



Partial periodate oxidation and thermal cross-linking for the processing of thermoset all-cellulose composites



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ABSTRACT

With the goal of preparing a new type of all-cellulose composites (ACCs), partial periodate oxidation of microcrystalline cellulose (MCC) was performed leading to specimens oxidized at C2 and C3 of the anhydroglucose moieties of cellulose. Samples having an overall degree of oxidation (DO) comprised between 0 and 1 were prepared. As confirmed by their absence in their ¹³C solid-state NMR spectra, the created carbonyl moieties were not detected, due to their immediate recombination with the available OH groups from untouched cellulose to yield hemiacetal cross-linkings. The high reactivity of the neo-carbonyl and the lability of the hemiacetals linkages were successfully used to prepare novel cross-linked ACCs resulting from the hot-pressing of samples with DOs ranging from 0.2 to 0.85. In these composites, the oxidized component acted as an in-situ reactive matrix, gluing the non-oxidized MCC part playing the role of filler.

Mechanical properties, measured with 3-point bending test, together with structural and thermal observations showed a direct correlation between the DO of the specimens, the cross-linking density, the macroscopic performances and the propensity to retain water when they were heated as shown by thermogravimetric (TGA) measurements. An optimum of the properties was reached for samples having a DO in the range of 0.4–0.65, where surface oxidized cellulose nanocrystals could be cross-linked with their oxidized or un-oxidized neighbors to yield nearly transparent samples of flexural modulus as high as 7 GPa and flexural strength of 177 MPa. Such values, obtained with samples resulting from the simple oxidation followed by thermosetting process presented here, match well the physical properties of ACCs resulting from more complex preparation scheme.

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1. Introduction

With the goal of designing eco-friendly composites, the deciphering of plant and tree ultrastructure is inspiring, as in these, one can find a perfect example of how nature is able to harmoniously mix amorphous matrices of lignin and hemicelluloses with crystalline microfibrillar cellulose to produce high strength structures. In plants, the performances of the fiber cell wall rely on the distribution of slender cellulose microfibrils, which combine linear orientation of the cellulose chains, peculiar crystalline ultrastructural organization and outstanding mechanical performances. Indeed, in its native form, crystalline cellulose (cellulose I) can reach a modulus as high as 120/150 GPa [1,2] and a strength as high as 6 GPa [3]. Due to these outstanding mechanical properties and to

their reduced CO₂ footprint, the use of cellulose fibers has generated a bloom of eco-composite developments and for years, fibers obtained from different sources (wood, flax, hemp, jute, sisal etc.) have been extensively processed with synthetic polymers and even bio-based products, such as polylactic acid (PLA), poly hydroxy alkanoate (PHA), starch etc. [4–7]. Due to the heterogeneity of the used fibers and their sensitivity toward hydration, the main drawback of such eco-composites is the weak interfacial adhesion between the fibers and the matrix [5]. Indeed, a poor compatibility between these two components leads to inefficient stress transfer, with the result of materials with low mechanical properties. To overcome these drawbacks, Nishino et al. have pioneered in 2004 the new concept of all-cellulose composites (ACCs) [8] demonstrated by impregnating untreated ramie fibers with LiCl/DMAc solutions of cellulose, followed by their regeneration. In such ACC composites the problem of interfacial incompatibility is thus avoided and the products possess superior mechanical and thermal

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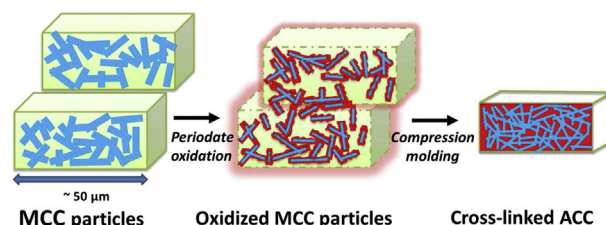
performances, while being totally biodegradable. Following this early seminal report, numerous ACC products have been processed. Their preparation and properties are summarized in a recent review, which distinguish the “non-derivatized all-cellulose composites” from the “derivatized all-cellulose composites” [9]. In the first processing strategy there is a partial or total dissolution of cellulose followed solvent removal, cellulose regeneration of the dissolved part and drying [8,10–13]. The second route relies on cellulose derivatization: a thermoplastic cellulose matrix is simply formed by benzylation [14,15], oxypropylation [16,17] or esterification [18,19]. The etherified or esterified amorphous cellulose derivatives are then hot-pressed with unmodified cellulose to form the ACCs. The mechanical properties of these derivatized ACCs are similar to those of cellulose-based composites with synthetic thermoplastic polymers, and in general display physical properties that are five to ten times lower than those of the non-derivatized ACCs counterparts [9].

The present work aims to go one step further with the elaboration of a third class of ACCs, namely thermoset ACCs. The idea is to use a single source of cellulose, but only to derivatize part of it in order to yield an in-situ thermosetting-prone matrix that can be further heat-processed with the remaining un-derivatized part of the sample. An early report of this concept can be found in an American Viscose 1963 patent by Battista et al. [20], where the authors pointed to the potential of ACCs resulting from partially oxidized microcrystalline cellulose. Today, the oxidation of cellulose is enjoying a renewed interest as the details of its implication for preparing improved products seem to be better understood [21,22]. In particular, it was confirmed that in paper products, the periodate oxidation improved not only the tensile strength [21–23] of the sheets but also reduced their hygroexpansivity [22]. Along this line, Larsson et al. [24,25] in two recent papers, have shown that cellulose nanofibrils that were partially converted to dialcohol in a sequential periodate oxidation followed by borohydride reduction, were processible into ductile ACC products. According to these authors, such ductility took its origin in the selectivity of the process whereby each initial crystalline nanofibril kept part of its core intact, but was covered by a shell of amorphous dialcohol.

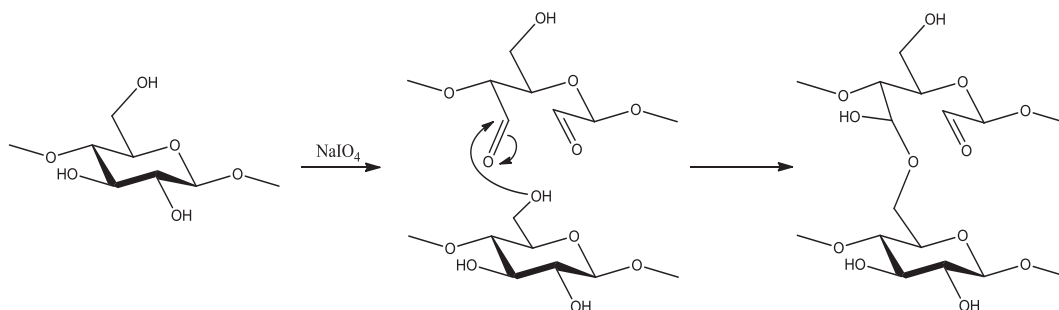
Our work also deals with the partial periodate oxidation of nanocellulose, but without going to the dialcohol reduction. In a former paper reporting on the periodate oxidation of dispersed cellulose microfibrils [26], we could define conditions where limited oxidation involved only the surface of the microfibrils, leaving intact their core. It was only with prolonged oxidation, typically above an overall degree of oxidation (DO) of 0.3/0.4, that the reaction progressed toward the center of the microfibrils, slowly destroying the integrity of the material. As outlined in Scheme 1, the periodate oxidation induces a glucosyl ring opening reaction that leads to the formation of two aldehyde groups at the

C2 and C3 position. In the resulting dialdehyde cellulose (DAC), the carbonyl moieties were found to be very reactive, leading to a fast recombination with adjacent unreacted OH groups to form intra-chain hemiacetal with 5 to 8-member fused rings. With individualized and isolated cellulose microfibrils, the hemiacetal groups, which are known to bear a substantial lability, are likely to reorganize into intra-microfibrillar bonds, but in aggregated cellulose systems, inter-particle cross-linking is probable, leading to cohesive ACC products with expected strong mechanical properties and low ductility. Thus, even if the diversity of the hemiacetals in DAC makes the structural analysis of this product difficult [26], their cross-linking capability could be turned into an advantage for the processing of thermosetting ACCs.

The sketch in Scheme 2 presents our strategy for preparing the thermosetting ACCs. We have selected microcrystalline cellulose (MCC), which consists of 50 μm particles [27] (symbolized by the two parallelepipeds) made of numerous agglomerated nanocrystals (symbolized by the blue (in web version) slender rectangles). The size of each nanocrystal is about 5 nm in width and 100 nm in length [28]. As depicted in Scheme 2, the MCC particles were first subjected to different degrees of oxidation (DO) by controlled action of sodium metaperiodate. Oxidation progressively leads to amorphous oxidized matrix at the surface (symbolized by the red waves), while the core of nanocrystals (blue (in web version)) remains untouched. To obtain the final ACCs, the oxidized MCC particles were then heated under compression molding to induce cross-linking. In these, the partly oxidized component is expected to act as an amorphous matrix (red (in web version)) while the non-oxidized inner core of the crystallites (blue (in web version)) could be considered as the reinforcement. The structure/property relationships of these ACCs were carefully examined. ^{13}C solid-state NMR spectroscopy data were collected on different processed samples in order to qualitatively and quantitatively highlight the ultrastructural evolution of crystalline cellulose as a function of the DO and the hemiacetals development. The thermal and mechanical properties of bulk samples were respectively investigated by thermogravimetric analysis and three-point



Scheme 2. Strategy for the processing of thermosetting ACCs after controlled periodate oxidation of MCC particle and hot-compression molding.



Scheme 1. The periodate oxidation induces a glucosyl ring opening reaction that leads to the formation of dialdehyde cellulose (DAC). The dialdehyde recombination with adjacent unreacted OH groups leads to the formation of hemiacetal linkages.

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