Structural Development of Nanoparticle Dispersion during Drying in Polymer Nanocomposite Films

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Abstract

Dispersions of nanoparticles (NPs) in a polymer matrix are a key element to set various properties of solution-cast polymer nanocomposite films. While the dispersion state of NPs in nanocomposite films has been extensively studied over the last decades, the structural development during drying and the relation of liquid and solid structure still remains poorly understood. In the present work, we study how NP dispersions develop during drying in polymer nanocomposite films, particularly focusing on the role of particle-polymer interaction in the structural development. Aqueous dispersions of nano-silica and poly(vinyl alcohol) are used as a model NP/polymer mixtures, where the particle-polymer interaction can systemically be varied via the pH. A novel *vertical* small angle X-ray scattering technique enables us to directly observe the development of NPs dispersion during drying. At a high pH 10, where silica particles have a poor affinity to PVA, SAXS intensity evolution shows phase separation during drying, resulting in the formation of dense aggregates of bare particles in the solid film. On the other hand, at a low pH 3, where silica particles have a good affinity with PVA, the SAXS data indicates a gradual densification of the NPs while maintaining a constant inter-particle distance, which is originating from adsorbed PVA. The resulting solid film after drying exhibits an improved dispersion of NPs. The evaluation of the inter-particle interaction suggests that the adsorbed polymer plays generally a key role in the uniform distribution of NPs in solid films, as it sterically stabilizes NPs over short ranges during all drying stages whereas depletion attraction dominates at longer ranges.

Keywords: Polymer nanocomposite film, drying, nanoparticle dispersion, particle-polymer interaction

1. Introduction

Polymer nanocomposite films prepared from solvent evaporation have received considerable interest over the last decades owing to the versatility of formulation and wide applicability of the processes. Recent applications include catalytic electrodes in fuel cells¹, organic photovoltaic solar cells², solid electrolytes for fuel cells³ or Li-ion batteries⁴, ceramic capacitors⁵, membranes for gas separation⁶, and antireflective coatings⁷. To realize the required properties in those applications, it is important to control the dispersion of nanoparticles (NPs) in the polymer matrix.

Controlling NP dispersion in polymer matrices is one of the most actively studied subjects in the field of polymer/colloid science and relevant industries⁸⁻¹¹. A well-known methodology to obtain a desired state of NP dispersion in polymer nanocomposites is to control the interparticle interaction. One possible route for this is to select a suitable solvent character or quality to tune the physicochemical affinity between the particle surface and the hosting polymer. Several studies report on the effect of the solvent on this affinity, and the resulting NP dispersion in the solid nanocomposite¹²⁻¹⁴. When casting onto a substrate, solvent evaporates and the liquid film inevitably experiences a significant volume change and structural evolution of the dispersion of the NPs. More specifically from the viewpoint of particle interaction, when drying occurs, solvent evaporation increases the volume fraction of particles, polymers and additives, which results in a significant change in the particle interactions and the resulting NP dispersion structure. In the case of a poor NP-polymer affinity, depletion attraction by non-adsorbed polymer or van der Waals attraction can result in NP aggregation in the solid film after drying^{12, 14, 15}. Conversely, in case of a good affinity between NPs and the hosting polymer matrix, the polymers may adsorb on the NP surface and introduce a steric repulsion, thus prevent NP aggregates in the final solid film^{12, 16, 17}. Therefore, a deeper understanding of the evolution of interparticle interaction and the impact

on the structural development of the NP dispersion during drying is required in order to control and achieve a desired NP dispersion in the dried polymer nanocomposite films.

While there is a considerable amount of studies on the dispersion state of NPs in the final polymer nanocomposite, the understanding on how NP dispersions are formed and evolve *during* drying is still lacking. Recent studies have observed the structural evolution of NP dispersion during solvent evaporation by means of in-situ or ex-situ small angle x-ray scattering techniques¹⁸⁻²⁵, but only dealt with colloid systems in the absence of polymers, which prevented to consider the affinity between particle and hosting polymer. Very recently, attempts have been made to understand the formation of NP dispersions in polymer films during drying^{15, 26}, but the role of the affinity between particle and hosting polymer, and the evolution of inter-particle interaction during drying was not adequately considered.

In the present study, we investigate the evolution of NP dispersion in polymer nanocomposite films during drying, with a particular focus on the role of the affinity of particle and the hosting polymer on the development of inter-particle interaction and resulting formation of NP dispersion. We directly observe the development of NP dispersion during drying by means of synchrotron *vertical* small angle X-ray scattering (*vertical* SAXS), where a vertical beam is directed through the film drying on a horizontal plate (see Fig. 1)²⁷. Vertical SAXS enables the direct observation of the structural development of NP dispersion during drying without any gravity-related restrictions, which conventional (horizontal) synchrotron beams cannot achieve¹⁸⁻²⁵. We use aqueous dispersion of nano-silica and poly(vinyl alcohol) as a model NP/polymer solution, where the particle-polymer interaction is systematically varied via the pH. The evaluation of the inter-particle interaction at different drying stages allows us to explain the respective development of NP dispersion at two selected pH values of 3 and 10 via steric repulsion and depletion attractions, and their dominance at different length scales.

2. Sample preparation and experimental method

Sample preparation Silica and poly(vinyl alcohol) (PVA) mixtures were prepared by mixing colloidal silica, PVA in solution, and deionized water. 30 wt% charge-stabilized colloidal silica (Ludox[®] HS-30, Aldrich, density $\rho = 2.2 \times 10^3 \text{ kg/m}^3$ according to the supplier) was used without further treatment. The average diameter d of the silica particles was determined from the SAXS intensity to be 15 nm, with $\sigma/d = 0.145$, where σ is the width parameter of the Schulz distribution function²⁷. A 15 wt% aqueous solution of PVA (Aldrich, $M_n = 31\text{-}51 \times 10^3 \text{ g/mol}$, degree of hydrolysis 87-88 %, and density $\rho = 1.2 \times 10^3 \text{ kg/m}^3$ according to the supplier) was prepared by dissolving PVA at 80°C for 2 h. After preparing a silica/PVA mixture with 10 wt% silica and 4 wt% PVA, the pH was adjusted by adding 0.3 M HCl solution to the suspension (which was initially at pH 10). When decreasing the pH to 3, the suspension abruptly becomes turbid. The radius of gyration R_g of PVA was set to be 6 nm based on the literature²⁸ and assumed to be independent of the pH. All measurements of liquid structure as well as the drying experiments were performed after 12 h of magnetic stirring of the final composition at room temperature.

Liquid structure The amount of adsorbed PVA on the silica surface Γ , zeta potential ζ , and zero shear viscosity η_0 were determined for all investigated suspensions. The amount of adsorbed PVA on the silica surface Γ was determined via centrifugation. Particles bearing adsorbed PVA were separated from the suspension by centrifuging at 23140 g for 1 h and the concentration of PVA in the supernatant was determined by weighing the polymer after evaporation of the solvent water at 70°C for 24 hours. We experienced difficulties with sedimentation at polymer concentrations of $\phi_{\text{PVA}} = 4 \text{ wt\%}$ (the actual polymer concentration

used for the drying experiments), thus we diluted the initial suspension so that ϕ_{PVA} was brought down to 1 wt%. Reproducibility of this procedure was confirmed by repeating the measurements at least three times for each of the three different samples at each pH. The zeta potential of the silica/PVA suspensions was measured using an electrophoretic technique (Zetasizer nano zs, Malvern instruments Ltd, UK). To confirm that interparticle interactions are negligible during the measurements, we diluted the original suspension with deionized water and confirmed that results are independent of the concentration when diluting by a factor of up to 500. The zero-shear viscosities η_0 were obtained from steady shear viscosities measured with an ARES strain-controlled rheometer (TA Instruments, Newark, USA) using a cone and plate geometry of 50 mm diameter and an angle of 0.0398 rad at 25 °C.

Drying behavior The organization of silica particles during drying was observed with the vertical SAXS setup at the BW1 line at DESY (Hamburg, Germany), as schematically shown in Fig. 1. The silica/PVA mixture was loaded onto a horizontal VESPEL plate with a pipette and spread to form a circular film with a radius of 10 mm. The vertical X-ray beam passed the sample at 5 mm from the center of the film. An extensive description on the setup, experiment and data treatment of SAXS intensity can be found in ref²⁷. To assure homogeneity of the sample in the beam direction during drying, we performed experiments with increasing sample volumes from 0.1 to 0.3 ml over the same area (corresponding to average film thicknesses of 0.3 mm to 1 mm) and obtained reproducible and height independent scattering results. The surface microstructure of the dried film was separately determined using a scanning electron microscope (JSM-840A, JEOL, Japan).

Figure 1. Sketch of a drying experiment with the *vertical SAXS* setup²⁷.

3. Results and discussion

3.1. Affinity between silica and PVA at different pH values, and dispersion state of NPs in silica/PVA suspensions

In this section, we first evaluate the physicochemical affinity between the silica surface and PVA in the initial suspension at different pH. It is well documented that, when the pH is reduced in silica/PVA suspensions, the silanol groups on silica surfaces are protonated (i.e. $\text{SiO}^- + \text{H}^+ \rightarrow \text{SiOH}$) and form hydrogen bonds with PVA²⁹. Measuring the zeta potential ζ and the amount of PVA adsorption Γ on the silica surface, it could be observed that ζ reduces and Γ increases with lowering pH as shown in Fig. 2A, implying that silica surface is neutralized, likely as a result of the protonation of silanol group, and thus of the increased PVA adsorption. This suggests that the affinity between silica and PVA becomes more favorable with lowering pH.

We now characterize the NP dispersion in the silica/PVA suspensions by means of SAXS intensity (Fig. 2B) and steady shear viscosity (Fig. 2C). At pH 10, a plateau in SAXS intensity is observed in the low q range, suggesting that the particles are stabilized as a result

of the strongly negative ζ (Fig. 2A). When the pH is decreased, the intensity at low q starts to exhibit a negative slope, implying that the particles gradually lose their stability. Finally, at pH 3, $I(q)$ exhibits a power law slope, indicating that particles form a fractal-like flocculated structure. The zero shear viscosity (η_0) significantly increases with decreasing pH (Fig. 2C), also suggesting that the particles are flocculating.

To further clarify the flocculated structure at pH 3, we have already measured SAXS intensities and Γ in an earlier publication when increasing the concentration ϕ_{PVA} from 0 to 4 wt%, and have found that NP particles experience bridging flocculation followed by steric stabilization as Γ increases up to $\phi_{\text{PVA}} = 2$ wt%³⁰. A further increase of ϕ_{PVA} resulted in the NPs experiencing a depletion flocculation, where the cluster size increased when increasing ϕ_{PVA} up to 4 wt%³⁰. This suggested that silica particles at $\phi_{\text{PVA}} = 4$ wt% form a depletion flocculated structure, where individual particles are sterically stabilized at short-range by adsorbed PVA. We are going to use this system and structure for the current drying study.

Figure 2. Surface chemistry of the silica surface and microstructure of silica/PVA suspension as a function of pH. (A) Closed symbol: amount of polymer Γ adsorbed onto the silica surface for a 1 wt% silica and 10 wt% PVA suspension. Open symbol: zeta potential ζ measured for the suspension of 4 wt% silica and 10 wt% PVA, diluted by a factor of 200 –

500. (B) SAXS intensity $I(q)$ of the suspension (4 wt% silica and 10 wt% PVA) for the different pH values. (C) Zero shear viscosity, η_0 of the suspension (4 wt% silica and 10 wt% PVA).

3.2. Structure of NP dispersion in the solid film after drying

In this section, we investigate the structure of NP dispersion in the solid film after drying. Figs. 3A-C display images of the initially liquid silica/PVA films at different pH levels. The liquid films at pH 10 (Fig. 3A) and pH 7 (Fig. 3B) exhibit a transparent appearance as a result of charge-stabilization. On the other hand, at pH 3 (Fig. 3C) the liquid film exhibits a turbid image as a result of depletion attraction and a lack of electrostatic repulsion. Figs. 3D-F exhibit the images of the solid, dry films, which changed their transparency significantly compared to the liquid state (thus cannot be predicted from the transparency of the liquid state). At pH 10 (Fig. 3D), the solid film exhibits a turbid appearance, with a porous microstructure consisting of dense aggregates (as seen from the SEM inset), suggesting that the charge-stabilized particles form aggregates during drying. On the other hand, the solid film at pH 7 (Fig. 3E) exhibits a less turbidity than at pH 10 and a disappearance of aggregates in the SEM image. In addition to this, we also observe a regular crack pattern at pH 7, whereas no cracks were observable at pH 10. Cracks occur when elastic stresses, caused by capillary pressure, exceed the strength of the material, resulting in a stress relaxation in form of cracks. The capillary pressure is proportional to γ/r_h where γ is the surface tension and r_h is the pore radius, respectively. The less porous structure observed in the SEM images at pH 7 suggests therefore a higher capillary pressure that results in the observed formation of cracks. At pH 3 (Fig. 3F), the initially turbid liquid film dries into a transparent solid film without observable aggregates in the SEM image. This implies that flocculate silica particles in the liquid state change their microstructure into a denser state

during drying. The solid film at pH 3 also exhibits a regular crack pattern that is also observed in drying films of stable suspensions as a result of close packed structure^{31, 32}. This suggests that NPs in the solid film at pH 3 and pH 7 form a dense structure, which results in a smaller pore size and introduces higher capillary pressures.

Figure 3. Silica/PVA film before and after drying at various pH. Visual image before (A-C) and after (D-F) drying of the coating film casted onto a borosilicate slide glass. E and F exhibit cracks in the dried film that are, however, not visible in D. Size of the logo in the images is 40 mm (width) $\times$ 15 mm (height). Insets: SEM images of the dried films (the scale bar is 1 μ m)

To further understand the NP organization in the solid film, we measured SAXS intensities and SEM images after drying at pH 10 and pH 3 as we increased ϕ_{PVA} . In Fig. 4, the SAXS intensities at pH 10 exhibit an upturn at the lowest q and a shoulder at $q = 0.43 \text{ nm}^{-1}$, suggesting that particles form disordered aggregates. The shoulder at $q = 0.43 \text{ nm}^{-1}$ allows us to approximate the center-to-center distance d between particles as $d = 2\pi/q = 14.6 \text{ nm}$, so nearly the same as the silica particle diameter. This implies that bare silica particles form aggregates in the polymer film, without any PVA in the aggregates. This also indicates that

the spherical aggregates observed in the SEM image of (Figs. 4B-D) are surrounded by PVA, probably with surface tension shaping the silica aggregates when air intrudes the drying film at the late stage of drying. Interestingly, increasing the PVA concentration does not change SAXS intensity or peak position, but only fills the pore space between aggregates without changing their size and shape as can be seen in the SEM images (Figs. 4B to D). This suggests that PVA does not improve the particle dispersion at pH 10 at all, due to the poor affinity between silica and PVA.

Figure 4. SAXS intensity and SEM images of solid film at pH10(a-d) and pH 3(e-h) at different ϕ_{PVA} of silica/PVA suspension. Films are dried from suspensions of $\phi_{\text{PVA}} = 4, 4.5, 5$ wt% (as noted in the image), respectively, and a constant silica concentration of 10 wt%. Volume ratio of the PVA and the silica in the film is 0.73, 0.83 and 0.92 for $\phi_{\text{PVA}} = 4, 4.5$ and 5 wt%, respectively.

In contrast to this, the SAXS intensity at pH 3 and $\phi_{\text{PVA}} = 4$ wt% (Fig. 4E) exhibits a broad peak at $q = 0.3 - 0.4 \text{ nm}^{-1}$ and a suppressed intensity at low q . This indicates that particles are

not aggregated, but rather form a dense and uniform structure (as supported by the regular crack pattern we mentioned in Fig. 3F). Furthermore, with increasing ϕ_{PVA} the SAXS intensity shows a gradual disappearance of the broad peak at $q = 0.3 - 0.4 \text{ nm}^{-1}$ and an upturn at the low q . This implies that the added PVA widens the distance among silica particles, but without changing the bulk structure, as shown in the SEM images (Figs. 4F-H).

The analysis of the solid structure in the silica/PVA film in comparison to the liquid state suggests that the structure of the NP dispersion strongly changes during drying. The affinity between particle and polymer seems to play a dominant role in the complex development of the NP dispersion during drying. To understand how the NP structure develops, we interpret the temporal evolution of vertical-SAXS intensities in the following section.

3.3. Drying behavior investigated by vertical SAXS

In this section, we examine how the SAXS intensity $I(q)$ and structure factor $S(q)$ change as solvent evaporates in the silica/PVA film at pH 10, 7 and 3, with the results shown in Figs. 5, 6 and 7, respectively. We note that, from an experimental point of view, the measured SAXS intensities of the suspensions exhibited a slight variation in the **overall** intensity for each sample loading, even for the same pH, due to slight variations of thickness of the liquid film loaded on the plate in the SAXS setup. Furthermore, since we were not able to directly measure the thickness of initial film, it was not possible to scale $I(q)$ with respect to the film thickness to correct for the intensity variation. Due to this experimental restraint, we ignore the absolute value of the vertical scale of $I(q)$ in Figs. 5A, 6A and 7A, and arbitrarily shift $I(q)$ in the vertical direction only for clarity issue. To obtain the structure factor $S(q)$ within this limit for a given intensity, we combine the form factor $P(q)$ with $I(q)$ so that $S(q) = I(q)/P(q) \sim 1$ at high q , where $P(q)$ was determined for the 0.1 wt% charge-screened silica suspension.

Figs. 5A and 5B exhibit $I(q)$ and $S(q)$ of the suspension at pH 10, respectively, with increasing τ , where τ is the drying time normalized by the time at which the scattering intensity does not change anymore.

Figure 5. (A) SAXS intensity $I(q)$ of the suspension of 4 wt% silica and 10 wt% PVA at pH 10 with respect to the reduced drying time τ . $I(q)$ is vertically arbitrarily shifted for clarity. Solid line: form factor $P(q)$, which is combined with $I(q)$ so that $S(q) = I(q)/P(q) \sim 1$ at high q .

(B) Structure factor $S(q)$ for different τ .

$S(q)$ in Fig. 5B shows an intensity peak around $q = 0.25 \text{ nm}^{-1}$, which gradually weakens and shifts to higher q during drying, and finally disappears at $\tau = 0.67$. This indicates that the charge-stabilized particles are gradually losing their long-range stability. At $\tau = 0.67$ a slight upturn is observed at the lowest q , suggesting that particles at this point start to weakly aggregate (see schematics in Fig. 8A at $\tau = 0.67$). In our previous drying study of identical charged-particles in the absence of PVA²⁷, we show that, when solvent evaporates, the upconcentrating sodium ions in the medium weaken the electrostatic repulsion as they reduce the distance over which electrostatic effects persist (i.e. the Debye length³³). The same will happen also in the present system, thus reducing electrostatic repulsion. In addition, the increasing concentration of PVA in the medium also contributes to the observed destabilization. This is because the amount of PVA that can be adsorbed is limited and set by the surface area of silica. Therefore, the concentration of non-adsorbed PVA in the medium is expected to increase as solvent evaporates, suggesting that depletion attraction may become stronger during drying, which possibly contributes to the observed destabilization in the drying film. In fact, the gradual disappearance of peak intensity at $q = 0.25 \text{ nm}^{-1}$ during drying shows a marked difference from our previous drying experiment in the absence of PVA²⁷, which exhibited a stronger peak intensity, followed by an abrupt disappearance at the near-end of drying. This suggests that depletion attraction plays an important role already from the early stage of drying as a driving force that leads to the destabilization in the following drying stage.

At $\tau = 0.83$, $S(q)$ develops a pronounced peak at $q = 0.4 \text{ nm}^{-1}$ and a significant upturn at the lowest q , indicating that the destabilized NPs form aggregates. This peak at $q = 0.4 \text{ nm}^{-1}$

shifts to 0.43 nm^{-1} over the time span $0.83 < \tau < 1$. The final value of $q = 0.43 \text{ nm}^{-1}$ is equivalent to the particle size (as discussed in Fig. 4A). This suggests that over this stage the increasing concentration of non-adsorbed polymers introduces a strong depletion attraction, which eventually leads to a separation into a phase of bare particles and a polymer phase. At $\tau = 0.92 \sim 1$, we observe an increase in the scattering contrast (see Supporting Information Fig. S1), indicating that air intrudes into the film²⁷, which results in a turbid film after drying (Fig. 3D).

Based on the analysis of $S(q)$, we suggest the following scheme of NP dispersion evolution in the silica/PVA suspension during drying as illustrated in Fig. 8A: The suspension shows dispersed NPs at $\tau = 0$ that gradually lose stability at $\tau = 0.33$, followed by the occurrence of disordered NP aggregates at $\tau = 0.67$. During the further drying process, the suspension contains strong aggregate of bare NPs with a direct contact of the bare surfaces, resulting in a separation of the polymer phase and the particle phase from $\tau = 0.83$ to 0.92 , consecutively. Finally, NP aggregates remain in the solid film after air intrudes inbetween the aggregates at $\tau = 1$.

Figure 6. (A) SAXS intensity $I(q)$ of the suspension of 4 wt% silica and 10 wt% PVA at pH 7 for different reduced drying times τ . $I(q)$ is vertically shifted for clarity issue. Solid line: form factor $P(q)$, which is combined with $I(q)$ so that $S(q) = I(q)/P(q) \sim 1$ at high q . (B) Structure factor $S(q)$ with respect to τ .

The evolution of $I(q)$ and $S(q)$ of the drying suspension at pH 7 is displayed in Fig. 6A and 6B respectively. The evolution of $S(q)$ from $\tau = 0$ to 0.7 shows a behavior similar to pH 10, indicating that also in this case silica particles gradually lose their long-range stability as the solvent evaporates, possibly due to the increasing depletion attraction. However, when comparing to pH 10 (Fig. 5B) for the time $0.83 < \tau < 1$, $S(q)$ at pH 7 for $0.8 < \tau < 1$ (Fig. 6B)

shows neither a significant upturn at the lowest q , nor the intensity peak at high q , suggesting that the silica/PVA film dries without phase separation, which leads to an improved transparency of the solid film at pH 7 (Fig. 3E) compared to pH 10 (Fig. 3D). However, this absence of strong aggregation and phase separation is on the first glance counterintuitive as charge stabilization at pH 7 is lower than at pH 10. This points at the important role that the polymer plays in this context. Compared to pH 10, the silica/PVA suspension at pH 7 has a slightly higher amount of polymer adsorption as seen in Fig 2. Studies on depletion attraction in the presence of grafting polymers³⁴⁻³⁶ showed that the presence of grafting polymer improves the dispersion stability, not only by introducing steric repulsion, but also by suppressing depletion attraction due to interpenetration of the free polymer into the steric layer of (anchored) polymer chains around the particles. Based on these studies, the improved NP dispersion in the solid film is likely to be caused by the increased PVA adsorption, which introduces steric repulsion and suppresses the depletion attraction during drying.

Figure 7. (A) SAXS intensity $I(q)$ of the suspension of 4 wt% silica and 10 wt% PVA at pH 3 with respect to the reduced drying time τ . $I(q)$ is vertically shifted for clarity issue. Solid line: form factor $P(q)$ which is combined with $I(q)$ so that $S(q) = I(q)/P(q) \sim 1$ at high q . (B) Structure factor $S(q)$ with respect to τ .

The evolution of $I(q)$ and $S(q)$ during drying at pH 3 is displayed in Figs. 7A and 7B, respectively. $S(q)$ shows a dramatic reduction of the upturn at the lowest q , which indicates that silica particles change their microstructure from depletion clusters to a uniform distribution as their volume fraction increases during drying. However, the intensity in the

high q range does not change, indicating that the distance between neighboring silica particles stays nearly the same throughout the drying process. This suggests a simple picture of the structural development during drying as illustrated in Fig. 8B: the initial aggregates are simply concentrating, with the particles eventually changing their relative positions within the aggregates to accommodate into the final close packing in the dry film (but keeping a constant inter-particle distance during the reorganization). The adsorbed polymers on the silica surface play a key role in the observed structural evolution as they sterically stabilize the particles on the short-range during all the drying process and thus enable the close range reorganization of particles.

Figure 8. Schematic of the structural evolution of silica dispersions during the drying of silica/PVA films at (A) pH 10 and (B) pH 3. Reduced values of film thickness are estimated from solvent loss measurements (See Supporting Information S2)

In order to further understand the evolution of SAXS intensity and corresponding NP dispersion during drying, we quantify $I(q)$ and the $S(q)$ as a function of τ . The intensity in the low q range of $I(q)$ reflects the long-range structure of NPs (for example, a power law slope at low q reflects the fractal dimension of NP clusters³⁰). Therefore, we determine the absolute value of the power law slope α from $I(q)$ for each different pH of the suspensions (Figs. 5A, 6A and 7A) over the range $0.1 \text{ nm}^{-1} < q < 0.2 \text{ nm}^{-1}$, with the results displayed in Fig. 9. The α value for pH 10 is initially zero, implying stabilized NPs in the suspension. With increasing τ , α rises gradually up to 1, implying that stabilized NPs are destabilized and then form NP clusters during drying as schematically depicted in Fig. 8A. For pH7 the value of α is 0.2 at the early stage of drying, indicating that NPs at pH 7 are initially less stabilized than at pH 10. However, α rises during drying only up to 0.8, which is smaller than for pH 10, implying that cluster formation during drying at pH 7 is less significant. The suspension at pH 3 shows $\alpha = 2.1$ in the beginning, indicating a significant initial presense of NP clusters in the suspension. However, α gradually decreases during drying down to the level observed for pH 7. This implies that the NP clusters disappears during drying with increasing concentrating, as schematically depicted in Fig. 8B.

Figure 9. Absolute value of the power law slope α as a function of τ , obtained from $I(q)$ of Figs. 5a, 6a and 7a over the range $0.1 \text{ nm}^{-1} < q < 0.2 \text{ nm}^{-1}$. All three suspensions are composed of 4 wt% silica and 10 wt% PVA.

Information about the arrangement of NPs over short ranges are mainly obtained from analyzing the primary peak in $S(q)$. For example, the average inter-particle distance and the degree of NP arrangement are obtained from the position and intensity of the primary peak in $S(q)$, respectively²⁷. Here we quantify the evolution of $S(q)$ during drying by tracking the position of the primary peak q_{peak} and the peak intensity S_{peak} as a function of τ , with results shown in Figs. 10A and 10B, respectively.

The q_{peak} data of pH 10 and pH 7 show a very similar time dependency in Fig. 10A; a gradual increase during drying, implying that the average interparticle distance reduces during drying in a similar way. However, Fig. 10B exhibits a marked difference in the evolution of S_{peak} for pH 10 and pH 7, in particularly from $\tau = 0.8$ onwards. A sudden rise of S_{peak} for pH 10 indicates the formation of dense aggregates of NPs, whereas no rise is observed for pH 7, indicating that no NP aggregates form. It is notable that this difference between the two pH occurs only at the late stage of drying, possibly when NPs are getting so

close that adsorbed polymers can mediate the NP arrangement. This again suggests that the adsorbed polymer plays a critical role in NP dispersion during drying.

It should be noted that q_{peak} for pH 3 (Fig. 10A) shows a nearly constant value over the whole range of τ , indicating that the particle arrangement remains constant throughout the drying process. The value $q_{\text{peak}} = 0.43 \text{ nm}^{-1}$ gives the averaged interparticle distance of NPs from $2\pi/q$, yielding 14.6 nm. This is equivalent to the diameter of silica particle, suggesting that NPs are touching the neighboring particles already from the beginning to the end of drying. On the other hand, S_{peak} in Fig. 10B gradually reduces during drying, indicating that the initially heterogeneous structure of aggregated NP clusters gradually compacts into a uniform distribution. The constant q_{peak} and the reduction of S_{peak} during drying at pH 3 suggest that the isolated NP aggregates are uniformly distributed during drying while maintaining their direct connection to neighboring NPs. We have noted in section 3.1 and also in ref 30 that the NPs in suspension at pH 3 are depletion flocculated at long-range, but sterically stabilized by adsorbed polymer at short-range. Thus it is expected that individual NPs are still allowed to change their relative position, even at close contact, with the help of the short-range steric repulsion, while they sustain their direct touching status due to the long-range depletion attraction. This leads then to the uniform distribution, as schematically shown in Fig. 8B. Again, this suggests that the adsorbed polymer plays a critical role in the stabilization of NPs during drying.

Figure 10. Quantification of $S(q)$ (obtained from Figs. 5b, 6b and 7b) as a function of τ . (A) Position of the primary peak q_{peak} of $S(q)$ and (B) intensity S_{peak} of this peak. The composition of all three suspensions is 4 wt% silica and 10 wt% PVA.

4. Discussion: The role of polymers in particle organization during drying

The analysis of SAXS intensity presented above on the drying film suggests that the evaporation of solvent significantly changes the particle interaction in the silica/PVA films in a way that could not be predicted a priori from the initial solution properties. The increasing volume fraction of silica particle and non-adsorbed polymer due to solvent evaporation contributes strongly to the evolution of particle interaction. In addition to this, also the

increasing salt concentration in the medium can reduce electrostatic repulsion²⁷. To elucidate and quantify the so far qualitatively assumed effect of solvent evaporation on the particle interaction, we calculate in the following the particle interaction potentials and their evolution; depletion interaction (V_{dep}), steric repulsion (V_s), electrostatic repulsion (V_e) and van der Waals attraction (V_{vdw}). To consider the effect of solvent evaporation on particle interaction, we assume that solvent evaporation increases the concentration of non-adsorbed PVA and ionic strength²⁷, but does not affect the amount of adsorbed PVA and the Hamaker constants. Therefore, solvent evaporation is assumed to affect only V_{dep} and V_e , without changing V_s and V_{vdw} . On the basis of these assumptions, we compare the particle interaction potentials at different pH values for the initial state (0 vol% solvent evaporation) with a representative intermediate state of 50 vol% solvent evaporation.

Steric repulsion V_s We employ scaling theory to determine the steric repulsion potential V_s ,^{37, 38}

$$V_s = \pi(r + \delta)K\Phi_{s0}^{9/4}D_{sc} \left\{ -16\Pi D_{sc} \ln\left(\frac{2\delta}{h-2r}\right) + \frac{4D_{sc}^{5/4}}{2^{5/4}}(8\Pi)^{9/4} \left[\frac{1}{(h-2r)^{1/4}} - \frac{1}{(2\delta)^{1/4}} \right] \right\} \quad (1)$$

where r and δ are the particle radius and adsorption layer thickness, respectively. D_{sc} is the effective thickness of the adsorbed polymer. Π and Φ_{s0} are the adsorption coverage ($\Pi = \Gamma/\Gamma_0$) and the volume fraction of an adsorbed layer at the saturation, respectively. To determine the parameters and calculate V_s at each pH, we employ the following assumptions about the adsorbed layer. Firstly, we assume that the volume fraction of the polymer in the adsorption layer is uniform and independent of the distance from surface. According to this

assumption $D_{sc} = \delta$. Secondly, based on a previous study³⁰, $\Pi = 0.8$ at $\phi_{PVA} = 4$ wt% at pH 3, and we assume $\Pi = 0.8$ for all pH. Thirdly, we set $\Phi_{s0} = 0.18$ at pH 3 according to ref.³⁷ and assume a decrease proportional to the measured Γ with increasing pH. As a result, we can calculate the adsorbed layer thickness from the amount of adsorbed polymer via $\delta = \Gamma / (\sigma \phi_{s0} \Pi)$. K is a constant expressed by $K = (\alpha_{sc} / a_m^3) k_B T$ where α_{sc} and a_m^3 are numerical constants that are proportional to the osmotic pressure and the segment length of a polymer chain, respectively³⁷. For this calculation, we use $K = 3 \times 10^5$ N/m² at all pH levels following ref³⁷, resulting in a magnitude of V_s that is comparable to the other potentials. The parameter values for the calculation of V_s used in Eq. (1) are summarized in Table 1.

pH	10	7	3
Γ (mg/m ²)	0.03	0.14	0.36
Φ_{s0}	0.05	0.1	0.18
δ (nm)	0.62	1.4	2.0

Table 1. Parameter values for the calculation of V_s , Eq (1).

Depletion attraction V_{dep} The current system includes both adsorbing and free polymers, thus an estimation of the interpenetration of the matrix polymer molecules with the adsorbed polymer needs to be done when evaluating depletion attraction. Vincent and coworkers^{35, 39} proposed a modified version of the classical Asakura-Oosawa model⁴⁰ considering an interaction between adsorbing and free polymer. In this study, we employ the V_{dep} of Vincent et al., which is given by³⁵

$$V_{dep} = -2\pi r P_2 \left(\Delta + \delta - p - \frac{h-2r}{2} \right)^2. \quad (2)$$

where P_2 is the osmotic pressure of the bulk polymer solution, which dominantly depends on the bulk polymer concentration. P_2 is given by

$$P_2 = - \left(\frac{\mu_1 - \mu_1^0}{\nu_1} \right) = \frac{kT}{\nu_1} \left[\ln(1 - \phi_2^b) + \phi_2^b + \chi (\phi_2^b)^2 \right] \quad (3)$$

where χ is the Flory-Huggins parameter (= 0.46 for PVA in water⁴⁵) and ν_1 is the molar volume of the solvent. Δ in Eq. (2) is the range affected by depletion attraction, which can be approximated as the diameter of the polymer coil, given by³⁵

$$\Delta = 1.4 r_g \left(\frac{1 - \phi_2^b}{1 - \phi_2^*} \right) \quad (4)$$

where r_g , ϕ_2^b and ϕ_2^* are the radius of gyration, bulk concentration and critical overlap concentration of free polymer, respectively. In this study, we determined $\phi_2^* = 1.4$ wt%. p in Eq. (2) is the interpenetration distance of the matrix polymer chain into the adsorbed layer, reflecting the degree of interaction between adsorbed and bulk polymer. p is given by³⁵

$$p = \frac{P_2 \Delta \nu_1}{kT(1-2\chi)\bar{\phi}_2^a \phi_2^b} \quad (5)$$

where $\bar{\phi}_2^a$ is the volume fraction of adsorption layer, which is equal to $\phi_{s0} \Pi$. p reflects the degree of interaction between adsorbed and bulk polymer, thus depends not only on the bulk and adsorbed polymer concentration but also on the thickness of the adsorbed layer³⁵. Since these values change during drying, the parameters calculated for conditions of 0 and 50 wt% solvent evaporation, respectively, are summarized in Table 2

pH	10	7	3
ϕ_{na} (vol%)	3.53 / 6.58*	3.28 / 6.34*	2.79 / 5.85*
P_2 ($\times 10^3$ Pa)	5.76 / 25.65*	4.62 / 23.32*	3.16 / 19.01*
Δ (nm)	16.55 / 16.01*	16.56 / 16.03*	16.64 / 16.10*
p (nm)	0.60 / 0.61*	0.95 / 1.28*	0.90 / 1.21*

Table 2. Parameter values for the calculation of V_{dep} from Eq. (2). *values used for the calculation after evaporation of 50% of the solvent from the suspensions.

Electrostatic repulsion V_e The Electrostatic repulsion potential (V_e) is given by⁴¹

$$V_e(h) = 4\pi\epsilon\epsilon_0 r^2 \psi_0 \exp[-\kappa(h-2r)]/h \quad (6)$$

where ψ_0 , and κ are the surface potential and the Debye Hückel inverse screening length, respectively. ϵ and ϵ_0 are the relative permittivity and the permittivity of vacuum, respectively. Our previous study²⁷ on drying of charged silica has shown that the solvent evaporation increases ion concentration, and thus reduces ψ_0 and κ^{-1} , resulting eventually in a weakening of V_e . The correlation of the solvent concentration with ψ_0 and κ^{-1} was derived as $\psi_0 \sim \kappa^{-1} \sim \sqrt{(1-\phi_s)/\phi_s}$ ²⁷, where ϕ_s is volume fraction of the solvent. This allows us to determine ψ_0 and κ^{-1} both at 0 and 50 wt% solvent evaporation, respectively, as summarized in Table 3.

pH	10	7	3
ψ_0 (mV)	45 / 24*	35 / 21*	5 / 3*

κ^{-1} (nm)	3 / 2*	3 / 2*	3 / 2*
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Table 3. Parameter values for the calculation of V_e from Eq. (6). *values used for the calculation for conditions after evaporation of 50% of the solvent from the suspension.

Van der Walls attraction V_{vdw} The adsorbed layer on the particles can affect the Van der Waals attraction potential between particles. Therefore, we calculate V_{vdw} in the presence of such an adsorbed layer, which is given by⁴²

$$V_{vdw}(h) = -\frac{1}{12} \left\{ \left(\sqrt{A_{22}} - \sqrt{A_{33}} \right)^2 \frac{r + \delta}{h - 2r} + \left(\sqrt{A_{33}} - \sqrt{A_{11}} \right)^2 \frac{r}{h - 2r + 2\delta} + 4r \left(\sqrt{A_{22}} - \sqrt{A_{33}} \right) \left(\sqrt{A_{33}} - \sqrt{A_{11}} \right) \frac{r + \delta}{(h - 2r + \delta)(2r + \delta)} \right\} \quad (7)$$

A_{11} , A_{22} , A_{33} in Eq. (7) are the Hamaker constants for particle-particle interaction, solvent-solvent interaction and polymer-polymer interaction, respectively. The Hamaker constants used for the calculation are $A_{11} = 0.85 \times 10^{-20}$ ³³, $A_{22} = 3.7 \times 10^{-20}$ ⁴³, and $A_{33} = 8.4 \times 10^{-20}$ ⁴⁴.

Figure 11. Particle interaction potentials of the silica/PVA suspensions at different pH values for 0 vol % solvent evaporation (so at the onset of drying). (A) total potential energy V_{tot} . (B) electrostatic repulsion V_e . (C) steric repulsion V_s . (D) van der Waals attraction V_{vdw} . (E) depletion interaction V_{dep} .

Fig. 11A shows the total potential energy V_{tot} of the silica/PVA mixtures, obtained as the sum of the single potential energies in Figs. 11B to 11E (i.e. $V_{\text{tot}} = V_{\text{dep}} + V_s + V_e + V_{\text{vdw}}$), calculated at the onset of drying (0 vol % solvent evaporation). From this it becomes obvious that for pH 10 an energy barrier of $\sim 3 kT$ observed in V_{tot} originates from V_e (Fig. 11B), implying particles are charge-stabilized in the initial liquid state. V_{tot} at pH 7 shows a positive wall as $h \rightarrow 2r$, arising from the combined potentials of V_e (Fig. 11B) and V_s (Fig. 11C). A minimum is observed at larger distance h , but the range is broad and the depth is below $|2 kT|$, so that it will not play a role as an attractive minimum. Therefore, particles at pH 7 are expected to be electrostatically and sterically stabilized in the initial liquid state. The

suspension at pH 3 shows a potential minimum of $\sim |3 kT|$ around $h - 2r = 4$ nm, followed by a potential wall as $h \rightarrow 2r$, suggesting that particles can be trapped at this distance of 4 nm, but are strongly sterically stabilized at shorter h . The potential minimum outside the steric wall is a result of V_{vdw} and V_{dep} , whereas V_e can be ignored. The presence of both an attractive minimum and a positive wall for $h \rightarrow 2r$ shows a good consistency with the analysis of the liquid structure at pH 3 in Fig. 2, indicating that indeed particles are sterically stabilized at short-range, but depletion flocculated at longer ranges.

Figure 12. Particle interactions of the silica/PVA suspensions at varying pH when 50 vol% solvent evaporates. (A) total potential energy V_{tot} . (B) electrostatic repulsion V_e . (C) steric repulsion V_s . (D) van der Waals attraction V_{vdw} . (E) depletion interaction V_{dep} .

Fig. 12 shows the potential energy after 50 vol % of the solvent has evaporated. Solvent evaporation increases both the salt and the polymer concentration in the medium, which

results in a weakening of V_e (Fig. 12B) and strengthening of V_{dep} (Fig. 12E) compared to the initial state (Figs. 11B and 11E, respectively). As a result, V_{tot} at pH 10 shows a disappearance of the energy barrier, causing the particles at pH 10 to fall into a primary minimum during drying, resulting in a permanent aggregation. In contrast to this, V_{tot} at pH 7 and pH 3 is still exhibiting an upturn as $h \rightarrow 2r$ that originates from V_s (Fig. 12C). At larger distances both pH 7 and 3 are dominated by the depletion potential and, as a result, both pH exhibit a potential minimum in V_{tot} at $h - 2r = 3-4$ nm. The minimum is deep enough ($> |7 kT|$) to cause the particles to aggregate, however, the potential wall at smaller distances for both pH prevents particle from further aggregation so that they can still locally rearrange. The presence of the potential wall even at later stages of drying represents a marked difference between the suspensions at lower pH and at pH 10

Calculations of the total potential energies from Eqs. (1), (2), (6) and (7) after 70 vol% solvent evaporation (See Supporting Information S3) are similar to 50% evaporation, however, with the difference that, for pH 7, the potential wall for $h \rightarrow 2r$ has disappeared. The new primary for pH 7 is, however, still much more shallow than for pH 10. This indicates that the particles at pH 7 will also eventually experience a permanent aggregation, but only at a higher particle concentration, so that the resulting clusters are much smaller and the structure is more homogeneous than for pH 10. This explains why the dry film at pH 7 is not totally clear, but exhibits a slight turbidity. For pH 3, the potential minimum slightly shifts to smaller h , however, positive values from steric repulsion prevent permanent aggregation.

The evaluation of potential energies with increasing evaporation shows that the pH dependent amount of adsorbed polymers plays a key role in the evolution of the interaction potential of silica during drying, in particular the possibility of a persistent steric stabilization even at later drying stages when the particles come into close proximity. As an extreme

example, V_{tot} at pH 3 shows an unchanged location of the potential minimum over the whole drying process ($h - 2r = 4$ nm at Figs. 11A and 12A), indicating that the inter-particle distance between neighboring particles does not change during drying. This again highlights the role of adsorbed polymer which stabilized the particles during drying at the short-range.

Conclusion

In the present study, we explore the development of NP dispersions during drying in NP/polymer solution films, with a focus on the interaction between particle and hosting polymer. We use an aqueous dispersion of colloidal silica and poly(vinyl alcohol), altering the affinity between particle and polymer via the pH. We observed the structural evolution of the NP dispersion state during drying *in-situ* by means of vertical x-ray scattering. For a poor affinity between NPs and hosting polymer, the suspension exhibits a phase separation during drying caused by an early domination of depletion attraction, resulting in dense and larger aggregates of bare particles. On the other hand, for a high affinity between NP and hosting polymer the suspension exhibits a gradual and homogeneous densification. This is caused by a sufficient steric stabilization that balances the depletion attraction sufficiently long during drying to maintain a constant minimum inter-particles distance. This retains the local mobility of the particle during drying and allows for particle rearrangement into a dense, homogenous and thus transparent dry film.

This possibility to tune the particle interaction and local mobility via the addition of polymer at different pH, and thus the structural evolution during drying into the solid state, has been demonstrated in this paper with apparently peculiar evolutions of the transparency of drying silica/PVA films:

- NPs at pH 10 are charge-stabilized in the suspension, but become destabilized during

drying by polymer induced depletion destabilization in the up-concentrating suspension, which leads finally to a flocculated during drying, thus a transparent liquid dried into a finally turbid solid state.

- On the other hand, NPs at pH 3 were initially flocculated in the suspension due to low charge stabilization, however, steric stabilization by the polymer during the whole drying process ensured mobility of the NPs allowing rearrangement into a finally uniform distribution, thus a turbid liquid dried into a transparent solid state.

The observed drying behavior of silica/PVA film seems to contradict the common belief that stabilized NPs dry into uniform distribution, whereas destabilized NPs form non-uniform distribution after drying^{46,47}. However, the quantitative analysis in the present study (based on in-situ determination of the structural evolution with vertical X-ray scattering and the calculation of the evolution of the interaction potentials) suggests that interparticle interactions can significantly evolve during drying and therefore alter the liquid structure to the point that initially stable suspensions destabilize into the solid structure in the drying silica/PVA film, and vice versa.

It should be noted that the evolution of interparticle interaction and corresponding NP dispersion at different stages of drying could be further understood by modeling of the experimental structure factors⁴¹, however, this will be a future study of SAXS experiments on drying suspensions.

Our systematic drying study focusing on the evolution of NP dispersion and its role of polymer on drying behavior will provide fundamental insights that enable novel design routes for a wide range of coating formulations.

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Supporting Information Available: Absolute Scattering intensities of drying film at pH 10, descriptions on the weight loss measurement during drying, and the calculation of potential energies at 70 vol% solvent evaporation are available free of charge *via* the Internet at <http://pubs.acs.org>.

Conflict of Interest: The authors declare no competing financial interest.

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