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FUNCTIONALIZATION OF CELLULOSE TO IMPROVE ITS HYDROPHILIZATION

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Introduction

Cellulose is known to be insoluble in water and in many organic solvents.

Context

- The market for wood cellulose derivatives is currently growing because of their bio-based origin and of their fibres properties.
- The creation of hydrophilic polar functional groups on cellulose backbone gives absorbent properties.
- Applications: medical and hygiene fields (absorbent products such as wound dressings, compresses, etc.), dissolving pulps.

Key issues

Cellulose hydrophilization is nowadays achieved by several processes⁽¹⁾, but having drawbacks: viscose process (highly volatile and toxic CS₂), Lyocell (costly reagent N-Methylmorpholine-N-Oxide), ionic liquids (particularly difficult recovery).

Aim of this study

Use selective reactions to optimize the formation of hydrophilic functional groups and their hydrophilization, by decreasing intra and intermolecular hydrogen bonding and substitution of some hydroxyl functions.

→ Study of the modification of the cellulose structure by: (i) grafting, (ii) oxidation.

Materials and Methods

Two types of cellulose modifications were studied (Figure 1):

- **grafting** of functional groups: sulfobutyl, sulfopropyl, sulfoethyl and carboxymethyl.
- **oxidation**: Tempo, sodium periodate⁽²⁾.

Two substrates were used:

- **microcrystalline cellulose** powder (reference system).
- **dissolving pulp** (industrial substrates).

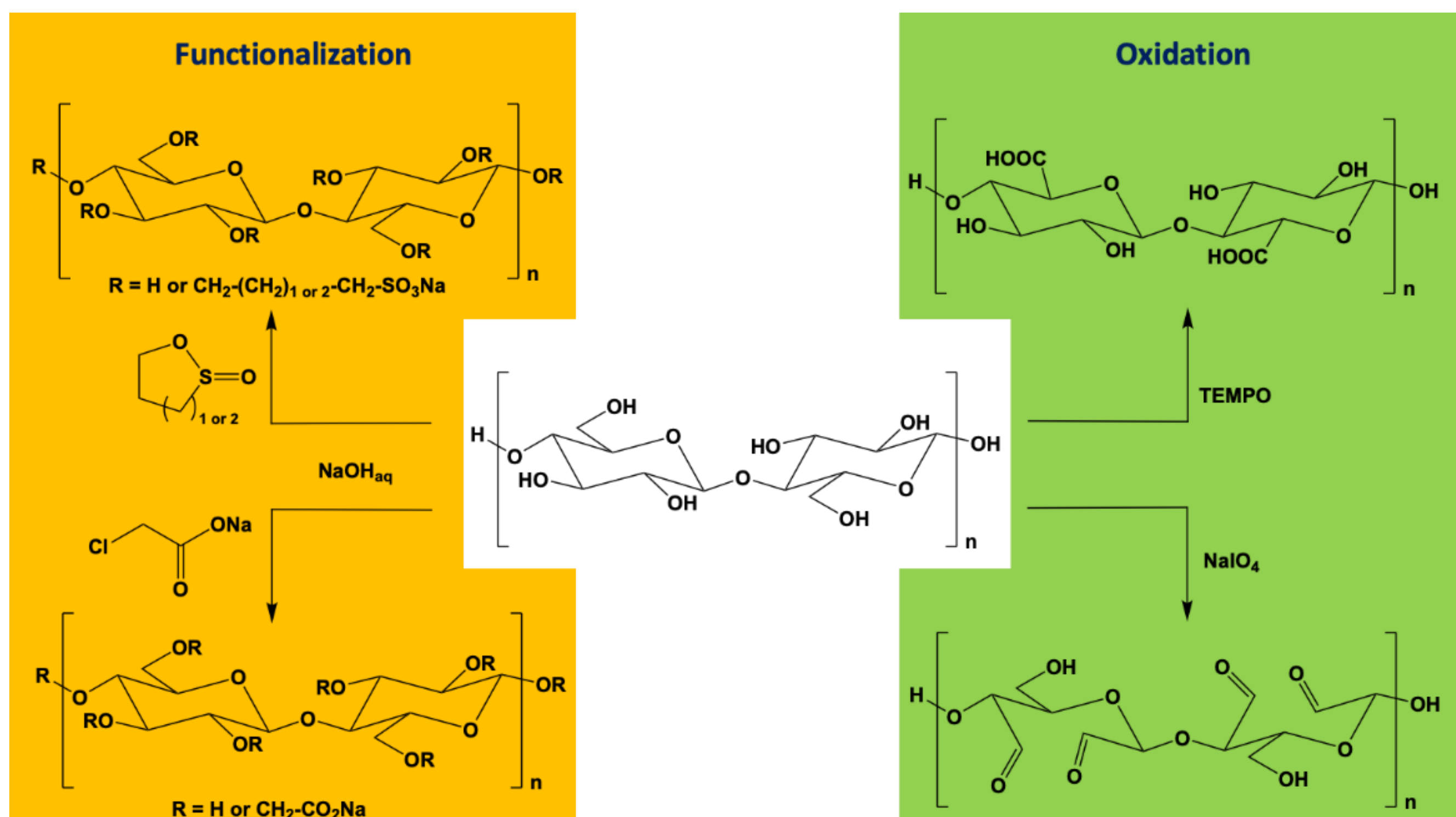


Figure 1. Grafting (left) and oxidation (right): the two pathways studied for cellulose modifications.

Studied parameters

Impact of time and temperature.

Conditions of experiments*

- **Sulfobutylation**: μC , 1,4 Butane sultone (6,3 mL, 61.53 mmol, 2 equ.).
- **Sulfopropylation**: μC , 1,3 Propane sultone (5.40 mL, 61.55 mmol, 2 equ.).
- **Sulfoethylation**: μC , 2 Bromo-ethane sulfonate (13.01 g, 61.66 mmol, 2 equ.).
- **Carboxymethylation**: μC , Sodium Chloroacetate (6 g, 51.51mmol, 1.67 equ.).
- **Oxydation NaIO₄**:
 - μC (1 g, 6.17mmol, 1 equ.), Sodium Periodate (1.6 g, 7.5mmol, 1.3 equ.).
 - fibres from dissolving pulp (10 g, 61.68mmol, 1 equ.), Sodium Periodate (13,20 g, 61.71mmol, 1 equ.).
- **Oxydation TEMPO**: μC (1 g, 6.17mmol, 1equ.), TEMPO (0.016 g, 0.102 mmol, 0.016 eq).

* μC : microcrystalline cellulose powder (5 g, 30.84 mmol, 1 mol equ.)

Samples characterization

- FT-IR and Raman spectroscopies: cellulose functional and crystallinity modifications.
- Elemental analysis and conductimetry: degree of substitution (DS).
- Light microscopy and SEM: surface and morphological modifications.
- Swelling/Dissolution in water.

Results

The following results are presented for microcrystalline cellulose (grafting) and dissolving pulp (oxidation).

Sulfobutylation

- Best DS value obtained: 0.15 (Table 1).
- Due the small %S, FT-IR shows a weak absorption band : 1200–1190 cm⁻¹.
- Hydrophilization: partial to total dissolution, depending on time and mixing (Table 2).

Sulfopropylation

- Best DS value obtained: 0.50 (Table 1).
- Hydrophilization: different behaviour (swelling-gel-dissolution).

Sulfoethylation

- Best DS value obtained: 0.10 (Table 1).
- Hydrophilization: non dissolution observed.

Carboxymethylation

- Best DS value obtained: 0.39 (for these conditions: 55 °C, 5 h).
- FT-IR : carboxyl band appeared at 1603 cm⁻¹ (Figure 2)
- Hydrophilization: total dissolution obtained.

Oxidation – NaIO₄

- Best DS value obtained: 3 eq IO₄⁻, R.T., 24 h).
- Raman spectroscopy: cellulose pretreatment led to glucopyranose ring deformations. The intensity of the signal at 379 cm⁻¹ decreased (from ref pulp to oxidized pulp – Figure 3).
- SEM analysis: the fibers of the reference cellulose pulp appeared linear and well separated with few visible microfibrils protruding from the longer fibers (Table 3). The oxidized fibers surface appeared smoother, more uniform and compact → oxidation affects the entire fiber and includes some level of polymer degradation.

	T (°C)	Time (h)	%S	DS
Sulfobutylation	45	6	3.01	0.15
Sulfopropylation	45	6	8.42	0.50
Sulfoethylation	45	6	0.26	0.10

Table 1. Optimal operating condition obtain for higher DS values.

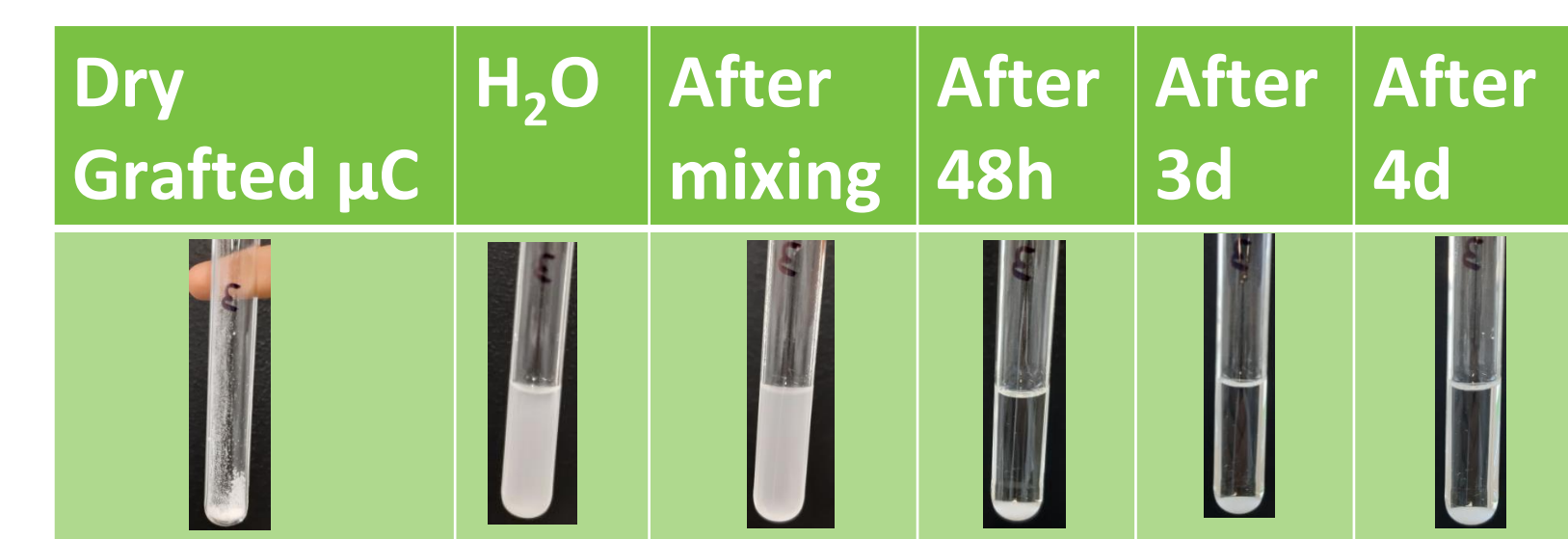


Table 2. Sulfobutylation: different hydrophilization behaviour.

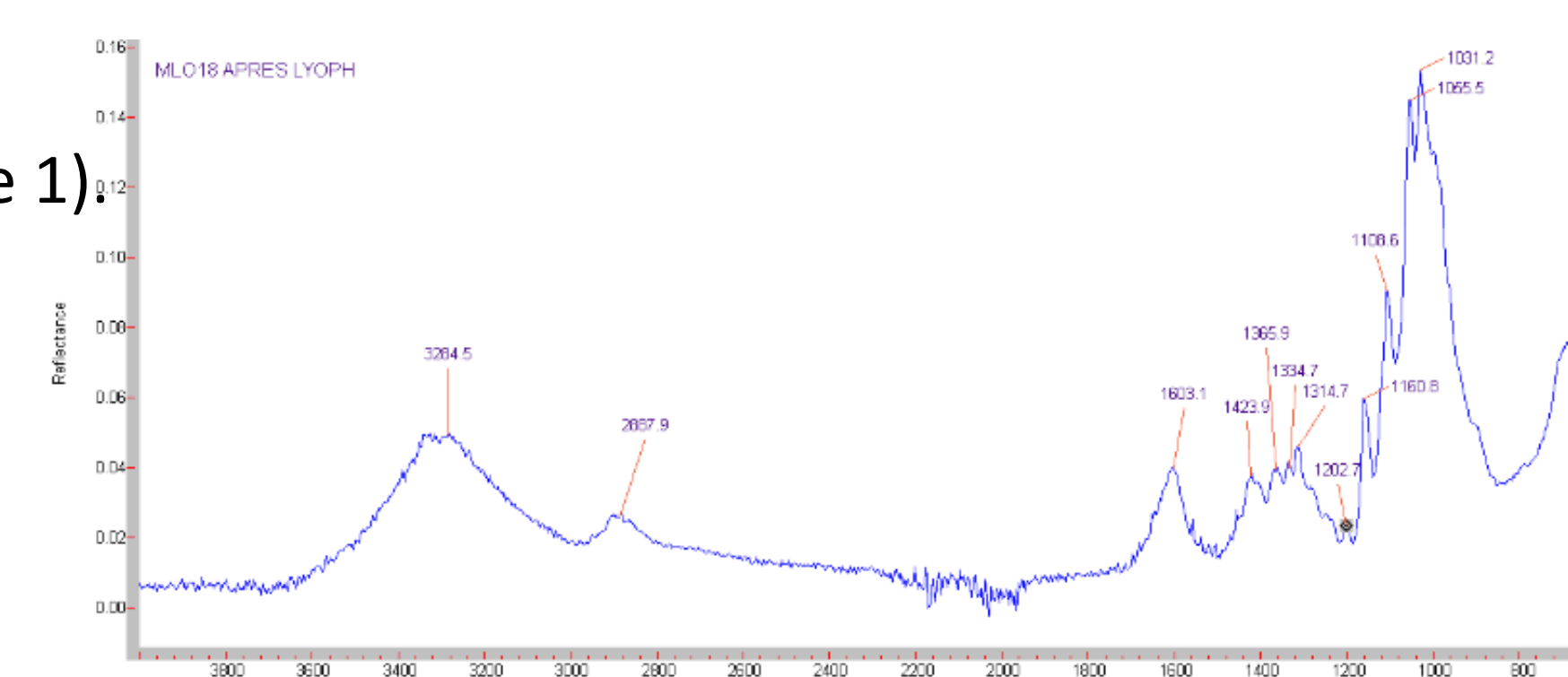


Figure 2. FT-IR spectrum – Carboxymethylation of microcrystalline cellulose.

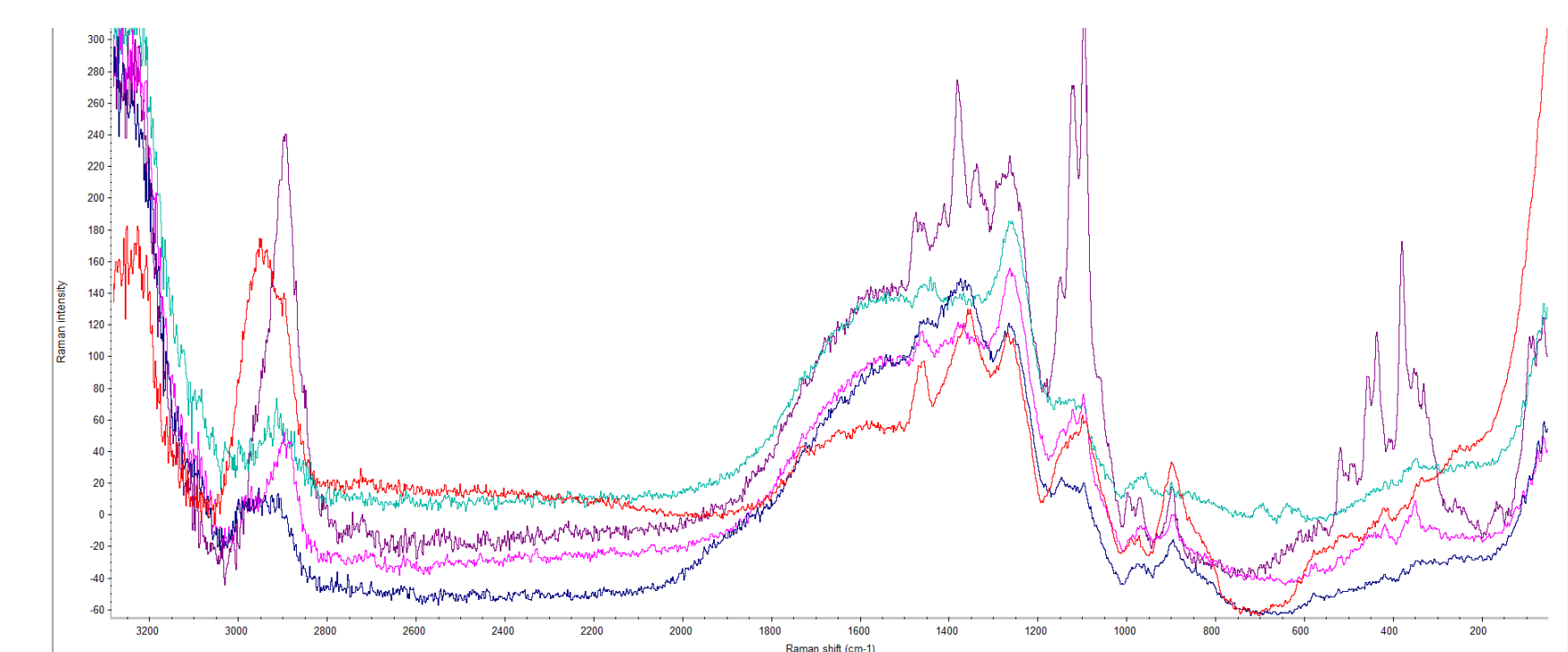


Figure 3. FT-IR spectrum – Carboxymethylation of microcrystalline cellulose.

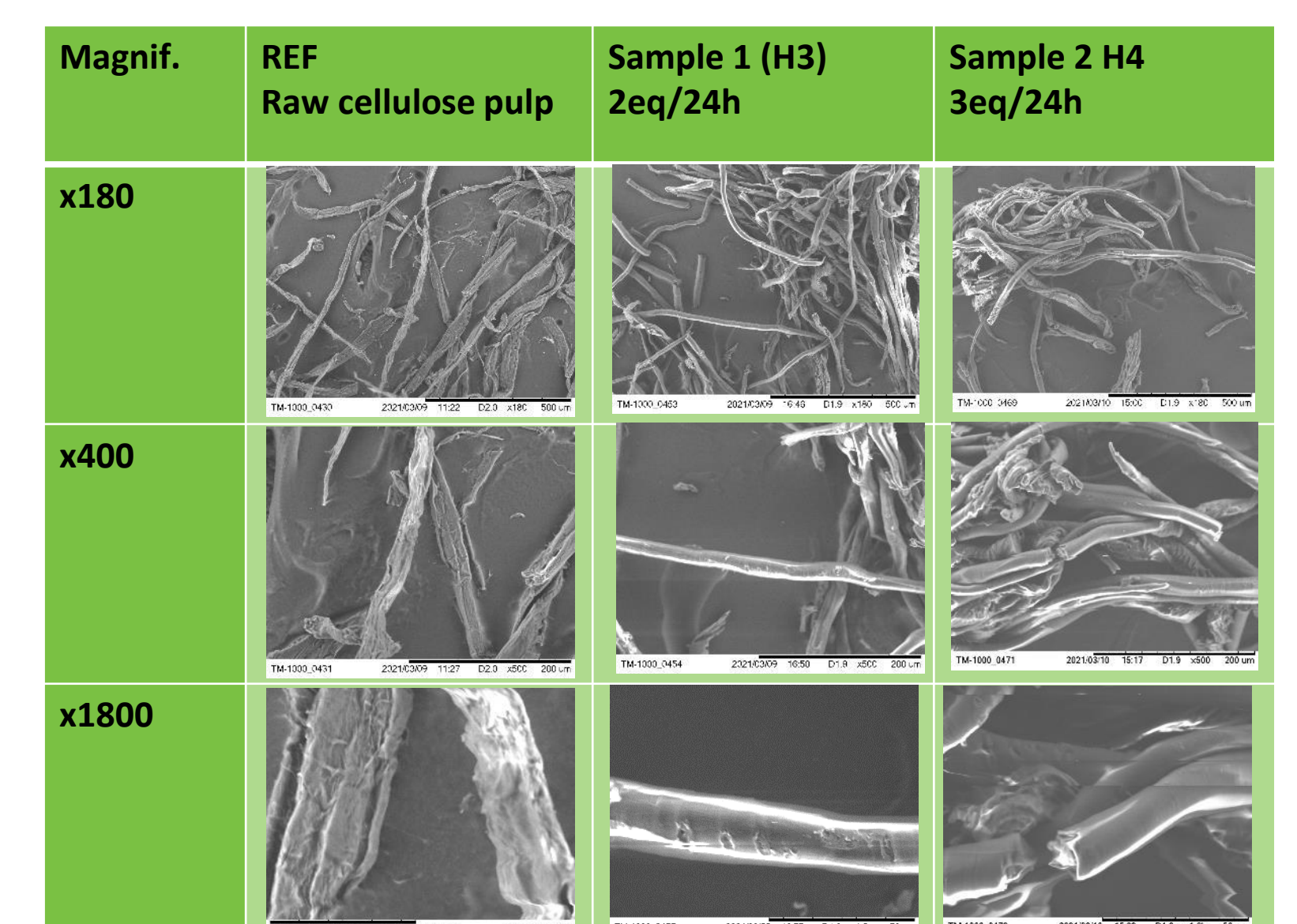


Table 3. SEM Imaging of oxidized cellulose pulps (2eq/3eq NaIO₄).

Conclusions and Perspectives

- Reaction conditions were optimized for each type of modification, to obtain degrees of substitution (DS, determined by elemental analysis for alkylsulfonates and conductimetric titration for carboxylates) ranging from 0.1 and 0.5, whatever the derivatization was.
- The hydrophilization of the modified celluloses was carried out by studying their swelling, behavior in water, and even their dissolution. The different treatments have also led to the homogenization of product morphology and fibre length.
- In the future, it would be interesting to deepen the studies of the solubility of cellulose derivatives and to characterize the increase in the hydrophilicity of modified fibers, for example by determining the value of the water retention.

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