



## Research Paper

# Effect of the dispersion state of minerals on the properties of cellulose nanofiber-based composite films

Luís Alves<sup>a,\*</sup>, Ana Ramos<sup>b</sup>, Eduardo Ferraz<sup>c,d</sup>, Pedro Sanguino<sup>e</sup>, Julio Santarén<sup>f</sup>,  
 Maria G. Rasteiro<sup>a</sup>, José A.F. Gamelas<sup>a,\*</sup>

<sup>a</sup> University of Coimbra, CIEPQPF, Department of Chemical Engineering, Rua Sílvio Lima, Pólo II, Coimbra 3030-790, Portugal

<sup>b</sup> FibEnTech, Department of Chemistry, University of Beira Interior, Rua Marquês d'Ávila e Bolama, Covilhã 6201-001, Portugal

<sup>c</sup> TECHN&ART, Polytechnic Institute of Tomar, Quinta do Contador, Estrada da Serra, Tomar 2300-313, Portugal

<sup>d</sup> Geobiotec, University of Aveiro, Geosciences Department, Campus Universitário de Santiago, Aveiro 3810-193, Portugal

<sup>e</sup> University of Coimbra, CEMMPRE, Mechanical Engineering Department, Rua Luís Reis Santos, Coimbra 3030-788, Portugal

<sup>f</sup> Formerly TOLSA, SA, Research & Technology for New Businesses, Ctra. de Madrid a Rivas Jarama, 35, Madrid 28031, Spain



## ARTICLE INFO

## Keywords:

Transmission electron microscopy

Clay dispersion

Composites

Cellulose nanofibrils

Transparency

Clay minerals

## ABSTRACT

The dispersion state and the efficiency of the mixture of the different components in a composite film have an important impact on its mechanical and optical properties. In the present work, the impacts of different dispersion treatments on the disaggregation state of fibrous clay particles in water, and on the properties of related cellulose nanofiber (CNF)-based composite films, were evaluated. X-ray diffraction studies, performed on samples of sepiolite and palygorskite, revealed only minor changes in the diffraction pattern when the minerals were subjected to ultrasonic treatment, with or without the addition of different chemical dispersing agents. Conversely, microscopic studies revealed important differences in the dispersion state of the samples, induced by the addition of the different dispersants, showing an improvement in the disaggregation of the mineral crystals. The composite films prepared with sepiolite (and carboxymethylcellulose, as chemical dispersant) dispersed using ultrasonic treatment, and different types of CNF, showed improved optical and mechanical properties when compared with composites of the same counterparts prepared with sepiolite dispersed using a high-speed shear disperser.

## 1. Introduction

New bio-based alternatives for plastic-based materials, mainly for the single-use ones, are a hot topic not only in academic research but also a concern for the population in general. Plastic materials are very well established, due to their good properties and low cost. However, the emerging environmental concerns, related to the macro- and micro-plastic pollution in soils, oceans and water streams are increasing every day (Magalhães et al., 2020). Thus, it is urgent to develop materials with properties suitable to substitute plastics in most common applications, mainly for single-use purposes, such as food packaging.

Cellulose nanofiber (CNF)-based films are regarded as new materials with great potential for the proposed end. CNFs are very attractive due to their high biocompatibility and biodegradability, superior film-forming capability and good mechanical properties (Zeng et al., 2021). Nevertheless, CNFs are expensive nanomaterials, being the high

cost related to the high energy and/or chemical pre-treatments, usually required for their preparation. Furthermore, the produced films also present some limitations, such as low water vapour barrier properties, mainly in high-moisture conditions. To improve the barrier properties and reduce costs, novel strategies are required to overcome the drawbacks of the CNF-based films and potentiate the industrialization of these bio-based materials. One of the most promising strategies involves the preparation of CNF-mineral composites (Alves et al., 2019; Gamelas and Ferraz, 2015; González del Campo et al., 2018).

Fibrous clay minerals, such as sepiolite and palygorskite, are interesting materials that find use in a wide range of applications, for instance, CO<sub>2</sub> capture (Cecilia et al., 2018), clay-rubber composites (Takei et al., 2013), nanofibrillated cellulose-clay nanocomposites (Alves et al., 2019; Gamelas and Ferraz, 2015) or drug delivery carriers (Wang et al., 2014). Sepiolite and palygorskite are natural fibrous clays whose structure is based on blocks alternating with cavities (tunnels),

\* Corresponding authors.

E-mail addresses: [luisalves@ci.uc.pt](mailto:luisalves@ci.uc.pt) (L. Alves), [jafgas@eq.uc.pt](mailto:jafgas@eq.uc.pt) (J.A.F. Gamelas).

which give rise to highly porous frameworks. The ideal formula for sepiolite is  $Mg_6Si_{12}O_{30}(OH)_4(OH_2)_4 \cdot 8H_2O$  and  $(Mg,Al,Fe)_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$  for palygorskite. An important characteristic of these minerals is the high density of silanol groups on the particle surface, much higher than that of platelet-like clay minerals. These groups originate from the bonding between non-shared oxygens from the tetrahedral silica sheets (located on channels) and hydrogen (Guggenheim and Krekeler, 2011).

Hydrogen bonding and Van der Waals interactions contribute to the presence of aggregates of the acicular individual particles of fibrous clays in aqueous suspensions, which limits the quality of the clay dispersion (Wang and Wang, 2019). For some applications, such as bionanocomposites, a good dispersion of the clay mineral in a selected medium, preferentially water-based, is essential to achieve superior properties in the final materials (Alves et al., 2019). To improve the dispersibility of fibrous minerals, several strategies have been evaluated mainly based on mechanical treatments, the addition of chemical dispersants to the suspension and the chemical modification of the mineral surface (Alves et al., 2020b; Ferraz et al., 2021; García et al., 2011).

Several different mechanical treatments have been tried, such as ultrasonication, high-speed shearing, or high-pressure homogenization, among others; some of these treatments demonstrated the ability to disrupt the bulk bundles into smaller bundles or rods (Wang and Wang, 2016). Ultrasonication has been presented as a relatively simple approach to disaggregate sepiolite fibers and enhance the stability of the suspension, which is not possible to be accomplished using low-power dispersing equipment, such as magnetic stirring (Alves et al., 2020b). Fibrous clays treated in water by ultrasonication were also demonstrated to have their properties improved. Ultrasonication has also been demonstrated to be a useful method to generate homogeneous and stable dispersions with other different materials in water (Lo Dico et al., 2019).

The addition of dispersing agents can also be used to improve the stability of the dispersions and extend the application of fibrous clays (Alves et al., 2020b; Ferraz et al., 2021). The added dispersing agents can interact, mainly, by physicochemical interactions such as hydrogen bonding and/or hydrophobic interactions with the mineral particles (Benli et al., 2012) and change the characteristics of the rods of the fibrous clay, namely their charge and surface chemistry, improving the dispersion quality. The choice of the dispersant is crucial for the target result. Phosphates like sodium hexametaphosphate are the most popular dispersing agents for minerals (Takei et al., 2013). Also, other agents have been tested, ranging from synthetic polymers to bio-based additives, such as cellulose derivatives (Alves et al., 2020b).

In the present work, the influence of ultrasonication and the addition of distinct chemical dispersants (sodium polyphosphate, hydrophobically modified poly(sodium acrylate) (HM-PAA), and sodium carboxymethylcellulose (CMC)) on the dispersion state of two fibrous minerals (sepiolite and palygorskite) in water, and the impact on the properties of CNF-based composite films, were evaluated. The capacity of each dispersing system was studied by transmission electron microscopy (TEM), and possible changes in the mineral structure, induced by the ultrasonication treatment, as well as by the additional interaction of the mineral crystal bundles with the dispersing agents were studied by X-ray diffraction. The CNF-based composite films were produced using sepiolite suspensions prepared by ultrasonication and compared with composite films produced with sepiolite dispersed in a high-shear disperser. In the literature, most of the reported works deal with planar minerals (Alves et al., 2019). Few studies reporting composites using fibrous minerals, such as sepiolite, are available (Ghanadpour et al., 2018; González del Campo et al., 2018; Martín-Sampedro et al., 2022). Additionally, to the best of our knowledge, no study in literature reports the effect of different dispersing equipment on the CNF-mineral composite film properties.

## 2. Materials and methods

### 2.1. Clays and chemicals

In this study, two sepiolite samples referred to as sepiolite 1 (Sep 1) and sepiolite 2 (Sep 2), obtained from the deposit of Vallecas-Vicálvaro (Madrid, Spain), and one palygorskite sample, from the deposit located in M'bour, region of Thiès (Senegal), were supplied by Tolsa, SA (Madrid, Spain). Sepiolite 1 was processed by a dry micronization process using a jet mill to break the fiber bundles down into micron-size particles. Sepiolite 2 was micronized using a wet process that produces an extensive deagglomeration of the sepiolite fiber bundles without affecting their aspect ratio (Alves et al., 2020b). Palygorskite (PAL) was processed using a roller mill treatment to a final particle size of less than 45  $\mu\text{m}$  (Ferraz et al., 2021).

The dispersing agents used were: sodium polyphosphate (Emplura grade, 99%, 106529) purchased from Sigma-Aldrich (Merck); hydrophobically modified poly(sodium acrylate) (Acusol 820, 30% (solids) emulsion consisting of 40% methacrylic acid, 50% ethyl acrylate and 10% stearyl oxypoly ethyl methacrylate) acquired from Rohm and Haas, USA; sodium carboxymethylcellulose (molecular weight of 250 kDa, degree of substitution of 0.7) obtained from Sigma-Aldrich (Merck). All chemicals were used as received without any further purification.

Cellulose nanofibers used in the present work were obtained and characterized following previously described procedures (Alves et al., 2022). Two different types of CNF were used in the present work, namely Mec CNF (mechanical) and TEMPO CNF (TEMPO-oxidised).

### 2.2. Preparation of the mineral suspensions with different chemical dispersants

Suspensions with 1.0 wt% of fibrous clay were prepared at room temperature from their respective dry powders. The clay powder was added to distilled water and the mixture was stirred using a magnetic stirrer at 200 rpm; right after, the dispersing agent was added at a mass ratio of 1:10 (dispersant/clay). Then, the suspension preparation was finished using an ultrasound probe (Vibra-cell VC 505, Sonics) working at 60% amplitude and 1 s pulse, for 10 min. Suspensions were also prepared without the addition of chemical dispersant. Then, suspensions containing 0.05 wt% clay were prepared for the transmission electron microscopy analysis by dilution of the concentrated samples.

### 2.3. Characterization of the mineral samples

Five samples of each clay mineral, i.e., the starting material and four suspensions prepared by dispersion of the mineral by ultrasonication, without and with additives, were characterized in terms of mineralogical characterization by powder X-ray diffraction using a Siemens D5000 X-ray diffractometer. A  $\text{CuK}\alpha 1$  radiation source with  $\lambda = 1.54056 \text{ \AA}$ , focused by a primary Ge crystal monochromator, was used. The detector is a standard scintillation counter. The Cu tube runs at 40 mA and 40 kV. The starting clay powders and the powders of the dispersed samples dried at 105 °C were placed in proper support. Diffractograms were collected by the counting method (step 0.02° and time 1.0 s) in the 2 $\theta$  range of 5–60°.

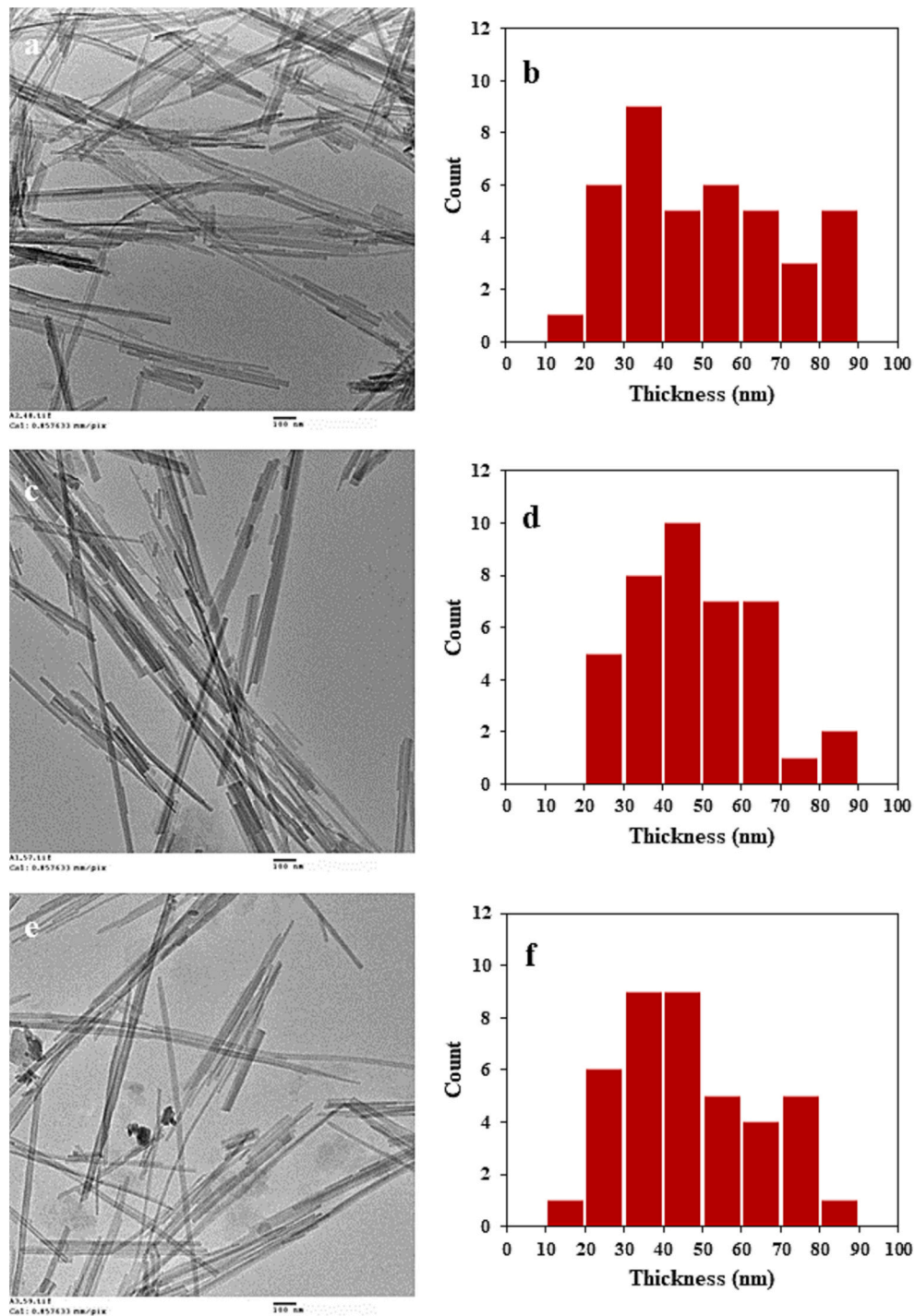
The morphology of the particles in the dry powders of the starting materials was evaluated by field emission scanning electron microscopy (FE-SEM) in a Carl Zeiss Merlin-61-50 microscope. Secondary electron mode and acceleration voltage of 1 kV were the operational conditions. The samples were previously sputter-coated with a thin film of Au/Pd.

High-resolution transmission electron microscopy (HR-TEM) was carried out in a JEOL JEM-2100 equipment to infer the dispersion state, morphology and size of the clay crystals in the suspensions, with and without dispersing agent, in aqueous medium. A small amount of each suspension (10  $\mu\text{L}$ ) was deposited on a carbon-coated copper grid, and the samples were observed using an accelerating voltage of 200 kV.

## 2.4. Preparation of the CNF-based composite films

Sepiolite (sepiolite 1) suspension in water (1.0 wt%), using CMC as dispersing agent, was prepared following the procedure described above (section 2.2). For comparison, sepiolite suspension (without CMC) was prepared using a high-shear disperser (Dispermat CV3-PLUS-E, VMA-Getzmann GmbH, Reichshof, Germany) at 5000 rpm for 15 min. Different films were prepared using filtration followed by hot pressing, according to a procedure previously described (Alves et al., 2022). Briefly, suspensions containing 0.2 wt% of the different CNF or CNF +

mineral were dispersed using the high-shear disperser at 1000 rpm for 10 min. After, the prepared suspensions were dewatered using a filtration unit purchased from Kimble Ultra-Ware Filtration Systems (DWK Life Sciences GmbH, Mainz, Germany) and membranes of cellulose acetate with 0.45  $\mu\text{m}$  pore and 90 mm diameter (Filtratech). The dewatered “wet cakes” were finally dried using a rapid dryer for laboratory sheets (Lorentzen & Wettre, model 257, Lorentzen & Wettre GmbH, Munich, Germany). The drying was performed using a temperature of 110  $^{\circ}\text{C}$  for 10 min.



**Fig. 1.** HR-TEM micrographs of the clay samples at 15,000 $\times$  magnification: a) sepiolite 1, c) sepiolite 2, and e) palygorskite suspensions in aqueous medium, treated with an ultrasonic probe. The scale bars correspond to 100 nm. Frequency distributions of the thickness (cross section) of the particles obtained from HR-TEM micrographs for b) sepiolite 1, d) sepiolite 2 and f) palygorskite samples.

## 2.5. Characterization of the CNF-based composite films

The prepared films were characterized following the procedures described elsewhere (Alves et al., 2022). The basis weight, thickness, transparency, and tensile properties (tensile strength, Young's modulus and elongation at break) were obtained according to the standards available. In brief, the thickness of the film was determined using a AdameL Lhomargy micrometer (model MI 20, Roissy-en-Brie, France), based on 10 measurements for 2 replicate films; the reported values correspond to the average values determined. The film transparency (average of 2 replicate films) was assessed according to the ISO 22891 standard, using a Technidyne Color Touch 2 spectrophotometer from Technidyne Corporation (New Albany, Indiana, USA), and applying the illuminant D65 and the observer 10°. The tensile properties were determined according to the ISO 1924-1 standard, at  $23 \pm 1$  °C and  $50 \pm 2\%$  RH, using a tensile tester from Thwing-Albert Instrument Co. (EJA series, West Berlin, NJ, USA), with the following setup: a tensile rate of 5 mm per minute and an initial gap (between grips) of 5 cm. The reported values of the tensile properties (tensile strength, Young's modulus and elongation at break) correspond to the average values of four specimens for each film type.

## 3. Results and discussion

### 3.1. Characterization of the fibrous clay dispersions through electron microscopy

The HR-TEM images of suspensions of the two sepiolite samples and the palygorskite sample in water, treated with an ultrasonic probe, are presented in Fig. 1.

The HR-TEM images revealed that the crystals were not fully individualized, using the ultrasound probe treatment, being observed aggregates of several crystals, "face-to-face", in the three samples. Bundles with thickness (cross section) in the range of 13–83 nm for Sep 1, 21–83 nm for Sep 2 and 15–84 nm for the palygorskite sample, can be observed. The frequency distribution of thicknesses (based on 40 measurements for each sample) shows that the mode thickness for Sep 1 is 30–40 nm, for the case of Sep 2 is 40–50 nm, and 30–50 nm for the palygorskite sample.

In length, all the samples present crystals with dimensions up to 1–2  $\mu\text{m}$ , being observed particles of 3–4 hundred nanometers, which can correspond to pieces of crystal bundles broken during the ultrasonic treatment.

The fibrous nature of these two minerals was also observed in the FE-SEM images of the starting sepiolite and palygorskite materials. The observed fibers have ca. 50–100 nm nanometers in thickness and a few micrometres in length (Fig. S1). The fibers consist of crystal bundles of small dimensions. The full disaggregation of the crystal bundles is a challenging step and an important parameter to obtain composite films with the desired properties. On the other hand, an extensive disaggregation treatment could eventually lead to critical changes in the mineral's structure. To access possible changes in the mineral structure, X-Ray diffraction was performed in the mineral samples before and after dispersion.

### 3.2. X-ray diffraction characterization of the clay dispersions

The X-ray diffractograms of the two sepiolite samples and the palygorskite sample are presented in Fig. 2. The parameters obtained for the different samples are resumed in Table 1.

The X-ray diffractograms of the sepiolite samples (dry powder), revealed that the dominant phase of these samples is sepiolite ( $2\theta = 7.3^\circ$ ,  $d = 12.1$  Å for both sepiolite samples); on the other hand, the palygorskite sample (dry powder), showed a dominant peak at  $2\theta = 8.4^\circ$ ,  $d = 10.5$  Å, corresponding to palygorskite phase, being the peak at  $2\theta = 26.6^\circ$  ( $d = 3.3$  Å), corresponding to quartz the second more intense. The

presence of contaminants was more pronounced for the palygorskite compared to the sepiolite samples, as reported before (Alves et al., 2020b; Ferraz et al., 2021).

After dispersion in aqueous medium, using ultrasonication as physical treatment, some slight changes in the X-ray diffraction patterns of the samples were noticed. However, no obvious changes in the characteristic diffraction peaks of the sepiolite and palygorskite phases were observed by treatment with the ultrasound probe, indicating that the basic structure of sepiolite and palygorskite was preserved. In particular, after the ultrasonic treatment the diffraction peak  $S_8$  (080), characteristic of sepiolite, became more intense, as measured by its relative intensity normalized to the  $S_1$  (110) peak (Table 1), for both the sepiolite samples, which can be attributed to disaggregation of the sepiolite fibers, which enabled the random orientation of the fibers in the dispersion (González del Campo et al., 2018). On the other hand, the  $S_2$  (130) peak of very low intensity disappeared after the ultrasound treatment (Sep 2) and the  $S_6$  (131) peak is absent in both the sepiolite samples after ultrasonication; the disappearance of these two peaks can suggest some disorder in the stacking of sepiolite polysomes, induced by the physical treatment (Krekeler and Guggenheim, 2008). For the palygorskite sample, the ultrasonication treatment did not lead to large changes in the intensity of the palygorskite characteristic peaks and did not result in the disappearance of these diffraction peaks confirming the preservation of the fibrous mineral structure.

### 3.3. Effect of additives on the dispersion state and structure of the mineral

The HR-TEM images of the three clay samples, dispersed using the ultrasonic treatment, with the addition of three different dispersing agents (polyphosphate, HM-PAA and CMC) are presented in Fig. 3.

The addition of the dispersing agents led, in general, to a better dispersion of the mineral crystals in aqueous medium. Comparing the images obtained without the addition of dispersing agents (Fig. 1) with the ones shown in Fig. 3 (with dispersing agents), it is possible to observe substantial differences in the aggregation/disaggregation state of the crystals.

With the addition of polyphosphate and CMC as dispersing agents, good performance in the dispersion was observed for the three mineral samples. Crystals with few nanometers in thickness (Sep 1 + polyphosphate: 10–30 nm; Sep 1 + CMC: 10–30 nm; Sep 2 + polyphosphate: 20–50 nm; Sep 2 + CMC: 10–40 nm; Pal + polyphosphate: 10–40 nm; Pal + CMC: 10–40 nm), and 300–1000 nm in length (for sepiolite samples) and 250–900 nm (for palygorskite) are observed (see Fig. S2 for thickness frequency distributions). Only a few "face-to-face" crystals could be observed in these samples. On the other hand, the use of HM-PAA can also reduce the "face-to-face" aggregates in the three mineral samples, but an extensive "random" reaggregation is observed, due to the lower stability induced by the use of this dispersing agent. The ability of this dispersing agent to disaggregate the crystal bundles of minerals was previously reported (Alves et al., 2020b; Ferraz et al., 2021), but due to the nature of this polymer, hydrophobically modified, the suspensions possess less stability (formation of gel occurred with time), and reaggregation was observed.

Some breaking of nanocrystals was observed, with this rupture being induced by the energy released by the ultrasonicator, operating by cavitation phenomena. Cavitation is very efficient to disaggregate the mineral crystal bundles; however, due to its great intensity, it can result in the breakage and consequent size (length) reduction of individualized nanocrystals (Neaman and Singer, 2000). In the samples without dispersing agent, this breaking occurred to a lesser extent due to the lower disaggregation achieved, which enables the bundles to support better the energy from the treatment.

Furthermore, possible structural changes in the minerals, induced by the addition of the dispersing agents, were studied by X-ray diffraction (Fig. 2 and Table 1).

The addition of the dispersing agents seemed not to produce

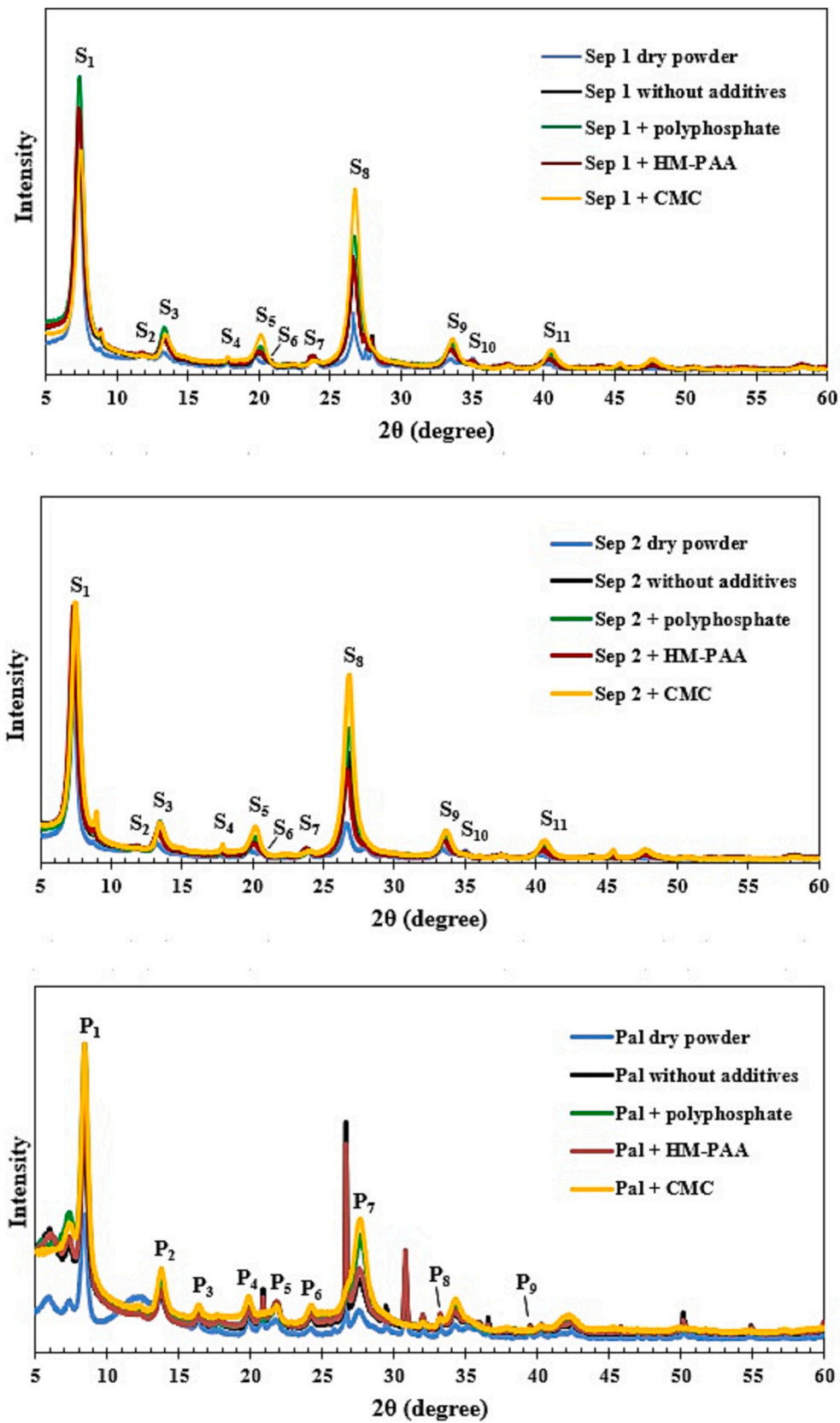


Fig. 2. X-ray diffraction of the sepiolite samples (Sep 1 – top; Sep 2 – middle) and palygorskite sample (Pal - bottom), with the identification of the clay minerals.

**Table 1**  
Parameters of Sep 1, Sep 2 and Pal from X-ray diffraction data.

Sample	Peak	hkl	Dry powder		Without additives		With polyphosphate		With HM-PAA		With CMC	
			d observed (Å)	I relative	d observed (Å)	I relative	d observed (Å)	I relative	d observed (Å)	I relative	d observed (Å)	I relative
Sep 1 / Sep 2	S <sub>1</sub>	110	12.1 / 12.1	100 / 100	12.0 / 11.9	100 / 100	12.0 / 11.8	100 / 100	12.1 / 12.0	100 / 100	11.8 / 11.9	100 / 100
	S <sub>2</sub>	130	7.4 / 7.5	3 / 2	7.5 / —	1 / —	7.4 / —	1 / —	7.5 / 7.5	2 / 1	— / —	— / —
	S <sub>3</sub>	200 or 040	6.7 / 6.7	4 / 5	6.6 / 6.6	9 / 10	6.6 / 6.6	12 / 14	6.7 / 6.7	9 / 8	6.6 / 6.6	13 / 11
	S <sub>4</sub>	150	5.0 / 5.0	2 / 1	5.0 / 4.9	2 / 2	— / 5.0	— / 1	5.0 / 5.0	2 / 2	5.0 / 5.0	2 / 3
	S <sub>5</sub>	060	4.5 / 4.5	5 / 3	4.4 / 4.4	5 / 6	4.4 / 4.4	7 / 8	4.4 / 4.4	6 / 5	4.4 / 4.4	14 / 11
	S <sub>6</sub>	131	4.3 / 4.3	3 / 2	— / —	— / —	— / —	— / —	— / —	— / —	— / —	— / —
	S <sub>7</sub>	260	3.7 / 3.7	6 / 4	3.7 / 3.7	4 / 3	3.7 / 3.7	2 / 2	3.7 / 3.7	4 / 3	3.7 / 3.7	2 / 1
	S <sub>8</sub>	080	3.3 / 3.3	26 / 18	3.3 / 3.3	48 / 51	3.3 / 3.3	49 / 57	3.3 / 3.3	46 / 37	3.3 / 3.3	90 / 76
	S <sub>9</sub>	510 or 0,10,0	2.7 / 2.7	3 / 4	2.7 / 2.7	7 / 8	2.7 / 2.7	8 / 10	2.7 / 2.7	7 / 6	2.7 / 2.7	14 / 11
	S <sub>10</sub>	281 or 441	2.6 / 2.6	4 / 3	2.6 / 2.6	2 / 1	2.6 / —	1 / —	2.6 / 2.6	2 / 1	— / —	— / —
	S <sub>11</sub>	312 or 062 or 2,10,1	2.2 / 2.2	3 / 3	2.2 / 2.2	4 / 5	2.2 / 2.2	5 / 6	2.2 / 2.2	4 / 4	2.2 / 2.2	9 / 7
Pal	P <sub>1</sub>	110	10.5	100	10.5	100	10.5	100	10.5	100	10.5	100
	P <sub>2</sub>	200	6.4	15	6.4	17	6.4	19	6.4	17	6.4	19
	P <sub>3</sub>	130	5.4	9	5.4	6	5.4	5	5.4	6	5.4	5
	P <sub>4</sub>	040	4.5	16	4.5	11	4.5	7	4.5	9	4.5	8
	P <sub>5</sub>	310	4.1	8	4.1	8	4.1	4	4.1	6	4.1	3
	P <sub>6</sub>	240	3.7	7	3.7	6	3.7	5	3.7	5	3.7	5
	P <sub>7</sub>	400	3.2	16	3.2	20	3.2	32	3.2	24	3.2	42
	P <sub>8</sub>	440	2.7	8	2.7	8	2.7	2	2.7	8	2.7	3
	P <sub>9</sub>	530	2.3	6	2.3	4	—	—	2.3	3	—	—

hkl indexes were obtained from (Nagy and Bradley, 1955) for sepiolite and from (Bradley, 1940) for palygorskite.

substantial changes in the main structural features of sepiolite and palygorskite, although some minor differences were noted, as follows. The addition of CMC led to an increase in the intensity of diffraction peak S<sub>8</sub> (080) for both the sepiolite samples, vs. the treatment with only ultrasonication, revealing a better disaggregation of the sepiolite fibers (González del Campo et al., 2018). Conversely, the low-intensity peaks, S<sub>2</sub> (130) and S<sub>10</sub> (281 or 441), disappeared after the ultrasound treatment when CMC was present, suggesting some disorder in the stacking of the polysomes; the same behaviour was observed for sepiolite 2 with the addition of polyphosphate. For the palygorskite sample, it was noted the disappearance of the low-intensity P<sub>9</sub> peak after the ultrasound treatment either with the addition of polyphosphate or CMC. However, as for the characteristic palygorskite diffraction peaks, the diffractograms after the ultrasonication treatment with added dispersants almost matched that of the initial palygorskite sample.

The favourable interaction of the biopolymer CMC with the crystal particles of the different clays is expected to allow a better dispersion, as well, as better stabilization of mineral particles in aqueous suspensions. Considering the nature of the biopolymer and sepiolite/palygorskite, the interactions involved are hypothesized to be of two types: hydrogen bonding between the hydroxyl groups of the biopolymer and the silanol groups on the outer surface of the mineral particles, and via Van der Waals forces, due to the amphiphilic nature of the cellulose derivative and sepiolite/palygorskite, with specific patches of their structure with different polarities (Benli et al., 2012; Lindman et al., 2021; Wang and Wang, 2016). The FTIR spectroscopy provided an additional information to this issue. The FTIR spectrum of sepiolite after ultrasonication (without added biopolymer) was reasonably similar to that of the original mineral sample (Fig. S3, for the region of the OH stretching in the Si-O-H, Mg-O-H and Mg-OH<sub>2</sub> bonds), showing the bands expected for the mineral. However, the spectrum of sepiolite after ultrasonication with added CMC (Fig. S3) showed a remarkable decrease of the intensity of all the bands in the mentioned region and, in particular, the very weak band due to the OH stretching in Si-O-H bonds at 3717 cm<sup>-1</sup> disappeared. The latter observation is an indication of the existence of interactions by hydrogen bonding between the silanol groups of the mineral surface and the hydroxyl groups of the CMC (Martín-Sampedro et al., 2022). Breaking of Mg-O bonds in the octahedral layer on the surface of the sepiolite crystals may also have occurred.

On the other hand, the use of HM-PAA, an amphiphilic polymer, as dispersing agent, also showed a low impact on the structural parameters

of the minerals, when dispersed in aqueous suspensions using ultrasonication. The type of interactions of this polymer with the clays is expected to be similar to the case of CMC, but the increased hydrophobicity (introduced by the presence of long hydrophobic chains) which delays the expansion of the polymer (Alves et al., 2015) led to poor stabilization of the suspensions, being observed aggregates of “random” oriented crystals in all the samples using this dispersant (Alves et al., 2020b; Ferraz et al., 2021).

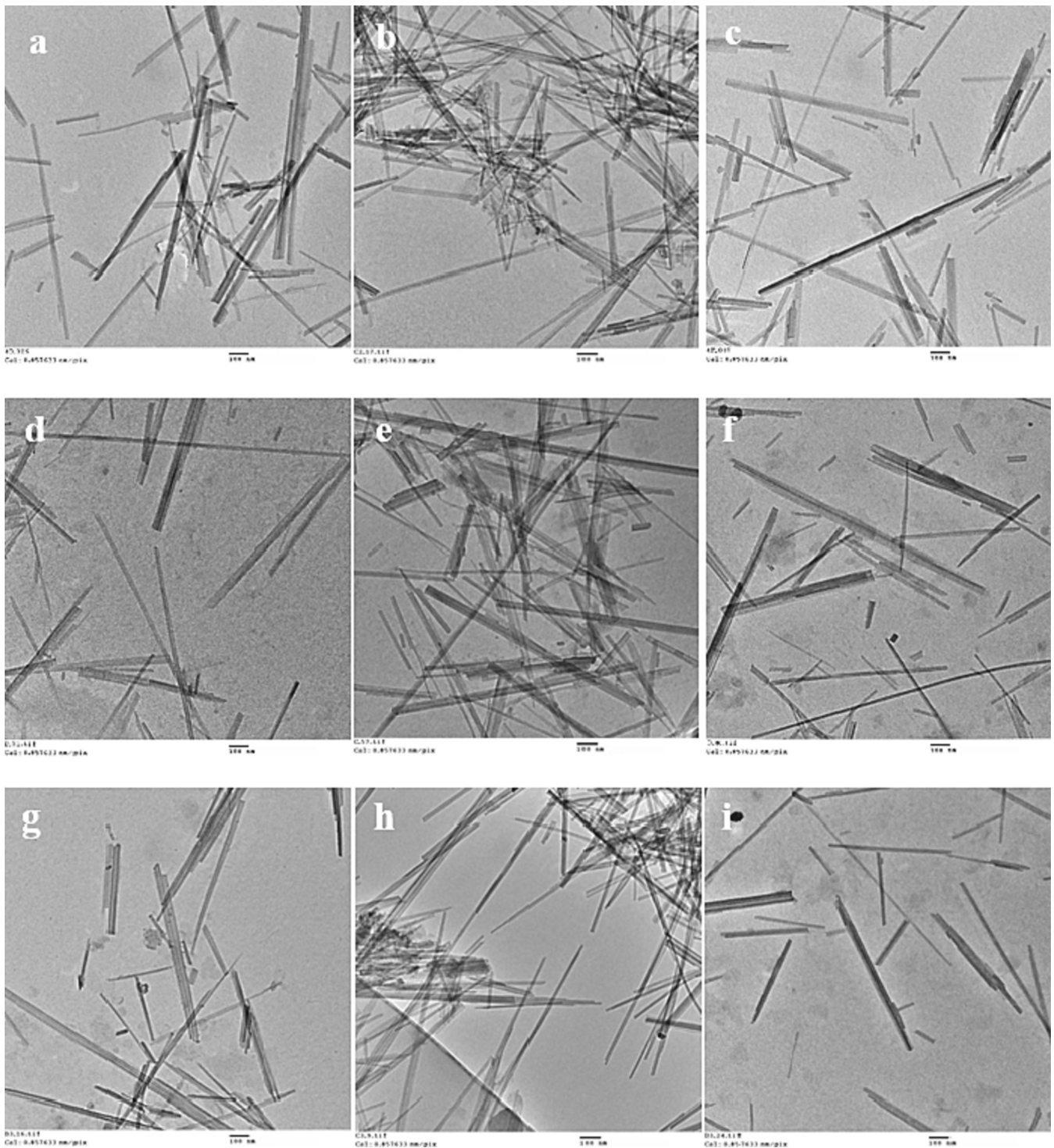
In sum, the obtained results indicate that the addition of dispersing agents, such as polyphosphate and CMC represents a good route to obtain fibrous clay suspensions with superior disaggregation and stability, without changing the fibrous mineral structure, when used as a complement to ultrasonic treatment.

#### 3.4. Effect of dispersion state of sepiolite on the CNF-based composite film properties

The dispersion state and mixture of the different components in composite films play a key role on the mechanical and optical properties of the composite (Alves et al., 2019). In Fig. 4 are presented photos of TEMPO oxidised CNF-based films, neat and with the addition of 20% sepiolite, with the mineral previously dispersed using different approaches: a high-shear disperser (TEMPO 55 + SEP) and applying ultrasonication and a chemical dispersant (TEMPO 55 + SEP Son).

CMC was chosen as dispersing agent, instead of the classical dispersant polyphosphate, due to its bio-based nature and good dispersion ability. Moreover, polyphosphate has in its composition phosphorous which can always induce unwanted water eutrophication. On the other hand, sepiolite 1 was chosen, due to the slightly better dispersion apparently obtained (i.e., slightly lower thicknesses of the dispersed crystals, as shown in section 3.3).

The transparency of the films containing 20% sepiolite is dependent on the dispersion method used, being the film prepared with sepiolite dispersed using ultrasonication more transparent than the film produced from the mineral suspension prepared with the high-shear disperser. The better dispersion state obtained using the first dispersion method allows a better mixture of both the components, being the size of the cellulose fibrils and the sepiolite crystals in the same order of magnitude (Alves et al., 2020a; Alves et al., 2020b), contrary to the case where the suspension of sepiolite was dispersed with the high-shear disperser, which provided particles of higher size, that can be inferred by the phase



**Fig. 3.** HR-TEM images at 15,000 $\times$  magnification of suspensions containing 0.05 wt% of fibrous clay treated with ultrasonic probe. a) sepiolite 1 with polyphosphate; b) sepiolite 1 with polyacrylate; c) sepiolite 1 with CMC; d) sepiolite 2 with polyphosphate; e) sepiolite 2 with polyacrylate; f) sepiolite 2 with CMC; g) palygorskite with polyphosphate; h) palygorskite with polyacrylate; i) palygorskite with CMC. The scale bars represent 100 nm.

separation observed for this suspension after few hours (Alves et al., 2020b). The smaller size of the mineral particles reduces the light scattering which resulted in films with higher transparency. The improvement in the transparency of the films (less opaque) when the mineral suspension was previously prepared by ultrasonication with added CMC occurred for the two tested CNF (see results for Mec CNF and TEMPO CNF in Fig. 5).

The smaller particle size of the sepiolite particles and the better

mixture allowed, not only had an impact on the optical properties of the composite films but also on their mechanical performance. The mechanical properties obtained for the studied composite films are shown in Table 2 and Fig. 6.

In general, it was observed an improvement in the properties of the CNF-based composites with a better dispersion state of sepiolite. As it can be seen, the addition of sepiolite to the films produced with Mec CNF led to a reduction in the mechanical properties, being this depletion



Fig. 4. Digital photos of TEMPO oxidised CNF-based films. Left – film obtained using neat CNF, without sepiolite; middle – composite film prepared with TEMPO-oxidised CNF and 20% sepiolite with the mineral dispersed using the high-shear disperser; right – composite film prepared with TEMPO-oxidised CNF and 20% sepiolite with the mineral dispersed using ultrasonication in the presence of CMC.

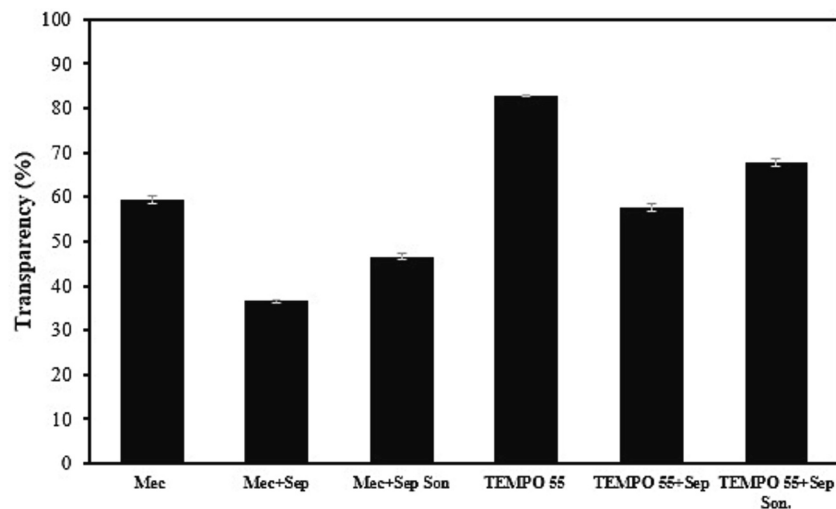


Fig. 5. Transparency of the CNF-based composite films prepared using sepiolite (Sep 1) dispersed using different dispersing equipment (Sep, using the high-shear disperser and Sep Son, using ultrasonication in the presence of CMC).

Table 2

Structural and mechanical properties of the prepared CNF-based composite films.

Film	Basis weight (g/m <sup>2</sup> )	Thickness (μm)	Max. Force (N)	Elongation at break (%)
Mec <sup>a</sup>	40.5 ± 0.5	34 ± 4	71.5 ± 4.9	10.5 ± 1.7
Mec + Sep <sup>b</sup>	38.0 ± 1.2	55 ± 15	44.4 ± 3.4	4.3 ± 0.6
Mec + Sep Son <sup>c</sup>	38.9 ± 0.8	45 ± 5	49.0 ± 2.8	7.6 ± 0.5
TEMPO 55 <sup>a</sup>	40.8 ± 0.8	39 ± 5	25.6 ± 13.5	2.0 ± 1.3
TEMPO 55 + Sep <sup>b</sup>	40.2 ± 1.1	37 ± 2	34.9 ± 8.0	4.1 ± 2.3
TEMPO 55 + Sep Son <sup>c</sup>	39.8 ± 0.3	37 ± 3	41.3 ± 2.8	3.6 ± 0.8

<sup>a</sup> neat CNF films.

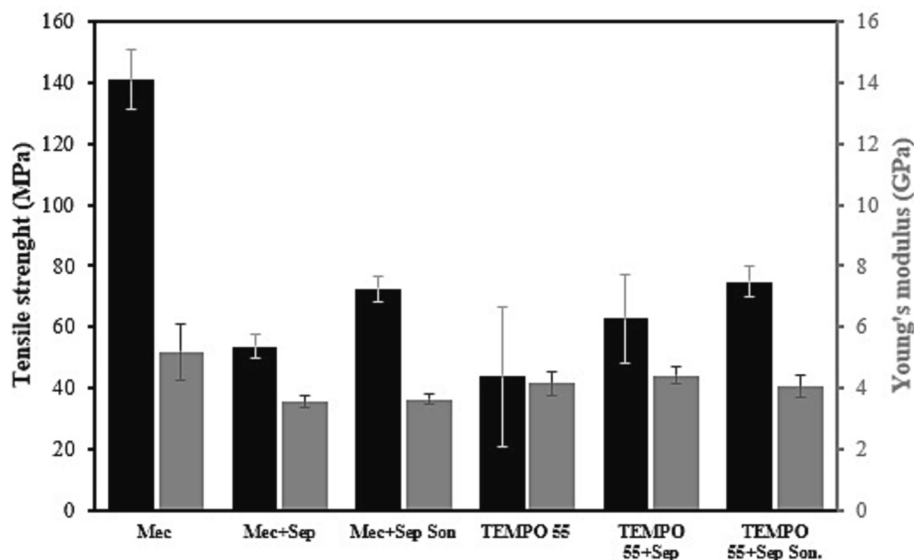
<sup>b</sup> composite films with 20% sepiolite with the mineral dispersed using the high-shear disperser.

<sup>c</sup> Composite films with 20% sepiolite with the mineral dispersed using ultrasonication in the presence of CMC.

mitigated with a better dispersion of sepiolite previously to the composite film preparation. In fact, the tensile strength, the maximum supported force, and the elongation at break of the composite films, prepared using sepiolite and Mec CNF, are improved with the better dispersion state of the sepiolite crystals, which not only allows a better mixture of the different components, but also results in a more compact structure, and thus in a lower decrease of the mechanical properties relatively to the corresponding film with neat CNF. The results obtained for TEMPO oxidised CNF-based composite films are somehow surprisingly positive, being possible to improve the mechanical properties of the composite films, compared with the neat film, even without previous

sonication of the mineral. However, the ultrasonication of sepiolite suspension, beyond an additional trend to a slight improvement in the tensile strength, allowed to keep the transparency of the film containing 20% of sepiolite with a value close to that of the neat TEMPO CNF film. The mechanical properties of the composite films obtained in the present work are in line to those of related films reported in the literature (González del Campo et al., 2018; Martín-Sampedro et al., 2022). For example, Martín-Sampedro et al. reported the preparation of hybrid nanopapers of TEMPO-oxidised CNF and sepiolite (20%) with a tensile strength of 79.0 MPa and Young's modulus of 4.7 GPa; our composite films presented comparable values for these properties (74.8 MPa and





**Fig. 6.** Mechanical properties of the CNF-based composite films prepared using sepiolite (Sep 1) dispersed using different dispersing equipment (Sep, using the high-shear disperser and Sep Son, using ultrasonication in the presence of CMC). The tensile strength corresponds to the black bars and the Young's modulus to the grey bars.

4.0 GPa, respectively), even though they were produced using a CNF from a different source (bleached eucalyptus pulp in the present study vs. bleached elm pulp in the previous literature study). The elongation at break was slightly higher in the present work (3.6% vs. 1.9%). However, when comparing the composite films with the neat CNF films, an improvement in the tensile strength from ca. 21 to 79 MPa was observed in the previous study, while in the present work this improvement was lower (from ca. 44 to 75 MPa). In another study, González del Campo et al. reported nanopapers of TEMPO CNF (from eucalyptus pulp) and sepiolite with a Young's modulus of 3.4 GPa and a elongation at break of 4.3%, which are also values comparable to those of the present work. However, in that study, the authors found a remarkable decrease in the elongation at break going from neat TEMPO CNF (19.5%) to TEMPO CNF + 20% sepiolite (4.3%), which we have not observed in the present work (elongation at break varied from ca. 2 to 3.6%). Some differences observed could be due mainly to the different procedures used to prepare the films (solvent casting or filtration method) and the different carboxyl content of the CNFs used. In sum, our results confirm that in addition to the good dispersion state of the mineral, the size and the shape of the used mineral have similarities with the size and shape of TEMPO CNF, both factors with a high impact on the optical and mechanical properties of the produced composite films.

#### 4. Conclusions

The starting sepiolite and palygorskite samples showed a fibrous nature, as expected, consisting of aggregates/crystal bundles and the HR-TEM images revealed that the crystals were not fully individualized when dispersed in aqueous medium using the ultrasound probe treatment, being observed aggregates, "face-to-face", of several crystals. The X-ray diffraction studies revealed only very minor changes in the diffraction pattern of the samples when subjected to the ultrasonic treatment, being these slight changes attributed to the disaggregation of the crystals of the minerals.

The further addition of dispersing agents did not lead to relevant changes in the fibrous mineral structure. On the other hand, the microscopic studies revealed important improvements in the dispersion state of the mineral samples induced by the addition of the different dispersants, mainly polyphosphate and CMC; when the clay samples were prepared using polyacrylate, an extensive "random" reaggregation was observed.

The dispersion state of the mineral, sepiolite, showed an important impact on the optical and mechanical properties of the composite films produced with nanocelluloses. The use of the same content (20%) of sepiolite dispersed with ultrasonication and CMC as dispersant led to a lower decrease in the mechanical properties and transparency of the films prepared using Mec CNF (vs. the neat CNF film) when comparing with the film preparation using sepiolite dispersed with high-shear disperser. The film produced using TEMPO CNF and sepiolite, with the mineral previously dispersed with ultrasonication and CMC, presented mechanical properties superior to those of the corresponding neat TEMPO CNF film, and a high transparency, close to that of the neat CNF film. These films could find applications in printed electronics, where the transparency of the films is a relevant issue. The incorporation of highly dispersed sepiolite not only can reduce the price of the films but at the same time improve the mechanical properties of the films. The present work intends to be the basis to develop a new generation of composite films, in which it will be possible to tune the properties of the film, according to the desired application, by changing the formulation and/or the dispersion state of the minerals used.

#### Funding

The present research was supported by the R&D Project "FILCNF-New generation of composite films of cellulose nanofibrils with mineral particles as high strength materials with gas barrier properties" (PTDC/QUI-OUT/31884/2017, CENTRO 01-0145-FEDER-031884), and the Strategic Research Centre Projects UIDB/00102/2020 and UIDB/05488/2020 funded by the Fundação para a Ciência e Tecnologia (FCT) and FEDER.

#### CRedit authorship contribution statement

**Luís Alves:** Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Ana Ramos:** Investigation, Writing – review & editing. **Eduardo Ferraz:** Methodology, Writing – original draft, Writing – review & editing. **Pedro Sanguino:** Investigation, Writing – review & editing. **Julio Santarén:** Writing – review & editing. **Maria G. Rasteiro:** Writing – review & editing, Funding acquisition. **José A.F. Gamelas:** Conceptualization, Investigation, Funding acquisition, Project administration, Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.clay.2023.106823>.

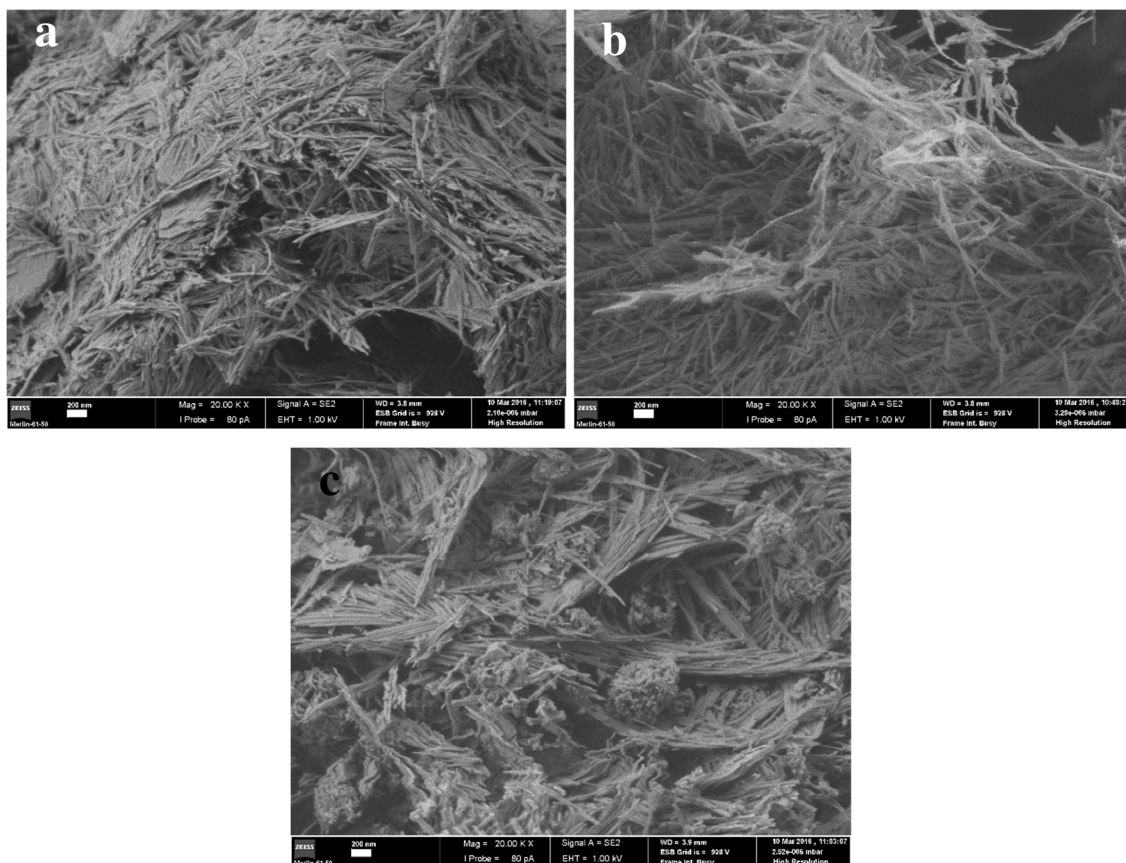
## References

- Alves, L., Lindman, B., Klotz, B., Böttcher, A., Haake, H.-M., Antunes, F.E., 2015. Rheology of polyacrylate systems depends strongly on architecture. *Colloid Polym. Sci.* 293, 3285–3293.
- Alves, L., Ferraz, E., Gamelas, J.A.F., 2019. Composites of nanofibrillated cellulose with clay minerals: a review. *Adv. Colloid Interf. Sci.* 272, 101994.
- Alves, L., Ferraz, E., Lourenço, A.F., Ferreira, P.J., Rasteiro, M.G., Gamelas, J.A.F., 2020a. Tuning rheology and aggregation behaviour of TEMPO-oxidised cellulose nanofibrils aqueous suspensions by addition of different acids. *Carbohydr. Polym.* 237, 116109.
- Alves, L., Ferraz, E., Santarén, J., Rasteiro, M.G., Gamelas, J.A.F., 2020b. Improving colloidal stability of sepiolite suspensions: effect of the mechanical disperser and chemical dispersant. *Minerals* 10, 779.
- Alves, L., Ramos, A., Rasteiro, M.G., Vitorino, C., Ferraz, E., Ferreira, P.J.T., Puertas, M. L., Gamelas, J.A.F., 2022. Composite films of nanofibrillated cellulose with sepiolite: effect of preparation strategy. *Coatings* 12, 303.
- Benli, B., Du, H., Celik, M.S., 2012. The anisotropic characteristics of natural fibrous sepiolite as revealed by contact angle, surface free energy, AFM and molecular dynamics simulation. *Colloids Surf. A Physicochem. Eng. Asp.* 408, 22–31.
- Bradley, W.F., 1940. The structural scheme of attapulgite\*. *Am. Mineral.* 25, 405–410.
- Cecilia, J.A., Vilarrasa-García, E., Cavalcante, C.L., Azevedo, D.C.S., Franco, F., Rodríguez-Castellón, E., 2018. Evaluation of two fibrous clay minerals (sepiolite and palygorskite) for CO<sub>2</sub> Capture. *J. Environment. Chem. Eng.* 6, 4573–4587.
- Ferraz, E., Alves, L., Sanguino, P., Santarén, J., Rasteiro, M.G., Gamelas, J.A.F., 2021. Stabilization of palygorskite aqueous suspensions using bio-based and synthetic polyelectrolytes. *Polymers* 13, 129.
- Gamelas, J.A.F., Ferraz, E., 2015. Composite films based on nanocellulose and nanoclay minerals as high strength materials with gas barrier capabilities: key points and challenges. *BioResources* 10, 6310–6313.
- García, N., Guzmán, J., Benito, E., Esteban-Cubillo, A., Aguilar, E., Santarén, J., Tiemblo, P., 2011. Surface modification of sepiolite in aqueous gels by using methoxysilanes and its impact on the nanofiber dispersion ability. *Langmuir* 27, 3952–3959.
- Ghanadpour, M., Carosio, F., Ruda, M.C., Wågberg, L., 2018. Tuning the nanoscale properties of phosphorylated cellulose nanofibril-based thin films to achieve highly fire-protecting coatings for flammable solid materials. *ACS Appl. Mater. Interfaces* 10, 32543–32555.
- González del Campo, M.M., Darder, M., Aranda, P., Akkari, M., Huttel, Y., Mayoral, A., Bettini, J., Ruiz-Hitzky, E., 2018. Functional hybrid nanopaper by assembling nanofibers of cellulose and sepiolite. *Adv. Funct. Mater.* 28, 1703048.
- Guggenheim, S., Krekeler, M.P.S., 2011. Chapter 1 - the structures and microtextures of the palygorskite-sepiolite group minerals. In: Galán, E., Singer, A. (Eds.), *Developments in Clay Science*. Elsevier, pp. 3–32.
- Krekeler, M.P.S., Guggenheim, S., 2008. Defects in microstructure in palygorskite-sepiolite minerals: A transmission electron microscopy (TEM) study. *Appl. Clay Sci.* 39, 98–105.
- Lindman, B., Medronho, B., Alves, L., Norgren, M., Nordenskiöld, L., 2021. Hydrophobic interactions control the self-assembly of DNA and cellulose. *Q. Rev. Biophys.* 54, e3.
- Lo Dico, G., Wicklein, B., Lisuzzo, L., Lazzara, G., Aranda, P., Ruiz-Hitzky, E., 2019. Multicomponent bionanocomposites based on clay nanoarchitectures for electrochemical devices. *Beilstein J. Nanotechnol.* 10, 1303–1315.
- Magalhães, S., Alves, L., Medronho, B., Romano, A., Rasteiro, M.D.G., 2020. Microplastics in ecosystems: from current trends to bio-based removal strategies. *Molecules* 25, 3954.
- Martín-Sampedro, R., Eugenio, M.E., Ibarra, D., Ruiz-Hitzky, E., Aranda, P., Darder, M., 2022. Tailoring the properties of nanocellulose-sepiolite hybrid nanopapers by varying the nanocellulose type and clay content. *Cellulose* 29, 5265–5287.
- Nagy, B., Bradley, W.F., 1955. The structural scheme of sepiolite\*. *Am. Mineral.* 40, 885–892.
- Neaman, A., Singer, A., 2000. Rheological properties of aqueous suspensions of palygorskite. *Soil Sci. Soc. Am. J.* 64, 427–436.
- Takei, T., Oda, R., Miura, A., Kumada, N., Kinomura, N., Ohki, R., Koshiyama, H., 2013. Effect of dispersion of sepiolite in sepiolite-NBR composite on the tensile strength. *Compos. Part B* 44, 260–265.
- Wang, W., Wang, A., 2016. Recent progress in dispersion of palygorskite crystal bundles for nanocomposites. *Appl. Clay Sci.* 119, 18–30.
- Wang, A., Wang, W., 2019. 1 - Introduction. In: Wang, A., Wang, W. (Eds.), *Nanomaterials from Clay Minerals*. Elsevier, pp. 1–20.
- Wang, Q., Zhang, J., Wang, A., 2014. Freeze-drying: a versatile method to overcome re-aggregation and improve dispersion stability of palygorskite for sustained release of ofloxacin. *Appl. Clay Sci.* 87, 7–13.
- Zeng, J., Zeng, Z., Cheng, Z., Wang, Y., Wang, X., Wang, B., Gao, W., 2021. Cellulose nanofibrils manufactured by various methods with application as paper strength additives. *Sci. Rep.* 11, 11918.

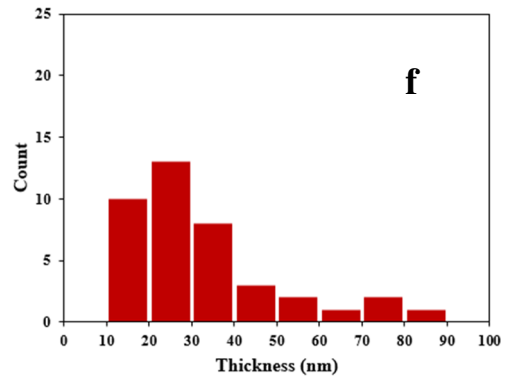
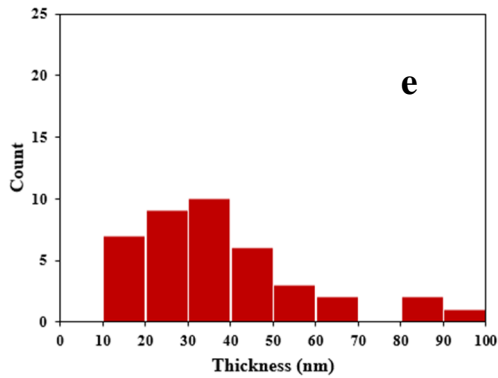
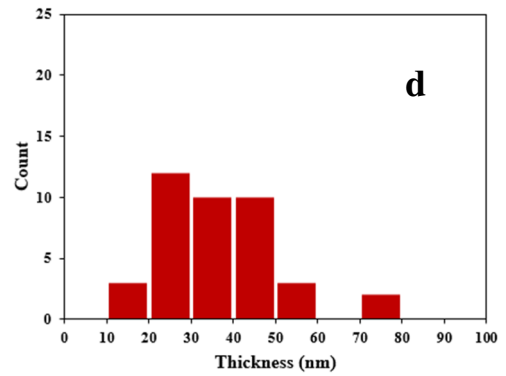
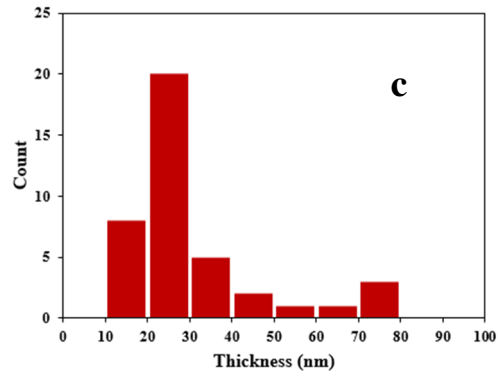
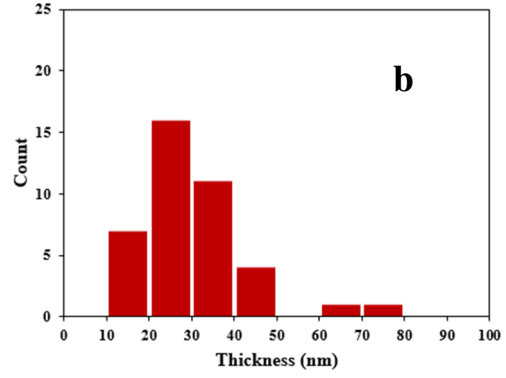
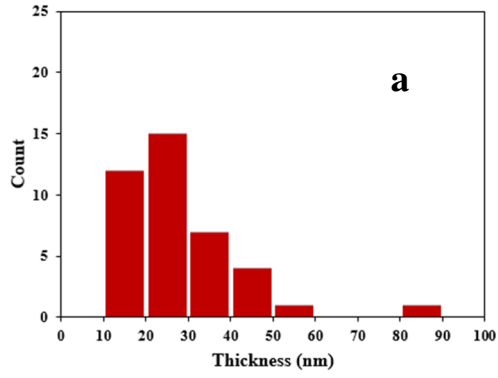


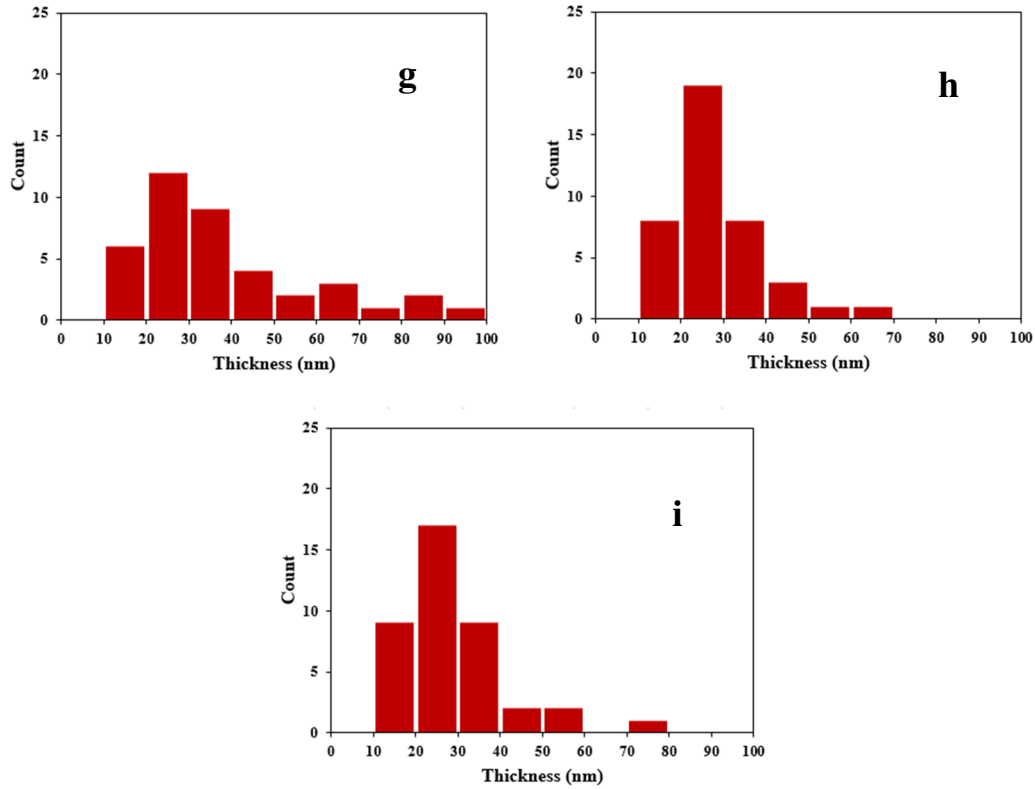
© 2020 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

## Supplementary material

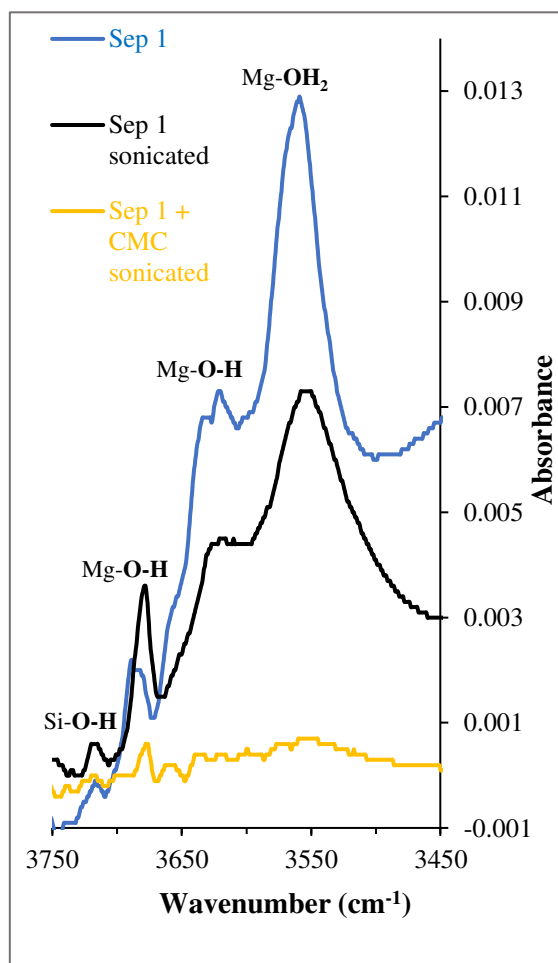


**Figure S1.** FE-SEM micrographs of a) sepiolite 1; b) sepiolite 2, and c) palygorskite, at a magnification of 20,000x. The scale bars correspond to 200 nm.





**Figure S2:** Frequency distributions (based on 40 measurements for each sample) of the thickness of the particles obtained from HR-TEM micrographs for a) sepiolite 1 with polyphosphate, b) sepiolite 1 with polyacrylate, c) sepiolite 1 with CMC, d) sepiolite 2 with polyphosphate, e) sepiolite 2 with polyacrylate, f) sepiolite 2 with CMC, g) palygorskite with polyphosphate, h) palygorskite with polyacrylate and i) palygorskite with CMC.



**Figure S3.** FTIR spectra of sepiolite (sepiolite 1), sepiolite after ultrasonication and sepiolite after ultrasonication with added CMC. Spectra were registered in a PerkinElmer Frontier spectrometer in the ATR mode, using 128 scans and a resolution of 4 cm<sup>-1</sup>. The bands attribution followed Frost et al., 2001 (Near-infrared and mid-infrared spectroscopic study of sepiolites and palygorskites. *Vibrational Spectroscopy*, 2001, 27, 1–13). Samples were previously dried at 55 °C before the spectra acquisition.