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Bridging flocculation of PEI-functionalized latex particles using nanocrystalline cellulose

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ABSTRACT

Polystyrene microspheres were functionalized by covalent binding of 250 kDa linear PEI and ethanolamine, acting as a blocking agent, through bioconjugation with EDAC. The functionalized spheres were found to become less susceptible to salt-induced flocculation due to electrosteric stability, caused by the PEI chains at low NaCl concentrations, and at high salt concentration, by steric repulsion by the ethanolamine layer, which in combination with van der Waals attraction results in a shallow energy minimum and the formation of a few unstable aggregates. The latex aggregated in the presence of nanocrystalline cellulose (NCC) with varying efficiencies, depending on the ratio of NCC to latex particles in solution. Polyelectrolyte titration showed that each latex sphere contained about 15 grafted PEI chains. The fastest aggregation was detected when about half of these chains were covered by a single NCC particle.

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1. Introduction

Microparticle retention aid systems have become popular additives in papermaking [1–9]. They promote the deposition of pigments (e.g., calcium carbonate) on fibres, and cause filler flocculation, which helps capture in a forming paper sheet. Most microparticulate retention aid systems comprise a cationic polyelectrolyte (e.g., cationic polyacrylamides, cationic starch, etc.) and an anionic nanocolloid (e.g., montmorillonite, silica, etc.). Typically the polyelectrolyte is added first, creating positive patches on fibres and filler surfaces. Then the nanocolloid is added to bridge the surfaces. We study the flocculation of a model latex system by a model nanocolloid. The latex consists of (polystyrene) microspheres with cationic polyelectrolyte (polyethylene imine (PEI)) grafted to their surface and the nanocolloid is nanocrystalline cellulose (NCC). Because NCC has a net negative charge from sulphate groups, a positively-charged polyelectrolyte, such as PEI, will increase the strength and likelihood of adsorption. However, the polymer needs to be covalently bound to the latex to avoid dissociation and bridge weakening. This can be accomplished by bioconjugation. To avoid looping of the (linear) PEI back onto the latex, we used ethanolamine as a blocking agent.

The latex-NCC system is a model for filler retention in papermaking, obviating the need for fibre modification. The system also models other colloidal systems that involve bridging, such as blood platelet aggregation induced by fibrinogen or the von Willebrand factor [10]. Mimicking the bridging of platelets can be accomplished by using 1 μm diameter polystyrene microspheres, which have a size that is reasonably close to platelet dimensions (1.4 and 0.9 μm axes).

Bioconjugation involves the covalent linking of two or more biological compounds at their termini [11]. PEI's primary amines can be easily bound to surface carboxyl groups on modified spheres via 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDAC), a compound often used to cross-link proteins. EDAC forms an unstable intermediate complex with carboxylic groups, which is susceptible to amide bond formation if it reacts with a primary amine. A recent example of EDAC use in bioconjugation can be found in the work of Aghdam and coworkers, who immobilized the N-terminus of lysine on gold nanoparticles and proceeded to bind interferons to the free C-termini [12].

2. Materials and methods

2.1. Functionalization of latex beads

1.09 mL of 1.64×10^{-5} M ethanolamine (Sigma) in MES buffer (2-(*N*-morpholino) ethanesulfonic acid, pK_a of 6.15) were com-

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bined in a centrifuge tube with 50 μL 5% green fluorescent carboxylate-modified Fluosphere sphere suspension (Invitrogen, sphere diameter 0.9 μm) and incubated for 30 min, followed by the addition of 0.5 mL 6.5×10^{-4} M EDAC solution (Sigma) and incubation for 2 h. Two millilitre of 8.76×10^{-7} M PEI solution and 0.5 mL EDAC were then added to the tube and incubated overnight. The solution was centrifuged for 20 min at 3000*g* and resuspended in 15 mL of water, repeated three times.

2.2. Polyelectrolyte titration

To determine the number of linear PEI chains with molecular weight 250 kDa (Polyscience, Inc.) grafted to latex particles, we performed a polyelectrolyte titration [13]. The titration was performed with a Wetrohm 665 Dosimat instrument. The solutions were titrated with the potassium salt of polyvinyl sulphonate (PVSK) (Aldrich) having a molecular weight of 170 kDa. We used potassium hydrogen phthalate (ACS acidimetric standard, Sigma Ultra) as a buffer to which 1 mL of o-toluidine blue (Aldrich) was added, acting as the titration end-point indicator. First, a calibration curve was established, which was shown to be linear. For a sample with an unknown PEI concentration, the amount of PVSK required to cause a colour change in o-toluidine blue was determined by titration, from which the PEI concentration could be obtained using the calibration curve. It was assumed that the titration of anchored PEI would be the same as for PEI in solution, as the PEI is only anchored by one end of the molecule and, hence, all other segments will be free to complex with PVSK. The low grafting density ensures single well-separated PEI chains on the surface.

2.3. Nanocrystalline cellulose

Nanocrystalline cellulose (NCC) was obtained by acid hydrolysis of black spruce cellulose fibres, in which the lignin and hemicelluloses were removed by a kraft pulping process. Cellulose fibres mainly consists of nanofibres, bundled in microfibrils. Each nanofibre contains crystalline and non-crystalline regions. Acid hydrolysis breaks down the amorphous regions, leaving only cellulose nanocrystals (NCC). These crystals are on average 141 nm long with a standard deviation of 60 nm. Their diameter is 5.0 ± 0.3 nm, and, thus, their axis ratio is 28 [14]. The acid hydrolysis introduces sulphate groups on the NCC surface resulting in a surface charge density of 0.33 charge groups per nm^2 [14].

2.4. Characterization

Sphere suspension images were obtained using a Nikon TE-2000U fluorescence microscope and its Hamamatsu camera. Dynamic light scattering (DLS) measurements were carried out, with readings taken every 10 ms for 1 min, in a light scattering apparatus (Brookhaven Instruments photon correlation spectrometer with a BI-2030, (64 + 8) channel, 6-bit autocorrelator), using 1 mL functionalized sphere suspension diluted with 5 mL of ultrapure water.

2.5. Stability in NaCl solution

Hundred microlitre of either normal or functionalized sphere suspension were added to 100 μL of 0.12 M, 0.18 M, 1.2 M, 1.8 M NaCl solution in ultrapure water. For 3 M final concentration, 100 μL sphere suspension was added to 100 μL 3 M NaCl and extra salt was added to achieve the desired concentration. The systems were allowed to incubate for 36 h and 20 μL samples were taken after a brief (∼5 s) period of gentle agitation.

2.6. Static incubation

Hundred microlitre of functionalized sphere suspension and 120 μL 2% nanocrystalline cellulose were added to a glass vial and incubated for 1 min. A 20 μL sample was placed on a microscope slide and analyzed using the Nikon fluorescence microscope with Hamamatsu camera and Nikon Elements software. For the purpose of object counting and sizing, the intensity threshold in binary mode was set to account for all well-focused visible singlets.

2.7. Mixing with shear

Five millilitre of ultrapure water and 1 mL of sphere suspension were added to a 15 mL beaker with a 2 cm long magnetic stirrer bar. The stirrer speed was regulated to approximately 15 rps and 1 mL diluted NCC suspension. The degree of dilution depended on the desired NCC per sphere ratio. Twenty micrelitre samples were collected after 1, 5, 10 and 15 min and analysed using the fluorescence microscope. The NaCl concentration in the ultrapure water added to the spheres and NCC was adjusted accordingly for the aggregation experiments at higher ionic strengths.

3. Results

3.1. Latex surface modification

Sphere functionalization with ethanolamine and PEI was successful: the sphere suspension did not present any visible aggregates, and the spheres were very mobile. From a polyelectrolyte titration, the number of PEI molecules grafted onto latex particles was 15 ± 3 per particle. The area between PEI molecules is occupied by grafted ethanolamine, with a surface concentration of 5×10^6 per sphere, or 1 molecule per 1.6 nm^2. These ethanolamine molecules reacted with the latex carboxyl groups, resulting in a hairy layer of chemisorbed molecules, exposing their hydroxyl group to the water.

Characterization of the sphere size using dynamic light scattering showed a distinct shift (∼200 nm) after modification with PEI (Fig. 1). Considering that the extended polymer length should be close to 2.6 μm (5800 segments), the PEI is likely to be in a mushroom conformation. As EDAC is specific to primary amines, conjugation of polymer loops and trains to the sphere surface is unlikely. The mushroom configuration also provides a plausible explanation for the increased peak breadth. While the non-functionalized

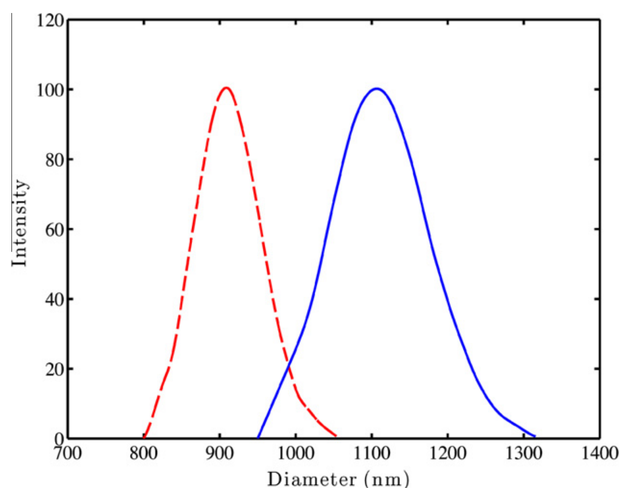

Fig. 1. Size distribution in suspensions of unmodified (dashed) and modified (solid) microspheres.

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