Nanocellulose-sepiolite bionanocomposite foams for oil adsorption applications

Amaret Sanguanwong (1,2), Adrian E. Flood (1), Makoto Ogawa (1), Raquel Martín-Sampedro (2), Margarita Darder (2), Bernd Wicklein (2), Pilar Aranda (2*), Eduardo Ruiz-Hitzky (2)

(1) School of Energy Science and Engineering. Vidyasirimedhi Institute of Science and Technology (VISTEC), Wangchan, Rayong 21210 (Thailand)
(2) Materials Science Institute of Madrid (ICMM-CSIC). C/ Sor Juana Inés de la Cruz 3, 28049 Madrid (Spain)
* corresponding author: pilar.aranda@csic.es

Palabras Clave: Sepiolita, Nanocelulosa, Bionanocomposites, Espumas hidrófobas. **Key Words:** Sepiolite, Nanocellulose, Bionanocomposites, Hydrophobic foams.

INTRODUCTION

Clay minerals, and especially sepiolite, has shown interesting properties for adsorption of different type of oils, being frequently employed as bleaching earths in the purification of oils. Bionanocomposites based on the combination of clays and biopolymers are attracting growing interest as adsorbent of pollutants in water (Alcântara & Darder, 2018; Orta et al., 2020). However, as these systems are often very hydrophilic, they have been rarely used in the removal of hydrophobic pollutants. For instance, oil spills are common and very often severe disasters in marine environments. In this context, we intended to develop bionanocomposite systems for removal of oils. In a previous work (González del Campo et al., 2018) we have observed that bionanocomposite films based on the combination of cellulose nanofibers (CNF) and sepiolite, both hydrophilic, could incorporate certain hydrophobic character. Thus, we now explore the preparation of CNF-sepiolite hydrophobic bionanocomposite foams using various approaches with the aim to produce efficient adsorbents for the removal of oil in water (Sanguanwong et al., 2021).

EXPERIMENTAL

Sepiolite (SEP) from Vallecas-Vicálvaro (Spain) of rheological grade, Pangel® S9 product, was supplied by Tolsa S.A. Cellulose nanofibers were obtained by treatment of a bleached eucalyptus Kraft pulp (obtained from La Montañanesa, Spain) with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO-mediated oxidation process) that, after subsequent washing and filtering, was passed twice through a microfluidizer (Microfluidics, M-110 P) to reach the formation of a CNF hydrogel. Foams were produced from pure CNF and CNF mixed with SEP (10–50% w/w) water dispersions with a 0.5% w/v total solid content, homogenized using high-shear stirring (IKA, Ultra-Turrax T25) and ultrasound irradiation (SONICS, Vibra Cell VCX 750) poured in molds and submitted to a freeze-drying process, either in one step (normal freezing at -18 ºC or directional using liquid nitrogen) or in a two-step process. This last method (refreezing) implies a first directional freezing using liquid nitrogen, a thawed step at room temperature for 12 h before a second normal freezing step. The final foams were silanized by placing them in a capped glassware where an atmosphere of methyltrimethoxysilane (MTMS, Sigma-Aldrich) is created by heating at 70 ºC for 1 day to complete the reaction.

SEM, gas pycnometry and mercury intrusion porosimetry were used to determine textural properties, density and pore size distribution. Hydrophobicity of the foams was analyzed by water contact angle measurements. MTMS modification was confirmed by FTIR. The stability and mechanical properties were determined from thermogravimetric analysis (TGA) and compressive strength tests. The oil sorption capacity of the foams was determined by means of the modified ASTM F726–12 standard, using olive oil and motor oil as adsorbates.

RESULTS

CNF-SEP foams prepared with different SEP contents (0–50% w/w) using the normal freezing method without silanization show that the SEP content did not have a strong effect on the mechanical properties of the foam, being the optimum for a content of 20% w/w SEP. After compression at a strain of 50%, the foams were able to recover 90% of their initial height (Fig. 1) but this behavior is different in consecutive compression tests due to the partial

damage of the cellular structure. After silanization with MTMS the foams become water-repellent showing an average contact angle of 121 ± 3º and 128 ± 5º for pure CNF and CNF-SEP (20%), respectively.

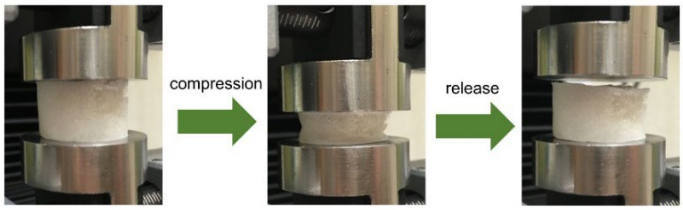

Fig 1*. Photographs of CNF-SEP (20%) foams after compression at a 50% strain and release of the applied strain.*

CNF-SEP foams prepared by the refreezing method and very low CNF contents could not be successfully prepared, an appropriate ratio of SEP content ≤ 20% being necessary to stabilize the required organization of the network. The combination of directional freezing and normal freezing results in an open channel porous structure through the axial direction of the refrozen sample that contrast with the small pore size observed when only applied directional freezing sample or the random porous structure produced in the normal freezing method. The presence of sepiolite improves the compressive modulus in the axial direction of the CNF foams prepared using the normal and directional freezing methods. The modulus of the refreezing samples was between those of the normal freezing and directional freezing samples for both pure CNF and CNF-SEP (20%) foams, probably because the orientation in refreezing samples results from the combination of the orientation of fibers caused by both type of freezing steps. Anyway, the modulus is still greater than that of the normal freezing foams and it is possible to recover 90% of their initial height after eight compression cycles applying a 50% strain. Though the three MTMS-modified CNF-SEP (20%) foams reach similar final oil adsorption values (≈ 138 g/g), their different porous structure leads to different oil sorption rates, with refreezing foams requiring only 5 min to reach their sorption capacity in contrast to 30 min and 10 min for the directional and normal freezing foams, respectively. Due to the elastic properties of the foams even after the oil sorption, 75% of the initial height can be recovered by compression.

CONCLUDING REMARKS

It is possible to produce CNF-sepiolite bionanocomposite foams of diverse characteristics by applying different freeze-drying methodologies. After silanization with MTMS the foams become hydrophobic and can be satisfactorily used for adsorption of oils, with the possibility of recovering it just by compression of the foam. The satisfactory results open way to explore the use of other cellulosic materials to produce suitable bionanocomposite foams for oil sorption applications.

ACKNOWLEDGEMENTS

Support from the Vidyasirimedhi Institute of Science and Technology (VISTEC), the MAT2015-71117-R (AEI, Spain and FEDER, EU), PID2019-105479RB-I00 & PID2019-107022RJ-I00 (AEI, Spain) projects, and the IJCI-2016-28403 contract ("Juan de la Cierva-Incorporación" Program, MINECO, Spain), is kindly acknowledged.

REFERENCES

Alcântara, A.C.S. & Darder, M. (2018): Building up functional bionanocomposites from the assembly of clays and biopolymers. Chem. Rec., **18**, 696–712. DOI: 10.1002/tcr.201700076.

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. DOI: 10.1002/adfm.201703048.

Orta, M.M., Martín, J., Santos, J.L., Aparicio, I., Medina-Carrasco, S., Alonso, E. (2020): Biopolymer-clay nanocomposites as novel and ecofriendly adsorbents for environmental remediation. Appl. Clay Sci., **198**, 105838. DOI: 10.1016/j.clay.2020.105838.

Sanguanwong, A., Flood, A., Ogawa, M., Martín-Sampedro, R., Darder, M., Wicklein, B., Aranda, P., Ruiz-Hitzky, E. (2021): Hydrophobic composite foams based on nanocellulose-sepiolite for oil sorption applications. J. Hazard. Mater., **417**, 126068. DOI: 10.1016/j.jhazmat.2021.126068.