Adsorption of a charged natural polysaccharide: role of pH and counterion on surface forces and film thickness

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In cosmetics, applications such as hair conditioning rely on the adsorption of polyelectrolyte films onto the charged surface of hair fibers, whose mechanical properties are central in determining the final sensorial perceptions. A current challenge for the cosmetic industry is to design high-performance products employing bio-sourced polyelectrolytes, with the aim of achieving eco-sustainable processes and products. Such design requires a deep understanding of the physico-chemical parameters controlling the adsorption and conformation of polyelectrolyte chains onto a charged substrate. We have used the Surface Force Apparatus (SFA) to investigate experimentally the effect of pH and counterion on the intersurface forces resulting from adsorption of chitosan onto negatively charged mica surfaces. Chitosan with 17% degree of acetylation and either acetate or lactate counterions was dissolved at 0.1 mg/mL in water with 100 mM of NaCl and pH adjusted to 3, 7 or 10. SFA measurements of the normal force vs intersurface distance were carried out, after chitosan adsorption onto the mica substrates and rinsing, in pure aqueous buffer with the same pH and salt content.

We find that, at pH 7, intersurface forces are repulsive and independent of the counterion. The range of such forces, on the order of 10-15 nm and larger than the Debye length at 100 mM of NaCl, is compatible with steric repulsion between chains forming a film whose thickness is about the Flory radius R_F of the chains. Repulsive forces measured at pH 3 are found to be comparable in range with pH 7. Surprisingly, we observe a twofold and reversible change in the range of repulsion when changing the pH between 3 and 10 (Fig. 1 A), with repulsion setting in at 20-30 nm at pH 10, suggesting a strong swelling of the adsorbed layer under basic conditions. This swelling at large pH is supported by numerical simulations of adsorbed chitosan chains, which demonstrate a spread of the monomer density profile and a decrease of the density peak at a distance of ~ R_F (Fig. 1 B).

Our study, combining force measurements and numerics, sheds light on the role of pH on adsorbed chitosan and suggests that the thickness of the adsorbed film is mainly controlled by the near-wall monomer density,.

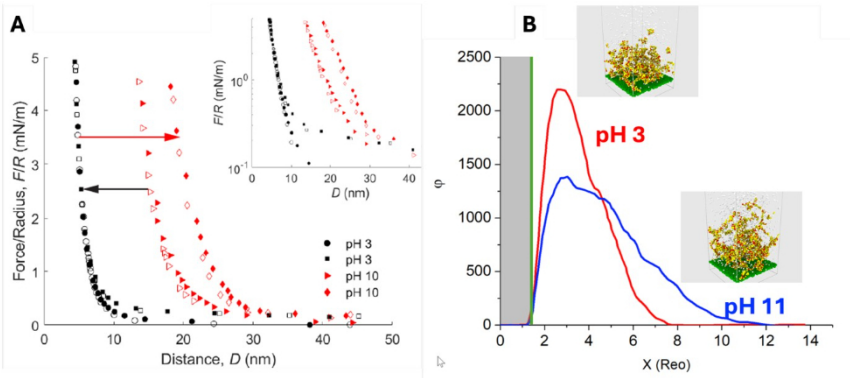

Fig. 1 – (A) Force vs distance curves obtained upon approach (full symbols) and separation (open symbols) at pH 3 and 10. (B) Monomer density profiles from numerical simulations of adsorbed chitosan

References:

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