Short Communication

Sleeving nanocelluloses by admicellar polymerization ☆

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ABSTRACT

This investigation reports the first application of admicellar polymerization to cellulose nanofibers in the form of bacterial cellulose, microfibrillated cellulose, and cellulose nanowhiskers using styrene and ethyl acrylate. The success of this physical sleeving was assessed by SEM, FTIR, and contact angle measurements, providing an original and simple approach to the modification of cellulose nanofibers in their pristine aqueous environment.

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1. Introduction

The most radical advances in cellulose-based materials in the last couple of decades are undoubtedly related to the preparation and exploitation of nanosized objects from both vegetable fibers and bacteria [1,2]. These highly crystalline fibrillar assemblies of macromolecules constitute the minutest forms of cellulose above its individual macromolecules, with thicknesses as small as a few nanometers and lengths ranging from 100 nm to continuous filaments in the shape of a physical network and include bacterial cellulose (BC) [3], microfibrillated cellulose (MFC) gels [4], and cellulose nanocrystals (NC) [5,6].

All cellulose-based composites with nonpolar macromolecular matrices encounter the classical problems of low interfacial compatibility (high interface tension) associated with the high polar character of the fibers, as well as of loss of mechanical properties after moisture uptake promoted by their well-known hydrophilicity. In order to reduce the hydrophilic character of cellulose fibers and improve the quality of their adhesion to the matrix, it is necessary to undertake a structural modification of their surface [7,8]. With nanocelluloses, however, the problem is more critical, because if they are dried, the cohesiveness of their ensuing assemblies makes it very hard to redisperse them. It follows that they should be kept in a liquid medium, preferably in an aqueous

suspension, in order to insure a good dispersion of their units within the matrix. Some chemical modifications of the surface of nanofibers have been reported, such as esterification with aliphatic carboxylic moieties [9–11] and grafting with an aliphatic isocyanate [12], poly(ε-caprolactone) [13], or poly(lactic acid) [14], but these processes are experimentally cumbersome, requiring transfer of the aqueous suspensions to organic solvents and sometimes the use of concentrated acids. The problem of their surface treatment remains therefore open to more straightforward approaches. This investigation calls upon a radically different strategy, which allows nanocelluloses to be kept in their pristine aqueous suspension, while their surface modification is attained by a physical deposition of a polymer generated in situ. This process, known as admicellar polymerization, was only previously applied to ordinary cellulose fibers, resulting in the formation of a thin polymer sleeve around them [15–18], and its extension to nanocelluloses is described for the first time in this communication.

2. Experimental

Commercial samples of hexadecylpyridinium chloride monohydrate (CTP), styrene (St), and all the other reagents and solvents were used as received, whereas the inhibitor present in ethyl acrylate (EA) was removed by standard alkali treatment. Bleached Eucalyptus cellulose pulp was kindly supplied by Suzano Papel e Celulose S.A, Bahia, Brazil, and the sugarcane bagasse provided by the Brazilian Bioethanol Science and Technology Laboratory.

The three types of nanocelluloses were prepared following conventional procedures: MFC (surface area $\sim$800 m^2/g) from the Eucalyptus pulp [4], NC (surface area $\sim$1300 m^2/g) from bagasse

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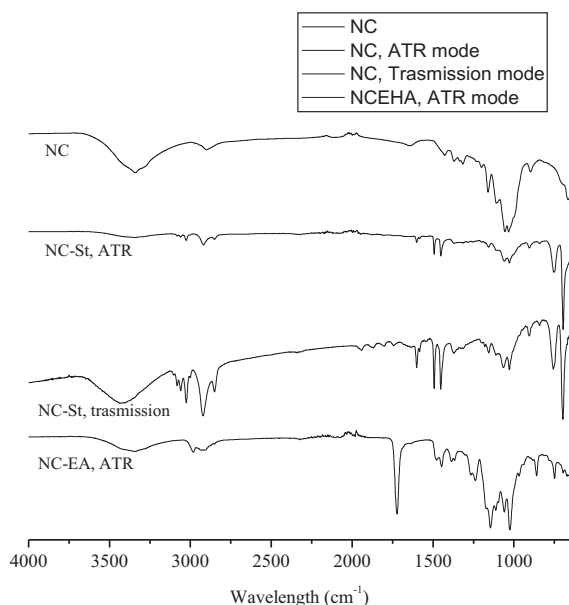E-mail address: agandini@iqsc.usp.br (A. Gandini).

Fig. 1. FTIR spectrum of NC, NC-St, and NC-EA.

[5], using concentrated sulfuric acid, and BC from *G. xylinus* fed with a standard culture medium [19] (surface area ∼400 m^2/g).

The aqueous dispersions of the nanofibers (BC 1 wt.%; MFC 0.45 wt.%, and NC 0.09 wt.%) in 0.6 mM CTP were equilibrated for 24 h under magnetic stirring to allow the surfactant to equilibrate its adsorption at the surface of the fibers. The hydrophobic monomer (3% v/v with respect to the aqueous medium for both St and EA) was then added, and the system maintained under magnetic stirring for 48 h at room temperature in order to promote its adsolubilization within the adsorbed surfactant bilayer. Ammonium persulfate (1% w/w with respect to the added monomer) and sodium metabisulfite (half of the molar amount of the initiator) were then added, the temperature increased to 80 °C, and the polymerization allowed to proceed for 2 h. After cooling to room temperature, the suspensions were centrifuged at 7000 rpm for 10 min, and the decanted solid washed and centrifuged first with a water/ethanol 70/30 v/v mixture and then several times with distilled water to remove all the surfactant, as monitored by UV spectroscopy. The samples were then dried to form thin films. The ensuing polymer-decorated nanofibers were labeled BC-St, BC-EA, MFC-St, MFC-EA, NC-St, and NC-EA, respectively.

3. Results and discussion

The success of these admicellar polymerizations at the surface of the different nanocelluloses was first assessed by FTIR spectroscopy, based on the appearance of the characteristic bands of each polymer superposed to the bands of the cellulose substrates (mainly the OH peak near 3500 cm^{-1} and the C—O one around 1100 cm^{-1}), namely the double peak at ∼700 and ∼750 cm^{-1} for the monosubstituted benzene ring in poly(styrene) and the band at ∼1730 cm^{-1} for the ester carbonyl group of poly(ethyl acrylate), as shown in Fig. 1.

Figs. 2–4 compare the typical SEM morphologies of MCF, BC, and NC, respectively, before and after the admicellar polymerization of St onto their respective surfaces. Fig. 4 also shows a typical TEM image of the pristine dispersed NCs, since clear SEM images could only be obtained for their compact forms. In all samples, polymer thicknesses approaching 10 nm were assessed on the basis of the SEM images.

Finally, static water contact angles increased appreciably with all modified samples, albeit by different amounts, as a function of the process conditions, the generated polymer, and the substrate. Typically, the untreated nanocelluloses films gave angles of ∼20° (MFC), ∼40° (BC), and ∼25° (NC), which decreased very rapidly to 0°. The modified films exhibited values ranging between
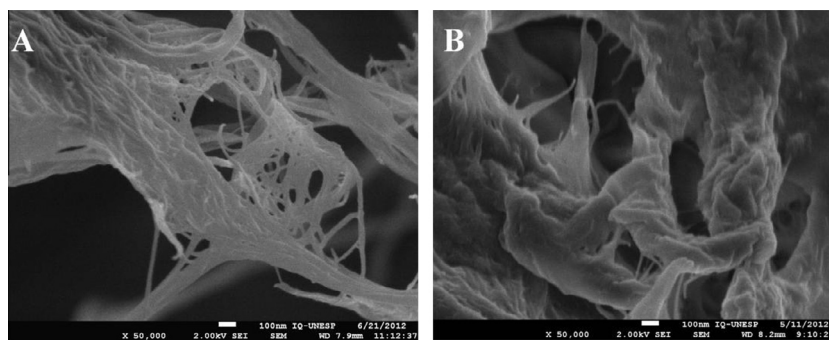

Fig. 2. SEM micrograph of MFC before (A) and after (B) the admicellar polymerization of styrene.
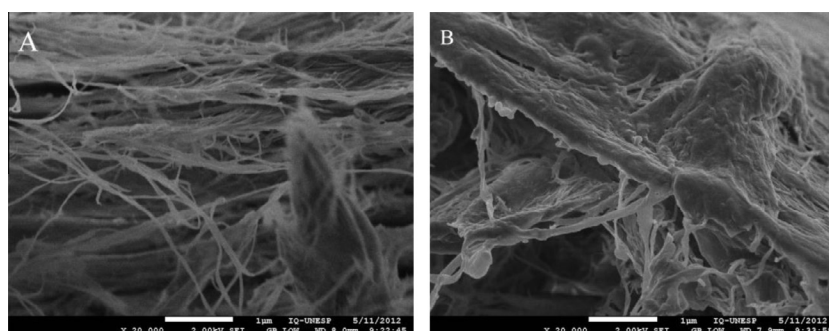

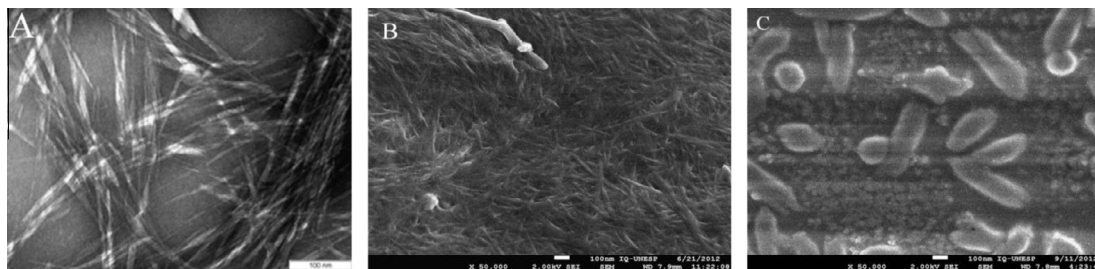**Fig. 3.** SEM micrograph of BC before (A) and after (B) the admicellar polymerization of styrene.

Fig. 4. TEM and SEM micrographs of NC before (A and B) and after (C) the admicellar polymerization of styrene.

50° and 70°, which were moreover much more stable with time, indicating the expected increase in hydrophobic character.

4. Conclusions

This preliminary study provided a clear-cut indication of the viability of the novel strategy for modifying the surface polarity of nanocelluloses. Work is in progress to optimize the process and broaden its scope in terms of the use of other monomers, together with the preparation of composite materials incorporating the sleeved nanofibers, using an aqueous process, e.g., with acrylic emulsions or natural rubber.

Acknowledgments

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