

Development of a green method for the preparation of cellulose nanofibers grafted with poly(butylene succinate)

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Abstract

Nanocellulose, such as cellulose nanofibers (CNF), has attracted great interest due to its good mechanical properties, low cost, non-toxicity, low density, and thermal stability¹. However, its high hydrophilicity remains a challenge for its application in many fields, where hydrophobic modifications of nanocellulose are necessary². Therefore, we aim to prepare chemically modified cellulose nanofibers using a three-step process: 1) oxidation of cotton linter cellulose fibers with sodium hypochlorite and a catalytic amount of sodium bromide and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)³; 2) subsequent mechanical treatment to extract cellulose nanofibers; 3) solventless polymer grafting process to bond poly(butylene succinate) (PBS) oligomers on to the cellulose molecular chains under mild conditions (80-150°C). The oxidation step is functional for two main reasons: promoting the subsequent disintegration of cellulose fibers into the nanometric scale; and introducing new functional groups that can be exploited during the polymer grafting process. For the polymer grafting process, we have used succinic acid and 1,4-butanediol in equimolar amounts, while evaluating different catalysts, stabilizers, temperatures, and reaction times. The final products were characterized by ATR-FTIR, ¹H-NMR, Gel Permeation Chromatography (GPC), Scanning Electron Microscopy (SEM), and Thermal Gravimetric Analysis (TGA). The results demonstrate the success of the oxidation and the polymer grafting process, allowing this work to progress further studying the incorporation of the chemically modified nanocellulose fibers in a PBS polymer matrix to produce green polymer composites.

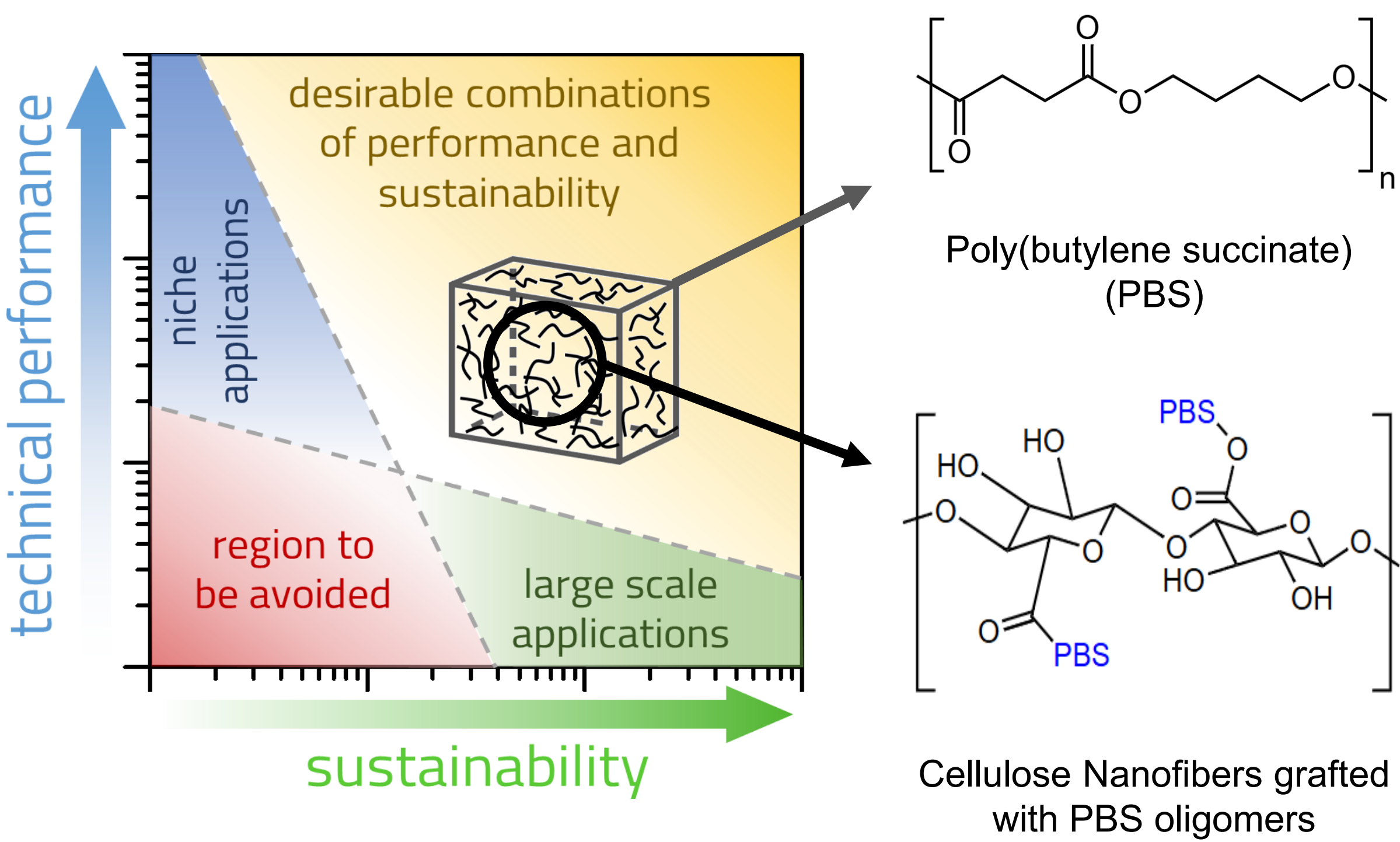


Figure 1: properties combinations and possible composition of the desired composite material.

CNF extraction and functionalization

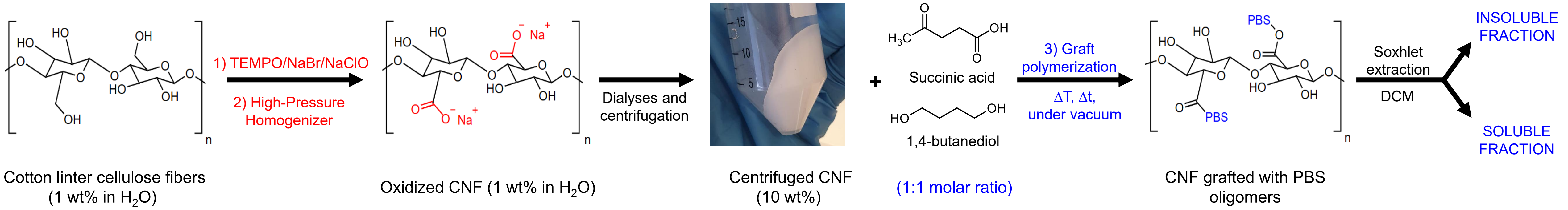


Figure 2: scheme of the proposed three-step process for the preparation of chemically modified cellulose nanofibers (CNF).

1) Oxidation

Table 1: reaction conditions and degree of substitution related to the oxidation step of the cellulose fibers.

NaClO (mmol/g)	Reaction time (min)	Degree of substitution
3	35	0.12

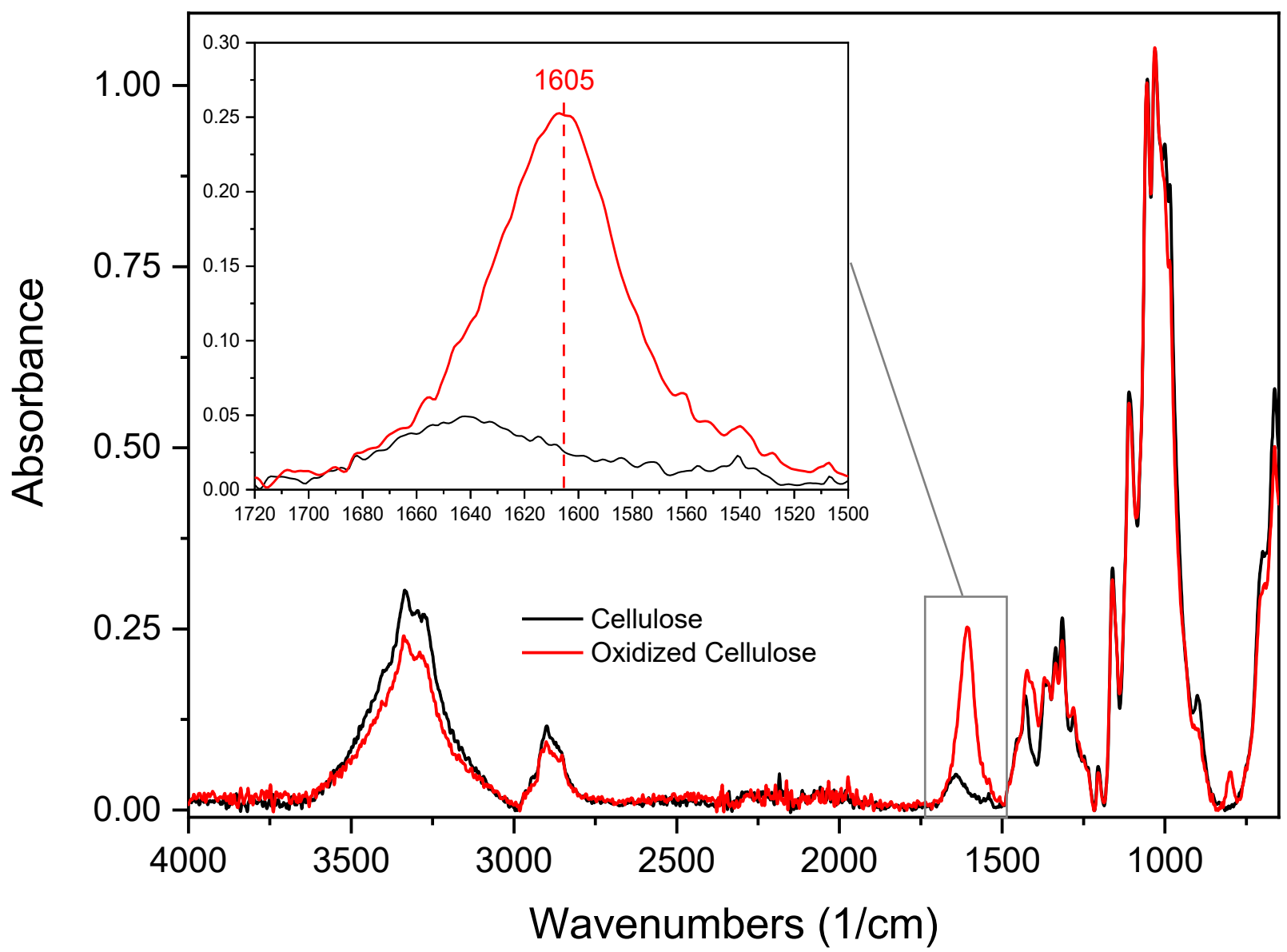


Figure 3: ATR-FTIR spectra of the starting cellulose material before and after the oxidation step.

2) CNF extraction

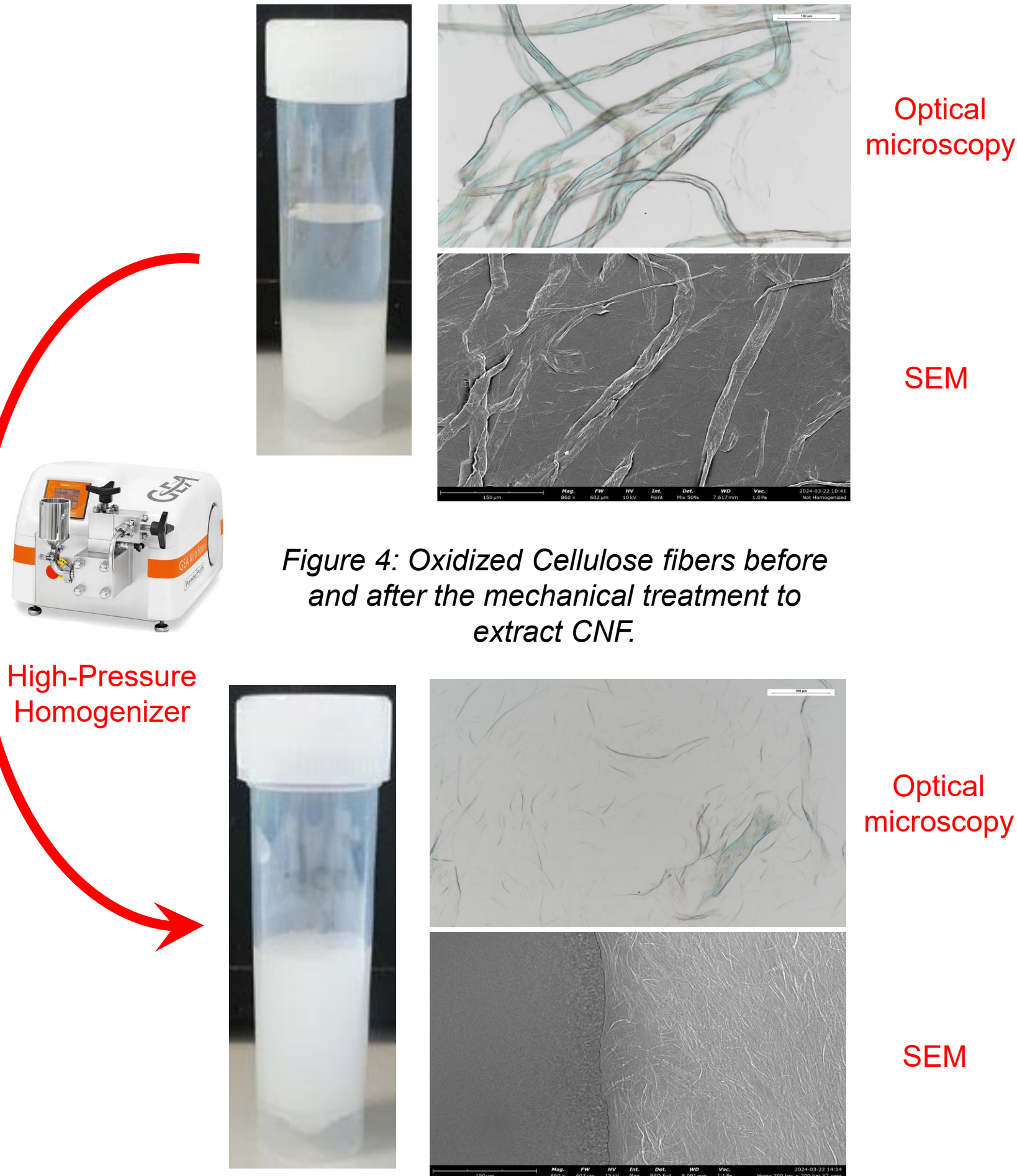


Figure 4: Oxidized Cellulose fibers before and after the mechanical treatment to extract CNF.

3) Graft polymerization

Table 2: tested reaction conditions for the graft polymerization of the simply oxidized cellulose fibers and results obtained from the characterization of the separated fractions.

Entry	Ti(OBu) ₄ (wt%)	80 °C (h)	100 °C (h)	150 °C (h)	Insoluble fraction ¹ (wt%)	¹ H-NMR (\overline{M}_n , Da) soluble fraction ¹
1	0	5	16	0	39	349
2	0	5	16	2*	22	659
3	0	3	19	22	24	359
4	2	3	0	22	14	450

*plus 20 h under atmospheric pressure

¹separated through Soxhlet extraction with Dichloromethane

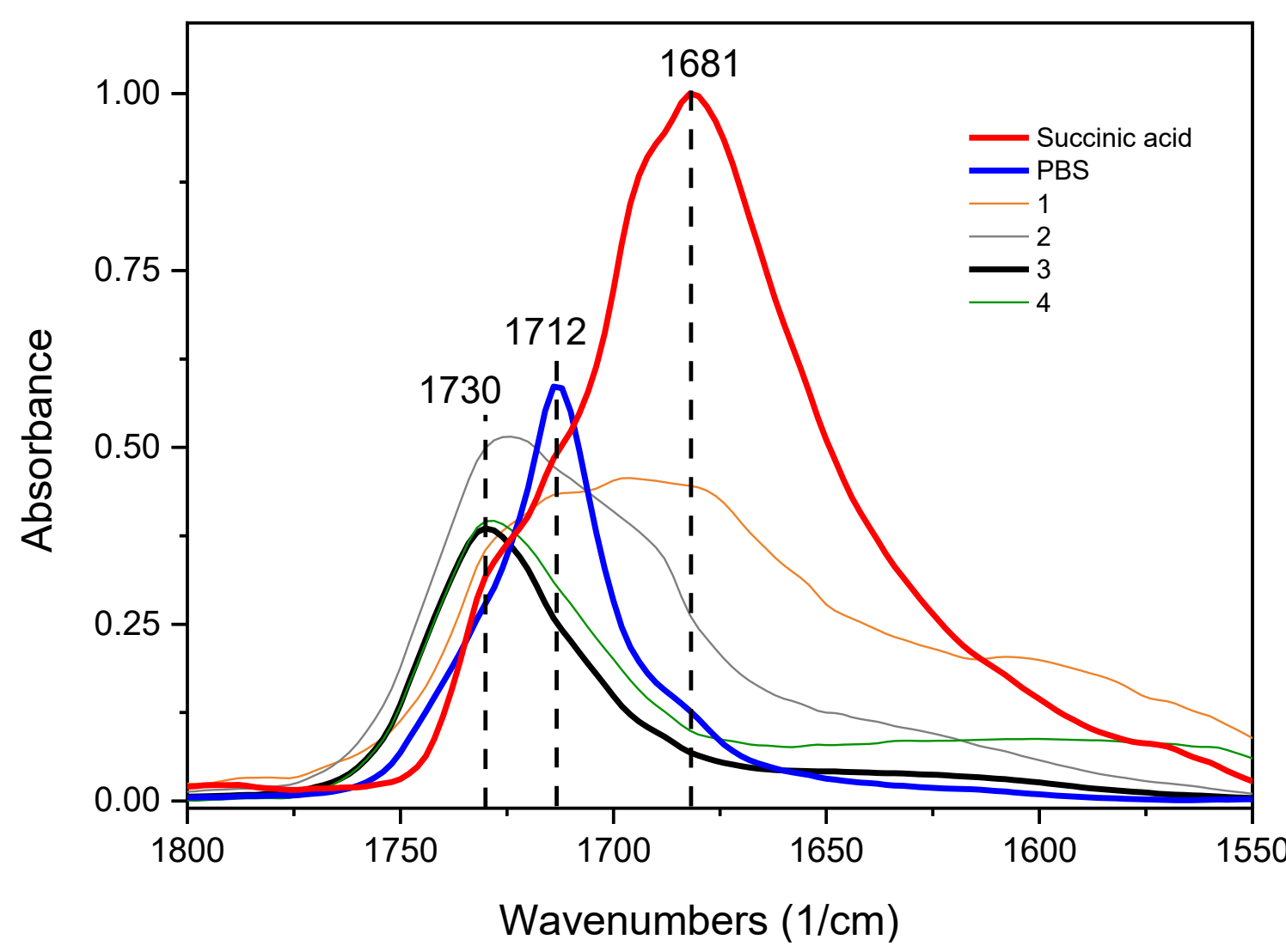


Figure 5: ATR-FTIR spectra, between 1800 and 1550 cm⁻¹, of commercial PBS, succinic acid, and the insoluble fraction of the samples obtained with the reaction conditions reported in Table 2.

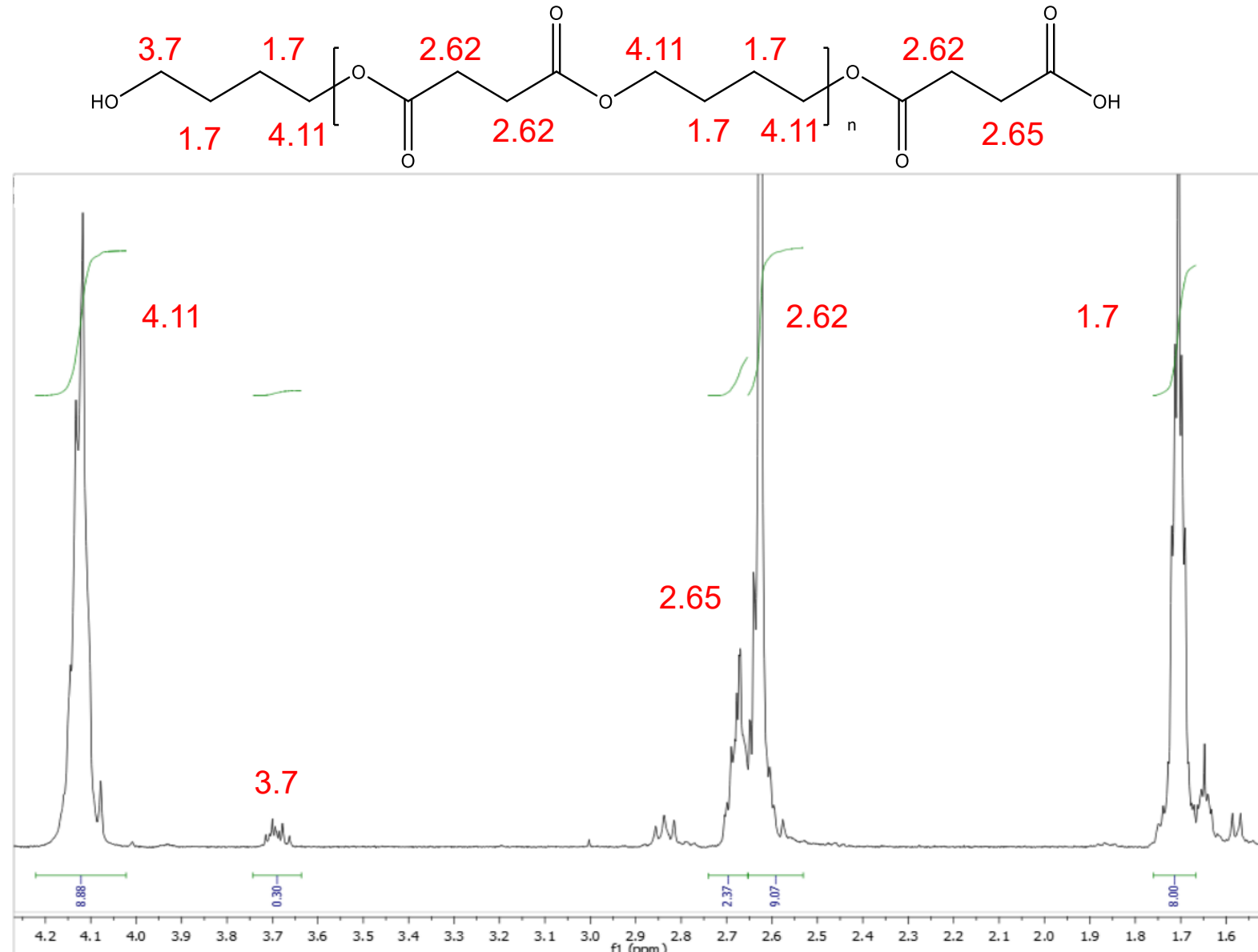


Figure 6: ¹H-NMR spectra of one of the soluble fraction obtained after the graft polymerization process, with the hypothetical chemical structure of the repeating PBS oligomer units.

Table 3: best reaction conditions for the graft polymerization of the simply oxidized cellulose fibers and the extracted CNF.

Entry	CNF	80 °C (h)	100 °C (h)	150 °C (h)	¹ H-NMR (\overline{M}_n , Da) soluble fraction ¹
3	X	3	19	22	359
5	V	3	19	22	568

¹separated through Soxhlet extraction with Dichloromethane

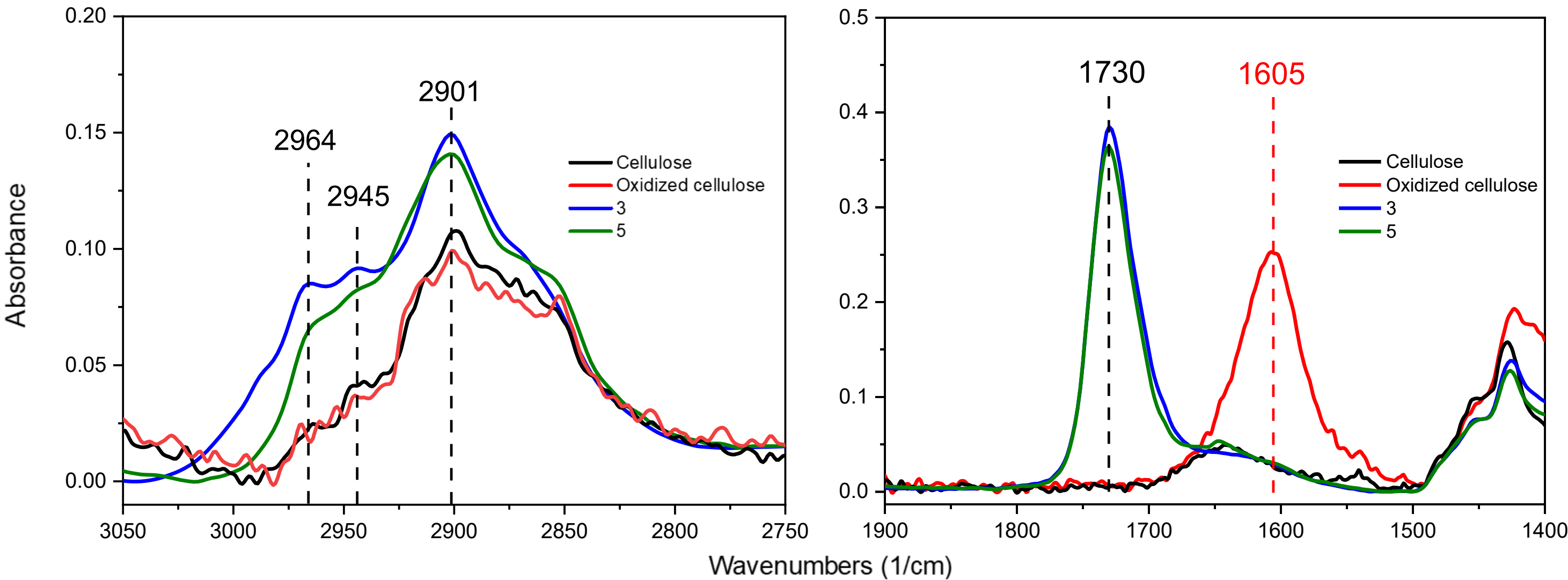


Figure 7: ATR-FTIR spectra between 3050-2750 cm⁻¹ and 1900-1400 cm⁻¹ of the starting cellulose material, oxidized cellulose, and the insoluble fraction of the samples obtained after the graft polymerization at the conditions reported in Table 3.

Conclusions

- Demonstrated the oxidation and the dimensional reduction of the cellulose fibers;
- Promising preliminary results of graft polymerization on/from the NFC under mild conditions.

Acknowledgments

Financially supported by the PRIN-GREENCO (Bando PRIN 2022 Prot. 20223LWKTC) - Research project title: Untapping the potential of **GREEN** Composites by combining performance and environmental sustainability.

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