Composite Films Based on Nanocellulose and Nanoclay Minerals as High Strength Materials with Gas Barrier Capabilities: Key Points and Challenges

José A.F. Gamelas,[a,]* and Eduardo Ferraz [b]

Composites of nanocellulose with layered silicates have recently emerged as a new type of composite materials offering superior strength, as well as thermal and gas barrier properties. These organic-inorganic hybrid composites with a nacre-like structure can be obtained from renewable resources and are environmentally friendly. They can potentially be presented as a serious alternative in the near future to several polymers or other polymer-inorganic composites, for applications in food packaging or electronic devices. The discussion here will be directed to: what are the new opportunities and challenges that arise for these materials aiming at their competition with well-established materials in the market.

Keywords: Nanofibrillated cellulose; Planar and fibrous minerals; Phyllosilicates; Composite films; Mechanical strength; Barrier properties; Food packaging; Flexible electronics

Contact information: a: Department of Chemical Engineering, CIEPQPF, University of Coimbra, Pólo II. R. Sílvio Lima, PT - 3030-790 Coimbra, Portugal; b: Polytechnic Institute of Tomar, Geobiotec Research Unit, Quinta do Contador, Estrada da Serra, PT - 2300-313 Tomar, Portugal.
** Corresponding author: jafgas@eq.uc.pt*

Composites of Nanofibrillated Cellulose and Nanoclay Minerals

The co-dispersion of nanocellulose and layered clay minerals (phyllosilicates) can give rise to composites having a structure similar to that of nacre, a natural material found in the shell of some molluscs. Typically, nanofibrillated cellulose (NFC) obtained using a chemical or enzymatic pre-treatment is used as matrix, and nanoclay minerals, either from natural or synthetic origin, such as smectites (montmorillonite and saponite) and vermiculite are used as filler. Superior strength and gas barrier properties, thermal stability, and transparency can be achieved.

Remarkable results were obtained by Wu *et al*. (2012, 2014), who prepared composite films using NFC, obtained by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation, with only 5 wt% of montmorillonite or 10 wt% of synthetic saponite. The resulting composites showed excellent mechanical properties (tensile strength of 509 MPa, Young's modulus of 18 GPa and elongation at break of 7.6% with montmorillonite and 425 MPa, 14.5 GPa, and 10.2%, respectively, with saponite). These results were even better than those of films of neat NFC (210 MPa, 11.6 GPa, and 3%, respectively). These composite materials represent a combination of strength, stiffness, and ductility, which is not common in biobased composites. For instance, composites with other biomaterials such as starch, poly-lactic acid or poly-vinyl alcohol have never approached these values. Since NFC is already stiff and strong, and these properties can be further enhanced in the organic-inorganic composite, the effect of the nanoclay mineral addition is worth being discussed.

The strength enhancement of the NFC film that can be achieved by the incorporation of small amounts of nanoclays contrasts to what happens for the addition of filler in papermaking, where the paper strength properties typically decrease with the increase of filler content mainly due to the low physico-chemical compatibility of the filler and cellulosic fibers (low adhesion) and dispersion problems. In the case of the NFC-layered silicates, the high dispersibility in water of anionic charged NFC and mineral platelets, together with the low interfacial energy between these components in the film (hydrogen bonding/ionic interactions) help to build a good matrix-filler interface, thus providing high strength properties to the composite.

The introduction of the nanoclay mineral into the NFC matrix also improves the gas barrier properties of the material, namely to oxygen and water vapor (Aulin *et al*. 2012; Wu *et al*. 2012, 2014), which is of high relevance for applications in food packaging or as substrate films for electronics. The gas barrier capability is mainly attributable to the inherent highly ordered nanoplatelet-like structure of the mineral (preserved in the composite with NFC). Such a structure presents a tortuous path for the diffusion of the gas molecules, thus hindering permeability. In addition to high strength and gas barrier properties, high transparency can also be obtained for composites of NFC with low incorporated amounts of layered silicate mineral.

If transparency of the composite material is not a final requisite, composites containing high mineral content can be attempted. It has been shown that "nanopaper" of enzymatic NFC incorporating more than 50 wt% of montmorillonite can be prepared with still some flexibility, high strength and stiffness (Liu *et al*. 2011). Besides, the oxygen transmission rate is considerably reduced at high humidity conditions, relative to neat NFC films. Thus, strong composite films with high gas barrier properties can also be produced using larger amounts of the platy clay mineral component.

Strengths and Weaknesses

Some strengths and weaknesses, in comparison with composites with other biopolymers and with synthetic polymers should be highlighted:

- NFC-layered silicate composites fulfill the condition of environmentally friendly materials obtained from renewable resources: nanocellulose derived from wood fibers; and nanoclay minerals obtained from natural georesources or alternatively as residues or by-products of industrial process with low added value.
- They can easily be prepared from aqueous co-dispersions of nanocellulose and nanoclay mineral particles. However, the quality of the composite films may be highly dependent on the process used for their preparation. If the time for film preparation is a limiting factor, then nanopapers may be preferred over films obtained by solvent casting.
- They may present astonishing strength properties (tensile strength, Young´s modulus), even superior to those of neat NFC.
- The gas (oxygen, water vapor) barrier properties are among the best that have been reported, sometimes even better than those of synthetic polymers-based commercial products. At high humidity conditions they are improved in comparison to NFC.
- Thermal stability up to about 250 ºC.
- NFC is still nowadays an expensive material for the composites production. It takes chemicals and energy to produce it from cellulose raw material.

- The mineral price is increased with the additional physical/chemical treatment required to obtain highly delaminated clays (necessary to achieve the desired strength and barrier properties).

Threats

Some constraints and vulnerabilities can be noted as threats:

- The efficiency of the composites is largely dependent on the morphological (*e.g.*, aspect ratio, volume fraction) and surface properties (*e.g.*, surface charge, surface energy, Lewis acid-base properties) of matrix and filler. The control of these parameters is important and may require not always available techniques (high-resolution electron microscopy, inverse gas chromatography, X-ray photoelectron spectroscopy).
- The dispersion of the matrix and filler individual components in aqueous medium is a critical factor for the quality and properties of the final product. NFCs and mineral particles that are poorly dispersed will give films with mediocre interfaces and weaker properties. Additional conditions (*e.g.* energy or polyelectrolytes) to allow more stable dispersions before film forming may be required.

Opportunities

The NFC-layered silicate nanocomposite films exhibit a versatile combination of properties. In order to harness all their potential for the society and environment, some important challenges must be underlined.

- The aforementioned cellulose-layered phyllosilicate nanocomposite films had been prepared from nanofibrillated cellulose typically obtained using a chemical or enzymatic pre-treatment before the mechanical homogenization. The nanocellulose production is still an expensive process, even considering that enzymatic NFC is cheaper than TEMPO-NFC. The possibility of using less-fibrillated cellulose, that is, obtained with a minimal consumption of chemicals in the chemical/enzymatic pre-treatment should be considered. Thus, the price of using high-cost NFC for the composite preparation could be mitigated. In this context, note that the properties claimed for the NFC-nanoclay composites, may exceed what is actually required for a specific situation. Using less costly and less-fibrillated cellulose may be enough to produce composites with still acceptable performances for the target application.
- There are some non-planar (fibrous) nanoclay minerals such as palygorskite or sepiolite that may be considered as hypothetical partial substitutes for the nanocellulose fibrous material. These minerals have morphological characteristics somewhat similar to NFC (thickness of 10 to 40 nm and lengths of 1 to 10 μm) and a layered chemical structure similar to planar minerals (both are phyllosilicates), which may anticipate a good compatibility between the several components in the blend. They can also add relevant mechanical and fire retardancy properties. A composite film combining three distinct nanocomponents, such as NFC matrix plus fibrous and planar nanoclay minerals acting as filler could thus be produced in the near future.

- For food packaging applications (delicatessen containers, laminate films) where high gas barrier properties, thermal stability and strength are essential, composite films with larger mineral content can be targeted.
- For applications where film transparency is also an important parameter to take into account (special packages, thin-film transistors, and organic light-emitting diodes), NFC-layered silicate composites with larger NFC content (more expensive) should be primarily considered.

References Cited

Aulin, C., Salazar-Alvarez, G., and Lindstrom, T. (2012). "High strength, flexible and transparent nanofibrillated cellulose–nanoclay biohybrid films with tunable oxygen and water vapor permeability," *Nanoscale* 4, 6622-6628.

Liu, A., Walther, A., Ikkala, O., Belova, L., and Berglund, L. A. (2011). "Clay Nanopaper with tough cellulose nanofiber matrix for fire retardancy and gas barrier functions," *Biomacromolecules* 12, 633-641.

Wu, C.-N., Saito, T., Fujisawa, S., Fukuzumi, H., and Isogai, A. (2012). "Ultrastrong and high gas-barrier nanocellulose/clay-layered composites," *Biomacromolecules* 13, 1927-1932.

Wu, C.-N., Yang, Q., Takeuchi, M., Saito, T., and Isogai, A. (2014). "Highly tough and transparent layered composites of nanocellulose and synthetic silicate," *Nanoscale* 6, 392-399.

DOI: 10.15376/biores.10.4.6310-6313