

# HYBRID SUSTAINABLE NANOCOMPOSITES CONTAINING NANOCELLULOSE FIBRES AND CROSS-LINKED ALUMINOSILICATES

B. Duchemin<sup>1,\*</sup>, D. Viet<sup>2</sup>

<sup>1</sup>LOMC, UMR 6294, CNRS-Université du Havre, 53 rue Prony, 76058 Le Havre, France

<sup>2</sup>LCA, UMR 1010, 4 allée Emile Monso, B.P.44362, 31432 Toulouse cedex 4, France

\*e-mail address of the corresponding author: benoit.duchemin@univ-lehavre.fr

**Keywords:** cellulose, clay, sol-gel, silica.

## Abstract

*A new class of nanocomposites was synthesized using cellulose nanofibres that were covalently linked in-situ with an inorganic matrix. The goal of this research project was to find a new material that: (i) can be produced from sustainable resources (ii) can be consolidated with a low temperature cycle with a low energy input and (iii) retains better mechanical properties than pure cellulose throughout its thermal degradation. The inorganic matrix belongs to the aluminosilicate family and the cross-linking was obtained by a sol-gel process involving the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) under mild acidic conditions. The cross-linking occurring between the matrix and the nanofibres was monitored using Fourier-Transform Infrared spectroscopy. X-ray diffraction was used to assess whether changes in the crystalline fractions occurred during the manufacture process. The thermal resistance of the composites was assessed by thermogravimetric analysis (TGA). The surfaces of these new materials were observed by atomic force microscopy.*

## 1 Introduction

In nature, proteins and polysaccharides are often associated with silicon in the form of silicon dioxide. These nanometric particles are polymerised *in-situ*, creating strong covalent bonds between the two entities. Examples such as diatoms (phytoplankton), radiolarians (zooplankton) and sponges are often cited in the literature, but silica can also coexist with mineral materials in rice, grasses, orchids, *etc* [1] Biomineralisation processes in which organic and mineral entities assemble into a composite are also commonplace in animals where they form structures such as teeth, bones, horns.[2] Hence, organic materials like collagen, elastin, keratin and various other proteins form composite structures with mineral compounds such as hydroxyapatite, calcium carbonate, *etc*. Remarkable mechanical and physiological structures thereby form at low temperatures by nanometric assembly processes. The goal of this project is to use a similar logic to form better materials from the two quasi-universal resources that are cellulose fibres and clays. In order to do so, an inorganic silicon alkoxide (TEOS) was self-assembled by condensation against the two starting materials in order to form covalent bonds between the two materials.

## 2 Materials and testing methods

### 2.1 Materials

Microfibrillated cellulose (MFC) was provided by the Laboratoire de Chimie Agro-Industrielle (LCA) in the hydrated form (~40 wt. % dry mass); it was stored in a freezer until use. An unmodified montmorillonite clay (Sigma-Aldrich) was used as the starting inorganic material. Distilled water was used for all experiments. Tetraethyl orthosilicate (Sigma-Aldrich), hydrochloric acid (Merck) and absolute ethanol (VWR) were used directly with no further purification or modification.

### 2.2. Material preparation

In a typical experiment, about 10 g of MFC (dry equivalent) were mixed in ~ 500 mL distilled water and stirred overnight at room temperature with a magnetic stirrer in a 1 L Schott bottle. The solution was poured in 250 mL Schott bottles. In order to produce homogeneous MFC films, bottles filled with 100 mL solution were first placed in an ultrasonic bath (ultrasonic cleaner Branson 200) at room temperature for 10 min. Hundred millilitres of distilled water were added to the solution before it was stirred with an ultra-turrax® at ~12000 rpm (T18 basic, IKA) for 5 min. The solution was then filtered over acrylic Versapor® filters (0.45 µm pore diameter) in a Buchner funnel assisted with a table-top vacuum pump. The films were then dried in a vacuum bag against a glass plate at room temperature for 40 hrs.

The clay/MFC mixtures were prepared with a slightly different procedure involving the addition of 1 g of clay to 100 mL of 1 wt.% MFC solution before the ultrasonic stirring step. The solution was stirred with a magnetic stirrer at room temperature overnight before the ultra-turrax step. The filtration and the film drying procedure were the same as those described in the previous paragraph. Clay contents of 50 wt.% were chosen in order to compare our results to the results obtained by Liu *et al.*[3]

The tetraethyl orthosilicate (TEOS) solution was prepared in slightly acidic conditions by mixing the TEOS, the diluted acid and the ethanol together. The stirring was carried out overnight at room temperature in order to hydrolyse the TEOS solution.

In order to prepare the consolidated MFC and clay/MFC films, films were immersed in Petri dishes in an excess of TEOS:H<sub>2</sub>O<sub>ac</sub>:C<sub>2</sub>H<sub>5</sub>OH solution at room temperature for 1 hr. They were then placed in a Petri dish filled with ethanol for 1 min in order to remove the excess TEOS solution. The films were stacked between perforated layers under a weight and dried for 48 hrs under ambient conditions.

A silicon matrix was obtained on its own by evaporating the hydrolyzed TEOS in a Teflon Petri dish.

### 2.2 Testing methods

TGA was performed on all materials on a Netzsch TG209. Samples between 5 and 14 mg were placed in Al<sub>2</sub>O<sub>3</sub> crucibles. A heating rate of 10°C/min was carried out between room temperature and 700°C under a constant flow of N<sub>2</sub> (12 mL/min).

Attenuated transmitted reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was performed on a Perkin Elmer Spectrum 65 apparatus equipped with a Miracle ATR accessory. The spectra were acquired in the 4000-450 cm<sup>-1</sup> range with a 4 cm<sup>-1</sup> resolution in 30 sec. All spectra were recorded with the Perkin Elmer spectrum V10 software.

X-ray diffraction patterns were acquired on a X'pert pro PAN'alytical diffractometer (CRISMAT, Caen) equipped with a K<sub>β</sub> Ni filter, 0.04 rad Soller slits on the tube side, anti-scatter slits, a PIXcel-1D detector. The measures were performed in 2θ angular range spanning from 5 to 90° in 8 min. The data was acquired on the Data Collector software and

the  $K_{\alpha 1}$  radiation was selected. The plots were then exported in the .xrdml format and analysed with the Maud software (<http://www.ing.unitn.it/~maud/>).

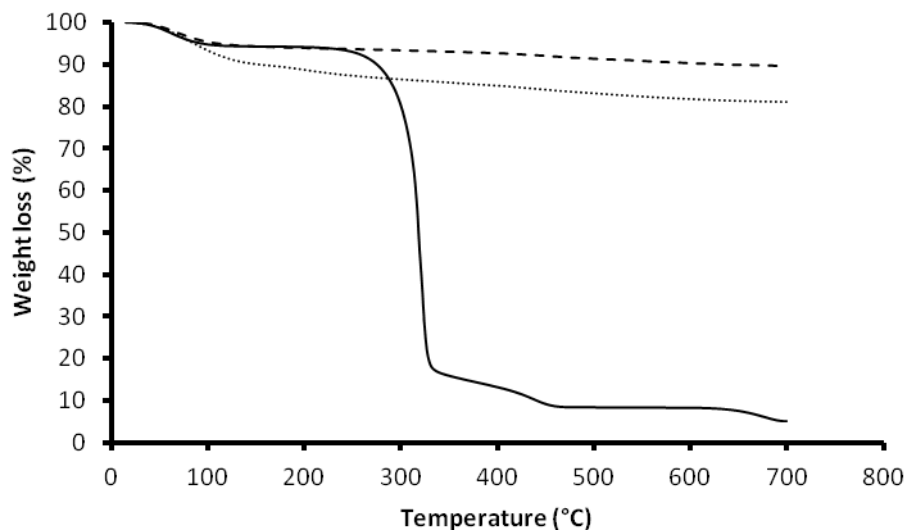
Atomic force microscopy (AFM) was obtained with a Brüker Innova microscope operated in tapping mode. The images were taken with a resolution of 1024X1024 pixels at a scan rate of 0.5 Hz. The cantilevers (RTESPA-CP) possess high-sensitivity silicon probes with a spring constant of 40 N/m and resonance frequency of 300 kHz. The software Nanoscope Analysis v.1.4 was used for lateral microfibril size determination. The initial MFC solution was diluted 25 X in order to obtain an 8 wt.% solution and the solution was stirred with ultrasound for 5 min. Droplets of solution were cast on clean glass slides and left overnight for drying at room temperature. A final drying step involved placing the glass slides in an oven at 105°C for 1 hr. The surfaces of the films tested with the other techniques were also imaged.

### **3 Results and discussion**

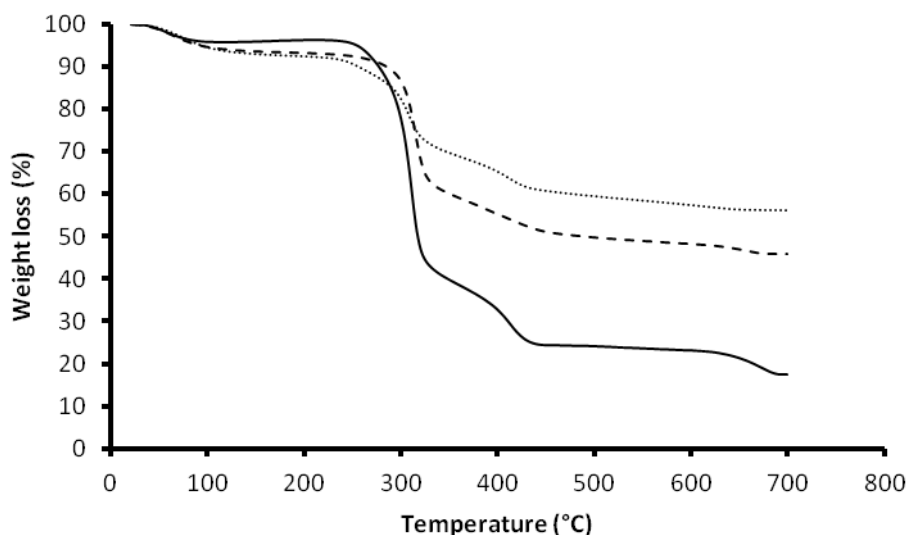
#### *3.1 TGA*

The samples show large differences in their thermal behaviours. The remaining weight fraction of the MFC after test completion was 5.02 wt.%, that of the silicon matrix was 80.97 wt.% and that of the TEOS-consolidated MFC was 17.57 wt.%. These results suggest a maximum SiO<sub>2</sub> contribution of 16.52 wt.% in the consolidated cellulose (Figures 1 and 2). When compared to the pure MFC material, the TEOS-consolidated MFC had a much better thermal resistance. The MFC underwent a fast thermal degradation at a maximum peak temperature of 320°C (DTG data) and at a rate of -3.38 wt.%/°C; the extrapolated completion of this degradation temperature occurred at 333°C with a remaining 17.7 wt.% of the initial material (Figure 1). In contrast, the TEOS consolidated MFC underwent a slower thermal degradation at a maximum peak temperature of 312°C and at a rate of -1.94wt.%/°C; the extrapolated completion of this degradation occurred at 321°C and the corresponding remaining weight fraction was 46.9 wt.% (Figure 2). This weight fraction is well above what would result from a mere uncoupled mixture of cellulose and silica. The cellulose degradation was not only slowed down by the silicon cross-linking at the surface of the fibres, it was also much limited in intensity, supposedly because of the creation of a molecular complex at the cellulose surface by condensation of the orthosilicate group on the cellulosic material. The resulting material is much more thermally stable than the cellulosic material on its own.

In a similar manner, the thermal properties of the silicified composite were enhanced when compared to the montmorillonite:MFC composite. From the residual weight fraction, the amount of condensed silica amounts to 10.25 wt.%. The degradation of the montmorillonite:MFC in the main cellulose degradation region around 310-315°C (as determined from the peak position of the DTG measures) was significantly slowed down by TEOS consolidation. The slope of this degradation was calculated to be -1.17 wt.%/°C without silicon consolidation and -0.51 wt.%/°C in the material consolidated by orthosilicate condensation (Figure 2). Such a slope change cannot be explained by the small amount of condensed silica in the composite. Once again, it is believed that this slope change is due to the creation of covalent bonding between the MFC and the orthosilicate groups. A weight loss in the 400-600°C region could indicate that the montmorillonite is in fact a synthetic mica-montmorillonite clay.[4]



**Figure 1.** Weight loss of the MFC (continuous line), montmorillonite (dashed line) and of the silicon matrix (dotted line)



**Figure 2.** Weight loss of the silicified MFC (continuous line), MFC:montmorillonite composite (dashed line) and of the silicified MFC:montmorillonite composite (dotted line)

### 3.2 ATR-FTIR

The peak at  $3620\text{ cm}^{-1}$  in the montmorillonite and montmorillonite composites is attributed unambiguously to hydrogen bonding (Figure 3). Cellulose has a strong hydrogen band made of several peaks in the  $3600\text{-}3000\text{ cm}^{-1}$  region and centred around  $3350\text{ cm}^{-1}$  (Figure 3). The cellulose signal strongly overlaps the clay one in this region, which makes conclusive remarks as to peak clay displacements uneasy. The main peak is located at  $3340\text{ cm}^{-1}$  in the untreated MFC, it is located at  $3360\text{ cm}^{-1}$  in the MFC:montmorillonite material and at  $3333\text{ cm}^{-1}$  both for the TEOS-consolidated MFC and MFC:montmorillonite. Besides the changes in peak position, a shoulder in the  $3300\text{-}3290\text{ cm}^{-1}$  region clearly appears on the TEOS-treated materials. These changes in the hydrogen bonding region towards lower frequency after treatment reflect an increasing -H bond stiffness, which could be due to more constrained free

hydroxyl groups in the vicinity of orthosilicate groups condensed on other neighbouring hydrogen bonds.

The peak at  $\sim 2900\text{ cm}^{-1}$  is usually assigned to C-H stretching. Whereas this peak appears as a fairly broad shoulder in the absence of silicon, it develops in a double peak with a sharper  $2900\text{ cm}^{-1}$  peak and a distinct shoulder at  $2870\text{-}2875\text{ cm}^{-1}$ .

Eventually, a shoulder around  $1052\text{ cm}^{-1}$  on the MFC spectrum develops into a distinct peak after TEOS treatment (Figure 3). This band is usually attributed to motions of silicon dioxide.[5-7] This band is also visible in the form of a shoulder on the consolidated MFC:montmorillonite composite, but its sharpness is strongly affected by both the C-O stretching of cellulose and the Si-O stretching of the clay.[8], [9]

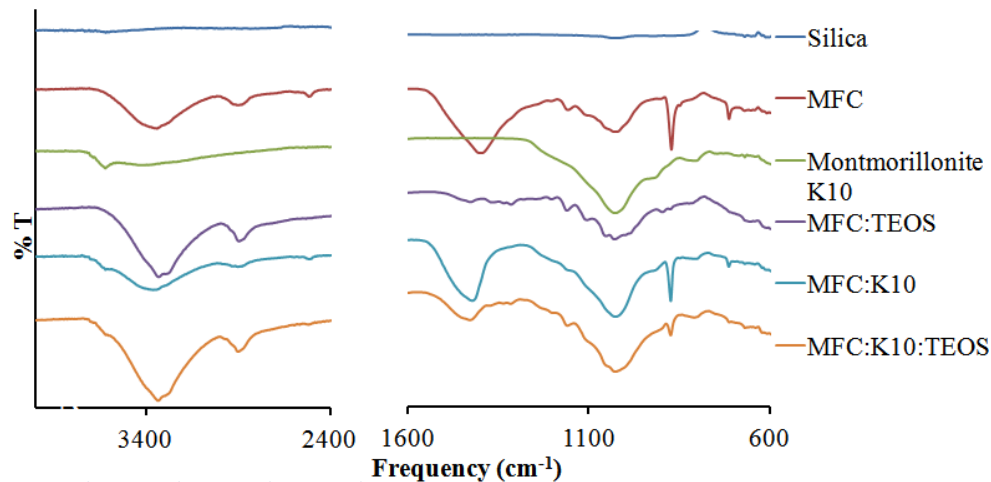


Figure 3. ATR-FTIR spectra

### 3.3 WAXD

The microfibrillated cellulose contained some calcite. This mineral is used in the refining and bleaching process of the recycled fibres during the MFC production. Montmorillonite peaks were visible in the MFC:montmorillonite composite before and after TEOS consolidation. Compared to the crystallinity of cellulose, the montmorillonite crystallinity was affected by the orthosilicate condensation, probably because of the orthosilicate reaction at the montmorillonite platelet surfaces inducing a loss of order. Qian *et al.* have indeed shown that mesoporous silicate could covalently attach to the montmorillonite surface when TEOS was used as a silicate precursor in sol-gel approach under acidic conditions.[10] The same team also demonstrated that the clay platelets could be exfoliated if the relative TEOS concentration in the starting solution was sufficiently high. This phenomenon was also evidenced in the present work by a sharp decrease of the (001) diffraction peak of the clay material at  $2\theta \sim 9.3^\circ$  (Figure 4).

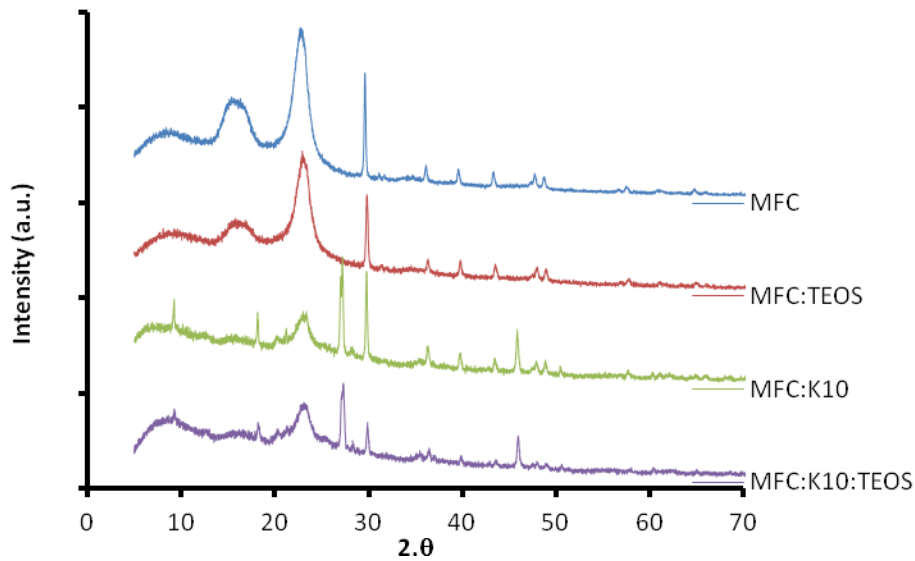
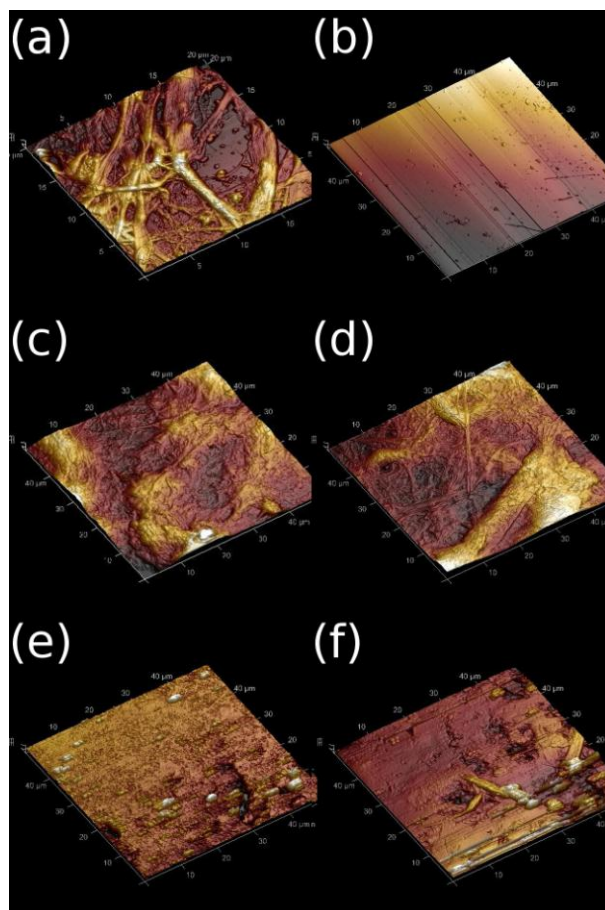


Figure 4. WAXD of the various materials before and after silicification

### 3.4 AFM

The various materials were analysed with the help of an AFM in tapping mode. The study of the MFC material revealed highly defibrillated plant cell wall. The largest fibres had a diameter of the order of 1  $\mu\text{m}$  and smaller fibres, usually around 100-200 nm in diameter, spanned from the former ones (Figure 5 a). The silica matrix on its own had a very flat surface (Figure 5 b). Whereas MFC films retained the fibrillar structure of the starting material after drying and compression, the MFC:montmorillonite composites exhibited a much smoother surface. This smooth aspect is probably due to the clay propensity to self-aggregate in the direction parallel to the film surface and to occupy interfibrillar porosities.[3], [11] The surface appearance of the MFC films did not change after they were consolidated by TEOS treatment (Figures 5c and d). However, the surface of the silicified MFC:montmorillonite composite appeared slightly smoother than that of the non-silicified one (Figures 5 e and f). This could be attributed to a partial reorganization of the clay by exfoliation and by the adhesion of the orthosilicate groups at their surface, as observed somewhere else.[10]



**Figure 5.** Three-dimensional rendering of topographical images obtained by atomic force microscopy in tapping mode for (a) diluted MFC fibres deposited on a glass slide (b) SiO<sub>2</sub> obtained by a sol-gel process and film surfaces of (c) MFC and (e) a 1:1 MFC:montmorillonite composite. (d) and (f) correspond, respectively, to (c) and (e) after impregnation in the hydrolysed TEOS solution and drying.

#### 4 Conclusions

It is well known that mixtures of clay and submicrometric forms of cellulose have better thermal behaviour than cellulose on its own.[3] Yet, consolidation *via* physical cross-linking of silicon species at the surface of the materials can slow down the thermal degradation even more. WAXD, FTIR and AFM provided clues as to the physical attachment of MFC to the clay platelets *via* siloxane bridges obtained by silicon alkoxide condensation. Further research need to be carried out in order to elucidate the changes in mechanical behaviour, wettability and manufacturing possibilities of these materials.

#### Acknowledgements

The authors would like to thank Ms Larisa Dobircan (LECAP, Rouen) for the help with the thermogravimetric analysis. One of the authors (B. Duchemin) is indebted to Professor Joël Bréard (LOMC, Le Havre) who offered his kind assistance all along the project organization.

#### References

- [1] Bond R., McAuliffe J. C. Silicon Biotechnology: new opportunities for carbohydrate science. *Aust. J. Chem.*, **56**, pp. 7-11 (2003).
- [2] McKittrick J., Chen P.-Y., Tombolato L., Novitskaya E. E., Trim M. W., Hirata G. A., Olevsky E. A., Horstemeyer M. F., Meyers M. A. Energy absorbent natural materials and bioinspired design strategies: a review. *Materials Science and Engineering: C*, **30**, pp. 331-342 (2010).
- [3] Liu A., Walther A., Ikkala O., Belova L., Berglund L. A. Clay Nanopaper with tough cellulose nanofiber matrix for fire retardancy and gas barrier functions. *Biomacromolecules*, **12**, pp. 633-

- 641 (2011).
- [4] Guggenheim S., Van Groos A. F. et al. Baseline studies of the clay minerals society source clays: thermal analysis. *Clays and Clay Minerals*, **49**, pp. 433-443 (2001).
  - [5] Yin Y., Wang C., Wang Y. Fabrication and characterization of self-assembled multifunctional coating deposition on a cellulose substrate. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **399**, pp. 92-99 (2012).
  - [6] Daoud W. A., Xin J. H., Tao X. Synthesis and characterization of hydrophobic silica nanocomposites. *Applied Surface Science*, **252**, pp. 5368-5371 (2006).
  - [7] Fardad M. A. Catalysts and the structure of SiO<sub>2</sub> sol-gel films. *Journal of Materials Science*, **35**, pp. 1835-1841 (2000).
  - [8] Carillo F., Colom X., Suñol J. J., Saurina J. Structural FTIR analysis and thermal characterisation of lyocell and viscose-type fibres. *European Polymer Journal*, **40**, pp. 2229-2234 (2004).
  - [9] Madejová J., Komadel P. Baseline studies of the clay minerals society source clays: infrared methods. *Clays and Clay Minerals*, **49**, pp. 410-432 (2001).
  - [10] Qian Z., Hu G., Zhang S., Yang M. Preparation and characterization of montmorillonite-silica nanocomposites: a sol-gel approach to modifying clay surfaces. *Physica B: Condensed Matter*, **403**, pp. 3231-3238 (2008).
  - [11] Liu A., Berglund L. A. Clay nanopaper composites of nacre-like structure based on montmorillonite and cellulose nanofibers: improvements due to chitosan addition. *Carbohydrate Polymers*, **87**, pp. 53-60 (2012).