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# Silicates as alternative pretreatment for cellulose pulp to obtain nanofibrils for application in biodegradable packaging: a technical review

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TECHNOLOGY OF FOREST PRODUCTS

## ABSTRACT

**Background:** The production of cellulose microfibrils/nanofibrils (CMF/CNF) has attracted increasing attention in recent decades due to their excellent barrier, mechanical, and surface chemistry properties. However, large-scale industrial production of CMF/CNF has been a major challenge due to their high energy consumption, limiting their application. In this context, in recent years many studies have focused on developing pre-treatments designed to facilitate the fibrillation of CMF/CNF by reducing energy consumption during their production. This review highlights the latest advances in the use of silicates as chemical pre-treatments for CMF/CNF production, covering the main aspects related to the effects of chemical modification on the production and the properties of materials for application in biodegradable packaging.

**Results:** Energy consumption reductions of up to 30% were achieved by pretreating cellulose pulps using silicates. In addition, the pre-treatments resulted in smaller CMF/CNF diameters and greater individualization of the nanofibrils. Studies evaluating the thermal stability, hydrophobicity, mechanical properties, and porosity of CMF/CNF pre-treated with silicates have reported promising results. The application of CMF/CNF pretreated with calcium and magnesium silicates in cardboard coating resulted in packaging with low water vapor permeability and high ductility.

**Conclusion:** Silicates interact well with cellulose surfaces, making them a promising material for the chemical pre-treatment of CMF/CNF. Furthermore, the modification by silicates could be an interesting strategy for expanding the use of CMF/CNF in the development of new products.

**Keywords:** barrier properties, energy consumption, fiber modification, paper coating.

## HIGHLIGHTS

Energy consumption in the production of CNF can be minimized with the use of silicates.
$Na_2SiO_3$ is a potential alkaline agent capable of facilitating mechanical fibrillation.
$Ca_2O_4Si$ and $MgO_3Si$ can functionalize CNF, expanding their use in new materials.
Coating cardboard with silicate functionalized CNF can improve the water vapor barrier.

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## INTRODUCTION

Non-biodegradable petroleum-based polymers can negatively impact ecosystems due to their accumulation and slow degradation. Studies have reported contamination of water and food by microplastics (COX et al., 2019), impairment of biogeochemical cycles (SEELEY et al., 2020), harm to the health of terrestrial and aquatic organisms (CHIA et al., 2020; JÂMS et al., 2020), and alteration of the landscape (LAVERS et al., 2019).

Thus, the use of biopolymers to fully or partially replace the use of non-biodegradable polymers has been increasingly investigated. In this context, cellulose is a plausible alternative because it is the most abundant natural polymer on Earth and has great versatility (KIM et al., 2020). Studies on cellulose have focused on its transformation, characterization, and applications on micro and nanometric scales.

Cellulose micro/nanofibrils (CMF/CNF) are fibrillar units resulting from the deconstruction of the cell wall and isolation of cellulose chains with nanometric dimensions (1-100 nm) and lower density (~ 1.5 g $cm^{-3}$) than other materials, such as metals and glasses (ARIFFIN et al., 2018). Due to its high mechanical strength, specific surface area, and biodegradability, besides low toxicity, this material has been investigated for applications in drug encapsulation (KUPNIK et al., 2020), packaging and films (AHANKARI et al., 2021), magnetic films (ARANTES et al., 2019), the textile industry (SAREMI et al., 2020), and reinforcement for polymer matrices (GUAN et al., 2020a; MÜLLER et al., 2020).

Mechanisms such as chemical treatments or mechanical processes can be performed to obtain CMF/CNF from plant fibers. These mechanical processes include microfluidization (PERRIN et al., 2020), sonication (ZHOU et al., 2020; WU et al., 2021), high-pressure homogenization (KARINA et al., 2020), and mechanical fibrillation in stone mills (LEAL et al., 2021).

The challenges in mechanical fibrillation concern the difficulty in deconstructing the crystalline structure of cellulose (BIAN et al., 2019; SÁNCHEZ-GUETIÉRREZ et al., 2020). The deconstruction of the cell walls of plant fibers without the use of chemical treatment leads to high energy consumption, varying from 30,000 to 50,000 kWh/t using a stone mill (ultrarefiner) (ESPINOSA et al., 2019; DU et al., 2020).

Chemical pretreatments of cellulosic fibers have been widely used to reduce energy consumption during the mechanical fibrillation of the cell walls (NECHYPORCHUK et al., 2016). Rol et al. (2019) highlighted the main pretreatments to modify the surface of the fibers to produce CMF/CNF with different properties, namely, sulfoethylation (NADERI et al., 2017); carboxymethylation (ARVIDSSON et al., 2015; IM et al., 2018); phosphorylation (NOGUCHI et al., 2017); and oxidation mediated by N-oxyl-2,2,6,6-tetramethylpiperidine-TEMPO (SAITO et al., 2007).

Although the use of these treatments considerably reduces energy consumption during the mechanical fibrillation of cellulose, some of these pretreatments may increase reagent costs, considering production on an industrial scale (LONG et al., 2017; HU et al., 2018; BIAN et al., 2020). TEMPO can result in costs above US$ 700,000.00/t, based on the required quantity described by Saito et al. (2007). In addition, there are inherent health risks arising from the presence of chemical substances adhered to the surfaces of CMF/CNF intended to be used in packaging and foods (STOUDMANN et al., 2020; AIMONEN et al., 2021).

Thus, the study of alternative pretreatments may yield CMF/CNF with lower energy consumption and physicochemical properties suitable for application in new products. One possibility is the silylation of cellulose (TRACHE et al., 2020), which may increase thermal and dimensional stability, water repellency, gas barrier properties, and mechanical strength (ANDRESEN et al., 2006; ROBLES et al., 2015; MIRI et al., 2021).

Most studies report the silylation of CMF/CNF and fibers for diverse applications but not as a pretreatment for mechanical fibrillation. Ventura et al. (2020) and Wang et al. (2021) reported applications of CMF/CNF in water treatment, air filtration, biomedical uses, additives in cosmetics, the pharmaceutical industry, the manufacture of electronic devices, and the production of paper and board packaging.

However, notably, the most commonly used silylating agents – tetraethyl orthosilicate (TEOS), methyltrimethoxysilane (MTMS), isobutyl trimethoxysilane (IBTMS), n-octyltriethoxysilane (OTES), chlorodimethyl isopropylsilane (CDMIPS) and 3-aminopropyl triethoxysilane (ATS) – are expensive and require solvents for their activation (ANDRESEN et al., 2006; ROBLES et al., 2015; MIRI et al., 2021).

Silicates are an alternative source of silica in this process; they are less expensive and exhibit high affinity with the hydroxyl groups of cellulose (HO et al., 2012a). On the other hand, considering the mechanical fibrillation processes, silica may cause premature wear of equipment components (discs, extruders, and microfluidizer mills).

Sodium ($Na_2SiO_3$), magnesium ($MgO_3Si$), and calcium ($Ca_2O_4Si$) silicates are options because they are already used in water treatment (LI et al., 2021); pulp bleaching (MOGHADDAM and KARIMI, 2020); the food industry as a stabilizing agent for emulsions (YOUNES et al., 2018); and as a source of nutrients in food supplements (MARTIN, 2007).

Some studies have shown that incorporating the aforementioned silicates into cellulose fibers and CMF/CNF suspensions resulted in composites and films with lower moisture and oxygen permeability, as well as greater mechanical and fire resistance, along with an increase in specific surface area (HUANG et al., 2018; GORGIEVA et al., 2020; LI et al., 2020). In addition, it has been observed that the use of silicates promoted greater stability in suspensions and improved dispersion in polymeric matrices (DEMILECAMPS et al., 2014; MÁRMOL et al., 2016).

Given the already proven potential of silicates, this review presents a survey of data available in the literature on the use of silicates as pretreatments for the production of CMF/CNF, addressing general concepts about chemical pretreatments and mechanical fibrillation of cellulose, the main types of silicates used and the main effects on the properties of the materials for application in biodegradable packaging.

## MECHANICAL FIBRILLATION OF CELLULOSE PULPS: GENERAL ASPECTS AND CHALLENGES

CMF/CNF are renewable products with diameters varying from 25 to 100 nm, obtained from plant fibers by chemical or mechanical processes aimed at deconstructing the cell wall (Figure 1), modifying its morphology and surface properties (ARIFFIN et al., 2018; SOLIKHIN et al., 2019; MIRI et al., 2021).

According to the ISO/TS 20477:2017 standard (ISO, 2017), CNFs are composed of at least one elementary fibril, containing crystalline, semicrystalline, and amorphous regions. In addition, CNF may contain longitudinal divisions, entanglement between particles, or network-like structures.

The terms nanofibrillated cellulose (NFC), microfibrillated cellulose (MFC), cellulose microfibrils (CMF), and cellulose nanofibrils (CNF) have been used to describe CNF produced by mechanical treatment of plant materials, often combined with steps of chemical or enzymatic pretreatment (PENNELS et al., 2020). CNF produced from plant sources by mechanical processes usually contain hemicelluloses and, in some cases, lignin. Some CNFs may have functional groups on their surface as a result of the manufacturing process (ISO, 2017).

The best-known mechanical processes for the production of CMF/CNF are microfluidization (PERRIN et al., 2020), sonication (ZHOU et al., 2020; WU et al., 2021), high pressure (KARINA et al., 2020), and mechanical fibrillation (LEAL et al., 2021). Most of the time, a "mill" induces fibrillation by desquamating the outer cell wall of the plant fiber, exposing the innermost layers (AFRA et al., 2013; SHARMA et al., 2015). The cellulosic fibers are forced at high speed into an opening between a rotating and a static stone disk in sequential stress cycles that, by abrasion, generate shear forces that break the hydrogen bonds of the cell wall. The discs in contact with the fibers, with the aid of grooves and pressure emitted by the mill, disintegrate the material into structural subcomponents. At the end of this process, aqueous suspensions consisting of interlaced and disordered networks of CMF/CNF are obtained (NAIR et al., 2014).

The challenges in the mechanical fibrillation process are related to the heterogeneity of the products and the difficulty in degrading the crystalline structure of cellulose (BIAN et al., 2019; SÁNCHEZ-GUETIÉRREZ et al., 2020). Another major difficulty is related to the high energy consumption necessary for the deconstruction of the cell walls of the fibers without the use of chemical treatment. Studies indicate that when using a stone mill in mechanical fibrillation, energy consumption can reach values between 30,000 and 50,000 kWh/t, depending on the desired degree of fibrillation (OSONG et al., 2016; ESPINOSA et al., 2019).

The heterogeneity of cellulosic products and the variation in energy consumption are associated with the origin of the raw material, the type and duration of the fibrillation process, the number of passes through the mill, and the pre-treatment of the lignocellulosic raw material and the pulp (THOMAS et al., 2020). These aspects were observed by Wang and Zhu (2016), who found that the time and distance between the disks used in the mill affected the characteristics of the films produced with CMF. The authors observed that the density and tensile strength of these films increased as the fibrillation time increased, as there was more exposure of the hydroxyl groups of the cellulose chains, which led to the establishment of hydrogen bonds.

Additionally, using the mechanical fibrillation method, Mihranyan et al. (2012) and Stanislas et al. (2020) showed that the types of raw material influence the crystallinity, porosity, and mechanical strength of CMF/CNF. Additionally, Dias et al. (2019) and Durães et al. (2020) found that the number of grinding cycles in the *grinder* and the effect of alkaline pretreatments significantly influence the displacement of the fiber wall, the morphological properties of the CMF/CNF, and the energy consumption during their production.

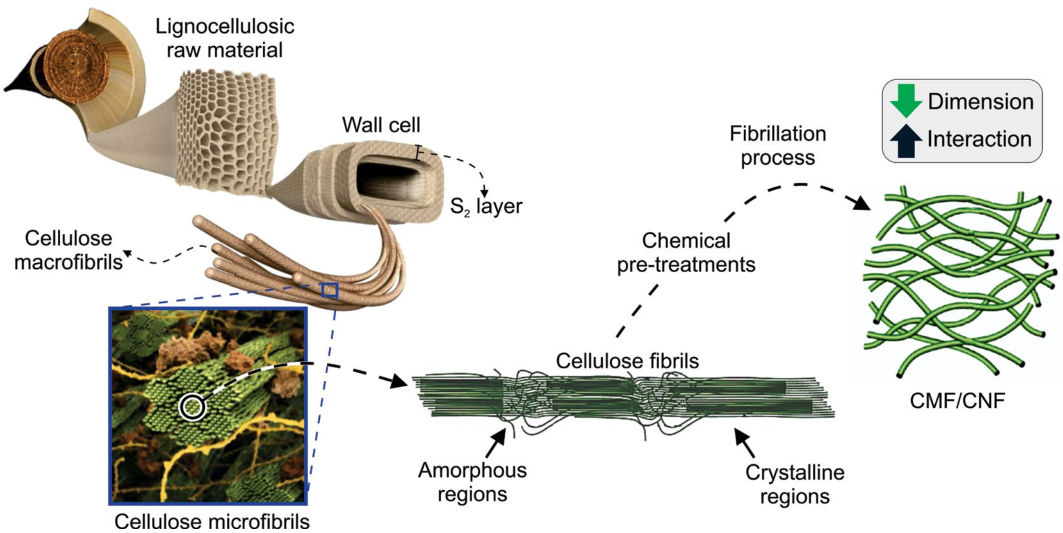


**Figure 1:** General scheme of obtaining cellulose micro/nanofibrils (CMF/CNF) from chemically pretreated lignocellulosic fibers and undergoing the fibrillation process. Source: adapted from Nishimura et al. (2018).

These variations are expected because different mechanisms account for the mechanical fibrillation of the plant cell wall, the most common being internal and external fibrillation. Internal fibrillation consists of the unpacking of the helical structure of cellulose macrofibrils in the $S_2$ layer of the cell wall (CHEN et al., 2014), which, due to the abrasive action of the millstones, are loosened to form CMF/CNF bundles (PHANTHONG et al., 2018; YUAN et al., 2021).

In the case of external fibrillation of the cell wall, the process of friction of the fibers with the millstones causes the individual microfibrils to burst, but they remain partially united to the cell wall (AFRA et al., 2013). Thus, there is an increase in the specific surface area and greater reactivity of the material with the medium, which is desirable for numerous applications (LIU et al., 2020; KUMAR et al., 2020).

Regarding the other mechanisms, studies have indicated that they are more closely related to excessive fibrillation of the cellulosic pulp (SCATOLINO et al., 2017; ARÉVALO et al., 2019). In this case, the formation of dispersed fines occurs due to the breakage of the CMF/CNF along their length, thus reducing their aspect ratio. This phenomenon leads to higher energy consumption and reductions in the crystallinity index, molar mass, and mechanical strength of the microfibrils (SERRA-PARAREDA et al., 2021). Figure 2 shows the main mechanisms of cell wall fibrillation.

Similarly, Lengowski et al. (2020) found that the use of different degrees of fibrillation of fibers can influence the physicochemical properties of films produced with CMF/CNF. These authors observed that the higher the degree of fibrillation, the greater the thermal stability and impermeability of cellulose films to air and water.

Thus, there are still gaps regarding the factors that influence mechanical fibrillation and the properties of the microfibrils obtained by this process. Several studies have shown that the application of pretreatments to cellulosic fibers, in addition to reducing energy consumption, can result in the functionalization of microfibrils, expanding their range of applications and reducing production costs (FILIPOVA et al., 2020; ONYIANTA et al., 2020; REN et al., 2020). Next, the main types of chemical pretreatments used in cellulosic pulps to facilitate the mechanical fibrillation process are discussed.

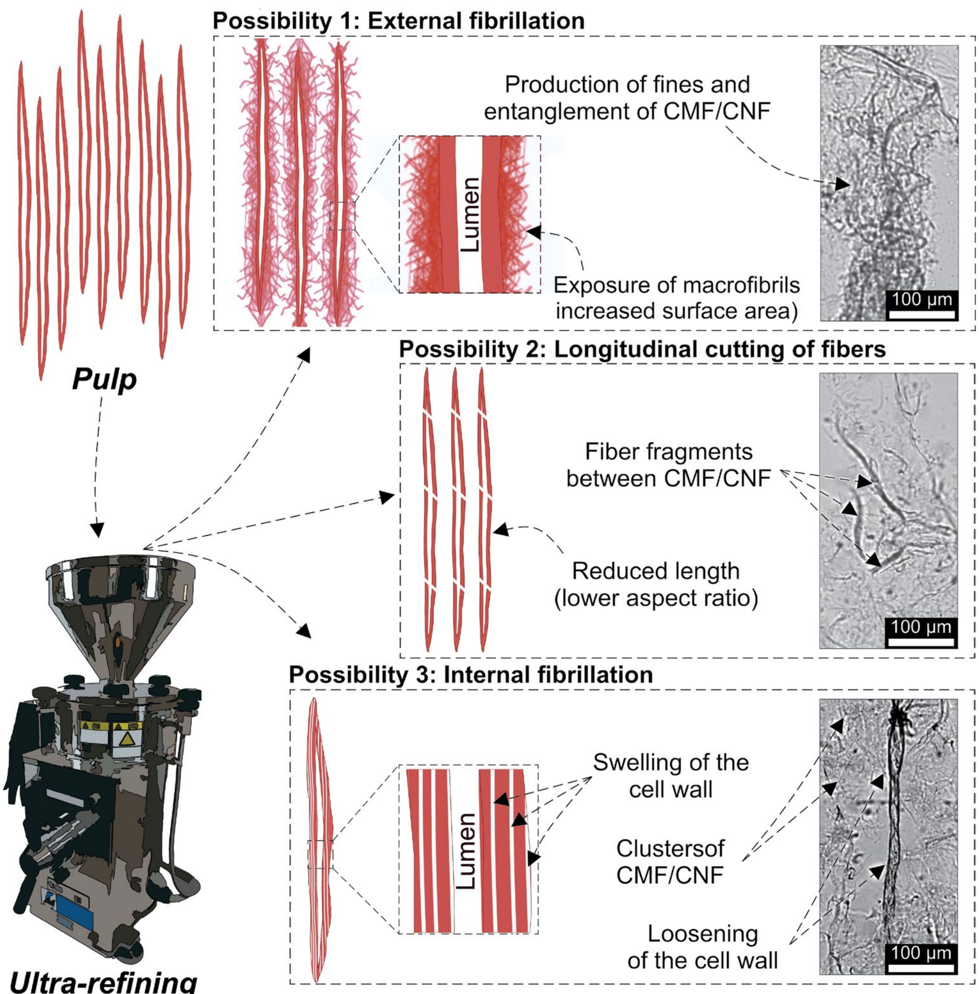


**Figure 2:** Schematic of the external and internal fibrillation mechanisms and their impacts on the characteristics of cellulose micro/nanofibrils (CMF/CNF).

## CHEMICAL PRETREATMENTS AND MECHANICAL FIBRILLATION OF CELLULOSE PULPS

As mentioned, due to the molecular structure of cellulose, the mechanical deconstruction of the cell wall is hindered. Thus, to reduce the energy consumption of this process and to obtain CMF/CNF with desirable quality, the pretreatments have been widely discussed (NECHYPORCHUK et al., 2016; TRACHE et al., 2020).

Studies conducted by Rol et al. (2019) presented the main pretreatments for modification of the fiber surface and production of CMF/CNF with different properties. These include sulfoethylation (NADERI et al., 2017); carboxymethylation (ARVIDSSON et al., 2015; IM et al., 2018); phosphorylation (NOGUCHI et al., 2017); and oxidation mediated by N-oxyl-2,2,6,6-tetramethylpiperidine - TEMPO (SAITO et al., 2007).

Among the mentioned pretreatments, TEMPO-mediated oxidation stands out because of the characteristics of the CNF produced. After employing this pretreatment in the bleached kraft pulp of conifers, Saito et al. (2007) obtained CNF diameters between 2 and 5 nm; increased water retention index (WRI) due to the higher specific surface of the CNF and, consequently, greater exposure of polar groups; improved CNF suspension stability; increased light transmittance through the suspension; and increased shear rate and viscosity of the CNF suspension. In addition, the use of TEMPO reduced energy consumption and accelerated the mechanical fibrillation process (ONYIANTA et al., 2018).

Studying the mechanical fibrillation of bleached kraft pulps from conifers, Isogai et al. (2011) and Filipova et al. (2020) reported that TEMPO pretreatment resulted in energy consumption varying between 13,000 and 19,000 kWh/t using a *grinder* and high-pressure homogenizer, respectively, in the production of CNF. Compared with the consumption presented by Osong et al. (2016) and Espinosa et al. (2019), which were between 30,000 and 50,000 kWh/t, the use of TEMPO saved an average of 50%. Such results are significant regarding the cost of producing CMF/CNF at an industrial scale.

However, the cost of using TEMPO is very high. Considering the protocol presented by Saito et al. (2007) and the average cost of the TEMPO solvent – US$122.00/g, for each dried ton of pulp, 16 kg of solvent would be required for US$1,952,000.00/t. In addition, both TEMPO and the other pretreatments mentioned in this study have the potential to generate chemically active wastes, which need to be neutralized for further disposal in the environment, adding more costs and environmental liabilities (LONG et al., 2017; HU et al., 2018; BIAN et al., 2020). Health risks due to the chemical modifications of CMF/CNF that cannot be completely ruled out are another problem (AIMONEN et al., 2021). These drawbacks limit the application of this material in food and packaging.

Thus, the issue of pulp pretreatments has not been fully resolved, making it necessary to explore new solutions. There are research initiatives aimed at using less expensive solvents for the mechanical fibrillation of cellulose. Dias et al. (2019) applied different concentrations of NaOH in the pretreatment of *Eucalyptus* sp. and *Pinus* sp. pulp, reducing the energy consumption to values between 4050 and 10,300 kWh/t, the number of cycles in the stone mill, and improving the fibrillation degree by using NaOH pretreatment at 5% and 80 °C for 2 h. Other studies have presented controversial results indicating that the use of NaOH does not reduce energy consumption and makes the CMF/CNF brittle, reducing their quality and stability (TRACHE et al., 2020).

Xu et al. (2020) used hydrothermal pretreatment (180 °C/ 30 min) without the application of additives to the cellulosic pulp, and after stone mill processing, they obtained an energy consumption of approximately 8150 kWh/t and an average CMF/CNF diameter of 8.4 nm.

Although hydrothermal pretreatment offers the advantage of producing CMF/CNF without the need for chemical reagents, using this material as a reinforcement in polymer composites or as an adsorption/release agent requires modifying its surface to increase chemical compatibility with the polymer matrix. It is also important to note that hydrothermal pretreatment on an industrial scale can entail significant costs since heating large volumes of water and pulp requires energy sources such as biomass, electricity, or fossil fuels. Therefore, the need to consider reducing energy consumption and maintaining the quality of CMF/CNF, making them compatible with uses in which health and the environment are not affected, is a great challenge. Some studies have already demonstrated the affinity between the hydroxyl groups of cellulose and silica sources (ANDRESEN et al., 2006; HO et al., 2012b; MENDES et al., 2015; LI et al., 2018). However, the potential of their use as cellulose pretreatments to facilitate mechanical fibrillation has not been addressed. Thus, in the next section, the characteristics of the aforementioned silicates are presented, and how their interaction with fibers and CMF/CNF can modify their surfaces is discussed.

## MODIFICATION OF CELLULOSIC FIBERS AND CMF/CNF WITH SILICA

Silylation is the main method used to modify the surface of cellulose through the addition of silica (TRACHE et al., 2020). In most studies, it was observed that this method is used for modification of CMF/CNF and fibers for various applications, but no studies were found using this method as a pretreatment of cellulosic pulp with the aim of mechanical fibrillation. The objective of these modifications is to make the surfaces of CMF/CNF more hydrophobic, increase their mechanical strength, and facilitate the miscibility of suspensions in polymer matrices (ROL et al., 2019).

Sequeira et al. (2009) produced hybrid composites of cellulose and silica by applying TEOS to bleached *Eucalyptus* sp. These authors found that TEOS increased the mechanical strength, and thermal and dimensional stability of the composites, making them suitable for packaging by providing a moisture barrier and thermal insulation.

Mendes et al. (2015) used silane agents to modify *Eucalyptus* sp. pulp using MTMS, IBTMS, and OTES. The authors found a high degree of substitution at carbons

2, 3, and 6 of cellulose. This resulted in increased water repellency, improving the properties of the fibers for applications in polymer and fiber-cement composites.

Regarding CMF/CNF, Andresen et al. (2006), using CDMIPS as the silylating agent, found an increase in the hydrophobicity of the material and the surface roughness. Robles et al. (2015) used ATS for surface modification of cellulose nanocrystals (CNC) to use them as reinforcement of poly (lactic acid) (PLA). In the study, it was reported that there was an increase in the hydrophobicity of cellulose with the addition of ATS, as well as improvements in the mechanical and thermal resistance of the CNF-PLA composites, due to the better dispersion of CNF in the polymer matrix.

Miri et al. (2021) modified CMF/CNF using TEOS in different proportions and observed that TEOS increased more the specific surface area of CNF than that of CMF. This resulted in an increase in the adsorption power of chemical components by cellulose in the form of an aerogel.

The main advantages of using chemical formulations based on silica as a cellulose surface modifying agent are related to mechanical strength and barrier properties. However, the reagents used for silylation mentioned above are expensive and require reagents for their activation. Thus, other sources of silica such as silicates have the potential for treating cellulosic fibers (HO et al., 2012a).

## POTENTIAL OF SILICATES AS PULP PRETREATMENT FOR THE PRODUCTION OF CMF/CNF AND ITS PACKAGING APPLICATIONS

There are few reports in both literature and industry regarding the use of silicates as pre-treatments for pulps to facilitate mechanical fibrillation for the production of CMF/CNF. The majority of accounts are focused on the use of silicates for fiber modification and subsequent application or incorporation of silicates into CMF/CNF suspensions. In other words, understanding the fundamental role of silicates in the early stages of cellulose pulp processing reveals untapped potential. The inherent ability of silicates to interact with cellulose fibers at a molecular level has the potential to revolutionize the efficiency and effectiveness of mechanical fibrillation processes.

By delving into this less-explored aspect, this review aims to present the potential of silicates in optimizing CMF/CNF production and their subsequent utilization in the burgeoning field of biodegradable packaging, composite production, paper coating solutions, enhancement of packaging barrier properties, and other applications that will be introduced below.

In a study carried out by Ho et al. (2012b), clays and micas were used to manufacture composites made up of CNF and silicates and there was significant impregnation of the silicate particles into the hydroxyl groups of the cellulose. This impregnation produced remarkable results, including a reduction in water vapor adsorption, an increase in hardness and the shear and tensile strength of the composites.

Guan et al. (2020b) and Liu et al. (2013), when applying mica and montmorillonite as silicate sources for CNF modification, obtained high fire resistance, increased mechanical strength, good gas barrier properties, and high optical transparency, combined with the low overall density of the material. Despite such advantages, micas and clays are not completely pure materials and may contaminate the material with inert or undesirable substances, depending on the application.

Thus, the use of silicate sources with high purity is necessary. Examples of this class include sodium ($Na_2SiO_3$), magnesium ($MgO_3Si$), and calcium ($Ca_2O_4Si$) silicates, which stand out for their availability and low cost compared to other reagents used for the conventional treatment of cellulosic pulp.

$Na_2SiO_3$ is an alkaline inorganic salt found in liquid and solid forms. Due to its homogeneity, chemical stability, viscosity, polymerization capacity, alkalinity, and ability to modify surface charges, it has been widely used in different industrial applications (NAHRAWY et al., 2018). This includes the production of adhesives (SONG et al., 2021), wood treatment (NEYSES et al., 2017), water cleaning (LI et al., 2021), the production of ceramics (EL-DIDAMONY et al., 2020), and pulp bleaching (MOGHADDAM and KARIMI, 2020).

Some studies report the modification of the cellulose surface through $Na_2SiO_3$. In this context, Demilecamps et al. (2014) found that the addition of $Na_2SiO_3$ reduced the specific surface area of the cellulosic fibers, inhibiting the formation of aggregates. These authors observed that there were considerable gains in the mechanical strength of the cellulose aerogel.

Additionally, studying the production of aerogels using $Na_2SiO_3$ in NFC of plant and bacterial origins, Sai et al. (2014) and Gorgieva et al. (2020) observed high reagent impregnation on the surface of the nanofibril network, increased hydrophobicity, reduced porosity, and improved mechanical properties and thermal stability with increasing $Na_2SiO_3$ concentration. The researchers also highlighted that although it requires the use of other reagents, the process generates little waste and is promising for obtaining materials for thermal insulation.

Mascarenhas et al. (2022a, b) investigated the use of $Na_2SiO_3$ as a pretreatment to obtain CMF/CNF from *Pinus* sp. and *Eucalyptus* sp. by a mechanical process. A reduction in energy consumption for production was observed, in addition to a reduction in the diameters and greater individualization of the CMF/CNF. Pretreatment with $Na_2SiO_3$ also increased the quality index (QI) of the CMF/CNF suspensions, reaching a maximum IQ value of 70 for CMF/CNF of *Eucalyptus* treated with 10% $Na_2SiO_3$. In the derived films, pretreatment with $Na_2SiO_3$ resulted in a reduction in transparency and an increase of up to 20% in tensile strength. The films with the treated fibers also presented an adequate barrier to UV-C radiation, water vapor, and oil.

Setter et al. (2023a) explored the use of CNF pretreated with sodium silicate and the cationic surfactant cetyltrimethylammonium bromide (CTAB) in the efficiency of the spray drying process and observed that there was an increase of up to 51% in the productivity of powdered CNF. The authors attributed this effect to the lower adhesion of the particles to each other and the dryer wall due to the low viscosity of the suspensions, provided by the addition of the surfactant CTAB, and to the higher degree of fibrillation of the CNF pre-treated with sodium silicate, which contributed to the formation of denser particles and, as a result, they were deposited more quickly by gravity, limiting their ability to adhere to the equipment wall. Setter et al. (2023b) found that alkaline pre-treatment with $Na_2SiO_3$ favored interaction with the cationic surfactant CTAB, which contributed to fewer hydrogen bonds being established among the CNF during spray drying. The authors produced cellulose films with these aggregates, redispersing them using the ultrasound process; the films had a compact and homogeneous internal structure, with good water vapor barrier and mechanical properties, characteristics attributed to the efficient redispersion of the agglomerates.

Magnesium silicate is characterized by being an adsorbent in the form of a very fine powder that is white or grey and odorless and can be natural or obtained synthetically. Its application is observed in various sectors of the industry, in the form of filler in paints, providing greater washability resistance to the coating (KRYSZTAFKIEWICZ et al., 2004); in the food industry as a stabilizing agent for emulsions and anti-wetting agents in salts and dehydrated fruits (YOUNES et al., 2018); and as a source of nutrients in food supplements (MARTIN, 2007). Another interesting feature of natural magnesium silicates is related to their low porosity and large specific surface area (PALEM et al., 2021).

Elsayed et al. (2018) studied the combination of magnesium silicate and cellulose for the production of capsules for medicines. In the study, it was found that the capsules remained intact for a longer time due to the moisture protection conferred by the magnesium silicate, without the need for additional substances. In addition, greater compatibility was observed, and the disintegration and release time of the drug was faster.

Huang et al. (2018) developed porous films with magnesium silicate for the adsorption of heavy metal ions in an aqueous solution and highlighted the low cost and high reactivity of magnesium silicate in the adsorption of heavy metals as the main advantages of this material. Studying the effect of adding magnesium silicate to the surface of carboxymethyl cellulose (CMC), Liu et al. (2019) found that the adhesion of magnesium silicate to the cellulose surface depends on the pH, and the best results are found for the range 4 to 6.

Mármol et al. (2016) studied the effect of adding magnesium silicate to modify the cellulose for reinforcement in fiber cement and observed that there was a significant gain in mechanical strength of the material using 30% magnesium silicate in the mixture, even after 200 cycles of accelerated aging after 28 days. The authors explained that the layer formed on the surface of the cellulosic fiber reduced exposure to the alkaline agents of the cement. Mascarenhas et al. (2022c) applied $MgO_3Si$ as a pretreatment to obtain CMF/CNF from *Pinus* sp. and *Eucalyptus* sp. and observed a reduction in water retention in the fibers and a reduction of approximately 30% in energy consumption for production.

Calcium silicate is a material obtained from natural raw materials such as quicklime (RICHARDSON, 2008; DAWOOD et al., 2017). It has high resistance to abrasion, humidity, and temperature and is nontoxic, and its applications are very similar to those of magnesium silicate. Biswas et al. (2019) studied the synthesis of cellulose and calcium silicate composites and found that there are large numbers of Ca and Si bonds in the cellulosic hydroxyl groups, demonstrating the affinity between the molecules. In addition, they concluded that the material obtained has high mechanical strength and is indicated for the manufacture of dental and orthopedic prostheses. Li et al. (2020) produced nanocomposites based on calcium silicate and CNF and found a high interaction between these components. The material produced presented a porous network, high specific surface area, and high water repellency.

Li et al. (2018) found similar results when they produced a calcium silicate composite structured with cellulose. In that study, the authors found that the addition of calcium silicate significantly increased the mechanical resistance to tearing and tensile strength and highly interacted with the cellulose surfaces. Ouyang et al. (2012) explained that this interactivity provides a homogeneous dispersion of calcium silicate on the surface of the cellulose, as they verified employing Fourier transform infrared (FTIR) spectroscopy that these particles bind strongly to the hydroxyl groups of cellulose.

In another study, calcium silicate was applied as a pretreatment to obtain CMF/CNF from *Pinus* sp. and *Eucalyptus* sp., which promoted a reduction in energy consumption of approximately 30%, in addition to a reduction in water retention by the fibers (Mascarenhas et al., 2022c).

Regarding applications, Mascarenhas et al. (2022c) applied CMF/CNF pretreated with $Ca_2O_4Si$ and $MgO_3Si$ as coatings on cardboard. The coatings caused a reduction in water vapor permeability and an increase in the ductility of the papers. It was also found that suspensions with 5% and 10% $Ca_2O_4Si$ increased the dispersion of PVAc, PVOH, and printing ink. On the other hand, the use of pretreated CMF/CNF as a coating reduced the strength and stiffness of the papers by approximately 50%, a fact attributed to the wetting and drying cycles conducted for the application. Therefore, future studies involving the optimization of application and drying techniques for CMF/CNF and silicate coating formulations should be conducted, as should studies involving its application in other packaging materials.

Given the above, it appears that silicates interact well with the reactive surfaces of cellulose; this is the initial premise for the possibility of using them as pretreatments for mechanical fibrillation. In addition, the modifications resulting from these interactions could be interesting for applications such as paper coating and packaging production in applications that require a great water barrier. Thus, there is an opportunity to associate these characteristics with CMF/CNF, which have great potential for this purpose.

## PERSPECTIVES AND CONSIDERATIONS ON PRETREATMENT OF PULP WITH SILICATES

According to the studies presented, there is great potential for the use of silicates as fiber pretreatments for the production of CMF/CNF given their affinity for interaction with cellulose.

The use of chemical pretreatments results in cellulose modifications, reducing energy consumption during mechanical fibrillation. Because $Na_2SiO_3$ makes it possible to obtain solutions with high alkalinity, it may facilitate the dissociation and swelling of the fiber cell wall, which indicates the potential for reducing energy consumption. In some cases, the reduction in energy consumption can achieve approximately 30%, in addition to a reduction in water retention by the fibers.

Regarding the pretreatments using $MgO_3Si$ and $Ca_2O_4Si$, it is expected that the impregnation of the fibers results in greater abrasiveness with the millstones, facilitating the breakage of the fibrils during mechanical fibrillation. In addition, considering the applications of these silicates, they can show interesting properties for the application of CMF/CNF in paper coatings, such as water repellency, lipid repellency, and higher mechanical strength.

However, information on the behavior of CMF/CNF suspensions produced with these silicates is incipient, and further study is needed. Future investigations involving the application of CMF/CNF treated with silicates are also necessary, including the exploration of different types of materials as substrates and the optimization of application techniques to potentiate their effects on the packaging properties.

## AUTHORSHIP CONTRIBUTION

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