Tailoring the properties of nanocellulose-sepiolite hybrid nanopapers by varying the nanocellulose type and clay content

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Abstract The development of nanocellulose-clay materials resulted of great relevance, as it opened up the applications of nanocellulose, but it still requires new approaches that could contribute to improve the preparation procedures and the features of this type of biohybrid materials. In this context, nanocellulose-sepiolite (NC-S) biocomposite foams and films have already been successfully tested for some applications. However, the influence of the nanocellulose properties on sepiolite-cellulose interactions, and consequently on the final properties and potential applications of NC-S biohybrid materials, has not been previously studied. To address this knowledge gap, four kinds of nanocelluloses produced from elm biomass (non-chemically pretreated lignocellulose and bleached cellulose nanofibers (LCNFs and CNFs, respectively), TEMPO-oxidized cellulose nanofibers (TOCNFs) and cellulose nanocrystals (CNCs)) were characterized and used to develop NC-S nanopapers. A stronger interaction was found between sepiolite and negatively charged nanocelluloses (TOCNFs and CNCs), improving their thermal stability and mechanical properties by increasing the sepiolite content. Furthermore, the type of nanocellulose and the sepiolite content could be adjusted to tune the flammability, water permeability and mechanical and optical properties of the NC-S nanopapers.
Graphical abstract

Keywords Lignocellulose nanofibers · Cellulose nanofibers · TEMPO-oxidized nanofibers · Cellulose nanocrystals · Sepiolite · Clays

Introduction

The interest in developing new processes capable of supplying energy, chemicals and materials from biomass has grown considerably in the last decades, with the aim of contributing to a bioeconomy based on biomass instead of fossil fuels. In this context, the development of new biohybrid materials based on nanocellulose, obtained from lignocellulosic biomass, and natural clays could be of great importance. The special interest of these hybrid materials is due to their expected improved thermal, mechanical, optical and physicochemical properties compared to pure nanocellulose, in accordance to that previously observed with other biopolymers, generating a large family of clay-based bionanocomposite materials (Darder et al. 2007; Chivrac et al. 2010; Aulin et al. 2012; Sárossy et al. 2012; Ruiz-Hitzky et al. 2013; Liu and Berglund 2013; Alcántara et al. 2016; Zheng et al. 2019; Cheikh et al. 2020). Several studies have already proved the outstanding properties of nanocellulose-clay biohybrids conformed as foams and films, claiming also a reduction in the cost of production by reducing the amount of required nanocellulose (Alves et al. 2018a; Zheng et al. 2019; Wang et al. 2019; Qin et al. 2019). On the contrary, fewer studies involve the incorporation of fibrous clays, such as sepiolite and palygorskite, instead of layered clays (Wicklein et al. 2015; Ghanadpour et al. 2018b; González del Campo et al. 2018, 2020; Gupta et al. 2019; Lisuzzo et al. 2020; Köklükaya et al. 2020; Sanguanwong et al. 2021).

Sepiolite is a natural hydrated magnesium silicate with a microcrystalline structure consisting of alternation of talc-like ribbons and cavities (tunnels) arranged parallel to the fiber direction (Fig. 1) (Brittle 1959; Ruiz-Hitzky 2001). Its microporosity and high aspect ratio (length of 1–5 μm and diameter of 50–100 nm for sepiolite from deposits in Spain) give rise to an elevated specific surface area (ca. 300 m² g⁻¹) and singular adsorption and rheological properties of paramount importance for many applications (Ruiz-Hitzky 2001; Ruiz-Hitzky et al. 2021). This fibrous clay presents non-accessible Mg-OH groups inside the structural blocks and silanol (Si-OH) groups on the external surface of the silicate. The latter could lead to the assembly to different kinds of biopolymers as well as nanoparticles that provide functional nanoarchitectures based on sepiolite, opening up a wide range of possible applications (Ruiz-Hitzky et al. 2011, 2013; Aranda and Ruiz-Hitzky 2018).

Sepiolite has recently been combined with nanocellulose giving rise to hybrid materials including highly flame-resistant and thermally insulating foams...
Thus, the performance of the biohybrid materials is largely dependent on the surface properties and the morphology of both components, i.e. the matrix (nanocellulose) and the filler (sepiolite) (González del Campo et al. 2018; Alves et al. 2019). Therefore, it is expected that the performance and final properties of the resulting nanocellulose-sepiolite biohybrids will depend not only on the surface properties of the clay component but also on the nature of the involved nanocellulose, mainly regarding its surface characteristics, such as charge and presence of functional groups, as well as its morphology, i.e. length and diameter dimensions.
Based on morphology, nanocellulose obtained from lignocellulosic biomass can be divided into two main groups: cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) (Jonoobi et al. 2015). The first one consists of needle-shaped or rod-like nanoparticles with diameter of 3–35 nm and length of 200–500 nm (Nechyporchuk et al. 2016). CNCs show highly crystalline nature, since they are produced by degrading amorphous regions of the cellulose fibers normally by acid hydrolysis with H$_2$SO$_4$ or HCl. When H$_2$SO$_4$ is used, sulfate groups (−OSO$_3^-$) are introduced on the surface of the nanocrystals improving their colloidal stability in water, but also reducing their thermal stability (Trache et al. 2017). On the other hand, cellulose nanofibers present higher aspect ratio, with diameters of 5–50 nm and length up to few micrometers, containing both amorphous and crystalline domains (Nechyporchuk et al. 2016). For their production, cellulose fibers are subjected to a high-shear mechanical treatment causing extensive fibrillation. This process is normally performed in a microfluidizer, a high-pressure homogenizer or a supermasscolloider friction grinder (Jonoobi et al. 2015; Nechyporchuk et al. 2016). To improve the performance of the mechanical treatment and reduce the energy consumption, a mechanical (refining), chemical (sulfonation, carboxymethylation, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation, etc.) or enzymatic (using endoglucanases) pretreatment can be carried out (Jonoobi et al. 2015; Nechyporchuk et al. 2016). Both the pretreatment and the high-shear mechanical process contribute to control the final properties of the resulting cellulose nanofibers. Furthermore, the composition and properties of the starting cellulose pulp also strongly influence the morphology and characteristics of the cellulose nanofibrils (Lavoine et al. 2012; Jonoobi et al. 2015). Thus, although bleached pulp is normally used, cellulose nanofibers have been successfully produced also from unbleached pulp observing both different behavior during microfibrillation and different final properties of the resulting lignocellulose nanofibers (LCNFs) (Rojo et al. 2015; Solala et al. 2020; Jiménez-López et al. 2020).

Taking into account the many differences that exist between the various types of nanocellulose (especially the surface properties and morphology), their interaction with sepiolite in the production of biohybrids is expected to be different. Several types of nanocellulose have been already used in the development of nanocellulose-sepiolite (NC-S) hybrids: phosphorylated nanofibers (Ghanadpour et al. 2018b), TEMPO-mediated oxidized nanofibers (Wicklein et al. 2015; González del Campo et al. 2018; Lisuzzo et al. 2020; Sanguanwong et al. 2021), non-chemically pretreated nanofibers (Gupta et al. 2019) and nanocellulose derived from microcrystalline cellulose by ultrasound irradiation (González del Campo et al. 2020). However, a comparison between results from these studies is very difficult because they refer to different raw materials and different procedures applied to produce the diverse NC-S biohybrid materials. Therefore, the main objective of this paper is to provide data to facilitate the comparative study of the interaction between sepiolite and different types of nanocellulose by using the same raw material and the same NC-S hybrid production process. In this way, cellulose-sepiolite interactions would be better understood contributing to the development of new approaches in the NC-S hybrid production which will improve their final properties. To this end, four types of nanocellulose produced from elm biomass, i.e. lignocellulose nanofibers (LCNFs) and bleached cellulose nanofibers (CNFs) both without chemical treatment, TEMPO-oxidized cellulose nanofibers (TOCNFs) and cellulose nanocrystals (CNCs), have been selected for the assembly with sepiolite nanofibers. After full characterization, their interaction mechanisms and the final properties of the obtained NC-S hybrid nanopapers have been investigated.

Materials and methods

Raw materials and chemicals

Elm pulps used in the production of nanocellulose were obtained at the Forest Research Centre (INIA, CSIC) from an Ulmus minor clone tolerant to Dutch elm disease, provided by the Spanish elm breeding program (agreement between the Polytechnic University of Madrid and the Spanish Environmental Administration). Unbleached pulp was obtained after kraft pulping (active alkali: 16 %, sulfidity: 21 %, liquid-to-wood ratio: 6 Lkg$^{-1}$, 90 min at maximum temperature: 165 ºC) and presented a chemical composition of 1.3 % ethanol extractives, 2.5 % total
lignin, 75.4 % cellulose and 18.4 % hemicelluloses. Unbleached pulp was further subjected to oxygen delignification (98 °C, 60 min, 0.6 MPa of oxygen pressure, 1.5 % NaOH over dry pulp (o.d.p.), 0.5 % MgSO₄ o.d.p. and 10 % (w/v) consistency) and total chlorine free (TCF) bleaching with hydrogen peroxide (two stages at 3 % H₂O₂ o.d.p., 2 % NaOH o.d.p., 0.1 % MgSO₄ o.d.p., 10 % (w/v) consistency; the first step at 105 °C during 140 min and the second one at 98 °C during 180 min). The chemical composition of resulting bleached pulp was: 0.9 % ethanol extractive, 1.4 % total lignin, 73.2 % cellulose and 16.1 % hemicelluloses. More complete information about this raw material and pulping and bleaching processes can be found in Jiménez-López et al. (2020).

Sepiolite (S) from Vicálvaro-Vallecas deposits (Madrid, Spain) was provided by TOLSA, S.A. This sepiolite, with a > 95 % purity, is a rheological degree product commercialized as Pangel S9.

2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) and other chemicals used in this work were reagent-grade and obtained from Merck (Barcelona, Spain). Ultrapure water (resistivity of 18.2 MΩ cm) was obtained with a Maxima Ultrapure Water from Elga.

Production of cellulose nanofibers and nanocrystals

Four different types of nanocellulose were used in this work, including lignocellulose nanofibers (LCNFs), cellulose nanofibers (CNFs), TEMPO-oxidized cellulose nanofibers (TOCNFs) and cellulose nanocrystals (CNCs). LCNFs and CNFs were obtained from unbleached and bleached elm pulp, respectively, after PFI refining pretreatment and 13 passes through a high-pressure microfluidizer (Microfluidizer M-110EH, Microfluidics Corp.). TOCNFs were produced from bleached elm pulp by chemical pretreatment (TEMPO-mediated oxidation with 10 mmol NaClO, 0.016 g TEMPO and 0.1 g NaBr per gram of dry pulp, at pH 10, room temperature and 1 % (w/v) pulp consistency), applying in this case a total of 4 passes through the microfluidizer. More details about nanofibrils production can be found in Jiménez-López et al. (2020). CNCs were produced from bleached elm pulp by acid-hydrolysis with 65 % (w/w) sulfuric acid at 55 °C and 7.5 % (w/v) pulp consistency for 45 min under continuous stirring. After several washing processes with deionized water and centrifugations (12,000 rpm, 15 min), the resulting suspension was dialyzed against deionized water for two weeks (Bondeson et al. 2006; Hoeger et al. 2011).

When cellulose nanofibers were produced without any chemical pre-treatment, a mixture between nanofibers and microfibers was obtained. Thus, nanofibrillation yield of produced elm nanofibers were 50.2 ± 2.4 %, 60.8 ± 2.5 % and 100.0 ± 0.0 % for LCNFs, CNFs and TOCNFs, respectively (Jiménez-López et al. 2020). To avoid a big difference in fiber sizes between samples and their effect on the characteristics of cellulose-sepiolite hybrid nanopapers, only cellulose particles at nanometric scale (nanofibers or nanocrystals) were used. To this end, all the cellulose samples were diluted to 0.2 % (w/v) and sonicated applying a total energy of 10 kJ (on/off pulses of 10 s to avoid overheating of the sample) at an amplitude of 50 % of the total capacity of the equipment (Vibra Cell VC 750: 750 W, 20 Hz). A titanium sonication probe with a diameter of 13 mm was used in the ultrasonic processor. After sonication, samples were centrifuged at 4500 rpm during 20 min, in order to remove the non-fibrillated and partially fibrillated particles in the pellet fraction (Besbes et al. 2011). For TOCNFs and CNCs no pellet fractions were obtained after centrifugation, as expected.

Characterization of nanocellulose

Lignin and carbohydrate contents of the different types of nanocellulose were determined based on NREL/TP-510-42618: Laboratory Analytical Procedures for determination of structural carbohydrates and lignin in biomass (NREL 2011). For carbohydrate analysis, a 1260 HPLC (Agilent Technologies) with a refractive index detector was employed using an Agilent Hi-PlexH column and running at 65 °C with 0.6 mL min⁻¹ of 5 mM sulfuric acid as mobile phase.

Carboxylate contents of the different cellulose nanofiber samples were determined by the conductivity titration method (Saito and Isogai 2004), using a platinum conductivity cell 50–70 and a GLP 31 conductivity meter from Crison.

Zeta potential measurements in a NanoBrook 90Plus PALS (Brookhaven Instruments, USA) were
performed in 0.025% (w/v) nanofiber suspensions to study their colloidal stability.

The morphology of the different types of nanocelluloses was determined by atomic force microscopy (AFM) using a Cervantes instrument (Nanotec Electrónica S.L., Spain) equipped with Nanosensors PPP-FMR cantilevers (2.8 N/m spring constant and 75 kHz resonance frequency). Modulated amplitude mode under ambient conditions was used to obtain the images. From the different AFM images of each sample, 50 measurements of the fibril height and length were taken into account to determine the diameter and length distribution.

Preparation of nanocellulose-sepiolite hybrid nanopapers

Nanocellulose-sepiolite hybrid (NC-S) nanopapers were prepared from 0.2 % (w/v) nanocellulose suspensions (after sonication and centrifugation, as mentioned above) and 0.2 % (w/v) sepiolite suspension. This sepiolite suspension was sonicated at the same conditions than cellulose suspensions (10 s on/off pulses and 50 % amplitude) but applying a total energy of 1 kJ instead of 10 kJ. For each nanocellulose type, mixtures of nanocellulose and sepiolite were prepared at 0, 5, 10 and 20 % (w/w) of sepiolite (referred to nanocellulose), and mixed in an Ultra-Turrax homogenizer (IKA T25) at 10,000 rpm for 5 min. Then, the mixture was sonicated applying a total energy of 2 kJ (10 s on/off pulses and 50 % amplitude) to achieve an appropriate homogeneous assembly between the organic and the inorganic particles (González del Campo et al. 2018). Finally, NC-S nanopapers were prepared by casting method using a Climacell EVO model 111 L stability chamber at 30 ºC and 50 % relative humidity (RH), resulting in films with thickness of ±1 μm (measured using a thickness gauge Mitutoyo NO.2118–50 Dial Indicator 0.001–5 mm). NC-S nanopapers were labeled as X-YS, where X indicates the type of nanocellulose used (LCNF, CNF, TOCNF or CNC) and Y represents the mass percentage of sepiolite related to total mass (0, 5, 10 or 20 %).

Characterization of the nanocellulose-sepiolite hybrid nanopapers

FTIR spectra of the different NC-S hybrids were directly registered on the nanopapers in the 4000–400 cm⁻¹ spectral range using a Bruker iFS 66VS spectrophotometer with a resolution of 2 cm⁻¹ and accumulation of 400 scans. X-ray diffraction (XRD) analysis of NC-S nanopapers was performed using a Bruker D8 Advance diffractometer (Bruker, USA) with CuKα radiation (Cu anode) and Ni filter. Measurements were carried out from 3º to 45º (2θ) with a step size of 0.04 and a goniometer speed of 1 s per step. Crystallinity indexes (CrI) of the different types of nanocelluloses were determined from X-ray diffractograms of NC-S nanopapers with 0% sepiolite using the Segal method (Eq. 1), after background subtraction:

\[
\text{CrI} = \frac{I_{200} - I_{AM}}{I_{200}} \cdot 100
\]

where \(I_{200}\) is the intensity of the crystalline (200)-peak and \(I_{AM}\) is the intensity of the amorphous phase (the minimum in the intensity near 2θ = 18.5º).

Hybrid nanopaper surfaces were characterized using field emission scanning electron microscopy (FE-SEM), using a FEI-NOVA NanoSEM 230 microscope equipped with an EDAX-Ametek detector. Samples were transferred into sticky carbon conductive tape and sputtered with Au for 30 s. Images were acquired with a low voltage high contrast detector (vCD) and an accelerating voltage of 4.45–4.70 keV.

Thermogravimetric analysis (TGA) was carried out to study the thermal behavior of the NC-S hybrids using a SDT-Q600 thermogravimetric analyzer (TA Instrument). Measurements were performed at a heating rate of 10 ºC min⁻¹ from room temperature to 900 ºC and under N2 atmosphere (100 mL min⁻¹). Degradation temperatures were calculated as the temperature at which the maximum degradation rate was observed for each degradation step. Char residue (CR) can be used to estimate the limiting oxygen index (LOI) of halogen-free polymers, according to van Krevelen (1975) (Eq. 2).

\[
\text{LOI} = 17.5 + 0.4\text{CR}
\]
where LOI is expressed in %, and CR is the char residue in wt% at 850 °C.

Water vapor permeability and sorption isotherms

Water vapor transmission rate (WVTR) and water vapor permeability (WVP) were determined gravimetrically following the desiccant method (ASTM E96 standard). Test cells were filled with dry silica-gel and sealed after mounting the NC-S nanopapers in the test cells using aluminum foil masks, with an inner diameter of 1 cm. Then, test cells were introduced in a humidity chamber at 75 % RH and room temperature and they were weighed each 24 h during a minimum of 4 days. Experiments were performed by triplicate for each hybrid nanopaper. WVTR were calculated dividing the slopes of the weight gain versus time curves, by the film area. WVP was calculated taking into account the thicknesses of each hybrid nanopaper according to the Eq. 3:

$$WVP = \frac{(WVTR \cdot L)}{\Delta P}$$

where L is the thickness of the nanopaper (mm); and ΔP is the partial water vapor pressure difference across both sides of the film (kPa). Tukey’s multiple comparison test (α=0.05) was used to determine differences between the various mean’s samples.

A dynamic water vapor sorption equipment (Aquadyne DVS, Quantachrome Instruments) was used to measure the water vapor sorption isotherms of the different hybrid nanopapers. Around 10 mg of NC-S nanopapers were purged at 80 °C until constant weight, and then mass changes due to water adsorption or desorption at 25 °C from 0 to 95 % RH were recorded.

Mechanical properties

A Model 3345 Instron Universal Testing Machine (Instron Engineering Corporation Canton, MA, USA) was used to determine mechanical tensile properties of hybrid nanopapers. NC-S nanopapers were cut into 60×10 mm test pieces. Initial grips separation was fixed to 30 mm and tensile test was carried out at a crosshead speed of 1 mm min⁻¹. A minimum of 4 measurements were performed for each sample of nanopaper. Tensile strength (MPa), Young’s modulus (GPa) and elongation at break (%) were calculated from stress-strain curves. Furthermore, tensile index (kN m kg⁻¹) and specific Young’s modulus (MN m kg⁻¹) were determined considering the apparent density of each hybrid nanopaper. Tukey’s multiple comparison test (α=0.05) was used to determine differences between the various mean’s samples of each mechanical property.

Optical transmittance and transmission haze

Optical transmittance and transmission haze of NC-S nanopapers were studied using a UV-1201 spectrophotometer, equipped with an integrating sphere (Shimadzu). Films samples were studied between 200 and 900 nm.

Opacity was calculated from absorbance at 550 nm ($A_{550}$, a.u.) and film thickness ($L$, mm), according to the following equation (Cheikh et al. 2020):

$$Opacity = \frac{A_{550}}{L}$$

### Table 1 Characteristics of nanocellulose samples: glucan, xylan and total lignin content (%), carboxylate group content (Carbox., µmol g⁻¹), zeta potential (Z-Pot, mV), crystallinity index (CrI, %) and dimensions (diameter: D, nm; and length: L, nm). LCNF: lignocellulose nanofiber sample, CNF: cellulose nanofiber sample, TOCNF: TEMPO-oxidized cellulose nanofiber sample and CNC: cellulose nanocrystal sample.

| Sample      | LCNF       | CNF        | TOCNF      | CNC         |
|-------------|------------|------------|------------|-------------|
| Glucan (%)  | 73.6 ± 1.3 | 77.6 ± 1.1 | 65.4 ± 0.2 | 81.1 ± 1.2  |
| Xylan (%)   | 22.8 ± 0.7 | 20.7 ± 0.4 | 10.5 ± 0.1 | 17.4 ± 0.1  |
| Total lignin (%)| 2.9 ± 0.4 | 1.9 ± 0.3 | 1.2 ± 0.2 | 1.0 ± 0.2  |
| Carbox. (µmol g⁻¹)| 55 ± 4 | 52 ± 7 | 1165 ± 31 | 53 ± 7 |
| Z-Pot. (mV) | −10 ± 1 | −26 ± 2 | −70 ± 1 | −65 ± 1 |
| CrI (%)     | 74.3 ± 0.6 | 77.0 ± 0.5 | 77.9 ± 0.1 | 94.4 ± 1.3 |
| D (nm)      | 4.0 ± 0.9 | 5.8 ± 1.5 | 2.7 ± 0.7 | 4.5 ± 2.1 |
| L (nm)      | 595 ± 142 | 892 ± 373 | 642 ± 179 | 199 ± 86 |
Results and discussion

Characteristics of the different nanocellulose samples

As it is known, both pulp sources and nanocellulose production process determine the properties of the resulting nanocellulose samples (Jonoobi et al. 2015; Nechyporchuk et al. 2016). Hence, LCNF and CNF samples presented different properties since they were obtained through the same production process (i.e. by refining pretreatment followed by microfluidization), but using an unbleached or a bleached elm kraft pulp, respectively. The higher lignin and hemicellulose (xylan) contents of the unbleached pulp influence not only the carbohydrate-lignin content of the nanofibers but also their crystallinity and dimensions. Thus, crystallinity index was lower on LCNF sample, due to a higher presence of amorphous components (lignin and hemicelluloses) (Table 1). Moreover, both amorphous components have been reported to enhance the fibrillation process: hemicelluloses contribute to inhibit hornification and fibril coalescence (Jonoobi et al. 2015; Solala et al. 2020; Ibarra et al. 2021), and lignin antioxidant capacity stabilizes cellulosic mechano-radicals reducing crosslinking between cellulose chains (Solala et al. 2012, 2020; Rojo et al. 2015; Tyagi et al. 2021). In agreement with these statements, AFM analysis showed nanofibers with lower diameter in LCNF sample compared to CNF sample (Table 1, for more information about size distribution see Supporting Information, Fig. SI.1, SI.2 and SI.3), indicating more extensive fibrillation in LCNF sample.

As expected, when the same pulp (bleached elm pulp) was subjected to different nanocellulose production processes, significant differences in the resulting nanocellulose were observed. The replacement of the refining pretreatment by a TEMPO-mediated oxidation pretreatment significantly increases the carboxylate groups content (52 vs. 1165 µmol g⁻¹ for CNF and TOCNF samples, respectively) due to the selective oxidation of C6 primary hydroxyl groups on the crystalline fibril surfaces (Isogai et al. 2011). These negatively charged groups introduce electrostatic forces causing repulsion between adjacent fibrils that ease fibrillation (Isogai et al. 2011; Lavoine et al. 2012), resulting in a colloidal stable suspension of thinner and shorter nanofibers (Table 1) with a zeta potential of -70 mV (compared to -26 mV for CNF suspension). Moreover, only completely nanofibrillated fibrils were found in this sample (100 % nanofibrillation yield), in contrast to LCNF and CNF samples, in which partially fibrillated and non-fibrillated fibrils were also found (50.2–60.8 % nanofibrillation yield) (Jiménez-López et al. 2020). Nevertheless, it should be remembered that these micro-fibrils were removed by centrifugation (as indicated in Materials and Methods section) and only nanofibril fractions are considered in this work. TEMPO-mediated oxidation pretreatment also contributed to the removal of hemicelluloses and lignin due to NaClO action (Table 1), as other authors have already reported (Okita et al. 2009). Finally, no big differences in crystallinity index were observed, indicating no significant changes in cellulose I crystal structure during
this pretreatment (Saito and Isogai 2004; Isogai et al. 2011).

As supposed, the biggest differences were observed when comparing nanocrystals and nanofibrils. During nanocrystals production, the strong acid treatment caused the cleavage of glycosidic bonds within cellulose chains in the amorphous domains, breaking the hierarchical structure of the fibrils into rod-like nanoparticles. Thus, compared to CNFs, CNCs showed higher crystallinity index (94 % vs. 77 %) and shorter length (199 nm vs. 892 nm) but similar diameter (4.5 nm vs. 5.8 nm). This sample also presented higher cellulose content than nanofibrils samples (Table 1), likely due to the removal of other amorphous components (mainly hemicelluloses and residual lignin) during the acid treatment (Malucelli et al. 2017; Trache et al. 2017). The use of sulfuric acid introduces negatively charged sulfate ester groups on the surface of the nanocrystals (Trache et al. 2017), improving colloidal stability (zeta potential of -65 mV).

FTIR analysis of NC-S hybrid nanopapers

FTIR spectra of NC-S hybrid nanopapers showed the typical vibration bands for cellulose rings (C-O-C) at 1164, 1111, 1060 and 1040 cm⁻¹ (Castro-Guerrero and Gray 2014) in all of them (Fig. SI.4 in Supporting Information). Typical bands at 3340 and 2890 cm⁻¹, corresponding respectively to ν O−H and ν C−H stretching vibrations, were also observed in all samples. One of the main differences between the FTIR spectra, is attributed to the presence of -COONa in TOCNF samples, indicated by the bands at 1607 cm⁻¹ (assigned to ν C=O in -COONa groups) and at 1410 cm⁻¹ (assigned to νC−O symmetric stretching of dissociated carboxyl groups) (Fujisawa et al. 2011).
This corroborates the oxidation of C6 primary OH groups in TEMPO-mediated oxidation pretreatment. Both bands can be better visualized in Fig. 2a, which shows FTIR spectra of the four nanocellulose papers (without sepiolite) in the 1700 – 1180 cm⁻¹ region. The presence of sulfate groups on CNC samples can be confirmed by the bands at 1356 and 1204 cm⁻¹, which are associated with S=O vibrations (Gaspar et al. 2014; Dasan et al. 2015). Finally, LCNF spectra showed a shoulder around 1510 cm⁻¹ which could be assigned to the aromatic skeleton vibration in lignin (Eugenio et al. 2021).

FTIR analysis confirms the interaction between sepiolite and the different nanocellulose samples based on the observed spectral modifications. Figure 2b shows the νOH stretching vibrations range (3730 – 3660 cm⁻¹) in the sepiolite infrared spectra, where the typical ν−OH bands of both silanol (Si-OH) and hydroxyl groups bonded to magnesium atoms (Mg-OH) were observed at 3719 and 3680 cm⁻¹, respectively. The first band completely disappears in the spectra of all NC-S hybrid nanopapers (Fig. 2b and Fig. SI.4), according to the hydrogen bonding interactions between the surface Si-OH of sepiolite and the C-OH groups at the nanocellulose surface (González del Campo et al. 2020; Lisuzza et al. 2020). The νOH band ascribed to Mg-OH is still appreciated in the resulting NC-S nanopapers, due to the inaccessibility of the –OH groups bonded to magnesium atoms (Lisuzza et al. 2020). In addition, the infrared spectrum of sepiolite shows bands at 986 and 472 cm⁻¹, assigned to Si-O-Si siloxane bridges, and at 444 cm⁻¹, assigned to Si-O-Mg bonds in the silicate network (Özcan and Özcan 2005; Perraki and Orfanoudaki 2008), which remain present in sepiolite-containing hybrid nanopapers, being especially visualized when sepiolite content increased (Fig. SI.4). Indeed, these bands appear less intense due to the dilution effect in the nanocellulose matrix but they do not modify their frequencies as they are due to vibrations of groups of atoms that are not accessible to interaction with the polymer. Finally, the intensity of the 1036 cm⁻¹ band, assigned to C-O-C bridges in cellulose (Castro-Guerrero and Gray 2014), apparently increased when sepiolite content increased due to overlapping with the νSi−O stretching vibrations band of the clay at similar wavenumber (Perraki and Orfanoudaki 2008).

XRD analysis of NC-S hybrid nanopapers

X-ray diffraction (XRD) patterns of all the NC-S hybrid nanopapers showed the typical peaks at ~15.1 and ~22.6 2θ degrees corresponding to the (1̅10) and (200) reflections of the crystalline planes of the Iβ allomorph of cellulose (Fig. 3). A shoulder at ~16.4 2θ degrees can also be observed, especially

![Fig. 4 FE-SEM images of the upper surface of the NC-S hybrid nanopapers made with the different nanocellulose types (LCNFs, CNFs, TOCNFs and CNCs) without sepiolite (a–d) and with 5 % of sepiolite (e–h)](image-url)

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in CNC patterns (Fig. 3d), corresponding to (110) crystalline plane of $I_{β}$ cellulose. As mentioned above, crystallinity indexes were calculated from the diffractograms of pure nanocellulose observing higher crystallinity for CNC sample, as expected. The presence of sepiolite in the NC-S hybrids was clearly confirmed even at the lower sepiolite content (5 %) by typical peaks at 7.4, 8.8 and 26.8 2θ degrees assigned to (110), (002) and (080) reflections of crystal planes of this silicate (Tang et al. 2012; González del Campo et al. 2018; Lisuzzo et al. 2020) (Fig. 3) (X-ray diffractogram for pristine sepiolite film is shown in Fig. SI.5 in Supporting Information). A peak at 13.4 2θ degrees, corresponding to the (003) crystal plane reflection of sepiolite is also observed especially in the diffractograms of TOCNF-S and CNC-S hybrid nanopapers (Fig. 3c and d, respectively). The changes in the relative intensity of the sepiolite reflection peaks indicate changes in the orientation of sepiolite fibers on the nanopapers (González del Campo et al. 2018; Lisuzzo et al. 2020). Thus, the intensity ratio of both (110)/(080) and (110)/(003) reflections decreased from 6.4 and 17.0, respectively, in pristine sepiolite film, to 1.0-5.7 and 4.8–12.6, respectively, in NC-S nanopapers, being more severe the decrease when sepiolite content increased (except for CNF-20 S). These results suggested that sepiolite has partially lost its tendency to orientate in the film plane (González del Campo et al. 2018) induced by the interactions with nanocellulose.

Surface morphology of NC-S hybrids nanopapers

Figure 4 shows FE-SEM images of the upper surfaces of NC-S hybrid nanopapers without sepiolite (a-d) and with 5 % sepiolite content (e-h) at 30,000× magnification. When sepiolite is not present, thin and long nanofibers can be distinguished in the surface of LCNF and CNF nanopapers (Fig. 4a and b), which consisted in a very entangled network films. However, a flatter and more homogeneous surface is observed for TOCNF and CNC nanopapers (Fig. 4c and d). According to AFM, TOCNF sample presented thinner nanofibers compared to mechanically pretreated nanofibers, which can contribute to more compacted nanopapers. Similarly, short nanocrystals (compared to nanofibers) can also contribute to form a more compacted CNC film. Furthermore, the reduced size of the nanoparticles in TOCNF and CNC samples makes difficult to distinguish them in FE-SEM images at this magnitude. In addition, the negative charges on the surface of TOCNF and CNC contributed to more homogeneous and stable nanocellulose suspensions, resulting in more homogeneous films.

Table 2 Characteristic parameters of thermogravimetric analysis (TGA) for NC-S samples: degradation temperature ($T_{deg}$), temperatures at which degradation begins ($T_{on}$) and ends ($T_{off}$), char residue at 850 ºC (CR) and limiting oxygen index (LOI)

| Sample  | $T_{deg}$ (ºC) | $T_{on}$ (ºC) | $T_{off}$ (ºC) | CR (%) | LOI (%) |
|---------|----------------|--------------|----------------|--------|---------|
| LCNF-0 S | 341            | 290          | 360            | 18.5   | 25.3    |
| LCNF-5 S | 348            | 297          | 365            | 16.8   | 24.7    |
| LCNF-10 S | 344          | 295           | 364            | 25.6   | 28.6    |
| LCNF-20 S | 342           | 294          | 364            | 34.3   | 32.3    |
| CNF-0 S | 345            | 294          | 360            | 11.7   | 22.5    |
| CNF-5 S | 341            | 305          | 361            | 19.5   | 25.9    |
| CNF-10 S | 335            | 302          | 359            | 25.1   | 28.2    |
| CNF-20 S | 341            | 300          | 363            | 30.6   | 30.8    |
| TOCNF-0 S | 238 / 297    | 222          | 340            | 20.6   | 26.4    |
| TOCNF-5 S | 244 / 301    | 221          | 349            | 25.8   | 28.8    |
| TOCNF-10 S | 244 / 302 | 224          | 351            | 32.7   | 31.8    |
| TOCNF-20 S | 247 / 307    | 225          | 366            | 38.9   | 34.7    |
| CNC-0 S | 266 / 359      | 174          | 461            | 34.1   | 31.5    |
| CNC-5 S | 272 / 361      | 236          | 454            | 35.8   | 32.5    |
| CNC-10 S | 272 / 364     | 235          | 461            | 39.4   | 33.8    |
| CNC-20 S | 274 / 357     | 249          | 447            | 27.8   | 29.4    |
In general, when sepiolite was present in the hybrid nanopapers made with cellulose nanofibers, it can be distinguished the presence of rigid and thicker sepiolite nanofibers (diameter of 30–100 nm) (Ruiz-Hitzky et al. 2011; Lisuzzo et al. 2020) compared to the typical curved and long cellulose nanofibers (Fig. 4e-g). However, the two fibrous components are hard to distinguish in some cases due to their morphological similarity, as previously reported in similar films (González del Campo et al. 2018; Lisuzzo et al. 2020), and the entangled network that they form in the nanopapers. Conversely, in hybrid nanopapers with CNCs (Fig. 4 h), only sepiolite fibers were distinguished, due to the small size of the cellulose nanocrystals. Interestingly, a highly oriented distribution of the sepiolite fibers was found in these CNC-S hybrid nanopapers, compared to the more random orientation observed in films with cellulose nanofibers.

Independently of the nanocellulose type and the sepiolite content, all the nanopapers showed an homogeneous assembly between the organic and inorganic component, probably thanks to the sequential high-shear dispersion and ultrasound treatment applied in the preparation of precursor NC-S suspensions (González del Campo et al. 2018, 2020; Lisuzzo et al. 2020; Ruiz-Hitzky et al. 2021). As an example, FE-SEM images of the surface of nanopapers made with CNFs and different sepiolite content (0 %, 5 %, 10 % and 20 %) are shown in Supporting Information (Fig. SI.6).

Thermal stability and limiting oxygen index of NC-S hybrid nanopapers

Thermogravimetric parameters for NC-S hybrid samples are detailed in Table 2. TGA curves can be found in Supporting Information (Fig. SI.7: for nanocellulose samples without sepiolite and Fig. SI.8: for the NC-S hybrid with different sepiolite content). As expected, the nanocellulose samples (i.e., without sepiolite) that showed lower thermal stability (lower $T_{on}$) were TOCNF and CNC samples, due to the presence of carboxylate and sulfate groups, respectively (Jiang and Hsieh 2013; Lichtenstein and Lavoine 2017). Hence, a new degradation temperature peak was observed at 238 °C in TOCNF sample due to the decarboxylation of sodium carboxylate groups (Lichtenstein and Lavoine 2017) and at 266 °C in CNC sample due to the lower activation energy of decomposition from the surface sulfate groups (Lu and Hsieh 2010; Gaspar et al. 2014). TOCNF sample also showed a shift in peak at 341–345 °C (for LCNF and CNF samples) to 297 °C likely due to the lower nanofiber diameter of TOCNF sample, leading to higher surface area exposed to heat and promoting a faster degradation (Jiang and Hsieh 2013; Gaspar et al. 2014). Contrarily, in CNC sample this peak shifted to higher temperature (359 °C), showing also higher $T_{off}$ probably because its higher crystallinity slowed down the thermal degradation process (Hernique et al. 2015).

Regarding the addition of sepiolite, it caused an increase of thermal stability in most NC-S hybrids, which can be ascribed to the hydrogen bonding interactions between nanocellulose and sepiolite. This effect has been previously reported for hybrid foams and/or films made with sepiolite and different types of cellulose: TEMPO-oxidized nanocellulose (Wicklein et al. 2015; González del Campo et al. 2018; Sanguanwong et al. 2021), phosphorylated nanocellulose (Ghanadpour et al. 2018b), mechanical nanocellulose (Gupta et al. 2019) and nanocellulose derived from ultrasonicated microcrystalline cellulose (González del Campo et al. 2020). The highest increase in thermal stability was found for CNC-S hybrids (increase in $T_{on}$ of 61–75 °C), while only a slight increase was observed for mechanically obtained nanocellulose hybrids (i.e. LCNF-S and CNF-S). Furthermore, both LCNF-S and CNF-S hybrids showed lower $T_{deg}$ and $T_{on}$ for 10 % and 20 % sepiolite content, compared to 5 %, while in TOCNF-S and CNC-S hybrids a progressive increase with the increase in sepiolite content was observed. It has been reported that negative charges on the surface of nanocellulose can positively influence the mixture of nanoclays and cellulose nanofibers (Alves et al. 2019). Hence, the negative charges in TOCNFs and CNCs (confirmed by Z-potential: -70 mV and -65 mV, respectively), enable their dispersion in water at the individual nanoelement level (due to charge repulsion effect) allowing a better interaction between nanocellulose particles and sepiolite nanofibers at the nanometric level. On the other hand, LCNFs and CNFs presented lower amount of negative charges in their surface (Z-potential of -10 mV and -26 mV, respectively), which could lead to aggregation of nanocellulose particles, reducing the surface interactions between nanocellulose.
and sepiolite. Thus, when sepiolite content increased from 5 % to 10 % or 20 %, LCNFs and CNFs may not dispose enough available surface area for the interaction with these higher amounts of sepiolite, causing a slight reduction in thermal stability. These different behaviors indicate the important role of the nature of nanocellulose on the clay-nanocellulose interactions, and therefore on the films preparation and final composite properties. Similar conclusion was reported by Torvinen et al. (2017), who combined different nano/micro-cellulose (TEMPO-oxidized, enzymatic, mechanical and lignocellulosic nanofibers) with kaolinite to form nanoporous composites for printed electronics.

Differences in the amount of char residue (CR) obtained after pyrolysis at 850 °C were also found. Among the nanopapers without sepiolite, the highest CRs were found for CNC sample, which can be attributed to the dehydration effect of the sulfate groups (Jiang and Hsieh 2013; Gaspar et al. 2014). LCNF sample showed higher CR than CNF sample, probably due to the higher hemicellulose content of this sample, which could form a coal residue on the surface of the nanofibers hindering the complete cellulose degradation (Claro et al. 2019). TOCNF sample also left higher CR than CNF sample, owing to the formation of sodium carbonate from chemical reaction between the residual products of decarboxylation (carbon dioxide) and dehydration (water).

Fig. 5 Water sorption isotherms of sepiolite and the nanocellulose-sepiolite (NC-S) hybrids with different sepiolite content prepared with (a) LCNF, (b) CNF, (c) TOCNF, and (d) CNC.
(Lichtenstein and Lavoine 2017). When sepiolite was added to the nanopaper, higher CRs were found for all nanocellulose types (except for LCNF-5 S and CNC-20 S) due to increased amount of inorganic material (González del Campo et al. 2018a, 2020).

According to van Krevelen (1975), the limiting oxygen index (LOI) can be estimated from the char residue upon pyrolysis of halogen-free polymers. LOI indicates the minimum volume percent of oxygen (in a mixture of oxygen and nitrogen) required to support flaming combustion. Thus, lower LOI values indicate higher flammability, and polymers with LOI values under 26 are considered flammable (Ranganathan et al. 2008). Increasing the char formation, as in the case of sepiolite addition, can limit the production of combustible carbon containing gases, decreasing the exothermicity due to pyrolysis reactions, and decreasing the thermal conductivity of the surface of burning materials (Ranganathan et al. 2008). Other authors have reported the flame retardant effect of sepiolite addition in nanocellulose-sepiolite foams (Wicklein et al. 2015; Ghanadpour et al. 2018b; Gupta et al. 2019). This effect has been more extensively studied for lamellar clay materials such as montmorillonite in both hybrid foams (Kökülkaya et al. 2017; Wang et al. 2019; Medina et al. 2019) and films (Liu and Berglund 2013; Carosio et al. 2015; Ming et al. 2017). According to van Krevelen (1975), the limiting oxygen index (LOI) can be estimated from the char residue upon pyrolysis of halogen-free polymers. LOI indicates the minimum volume percent of oxygen (in a mixture of oxygen and nitrogen) required to support flaming combustion. Thus, lower LOI values indicate higher flammability, and polymers with LOI values under 26 are considered flammable (Ranganathan et al. 2008). Increasing the char formation, as in the case of sepiolite addition, can limit the production of combustible carbon containing gases, decreasing the exothermicity due to pyrolysis reactions, and decreasing the thermal conductivity of the surface of burning materials (Ranganathan et al. 2008). Other authors have reported the flame retardant effect of sepiolite addition in nanocellulose-sepiolite foams (Wicklein et al. 2015; Ghanadpour et al. 2018b; Gupta et al. 2019). This effect has been more extensively studied for lamellar clay materials such as montmorillonite in both hybrid foams (Kökülkaya et al. 2017; Wang et al. 2019; Medina et al. 2019) and films (Liu and Berglund 2013; Carosio et al. 2015; Ming et al. 2017).

Water vapor interactions with NC-S hybrid nanopapers

The water adsorption isotherms of NC-S hybrid nanopapers are shown in Fig. 5, while adsorption-desorption isotherm curves can be found in the Supporting Information (Fig. SI.9). A sigmoidal or S-shape profile can be observed for all NC-S hybrids and pristine nanocellulose types (except for LCNF-5 S and CNC-20 S) due to increased amount of inorganic material (Lichtenstein and Lavoine 2017). When sepiolite was added to the nanopaper, higher CRs were found for all nanocellulose types (except for LCNF-5 S and CNC-20 S) due to increased amount of inorganic material (González del Campo et al. 2018a, 2020).

According to Tukey’s multiple comparison test, values followed by the same letter in the same column do not differ significantly (p < 0.05) to Ming et al. (2017) and Darder et al. (2017), self-extinguishing behavior of hybrid films or foams improved sharply for clay content over 25–30 %, observing an immediately extinguishing of the flame after its removal. Therefore, if sepiolite content were increased over 30 % in NC-S nanopapers, even higher LOI values than those showed in Table 2 could be expected. Moreover, self-extinguishing properties of NC-S hybrid nanopapers can be tunable not only by the addition of different content of sepiolite, but also by the selection of the nanocellulose type used. Thus, NC-S hybrid nanopapers made with CNCs or TOCNFs showed higher LOI values than those made with LCNFs or CNFs.

### Table 3 Water vapor permeability (WVP) and mechanical properties of NC-S hybrid nanopapers: tensile index (TI), specific Young’s modulus (SYM) and elongation at break (EB). According to Tukey’s multiple comparison test, values followed by the same letter in the same column do not differ significantly (p < 0.05)

| Sample       | TI (kN m kg⁻¹) | SYM (MN m kg⁻¹) | EB (%)   | WVP x 10¹¹ (g m m⁻² s⁻¹ Pa⁻¹) |
|--------------|---------------|----------------|---------|-----------------------------|
| LCNF-0 S     | 45.6 ± 7.9 D  | 4.5 ± 0.2 A    | 1.0 ± 0.4 FGH | 1.6 ± 0.2 D                |
| LCNF-5 S     | 54.6 ± 1.0 CD | 4.0 ± 0.1 ABCDE | 1.4 ± 0.4 EF | 1.4 ± 0.2 D                |
| LCNF-10 S    | 49.7 ± 9.0 CD | 3.8 ± 0.6 BCDEF | 2.1 ± 0.3 CDE | 1.5 ± 0.2 D                |
| LCNF-20 S    | 62.1 ± 3.2 BC | 4.3 ± 0.2 ABC | 2.4 ± 0.2 CD | 1.8 ± 0.2 CD                |
| CNF-0 S      | 83.5 ± 10.3 A | 3.8 ± 0.2 CDEF | 3.1 ± 0.6 AB | 1.4 ± 0.2 D                |
| CNF-5 S      | 82.5 ± 5.7 A  | 4.4 ± 0.3 AB   | 2.6 ± 0.3 BC | 1.7 ± 0.2 D                |
| CNF-10 S     | 35.7 ± 6.6 DE | 4.3 ± 0.4 ABC | 1.7 ± 0.2 DEF | 1.7 ± 0.2 D                |
| CNF-20 S     | 72.7 ± 4.2 AB | 3.7 ± 0.2 DEFG | 3.6 ± 0.4 A | 2.6 ± 0.3 B                |
| TOCNF-0 S    | 14.3 ± 2.2 EF | 3.3 ± 0.4 FGH  | 1.1 ± 0.4 FG | 2.9 ± 0.2 AB                |
| TOCNF-5 S    | 17.7 ± 7.4 EF | 2.2 ± 0.2 I    | 1.2 ± 0.1 FG | 2.6 ± 0.3 BC                |
| TOCNF-10 S   | 57.8 ± 4.5 CD | 3.0 ± 0.0 H    | 3.1 ± 0.2 AB | 2.8 ± 0.3 AB                |
| TOCNF-20 S   | 53.4 ± 3.1 CD | 3.2 ± 0.0 FGH  | 1.9 ± 0.5 CDE | 3.6 ± 0.3 A                |
| CNC-0 S      | 7.1 ± 3.7 F   | 2.9 ± 0.2 H    | 0.3 ± 0.1 I | 1.8 ± 0.1 CD                |
| CNC-5 S      | 8.8 ± 3.2 F   | 3.1 ± 0.4 GH   | 0.3 ± 0.1 I | 1.8 ± 0.2 CD                |
| CNC-10 S     | 11.5 ± 4.6 F  | 3.4 ± 0.3 EFGH | 0.4 ± 0.1 HI | 1.8 ± 0.2 CD                |
| CNC-20 S     | 18.4 ± 2.5 EF | 4.3 ± 0.1 ABCD | 0.6 ± 0.2 GHI | 3.6 ± 0.4 A                |
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2018; Jiménez-López et al. 2020) and lower hydrophilic character for CNC sample, due to its higher crystallinity (Table 1) (Guo et al. 2017). When sepiolite (with higher hydrophilic character than nanocellulose) was introduced in the nanopapers, no significant changes in water sorption properties were found for LCNF-S, CNF-S and TOCNF-S hybrids. However, in the case of CNC-S hybrids, a progressive increase in hydrophilic character was found while increasing the sepiolite content. Similarly, González del Campo et al. (2020) reported an increase in hydrophilicity due to the sepiolite content in nanopapers made of nanocellulose from ultrasonicated microcrystalline cellulose and sepiolite. This effect could be due to a progressive reduction in the apparent bulk density of the CNC-S hybrid nanopapers while increasing the sepiolite content (1.65, 1.53, 1.49 and 1.28 g cm⁻³ for CNC-0 S, CNC-5 S, CNC-10 S and CNC-20 S, respectively). A reduction in apparent bulk density is related to an increase in porosity, which can result in an increase of water adsorption (Tyagi et al. 2021), since it depends on both surface energy and pore structure near the surface. Lower differences in apparent bulk densities were found in the NC-S nanopapers prepared with cellulose nanofibers and varying sepiolite content (1.50–1.33, 1.47–1.39 and 1.63–1.46 g cm⁻³ for LCNF-S, CNF-S and TOCNF-S nanopapers, respectively) explaining the lack of this effect on water adsorption for these samples. Contrarily, González del Campo et al. (2018) reported a reduction in hydrophilicity for nanopapers made with TEMPO-oxidized nanocellulose and 2–10% sepiolite, attributing this effect to the blocking of available sorption sites due to hydrogen bonds between nanocellulose and sepiolite fibers and to an increase in surface roughness. However, this effect was not observed herein for TOCNF-S hybrids.

Table 3 shows the water vapor permeability (WVP) for the different NC-S hybrid nanopapers, calculated from the water vapor transmission rate (WVTR) measurements and the film thickness. TOCNF nanopapers presented the highest WVP values (lowest barrier properties), due to the presence of carboxylate groups on the surface. These groups not only increased the water affinity of the nanofibers, as mentioned above, but also reduce the interfibrillar hydrogen bonds between nanofibers (Isogai et al. 2011), contributing to lower compaction of the film and easier swelling at high relative humidities (Jiménez-López et al. 2020). When 5–10 % sepiolite content was introduced in the nanopapers, no significant changes were found in permeability, indicating a good interaction between nanocellulose and sepiolite. However, when sepiolite content increased to 20 %, more significant increases in water vapor permeability were found, independently of the involved nanocellulose type. In agreement with these results, González del Campo et al. (2020) reported that sepiolite should be kept lower than 20 % in order to preserve the barrier properties of nanocellulose-sepiolite films. Similar results were found when sepiolite was added to other polysaccharides films such as alginate or arabinoxylan (Sárossy et al. 2012; Cheikh et al. 2020). Finally, it should be mentioned that although WVP of NC-S nanopapers (1.6–3.6·10⁻¹¹ gm⁻¹ Pa⁻¹ s⁻¹) was higher than that of traditional plastic (low-density polyethylene (LDPE): 0.014–0.007·10⁻¹¹ gm⁻¹ Pa⁻¹ s⁻¹; high-density polyethylene (HDPE): 0.002–0.004·10⁻¹¹ gm⁻¹ Pa⁻¹ s⁻¹; polyethylene terephthalate (PET): 0.002–0.023·10⁻¹¹ gm⁻¹ Pa⁻¹ s⁻¹; polyvinyl alcohol (PVOH): 0.343·10⁻¹¹ gm⁻¹ Pa⁻¹ s⁻¹) (Bastarachea et al. 2011), it was similar to that reported for other bioplastic such as polyactic acid (PLA): 1.9–2.5·10⁻¹¹ gm⁻¹ Pa⁻¹ s⁻¹ (Dadashi et al. 2014; Li et al. 2017), polyactic acid/poly(3-hydroxybutyrate) composites (PLA/PHB): ~4.8·10⁻¹¹ gm⁻¹ Pa⁻¹ s⁻¹ (D’Amico et al. 2016) or trilayer policaprolactone/methylcellulose: 3.9·10⁻¹¹ gm⁻¹ Pa⁻¹ s⁻¹ (Takala et al. 2013).

Mechanical properties of NC-S hybrid nanopapers

Mechanical properties of the diverse NC-S hybrid nanopapers were determined based on tensile test (Table 3). All the nanopapers presented a basis weight of 10.4 ± 1.3 g m⁻², a thickness of 7.0 ± 1.1 μm and an apparent bulk density of 1.48 ± 0.11 g cm⁻³. When pure nanocellulose samples were compared, higher mechanical properties were found for mechanically pretreated nanofibrillated cellulose (LCNF and CNF samples), especially for bleached nanofibers (higher tensile index and elongation at break, and only slightly lower specific Young’s modulus than LCNF sample). Despite the controversial results published about the effect of lignin on mechanical properties of lignin-containing nanocellulose (Ferrer
et al. 2012; Rojo et al. 2015; Solala et al. 2020; Jiménez-López et al. 2020), most of the works agree that unbleached and bleached nanopapers showed comparable mechanical properties, although a loss of ductility (lower elongation at break) could be associated with the lignin content (Rojo et al. 2015). When the TEMPO-mediated oxidation was applied as pretreatment in nanocellulose production, resulting TOCNF nanopaper showed lower mechanical properties, due to lower hydrogen bonding between nanofibers caused by the presence of carboxylate groups (Isogai et al. 2011). Finally, CNC nanopaper presented the lowest mechanical properties, as expected, due to the lower length of nanocrystals compared to nanofibers (199 nm vs. 595–892 nm, respectively) yielding lower crosslinking into the film.

The addition of sepiolite caused an increase in specific Young’s modulus, tensile index and elongation at break in most of the nanopapers (especially those made with TOCNFs and CNCs). In line with these results, several authors have reported an increase in Young’s modulus and tensile index related to the increase in sepiolite content not only in composite films made of nanocellulose (González del Campo et al. 2018, 2020) but also made of other polysaccharides or cellulose derivatives (such as alginate, starch, pectin, xanthan, chitosan, hydroxypropylmethylcellulose or carboxymethylcellulose, among others), even with high loading of fibrous clay (Darder et al. 2006; Chivrac et al. 2010; Alcântara et al. 2014, 2016; Cheikh et al. 2020). This behavior could be attributed to a good dispersion in the hybrid suspension (especially those made with negatively charged nanocellulose: TOCNFs and CNCs) and to strong interactions at the nanometer scale between the fibrous clay and the biopolymer (Alcântara et al. 2014, 2016).

In spite of the general positive effect of sepiolite on mechanical properties, some reductions in specific Young’s modulus, tensile index and/or elongation at break were found for LCNF-S and CNF-S hybrid nanopapers, especially in CNF-10 S. These results could indicate a weaker interaction between sepiolite and mechanically pretreated nanocellulose, which was also suggested by the lower thermal stability of LCNF-S and CNF-S nanopapers with 10–20 % sepiolite content. Regardless of these reductions, LCNF-S and CNF-S hybrid nanopapers still showed higher mechanical strength than TOCNF-S and CNC-S hybrid nanopapers, due to the most outstanding properties of pure LCNFs and CNFs. These results, along with their better barrier properties (lower WVP) make LCNF-S and CNF-S hybrid nanopapers good candidates for packaging applications.

### Table 4

Optical properties of NC-S hybrid nanopapers: total transmittance at 550 nm and 280 nm, and transmission haze and opacity at 550 nm (nanopapers thickness of 7.0 ± 1.1 μm)

| Sample   | Total Transmittance (%) | Transmission Haze (%) | Opacity (a.u. mm⁻¹) |
|----------|-------------------------|-----------------------|---------------------|
|          | (at 550 nm) | (at 280 nm) | (at 550 nm) | (at 550 nm) |
| LCNF-0 S | 85.9          | 35.6      | 7.9          | 9.9          |
| LCNF-5 S | 83.1          | 28.5      | 15.6         | 11.9         |
| LCNF-10 S | 83.7        | 36.5      | 19.0         | 12.4         |
| LCNF-20 S | 75.5         | 23.3      | 44.4         | 14.8         |
| CNF-0 S  | 88.9          | 71.6      | 5.5          | 6.2          |
| CNF-5 S  | 86.8          | 64.8      | 11.9         | 7.7          |
| CNF-10 S | 83.7          | 56.1      | 22.1         | 9.4          |
| CNF-20 S | 73.1          | 34.8      | 45.0         | 16.7         |
| TOCNF-0 S | 89.8        | 78.5      | 2.0          | 6.8          |
| TOCNF-5 S | 88.4         | 68.9      | 11.4         | 7.6          |
| TOCNF-10 S | 86.6        | 58.7      | 15.8         | 8.7          |
| TOCNF-20 S | 80.0        | 42.1      | 41.4         | 11.9         |
| CNC-0 S  | 88.1          | 76.3      | 1.6          | 11.4         |
| CNC-5 S  | 87.2          | 72.4      | 3.3          | 10.8         |
| CNC-10 S | 85.2          | 52.6      | 6.3          | 12.7         |
| CNC-20 S | 86.1          | 60.4      | 7.2          | 8.9          |
Optical properties of NC-S hybrids nanopapers

In order to evaluate optical properties of NC-S nanopapers, total transmittance and transmission haze were determined between 200 and 900 nm (Fig. SI.10 and SI.11 in Supporting Information). Most significant optical properties are shown in Table 4. All 100 % cellulose nanopapers presented high transparency: total transmittance higher than 86 % and opacity lower than 11 a.u. mm$^{-1}$ at 550 nm, indicating a dense packaging of small nanofibers/nanocrystals without voids between them able to cause light scattering (Hsieh et al. 2017). Interestingly, LCNF samples showed a relative UV-protection indicated by a low total transmittance at 280 nm (36 %, compared to 72–79 % for the other nanocellulose types), due to the presence of phenolic structure in lignin able to absorb UV light (Sadeghifar et al. 2017). Sepiolite content also improved UV-protection, as previously reported by Gonzalez del Campo et al. (2018). On the contrary, only a slight progressive reduction in transparency (550 nm) was found when sepiolite was incorporated in the nanopapers, being slightly more significant this effect in CNF-S hybrid nanopapers. Nevertheless, all NC-S nanopapers with up to 10 % sepiolite content presented very high transparency (total transmittance at 550 nm higher than 84 %) and only LCNF-20 S and CNF-20 S nanopapers presented...
transmittances lower than 80 % (75.5 % and 73.1 %, respectively) and opacity higher than 13 a.u. mm⁻¹ (14.8 a.u. mm⁻¹ and 16.7 a.u. mm⁻¹, respectively).

Thus, when NC-S hybrid nanopapers were placed right on a printed paper, the letters can be clearly read (Fig. 6). The small changes in transparency and opacity indicated that NC-S hybrid nanopapers were densely packed together, although a more heterogeneous structure when sepiolite content increased over 10 % could promote light dispersion. In this context, other authors have found high transparency in cellulose nanopapers with layered-clays, reporting total transmittances of 72–92 % even with 50 % clay content (Wu et al. 2014; Ming et al. 2017; Liu 2018; Qin et al. 2019). However, other authors observed a significant reduction in transparency when the fibrous or layered clays content increased (Aulin et al. 2012; Wu et al. 2012; González del Campo et al. 2018).

Optical transparency, combining with high mechanical strength and flexibility, is of interest in applications such as optoelectronics and barrier coating (Liu 2018). Furthermore, tunable transmission haze, i.e. the percentage of the transmitted beam of light that deviates from the incident beam by more than 2.5° due to light scattering, is also very important in optoelectronic devices (Jiang et al. 2018). In this regard, different approaches have been proposed such as varying the nanofibers/microfibers rate (Fang et al. 2014; Jiménez-López et al. 2020), the nanofibers/carboxymethyl cellulose (CMC) rate (Kim et al. 2020).
In this work, we propose to tune haze properties by changing the sepiolite content of the NC-S hybrid nanopapers, since a significant increase in transmission haze was observed for increasing sepiolite content. Thus, when the NC-S hybrid nanopapers were placed 3.5 cm separated from a printed paper, the letters become fuzzy when increasing sepiolite content (except for CNC hybrid nanopapers) because the light through the hybrid nanopaper becomes scattered by its higher haze (Fig. 7). This effect is probably due to the higher size of sepiolite fibers compared to nanocellulose particles. Nevertheless, low haze was observed in all CNC-S hybrid nanopapers, probably due to the smaller length of nanocrystals, compared to nanofibers, and the stronger intimate interaction between nanofibers and sepiolite, as suggested by the resulting thermal stability and mechanical properties. It is worth mentioning that although other authors have achieved higher optical haze for cellulose nanopapers, LCNF-20 S, CNF-20 S and TOCNF-20 S hybrid films presented high haze per unit thickness (5.1–5.5 % μm^-1). These values are comparable to those reported by Li et al. (2020) for highly transparent cellulose nanopapers with varying hemicelluloses and lignin content (3.55–5.5 % μm^-1) and by Kim et al. (2021) for all cellulose transparent films with different CNF/CMC ratio (6.1–8.9 % μm^-1). These authors claimed the outstanding optical properties of their films compared to other cellulose paper/nanopapers previously reported (0.05–2.28 % μm^-1) (Kim et al. 2021).

Taking into account these results, NC-S hybrid nanopapers made with nanofibers and high sepiolite content (especially TOCNF-20 S), which presented high transparency and transmission haze, could be applied in devices such as solar cells (providing diffuse scattered light) and LED lighting or backlight units in Liquid Crystal Display (LCD) (rendering uniform light distribution). LCNF-S, CNF-S and TOCNF-S with low sepiolite content, could be used in outdoor devices such as touch panels, since moderate haze would contribute to anti-glaring, providing comfortable visibility. Finally, CNC-S hybrid nanopapers, which presented high transparency and low transmission haze, could be applied in displays requiring high clarity with vivid and clear images (Fang et al. 2014).

Conclusions

Differences in the interaction between sepiolite and cellulose have been found due to variations in the surface chemistry (charge, functional groups) and morphology of the different types of nanocellulose used to make the NC-S nanopapers. The negative surface charges in TOCNFs and CNCs appear to enhance their dispersion in the hybrid suspension and the interaction between nanocellulose and sepiolite, improving the thermal stability and mechanical properties of NC-S hybrid nanopapers. Nevertheless, NC-S hybrid nanopapers made with chemically untreated nanofibers (LCNFs and CNFs) showed not only better thermal stability but also better mechanical and barrier properties than those made with TOCNFs and CNCs, being potentially valid for packaging applications. The prepared nanopapers showed suitable optical transparency for potential application in optoelectronic devices, with the great advantage of tuning the transmission haze by choosing the type of nanocellulose and adjusting the sepiolite content. Thus, LCNF-20 S, CNF-20 S and TOCNF-20 S, with high transmission haze, could be useful in solar cells and LED lighting or LCD backlight units, while those based on the same nanofibers with lower sepiolite content could be suitable for outdoor devices due to their moderate haze. Conversely, the high transparency and low transmission haze of CNC-S hybrid nanopapers make them useful for electronic devices and displays requiring high clarity. Furthermore, the flammability, permeability as well as mechanical and optical properties of all NC-S hybrid nanopapers can be tuned by selecting nanocellulose type and sepiolite content, depending on the requirements of the intended final application.

Associated Content

Supporting Information: Fig. SI.1: Diameter distribution of nanocellulose samples determined by
AFM; Fig. SI.2: Length of nanocellulose samples determined by AFM; Fig. SI.3: AFM images of nanocellulose samples; Fig. SI.4: Fourier Transform Infrared (FTIR) spectra of the nanocellulose-sepiolite (NC-S) hybrid nanopapers with different sepiolite content; Fig. SI.5: X-ray diffractogram of pristine sepiolite film; Fig. SI.6: FE-SEM images of NC-S hybrid nanopapers made with CNF nanocellulose and different sepiolite content (0–20 %); Fig. SI.7: Thermogravimetric curves of the nanocellulose samples under N₂ atmosphere; Fig. SI.8: Thermogravimetric curves obtained under N₂ atmosphere of the nanocellulose-sepiolite (NC-S) hybrid nanopapers with different sepiolite content; Fig. SI.9: Water sorption and desorption isotherms of sepiolite and the nanocellulose-sepiolite (NC-S) hybrid nanopapers with different sepiolite content; Fig. SI.10: Total transmittance of the nanocellulose-sepiolite (NC-S) hybrid nanopapers with different sepiolite content; Fig. SI.11: Transmission haze of the nanocellulose-sepiolite (NC-S) hybrid nanopapers with different sepiolite content.

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Declaration

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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