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Coupling onto surface carboxylated cellulose nanocrystals

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ABSTRACT

Non-flocculating aqueous suspensions of cellulose nanocrystals with different sizes were prepared by the combination of acid hydrolysis and surface TEMPO oxidative carboxylation of cotton linter and microfibrils of parenchyma cell cellulose (PCC). A decrease of the crystal size occurred and the introduction of negative charges at the interface of the crystalline domains induced a better individualization of the crystallites. These suspensions were further amidated by interaction with 4-amino TEMPO; a nitroxide radical containing a terminal amino group. The products were characterized by elemental analysis, conductimetry, solid-state ^{13}C NMR, FTIR and EPR spectroscopies, together with X-ray diffraction analysis and the coupling performance was deduced with a high correlation. The results indicated that the amidation was effective with yield roughly of 30%, the reaction yield being somewhat more important on samples from cotton origin. In all samples, the amidation was realized at the surface of the samples from carboxylated functions, which kept their intrinsic crystallinity, integrity and perfection throughout the preparation protocol. Their hydrophobic character was evaluated by observing their behavior in polar and non-polar solvents.

1. Introduction

With the current incentive to produce polymer-based materials from sustainable resources, the abundant and renewable cellulose stands out as choice candidate to fulfill this demand. Besides the classical uses of cellulose in the field of textile, paper and derivatives industries, new developments based on the advantageous utilization of the unique ultrastructural morphology of cellulose are pursued. Indeed at the sub micrometer level, all cellulose containing organisms display an assembly of microfibrils of few nanometers in width and many micrometers in length. In view of their ubiquity, it is commonly accepted that the microfibrils are the basic building blocks of all cellulose materials [1–4]. The occurrence of the microfibrils takes its origin in the mode of cellulose biosynthesis, whereby enzymatic spinnerets, commonly called terminal complexes, extrude slender microfibrils of uniform diameter, that result from the continuous biopolymerization, spinning and crystallization of nearly endless cellulose molecules [2]. The perfection of this enzymatic machinery is such that within any given cellulose microfibrils, the chains are fully extended, and there is only a limited number of defects along the microfibrillar length [5,6]. After an acid treatment, the microfibrils become cut longitudinally at their defects, with the result of shorter elements: the cellulose nanocrystals [1]. These nanocrystals have the same diameter as the initial microfibril, but lengths ranging from tenth of nanometer for samples from wood or cotton origin to several micrometers for tunicin or Valonia cellulose. It is generally accepted that these nanocrystals consist of fully extended cellulose chain segments well organized in perfect crystalline arrangement. Typically, these nanocrystals sometimes named “cellulose whiskers”, display mechanical properties that approach the theoretical value of perfect cellulose crystal, with a modulus close to 150 GPa and strength of the order of 10 GPa [7–9]. These high values, together with the abundance and renewability of cellulose has been attracting a great interest for their incorporation as reinforcing agents in bio-based composites and nanocomposites [10].

It is as early as 1991 that in a first report, it was observed that a substantial reinforcement effect was obtained by impregnating tunicin – animal cellulose – nanocrystals mats with water-soluble thermosetting resins [11]. Following this early results, it was further revealed that an adequate mixing of small amounts of non-flocculated aqueous suspensions of cellulose nanocrystals with aqueous solutions or suspensions of polymers, followed by drying of the mixture could lead to a drastic increase in the physical properties of the resulting nanocomposites [12]. This effect was particularly spectacular above the Tg of the polymer matrix, as it was shown that the reinforcing effect could be maintained until the softening

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temperature of cellulose [13]. A major drawback of these results is that in order to get homogenous dispersions of the cellulose elements within the nanocomposites, the reinforcing nanocrystals need to be initially surface sulfated or carboxylated in order to be handled as non-flocculated aqueous suspensions [13,14]. In most apolar organic solvents, these suspensions invariably flocculate and are therefore not suited to be homogenously dispersed in the solutions of most commodity polymers. To circumvent this hurdle many studies have been devoted to modify the skin of the cellulose nanocrystals in order to render them hydrophobic, without affecting the integrity of their cores and thus keeping the initial mechanical properties of the corresponding nanocrystals. After modifications these hydrophobic nanocrystals become dispersible, without flocculation in apolar solvents and can thus be homogenously incorporated in most polymers. For this, typical modifications range from the selective adsorption of surfactant [15] to the chemical derivatization of cellulose surface hydroxyl groups [16,17].

This work was undertaken in this context. We have taken advantage of the possibility to convert the surface hydroxymethyl groups of cellulose nanocrystals into carboxyl groups, following the classical TEMPO-mediated oxidation reaction [18–20]. It was shown that these surface carboxylated nanocrystals could be further modified by an amidation coupling with a series of amines using water-soluble carbodiimide, thus giving the possibility to modify the hydrophilic/hydrophobic surface property of the cellulose nanocrystals, using amines presenting hydrophilic or hydrophobic moieties. So far, only few reports have described the details of such coupling [20–22]. Here, we have followed such amidation reaction on nanocrystals from cotton linters and from sugar beet pulp cellulose, by using 4-amino TEMPO as a probe [22]. The quantification of the coupling reaction was achieved by a using a series of spectroscopic analyses as well as other analytical tools. In particular, the nitroxide moiety of the probe was found very valuable to quantify the coupling reaction accurately and unambiguously by analyzing the electron paramagnetic resonance spectroscopy data from the modified samples.

2. Experimental section

2.1. Materials

2.1.1. Chemicals

TEMPO, 4-amino TEMPO, sodium bromide and sodium hypochlorite were purchased from Aldrich whereas N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were obtained from Sigma.

2.1.2. Cellulose

Two cellulose samples were used in this work, (i) a batch of cotton linters from Tubize Plastics, Rhodia (Belgium), which was used as received and (ii) a sample of dried parenchyma cell cellulose (PCC) from sugar beet pulp (SBP) from General Sucrière Saint Louis Sucre (Nassandres, France). This last sample was desincrusted according to the procedure of Dinand et al. [23] and dispersed in water with a Waring Blender operated at full speed for 5 min at a concentration between 1% and 2% (w/v). The slurry which had reached a temperature of 60 °C was immediately further treated in a laboratory scale Manton–Gaulin homogenizer 15MR-8TBA, from APV Gaulin Inc., Wilmington, Mass. Fifteen passes were applied using a pressure of 500 bar and keeping the temperature below 95 °C to avoid cavitation. The resulting creamy suspension did not flocculate as it was stabilized by the presence of charged glucuronic and galacturonic acid residues at the microfibril surfaces, as already published [24,25]. The suspension was either freeze-dried or kept at 3–4 °C for further use.

2.1.3. HCl hydrolysis

20 g of cotton linters or 16 g (based on dry weight) of dispersed PCC from SBP were hydrolyzed with 1 L of 2.5 M HCl at 100 °C for 20 min to yield suspensions of cellulose nanocrystals, which were filtered and washed with water until neutral pH. The weight loss resulting from the hydrolysis step was around 10% for cotton linters and 20–25% for PCC from SBP. For both samples, this product loss corresponded to the hydrolysis of the cellulose amorphous zones, as already transcribed in the literature, in particular by Araki et al. [20] and Montanari et al. [26]. In addition, for PCC from SBP, the additional product loss was due to the removal of the residual hemicellulose and pectic polysaccharides located at the surface of the microfibrils [24,25]. In the text, these samples are named cellulose nanocrystals indexed to their cellulose origin.

2.1.4. TEMPO-mediated oxidation

Oxidation experiments, schematized in Fig. 1, were carried out as previously published [27,28] with minor modifications [22].

In a typical run, cellulose samples (1.95 g, 12 mmol anhydro glycosyl units or AGU) were dispersed in distilled water (180 mL) for 3 min with a high speed T25 basic Ultra-Turax homogenizer (Ika-Labortechnik, Staufen, Germany). 90 mL of water, which was used to wash the homogenizer, was then added to the suspension. TEMPO (30 mg, 0.19 mmol), NaBr (0.63 g, 6.1 mmol) and NaOCl (1.76 M solution, 1.5 mL, 2.64 mmol) was stirred in 20 mL of water until complete dissolution. This solution was then added to the cellulose

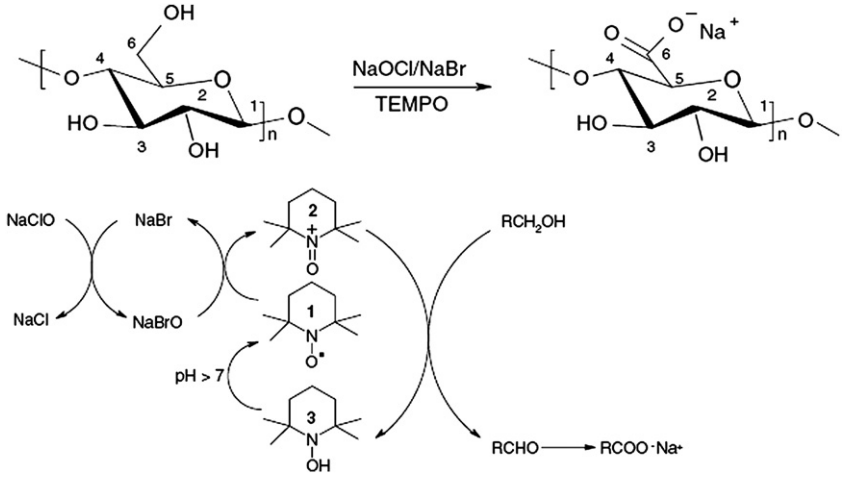

Fig. 1. Oxidation scheme of cellulose with TEMPO mediation [28].