



Assembly of nanoparticles–polyelectrolyte complexes in nanofiber cellulose structures



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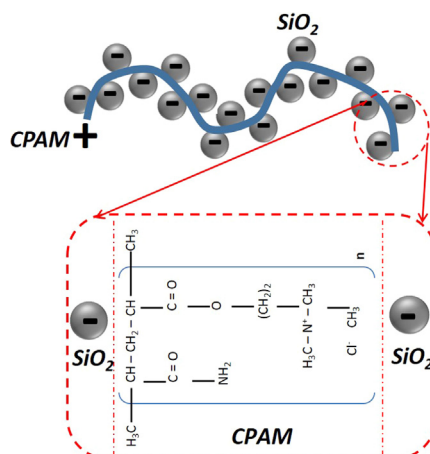
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HIGHLIGHTS

- We quantify the effect of cationic polyacrylamide (CPAM) dosage on the assembly of silica nanoparticles (NPs) within a nanocellulose composite.
- Increasing CPAM dosage increases retention of NPs within the cellulose matrix with stronger interparticle interactions.
- Small angle X-ray scattering (SAXS) and microscopic reveal that CPAM concentration affects the aggregates size of SiO₂ NPs within the composite.
- We show a bimodal distribution of spherical particles (8–20 nm in diameter) in nanocellulose composites by modelling the SAXS curves.
- Data analysis allow understanding interparticle interactions within assemblies of SiO₂ NPs at the nanometer scale with different dosage of CPAM.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 September 2016

Received in revised form 23 October 2016

Accepted 30 October 2016

Available online 1 November 2016

Keywords:

Small angle X-ray scattering (SAXS)

TEM

Silica nanoparticles (NPs)

Cationic polyacrylamide (CPAM)

ABSTRACT

We report the effect of cationic polyacrylamide (CPAM) addition on the structural assembly of silica nanoparticles (NPs) within a nanocellulose fibre matrix. Paper like composites are fabricated by first forming complexes of NPs with CPAM, then adding those to a suspension of nanocellulose fibres; followed by filtration, pressing and drying of the final suspension. Complementary small angle X-ray scattering (SAXS) and microscopy (SEM, TEM) investigations of these composites showed a lognormal bimodal distribution of NP sizes. Data analysis allows understanding interparticle interactions within assemblies of SiO₂ NPs at the nanometer scale with respect to different dosage of CPAM. Increasing CPAM dosage increases retention of NPs within the cellulose matrix with stronger interparticle interactions and produces composites with smaller pores. The correlation length of NPs, indicative of the size of the NP clusters increased from 30 to 70 nm as the CPAM dosage increased from 16.5 to 330 mg/g NPs. Retention

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<http://dx.doi.org/10.1016/j.colsurfa.2016.10.068>

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1. Introduction

Cellulose nanofibres are fast becoming widely available low-cost organic nanomaterials with specific properties such as tuneable opacity, low thermal expansion, high stiffness, high strength and flexibility. Cellulose is the most abundant, renewable and biodegradable biopolymer, efficiently produced by well-established manufacturing processes and infrastructures [1–3]. Nanocellulose fibres result from the intense fiberizing of cellulose pulp fibres. Cellulose nanofibres “paper” composites have exciting prospects and emerging applications such as smart clothing [4], transparent conductive films for electronics [5,6], tissue engineering [7] and barriers [8]. Even though the full commercial scale production of cellulose nanofibres has not yet been fully achieved, the wide availability of cellulose is promoting the production of new materials with cellulose nanofibres as the main component [9].

Nanocomposites are usually two phase materials consisting of a continuous polymeric phase reinforced by a discontinuous phase consisting of high surface area nanofillers [10]. When the size of fillers shrinks from microscale to nanoscale, the resulting composite develops unusual properties primarily due to the concomitant increase in interfacial area [11]. The properties of nanocomposites depend not only on the properties of their individual components but also on the morphological and interfacial characteristics arising from assembling the individual constituents [12]. In the materials investigated here, nanocellulose is the semi-continuous or connecting phase where silica nanoparticles (NPs) are linked through a retention aid to provide a new structure with voids, in which porosity and pore structure are dependent on NPs. The terms “cellulose nanofibres” and “nanocellulose” are used interchangeably in this paper and nanosilica was selected as model of functional NP.

Since both silica NPs and nanocellulose are negatively charged, an electrostatic repulsion is opposing the retention of NP's in the composite. In such cases, cationic polyelectrolytes are widely used in paper industries as retention aids [13,14]. Common industrial cationic polyelectrolytes include: cationic dimethylamino-ethyl-methacrylate polyacrylamide (CPAM), polyethylenimine (PEI), Polydiallyldimethylammonium chloride (polyDADMAC) and polyamide-amine-epichlorohydrin (PAE). Among those, CPAM is the most prevalent in industry for its low cost, high performance, and wide range of morphologies available. Also, it has the ability to strongly adsorb onto the negatively charged cellulose fibres [15,16] and is a stable polymer soluble in water and many organic solvents [17]. Important industrial applications for CPAM include water treatment, oil well stimulation and mineral processing [17]. Previously, we used CPAM to coagulate and retain NPs into nanocellulose and demonstrated that composite pore structure can be controlled [18]. However, the interaction of the CPAM with NPs and the mechanism of structural formation by CPAM induced NPs assembling within the composite at nanoscale have not been explored and there are no good methodology available to quantify NP aggregate at the critical length scale ranging from 1 nm to 1 μ m.

Generally, for characterization, direct methods such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used, but they evaluate a limited area of the composite and it is difficult to measure interparticle interactions between NPs

[19,20]. Indirect inverse space techniques such as X-ray, neutrons or light scattering provide a complementary statistical perspective on the internal structure of the material. Small angle X-ray scattering (SAXS) is a powerful method to characterize particle or structure size in ranges from \sim 1 to 100 nm [21,22].

In this study, a novel structural characterization approach is developed to elucidate NPs interactions within the respective formed assemblies dispersed in the cellulose matrix. We prepared nanocellulose/SiO₂ nanocomposites using CPAM as a retention aid. SAXS, TEM and SEM were used to quantify and optimize the interaction within silica NP assemblies with respect to different dosage of CPAM and distribution of assemblies within the cellulose matrix. Results from this study will contribute to engineer nanocomposites efficiently with polyelectrolytes. It is the objective of the study to characterize the structure of novel inorganic NP –organic fibre composites at the critical length scale affecting catalysis, permeability and biocompatibility.

2. Experiments

2.1. Materials

Microfibrillated cellulose (MFC) was purchased from DAICEL Chemical Industries Limited, Japan (grade Celish KY-100G). The MFC was supplied at 25% solids content and stored at 5 °C as received. The surface area of MFC is 31.1 m²/g [22,23]. Cationic dimethylamino-ethyl-methacrylate polyacrylamide (CPAM) polymer of high molecular weight (13 MDa) and with a charge density of 40 wt% (F1, SnowFlake Cationics) was graciously supplied by AQUA + TECH, Switzerland. NexSil 8 Aqueous Colloidal Silica was provided by IMCD Australia Ltd as 30 wt% suspensions. The manufacturer reported a colloidal silica average diameter of 8 nm and a specific surface area of 330 m²/g.

2.2. Method

2.2.1. Preparation of MFC, CPAM and NP suspensions

MFC suspensions (0.2 wt%) were prepared by dispersing fibres in deionized water uniformly using a disintegrator equipped with a 3 L vessel at 15000 propeller revolutions. CPAM solutions (0.01 wt%) were prepared by dissolving CPAM powder in deionized water for 8 h using a magnetic stirrer prior to nanocomposite fabrication. SiO₂ NP (0.1 wt%) suspensions were prepared by diluting 30 wt% original silica NP suspension using deionized water, and the suspension was stirred using a magnetic stirrer for 10 min before use. Mixing time is important in both cases to obtain homogenous suspensions. All suspensions were prepared at room temperature. The pH of final solutions is about 8 and does not vary significantly with different dosage of CPAM.

2.2.2. MFC sheet preparation

MFC sheets were prepared [24], using a standard British hand sheet maker (model T205). Concentrated MFC suspension (0.2 wt%) was poured into the hand sheet maker column and allowed to drain under gravity. After the water drained, the formed film was

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