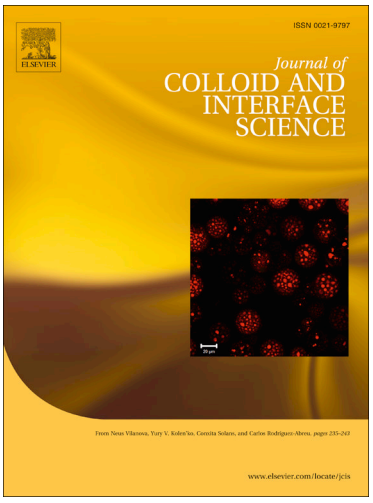

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Understanding heat driven gelation of anionic cellulose nanofibrils: combining Saturation Transfer Difference (STD) NMR, Small Angle X-ray Scattering (SAXS) and rheology

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†Electronic Supplementary Information (ESI) available: STD and reference NMR spectra, rheological data for other OCNF and CCNF dispersion concentrations, ^{1}H ^{13}C HSQC spectra and NOESY build up curves for OCNF before and after heating, fluorescence data, contributions to STD signal, temperature evolution of STD signal, and further NMR characterisation data. See DOI: 10.1039/x0xx00000x

Keywords. Water confinement, hydrogel, TEMPO oxidised cellulose, heat induced gelation, saturation transfer difference NMR, SAXS, rheology

Abstract

A novel mechanism of heat-triggered gelation for oxidised cellulose nanofibrils (OCNF) is reported. We demonstrate that a synergistic approach combining rheology, small-angle X-ray scattering (SAXS) and saturation transfer difference NMR (STD NMR) experiments enables a detailed characterisation of gelation at different length scales. OCNF dispersions experience an increase in solid-like behaviour upon heating as evidenced by rheological studies, associated with enhanced interfibrillar interactions measured using SAXS. Interactions result in an increased fibrillar overlap and increased population of confined water molecules monitored by STD NMR. By comparison, cationic cellulose nanofibrils (produced by reaction of cellulose with trimethylglycidylammonium chloride) were found to be heat-unresponsive.

Introduction

There is an enormous interest in cellulose based hydrogels as inexpensive and biodegradable gels, for their industrial and sustainable applications. Cellulose naturally occurs in plant cell walls as a hierarchical assembly of fibrils, tightly bonded via multiple hydrogen bonds.[1,2] Cellulose and cellulose derivatives are becoming of great importance for the production of a wide range of biodegradable materials, as their rheological properties have gained great importance for several applications ranging from drug release,[3] microbeads,[4] to functional ingredients in food (e.g. thickeners, stabilizers, gelling agents).[5–7]