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Adsorption of Poly(vinyl formamide-*co*-vinyl amine) onto Silica Particle Surfaces and Stability of the Formed Hybrid Materials

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Summary: In order to produce silica/polyelectrolyte hybrid materials the adsorption of the polyelectrolyte poly(vinyl formamide-*co*-vinyl amine), P(VFA-*co*-VAm) was investigated. The adsorption of the P(VFA-*co*-VAm) from an aqueous solution onto silica surface is strongly influenced by the pH value and ionic strength of the aqueous solution, as well as the concentration of polyelectrolyte.

The adsorption of the positively charged P(VFA-*co*-VAm) molecules on the negatively charged silica particles offers a way to control the surface charge properties of the formed hybrid material. Changes in surface charges during the polyelectrolyte adsorption were studied by potentiometric titration and electrokinetic measurements.

X-ray photoelectron spectroscopy (XPS) was employed to obtain information about the amount of the adsorbed polyelectrolyte and its chemical structure.

The stability of the adsorbed P(VFA-*co*-VAm) was investigated by extraction experiments and streaming potential measurements. It was shown, that polyelectrolyte layer is instable in an acidic environment. At a low pH value a high number of amino groups are protonated that increases the solubility of the polyelectrolyte chains. The solvatation process is able to overcompensate the attractive electrostatic forces fixing the polyelectrolyte molecules on the substrate material surface. Hence, the polyelectrolyte layer partially undergoes dissolving process.

Keywords: dissolving mechanism; hybrid material; polyelectrolyte adsorption; poly(vinyl formamide-*co*-vinyl amine); silica; stability of polyelectrolyte layer

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Introduction

The adsorption of polyelectrolytes onto various kinds of solid materials, for example inorganic oxide particles, resins, flat surfaces or fibres, is an intensively studied field of material research, due to the practical relevance of PE in adhesion, flocculation or wetting [1-4]. Decher *et al.* developed a new technology for synthesizing stable polyelectrolyte multilayers [5]. The authors used oppositely charged polyelectrolyte that have been adsorbed consecutively from the diluted aqueous solutions onto flat surfaces. Möhwald *et al.* [6-7] used similar techniques for synthesis of novel polymeric hollow spheres. The polyelectrolytes used by the mentioned authors, poly(sodium styrenesulfonate) or quaternary polyammonium salts are strong polyelectrolytes with a fixed number of charges along the polymer chain that do not form an equilibrium controlled by the surrounding media. The electrostatic interactions between the oppositely charged polyelectrolyte layers are also not influenced by the pH value of an aqueous solution. Hence, those multilayer systems are very stable in aqueous media. But these polyelectrolytes seem not suitable for further functionalization reactions under mild conditions.

P(VFA-*co*-VAm) is a weak polyelectrolyte containing a controllable number of reactive and accessible primary amino groups on the polymer backbone. It is an interesting candidate for silica surface functionalization in aqueous solutions [8-10], because it has a high chemical potential for subsequent derivatization reactions with electrophilic agents.

The present study reports the coating of silica particles with well-defined P(VFA-*co*-VAm) in order to control the surface properties of the formed hybrid material, like its surface charge density, acid-base characteristics and stability. Beside the entropy, the adsorption of P(VFA-*co*-VAm) and its adhesion is driven by electrostatic forces between the oppositely charged silica surface and the P(VFA-*co*-VAm)'s amino groups. However, the charge degree of P(VFA-*co*-VAm) depends on the protonation/deprotonation equilibrium of the amino groups. The protonation/deprotonation equilibrium can be easily influenced by the pH value of a surrounding aqueous media. Hence, the stability of the adsorbed polyelectrolyte layer can be also affected by the environmental conditions. Investigations of the polyelectrolyte layer stability show that weakly bounded polyelectrolyte molecules can be easily removed. But it seems impossible to remove the complete P(VFA-*co*-VAm) layer from the silica particles. Nevertheless, for practical applications and subsequent functionalization reactions it is recommended that the P(VFA-*co*-VAm) layer to be stabilized by cross-linking reactions [8].

To study the adsorption process of P(VFA-*co*-VAm) onto silica surfaces and the hybrid's stability, polyelectrolyte and potentiometric titration as well as electrokinetic measurements were employed. In addition, X-ray photoelectron spectroscopy (XPS) was applied to study the molecular structure of the produced hybrid materials.

Experimental

Materials

Kieselgel 60 (Merck, Darmstadt, Germany) a commercially available spherical silica was used as the inorganic substrate material. The diameter of the silica particles ranged between 15 and 40 µm. Kieselgel 60 particles are micro-porous (pore diameters ca. 5 nm).

The P(VFA-*co*-VAm) sample with molar mass of M_n = 15.000 g mol^{-1} was provided by BASF (Ludwigshafen, Germany). The degree of hydrolysis was 96 mol-%. This means that 96 mol-% of the former formamide groups of the PVFA chains were converted into amino groups.

Adsorption procedure

For the adsorption experiments, an aqueous stock solution containing 11.4 wt.-% P(VFA-*co*-VAm) was diluted to different concentrations. Then, 0.5 g silica was suspended in 50 ml of the diluted P(VFA-*co*-VAm) solutions. During the adsorption process, the suspension was gently shaken at room temperature. The modified particles were filtered off by slight suction. The hybrid materials were carefully washed with distilled water and dried in vacuum at 40 °C for 24 h.

X-ray photoelectron spectroscopy

XPS studies were carried out by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, UK). The spectrometer was equipped with a monochromatic Al Kα ($h \cdot \nu$ = 1486.6 eV) X-ray source of 300 W at 15 kV. The kinetic energy of the photoelectrons was determined with a hemispheric analyzer set to pass energy of 160 eV for wide scan spectra. During all measurements electrostatic charging of the sample was over-compensated by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same amount that was necessary to set the C 1s peak to 285.00 eV for saturated hydrocarbons.

Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function.

Polyelectrolyte and potentiometric titration

Polyelectrolyte and potentiometric titration were performed with the particle charge detector PCD 02 (Mütek, Germany). For polyelectrolyte titration a 10^{-3} mol·l^{-1} solution of poly(sodium ethylenesulphonate) was used. Potentiometric titration was carried out between pH 3.5 and 10, using 0.1 mol·l^{-1} KOH and HCl, respectively.

Electrokinetic measurements

The electrokinetic measurements were performed as streaming potential experiments employing an EKA (Anton Paar, Austria). In a specially designed powder-measuring [11] cell the hybrid materials were packed as diaphragm, which was flown through by an aqueous KCl solution (c = 0.001 mol·l^{-1}). The pH dependent measurements start from pH = 6.8. The addition of 0.1 mol·l^{-1} HCl lowered the pH values, while the addition of 0.1 mol·l^{-1} KOH increased the pH values. After recording the streaming potential values of the acidic pH range the sample was exchanged for measuring the streaming potential values of the basic pH range. The values of the electrokinetic potential (zeta-potential ζ) were calculated from the measured streaming potential values according to the Smoluchowski's equation [11].

Results and discussion

Bare silica surface and P(VFA-co-VAm)

Silica particles suspended in water or in aqueous electrolyte solutions may be considered as a polyelectrolyte. The surface charging of the silica particles is either the result of dissociation processes of Brønsted-acidic silanol groups (Si–OH) forming negatively charged silanolate ions (Si–O^-) or proton adsorption yielding Si–OH_2^+ species. In a wide pH range the two charge generation mechanisms may take place simultaneously on the silica surface because the acidity of surface silanol groups can be quite different.

P(VFA-*co*-VAm) chains also have discrete charges; therefore, an important component of the driving force of P(VFA-*co*-VAm) adsorption onto silica surfaces should be the Coulomb force between the charge centres of the solid surfaces and the polycation.

Potentiometric titration in water shows that the point of zero charge ($pzc = pH|_{\Psi = 0}$, where Ψ is the potential) is reached at pH = 2.5 for bare silica and at pH =10.2 for P(VFA-*co*-VAm) (Figure 1). As mentioned above, the dissociation reactions form negatively charged silanolate ions on the silica surface. The formation of ammonium groups lead to positively charged P(VFA-*co*-VAm) over a wide pH range (pH < pzc).

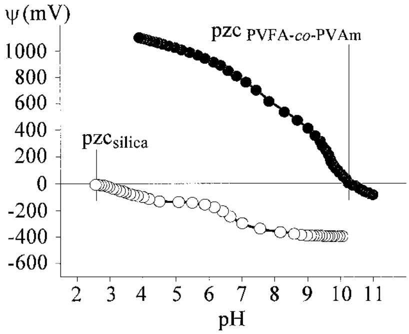

Figure 1. Potentiometric titration of bare silica (○) and P(VFA-*co*-VAm) (●)

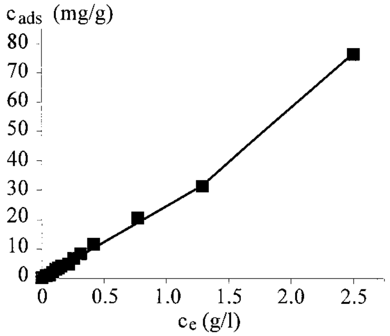

Figure 2. Isotherm (T = 22 °C) of the adsorption of P(VFA-*co*-VAm) onto silica from aqueous solution (c_e = equilibrium concentration of P(VFA-*co*-VAm) in the solution, c_{ads} = adsorbed amount of P(VFA-*co*-VAm)

Adsorption behaviour of P(VFA-co-VAm) onto silica surface

The adsorption behaviour of P(VFA-*co*-VAm) is shown in Figure 2. Surprisingly, results of polyelectrolyte titration of supernatant P(VFA-*co*-VAm) solution illustrate that no plateau region is observed (Figure 2). It is assumed that beside the adsorption of P(VFA-*co*-VAm) onto the silica particle surface an additional polyelectrolyte aggregation is initiated by increasing the polyelectrolyte concentration in the stock solution. Hence, the remained P(VFA-*co*-VAm) content in the supernatant solution appears smaller.

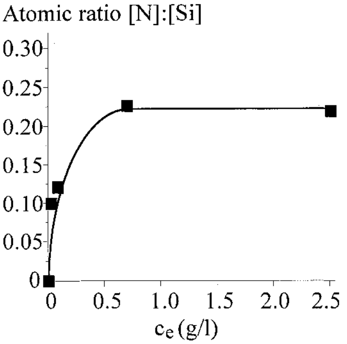

Figure 3. Amount of P(VFA-*co*-VAm) adsorbed onto silica surfaces determined by means of XPS. The amount of the P(VFA-*co*-VAm) is indicated by the nitrogen content [N], the number of unoccupied silica surface sites is indicated by the silicon value [Si] (c_e = equilibrium concentration of P(VFA-*co*-VAm) in the solution)

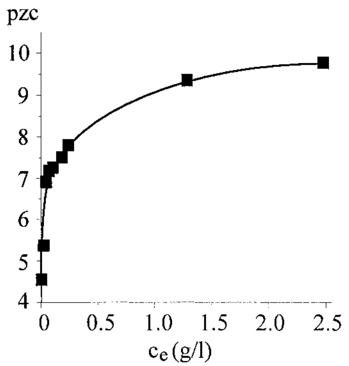

Figure 4. Amount of P(VFA-*co*-VAm) adsorbed onto silica surfaces measured by potentiometric titrations (c_e = equilibrium concentration of P(VFA-*co*-VAm) in the solution, the adsorbed amount of P(VFA-*co*-VAm) is expressed by the shift of the point of zero charge, pzc)

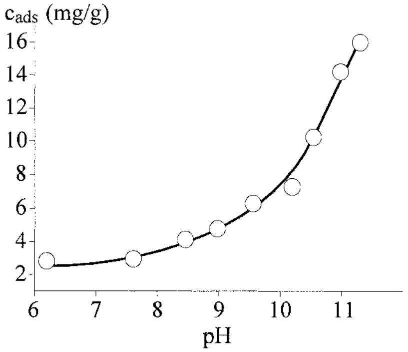

Figure 5. Influence of the stock solution's pH value on the P(VFA-*co*-VAm) amount adsorbed onto silica ($c_{P(VFA\text{-}co\text{-}Vam)} = 10^{-2}$ mol·l^{-1}, c_{ads} = adsorbed amount of P(VFA-*co*-VAm))

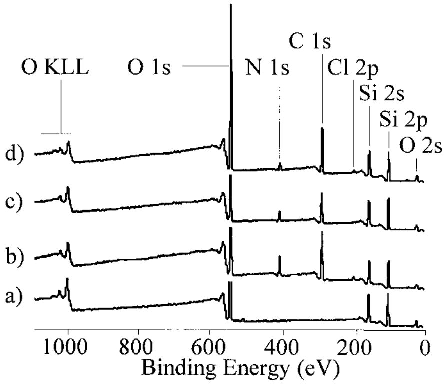

Figure 6. Wide-scan XPS spectra of bare silica (a), P(VFA-*co*-VAm) adsorbed onto silica (b), P(VFA-*co*-VAm) adsorbed onto silica after extraction (c), and P(VFA-*co*-VAm) adsorbed onto silica pre-treated with 2 mol·l^{-1} HCl (d)

During washing the freshly prepared P(VFA-*co*-VAm)/silica hybrid materials, all weakly bounded macromolecules will be removed. Only the polyelectrolyte molecules that are bound via strong interaction forces remain on the particle surface. Adsorption isotherms determined from XPS measurements (Figure 3) and potentiometric titration (Figure 4) of the P(VFA-*co*-VAm)/silica hybrid particles confirm this assumption by showing a clear plateau region. In the case of XPS it can be assumed that the N 1s peak appears only from the polyelectrolyte layer and Si 2p is a specific signal of the substrate material. Then, the [N]:[Si] atomic ratio should be an accurate measure of the amount of adsorbed polyelectrolyte. Potentiometric titration shows an increased shift of the pzc with increasing the polyelectrolyte concentration in the stock solution, which indicates the progress of compensation of the originally negative charge carriers on the silica surface by the adsorbed polycation (Figure 4).

Figure 5 shows the influence of the solution pH value on the adsorbed amount of P(VFA-*co*-VAm). At low pH values, the macromolecules have a high charge density and as a result of this the chains are stiff and stretched. Hence, the P(VFA-*co*-VAm) amount adsorbed onto silica surface is low. As can be seen in Figure 1 an increased pH value decreases the charge density of the P(VFA-*co*-VAm) molecules. The macromolecules will be more flexible and no electrostatic repulsion between the P(VFA-*co*-VAm) molecules could prevent the adsorption process. A higher amount of P(VFA-*co*-VAm) is adsorbed onto the silica surface (Figure 5).

Stability of the P(VFA-co-VAm) layer

The stability of the formed P(VFA-*co*-VAm) layers was tested by extraction experiments. Samples were put in a Soxhlet apparatus and extracted with distilled water over 72 h. As can be seen in Figure 6 and Table 1 during the extraction procedure the relative amount of nitrogen expressed as ratio [N]:[Si] is significantly decreased.

From this result it can be concluded that the adsorbed polyelectrolyte layer is not stable. The formation of ionic species on the polyelectrolyte chains may enhance the electrostatic interaction to the negatively charged silica surface, but with increasing the charging degree the solubility of the polyelectrolyte molecule is also increased. New amounts of pure water disturbs the primary adjusted adsorption equilibration and dissolves part of the weekly adsorbed macromolecules.

The partially removal of the polyelectrolyte layer was also observed in streaming potential experiments. It is expected that during the experiment the streaming liquid generates an additional mechanical stress, which should enhance the abrasion of the polyelectrolyte layer.

Table 1. XPS quantification report of P(VFA-*co*-VAm)/silica hybrid material before and after a Soxhlet extraction, and after the pre-treatment with 2 mol·l^{-1} HCl. The atomic ratio [N]:[Si] indicates the adsorbed amount of P(VFA-*co*-VAm).

	Atomic ratio [N]:[Si]		
	Before Soxhlet extraction	After Soxhlet extraction	After pre-treatment with 2 mol·l^{-1} HCl
Bare silica	0.000	0.000	0.000
P(VFA-*co*-VAm) adsorbed onto silica	0.231	0.204	0.178

Figure 7 shows the zeta-potential of a P(VFA-*co*-VAm)/silica hybrid material in dependence on the pH value of the streaming aqueous KCl solution. In the pH range 5 ≥ pH ≥ 9, the positive zeta-potential remains nearly constant (plateau, region *A* in Figure 7). Here, all amino groups that are able to form positively charged ammonium salt species are protonated. At pH > 9 the ammonium species are gradually deprotonated by the excess of OH$^-$ ions in the aqueous solution and as a consequence the zeta-potential value decreased. The isoelectric point (iep = $pH|_{\zeta = 0}$) of the P(VFA-*co*-VAm)/silica hybrid excellently agrees with the pzc of the P(VFA-*co*-VAm) solution (Figure 1). This indicates that the P(VFA-*co*-VAm) fully covers the silica surface and determine the charging behavior of the hybrid material. In the acidic range (pH < 5, region *B* in Figure 7), a high content of protonated amino groups is expected and the measured zeta-potential should agree with the potential of the plateau phase. However, at pH ≈ 3.4 the zeta potential shows a minimum. That minimum can be explained by the instability of the adsorbed polyelectrolyte layer in an acidic environment. The stepwise addition of HCl results in an increased solvatation of macromolecules, which is the first step of their dissolution. The streaming liquid removes the dissolved polymers, and support so the dissolving process by changing the adsorption equilibrium to the side of the solved species. In order to proof the assumption mentioned above, the hybrid material was treaded with 2 mol·l^{-1} HCl. As can be seen in Figure 7, the HCl treatment does not change the shape of the function $\zeta = \zeta(\mathrm{pH})$ in the region *A*. The minimum observed for the non-treated sample was not found. The plateau phase is on a lower level and the iep is shifted to a lower value of pH. The iep corresponds with the number of Brønsted base sites on the sample surface. The shift of the iep to a lower value indicates that the weakly bound P(VFA-*co*-VAm) layer is removed by the HCl treatment. Hence, a decrease of the zeta-potential in the region *B* cannot be observed for the HCl pre-treated sample.

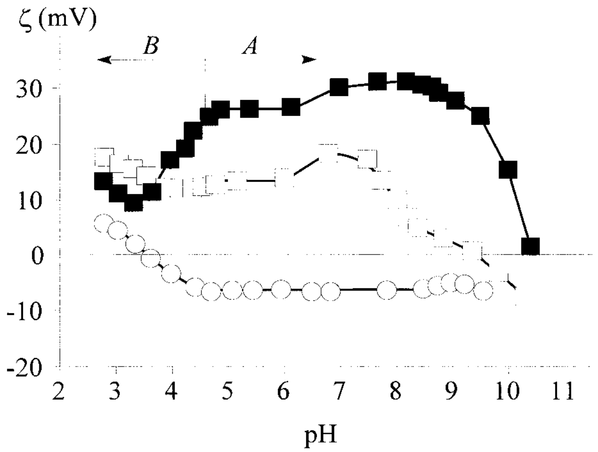

Figure 7. Zeta-potential values determined from streaming potential measurements in dependence on pH of an aqueous 0.001 mol·l^{-1} KCl solution. The measurements were carried out with bare silica (O), P(VFA-*co*-VAm)/silica hybrid material ([N]:[Si] = 0.231, ■), and the same P(VFA-*co*-VAm)/silica hybrid material pre-treated with 2 mol·l^{-1} HCl for 24 h ([N]:[Si] = 0.178, □)

The curves of the zeta-potential-pH dependence of the P(VFA-*co*-VAm)/silica hybrid materials show that the polyelectrolyte layer is not stable in strong acidic aqueous solutions. They show also that it is not possible to completely wash-off the polyelectrolyte layer. For subsequent functionalization reactions and the hybrid's applications it is recommended to enhance the polyelectrolyte layer stability by cross-linking reactions. The free and reactive amino groups of the P(VFA-*co*-VAm) chains offer the possibility to carry out such cross-linking reactions employing bi-functional low-molecular weight agents, metal clusters or fullerenes [8].

Conclusions

The adsorption of P(VFA-*co*-VAm) onto silica particle surfaces was studied. During the adsorption process, the excess of the polyelectrolyte forms aggregates that were weakly adsorbed on the silica surface. Those polyelectrolyte aggregates can be easily washed-off. On the silica particle surface remains a certain amount of P(VFA-*co*-VAm) that can be controlled by the adsorption conditions. The adsorbed polyelectrolyte layer is partly instable in acidic aqueous media. The protonation of the amino groups increases the solubility of the adsorbed P(VFA-*co*-VAm) molecules, attractive electrostatic interactions can be overcompensated and part of the polyelectrolyte chains can be desorbed, while the major part of the adsorbed polyelectrolyte molecules remain stable. For the subsequent derivatization reactions, which can be carried out using the reactive and accessible primary amino groups of the P(VFA-co-VAm)/silica hybrid particles, cross-linking reactions are recommended to stabilize the adsorbed P(VFA-co-VAm) layer.

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