ICAM2009
11th International Conference on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25

Surface Chemical Modification of Ramie Cellulose Nanocrystals

A. J. de Menezes[(1)*], G. Siqueira[(2)], A. A. S. Curvelo[(3)] and A. Dufresne[(2)]

(1) Universidade Federal de São Carlos – UFSCar/campus Sorocaba, 18052-780, Sorocaba, Brasil. jrmenezes@ufscar.br
(2) Grenoble Institute of Technology, The International School of Paper, Print Media and Biomaterials, (PAGORA), BP65, 38402 Saint Martin d'Hères cedex, France. gilberto.siqueira@efpg.inpg.fr ; dufresne@efpg.inpg.fr
(3) Instituto de Química de São Carlos da Universidade de São Paulo IQSC/USP, C.P. 780, 13560-970 São Carlos, Brasil. aprigio@iqsc.usp.br

* jrmenezes@ufscar.br

Abstract – The surface of ramie cellulose whiskers has been chemically modified by grafting organic acid chlorides presenting different lengths of the aliphatic chain by an esterification reaction. The occurrence of the chemical modification was evaluated by FTIR and X-ray photoelectron spectroscopies, elemental analysis and contact angle measurements.

Aqueous suspensions of cellulose nanocrystals can be prepared by acid hydrolysis of the biomass. The object of this treatment is to dissolve away regions of low lateral order so that the water-insoluble, highly crystalline residue may be converted into a stable suspensoid by subsequent vigorous mechanical shearing action. The resulting nanocrystals occur as rod-like particles or whiskers, which dimensions depend on the nature of the substrate, but range in the nanometer scale. Because these whiskers contain only a small number of defects, their axial Young's modulus is close to the one derived from theoretical chemistry and potentially stronger than steel and similar to Kevlar. It has been first experimentally determined in 1962 and a value of 137 GPa was reported [1]. This value differs from the theoretical estimate of 167.5 GPa reported by Tashiro and Kobayashi [2]. More recently, Raman spectroscopy technique has been used to measure the elastic modulus of native cellulose crystals. A value around 143 GPa has been reported [3]. These nanoparticles are therefore suitable for the processing of green nanocomposite materials.Then, the main problem is related to the homogeneous dispersion of these nanoparticles within a polymeric matrix. Because of the high stability of aqueous suspensions of cellulose whiskers, water is the preferred processing medium. Hydrosoluble polymers are therefore well adapted for the processing of cellulose whiskers reinforced nanocomposites [4]. In the present work, cellulose whiskers were functionalized by an esterification reaction with organic acid chloride aliphatic chains of different sizes. The objective of this surface chemical treatment was to enhance the non polar nature of the grafted nanocrystals and improve their dispersibility in a hydrophobic polymeric matrix.

Acid hydrolysis of native ramie cellulose fibers leads to aqueous suspensions of elongated nanocrystals with high aspect ratio. The rod-like nanocrystals from ramie exhibit an average diameter of 6–8 nm and a length of about 150–250 nm as estimated by transmission electron micrographs (Figure 1). The occurrence of the chemical modification was evaluated by FTIR and X-ray photoelectron spectroscopies, elemental analysis and contact angle measurements. From the latter, the surface energy of the materials under investigation was deduced and it was shown that chemical modification led to more hydrophobic nanoparticles. The crystallinity of the particles was not altered by the chain grafting.

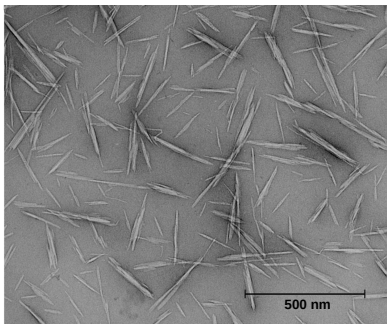

Figure 1: Transmission electron micrograph of ramie cellulose nanocrystals

References

[1] I. Sakurada, Y. Nukushina and T. Ito, J. Polym. Sci., 57(1962) 651.

[2] K. Tashiro and M. Kobayashi., Polymer, 32(1991) 1516.

[3] A. Šturcová, G.R. Davies and S.J. Eichhorn, Biomacromolecules, 6(2005) 1055.

[4] M.N. Anglès and A. Dufresne, Macromolecules, 33(2000) 8344.