

Enzymatic vs. chemical phosphorylation of cellulose nanofibers (CNFs)

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Aim

- ✓ To elaborate new site-specific & non-aggressive enzymatic approach for phosphorylation of cellulosic nanofibers (CNFs) of $d = 10-70 \text{ nm}$ & $l \leq 4-5 \text{ }\mu\text{m}$
- ✓ To compare enzymatic *vs.* chemical phosphorylation
- ✓ To characterize phosphorylated CNFs
- ✓ To establish structure- morphology-properties relationship
- ✓ To utilize phosphorylated CNFs properties

Enzymatic

vs.

Chemical

¹³C –NMR spectroscopy

Phosphorylation **occurred at C6-OH** group of the glucose, resulting to minor crystal structure reduction.

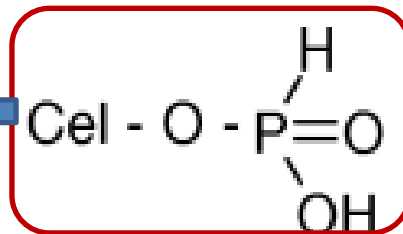
¹³C –NMR spectroscopy

Phosphorylation **occurred at C6, C2 and/or C3-OH groups** of the glucose, resulting to huge crystal structure reduction.

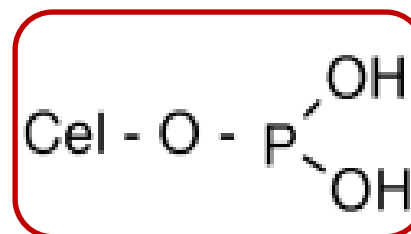
ATR-FTIR spectroscopy

Appearance of two IR bands; at 2360 cm⁻¹ (P-H) and 1210 cm⁻¹ (P=O)

Tautomeric equilibrium



or



Potentiometric titration

Appearance of two inflexion points being almost in the ratio of

1:2

↓
Dibasic acid behavior

Both structures confirmed by both process

Utilization of phosphorylated CNFs

Technical applications:

Total weight loss of native CNF was ~86 %, while phosphorylated-CNF decreased to ~43 % at 600°C.

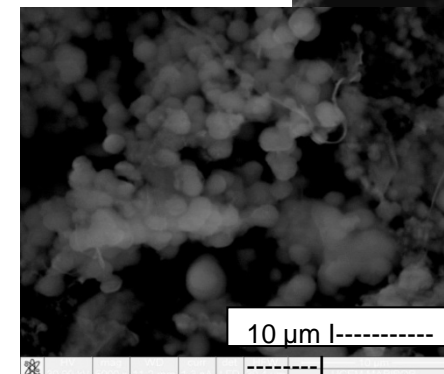
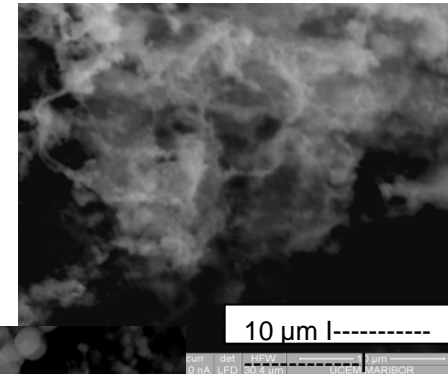
Excellent flame-resistance properties.

Biomedical application:

Biomimetic growth of Ca-P crystals (hydroxyapatite).

Removal of heavy metal from water:

High adsorption capacities of Fe³⁺ ions.



Conclusions

- The enzymatic and chemical phosphorylation of CNF can be used in its modification and functionalization.
- Although the enzymatic processing can not be so efficient as chemical one, the enzymatic procedure
 - is very selective & not aggressive to the cellulose,
 - is eco-toxicologically friendly and fully re-usable.
- New types of functionalities and applications can be expected.