Cellulose Nanostructures from Agricultural Wastes as building block for functional materials

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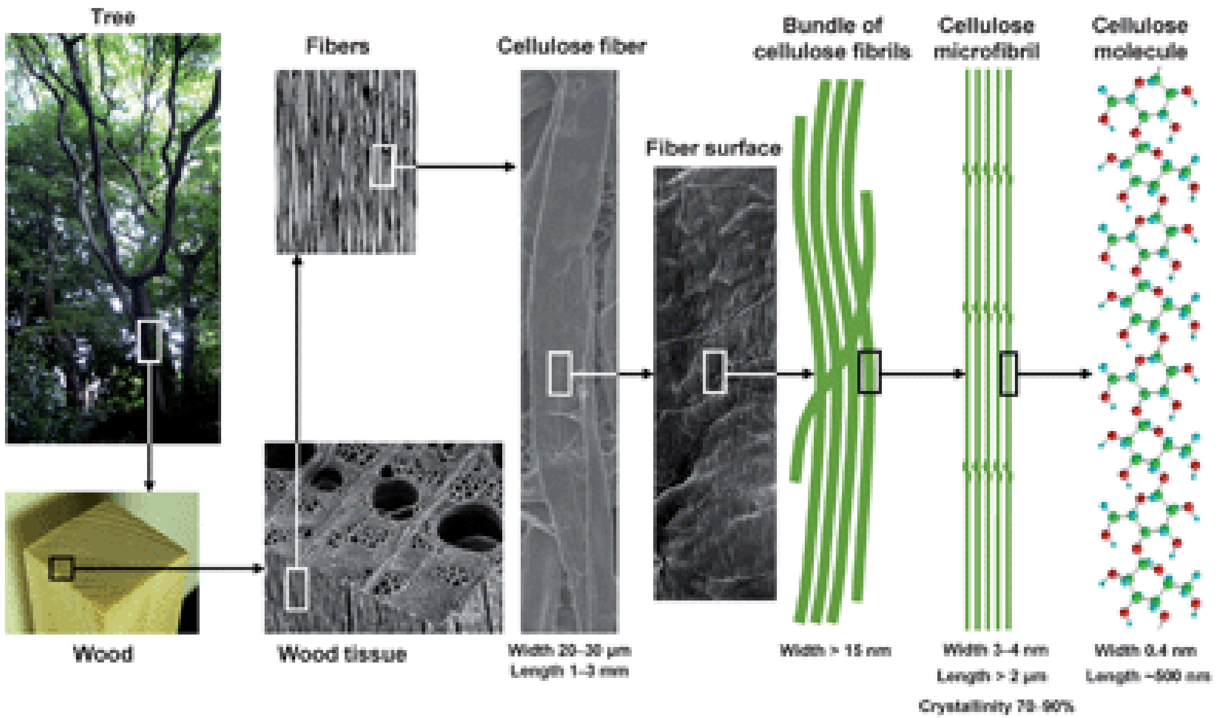
Introduction – Nanocellulose

- Cellulose is the most abundant organic polymer made of glucose chains
- Some interesting properties include hydophylicity, biodegradability, and renewability.
- Nanocellulose are made of isolated units of cellulose microfibers



(Isogai, A., Saito, S., & Fukuzumi, H. 2011. TEMPO-oxidized cellulose nanofibers. *Nanoscale,3,* 71-85)

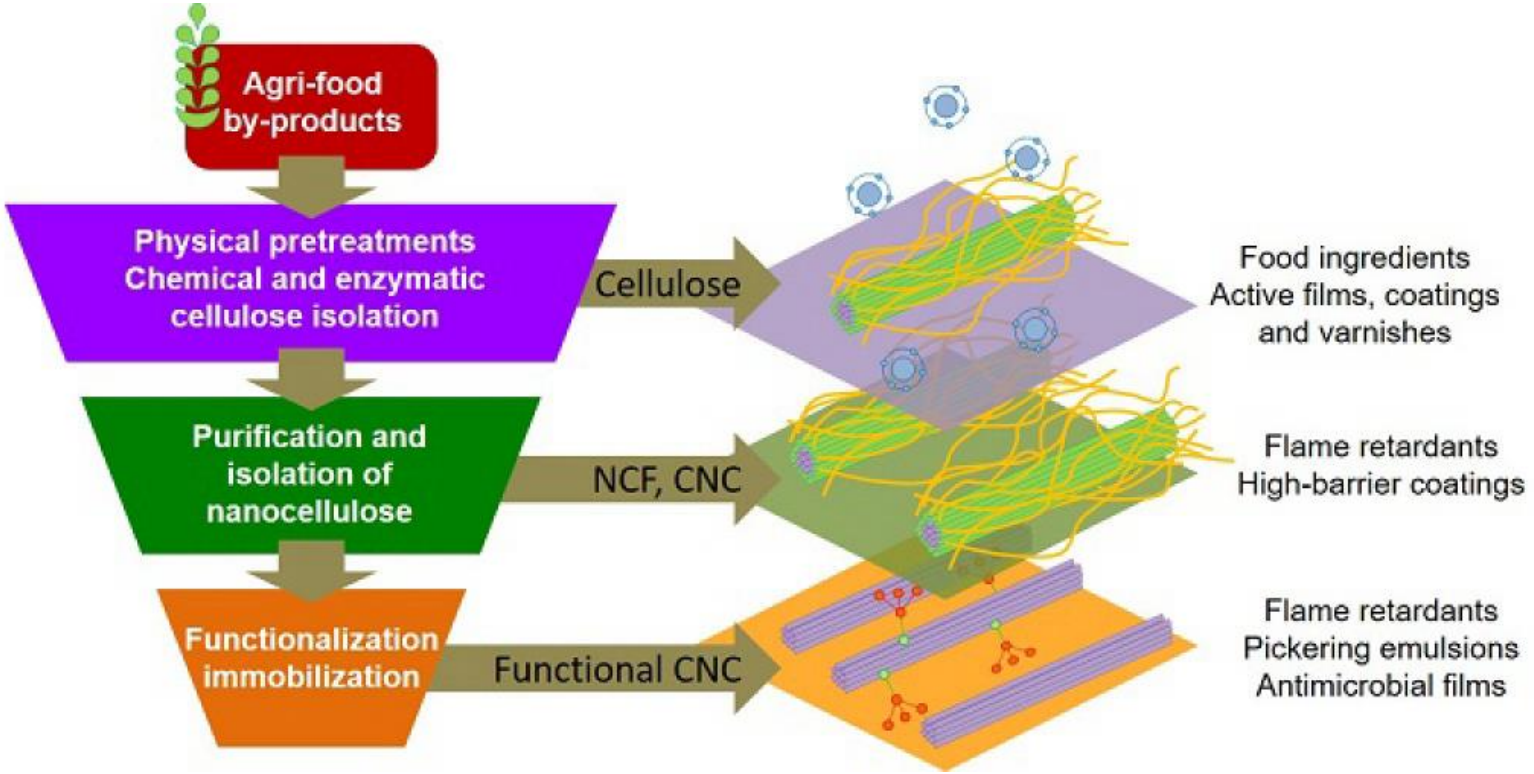
Introduction – the PANACEA Project

- A technology **PlAtform** for the sustainable recovery and advanced use of **NAnostructured CEllulose** from **Agri-food residues** (PANACEA)
- Main objective is to **develop** a technology **platform** to **process agri-food residues** for the **recovery of cellulose** and **high added value compounds** to be used as building blocks to develop more sustainable advanced materials
- Aims to **address the problem of waste generation** by the European food sector (i.e. out of about 250 million ton/year, around 10% are from fruit and vegetable processing)

Introduction – the PANACEA Project

- Partners in the PANACEA project:
  - Prof. Francesco Donsi (Università degli Studi di Salerno)
  - Prof. Marina Scarpa (Università degli Studi di Trento)
  - Patrizia Contursi (Università degli Studi di Napoli Federico II)
  - Prof. Biogia Spigno (Università Cattolica del Sacro Cuore)
  - Dr. Gennaro Gentile (Consiglio Nazionale delle Ricerche)
  - Dr. Federico Carosio (Politecnico di Torino)

Introduction – the PANACEA Project



My research falls in these parts of the PANACEA Project

Abstract

- The main goal of the research is to **develop** a more **sustainable industry-scale** method to **recover nanocellulose** from more coarse **agricultural wastes**.
- We consider different chemical reactions to **reduce the macroscopic fiber into their nanosized building blocks**. Starting materials used were cellulose fibers, farina di agrumi, and already TEMPO-oxidized nanocellulose.
- Moreover, different methods of **functionalizing nanocellulose to** impart desired properties like **hydrophobicity** and **improved thermal stability** are also being investigated.

Strategies:

- For the recovery of nanocellulose, we oxidized the starting coarse material by periodate oxidation[1] (under acid conditions).
- To modify nanocellulose (i.e. for hydrophobicity and for improved thermal stability), we chose silanization[2].
- Both chemical reactions were chosen for their relative simplicity (compared to others) and with green chemistry considerations.

[1] Periodate Oxidation – Use of $NaIO_4$ to break the C2-C3 bonds in glucose repeat units to form 2,3 dialdehyde groups
[2] Silanization – Surface modification process using silanes. Silanes can act as coupling agents to address polarity incompatibility between natural fibers (polar) and polymer reinforcements (non-polar) → promote interfacial adhesion

Nanocellulose Extraction – Periodate Oxidation

Dissolve $NaIO_4$ and NaCl in water. **Add** to wet pulp

→

Perform oxidation reaction at room temperature away from light, stirring for 96 hrs (4 days)

→

Stop the reaction and **rinse** the suspension by centrifugation

→

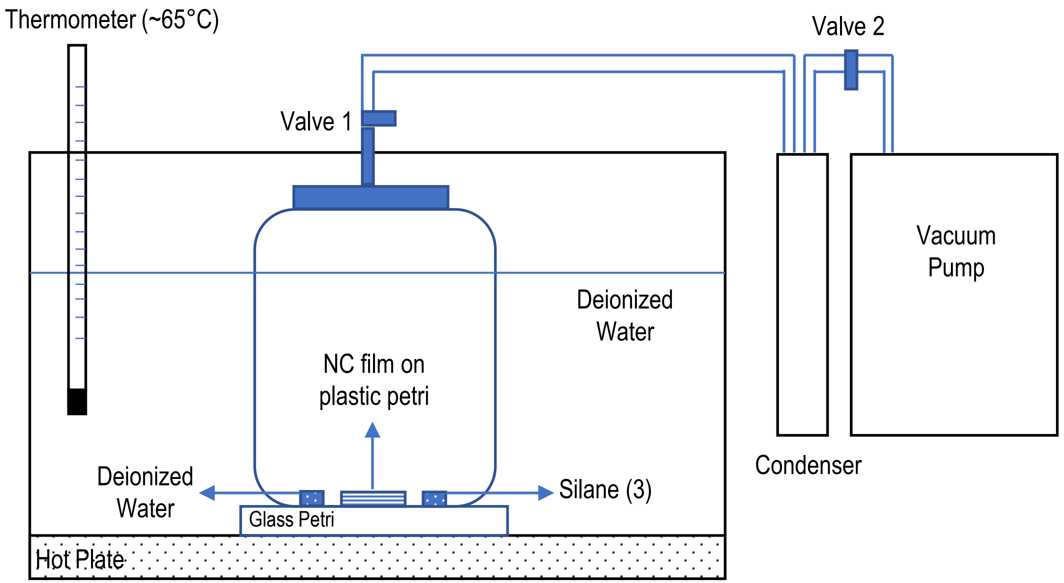
Suspend pre-oxidized cellulose and **heat** at 80°C with stirring for 6hrs

→

Recover nanocellulose after centrifugation

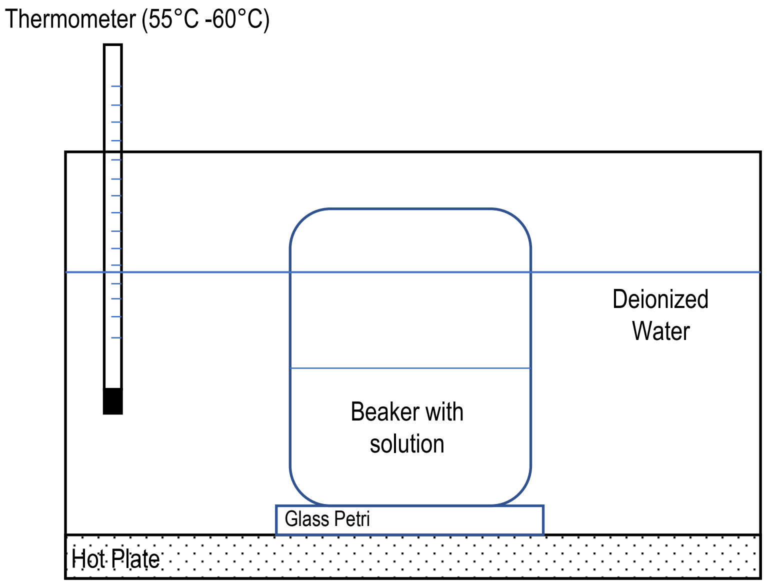
Nanocellulose Functionalization – Silanization (Gas phase)

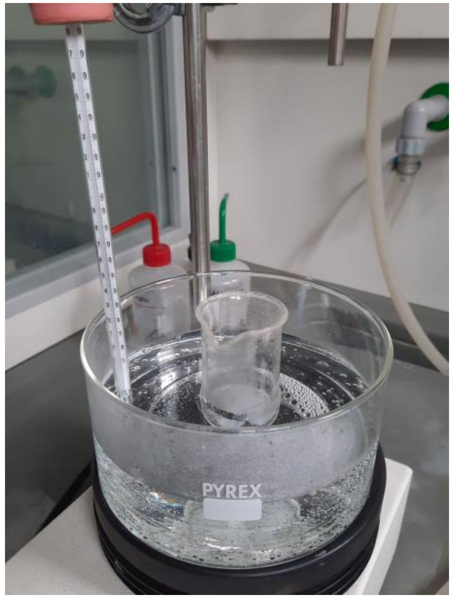
- Gas phase silanization was done on **already dried nanocellulose films**
- Functionalization is therefore done on the **surface of the film**
- **Pro:** Simpler process, can be done on already prepared films
- **Con:** Functionalization is limited to the surface of the film



Nanocellulose Functionalization – Silanization (Liquid Phase)

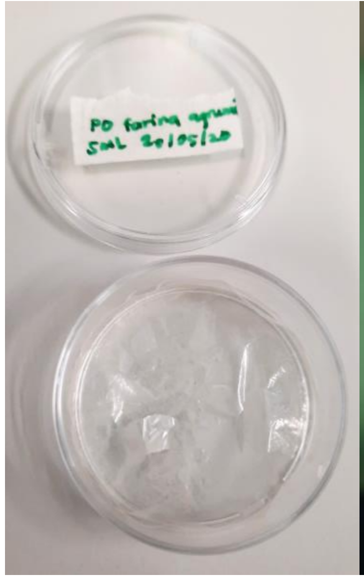
- Liquid phase silanization was performed on **nanocellulose suspensions**
- Modification was done on the **bulk material**, instead of just the surface
- **Pro:** Better functionalization of the entire material
- **Con:** Takes up more time (i.e. need to rinse the solution after)

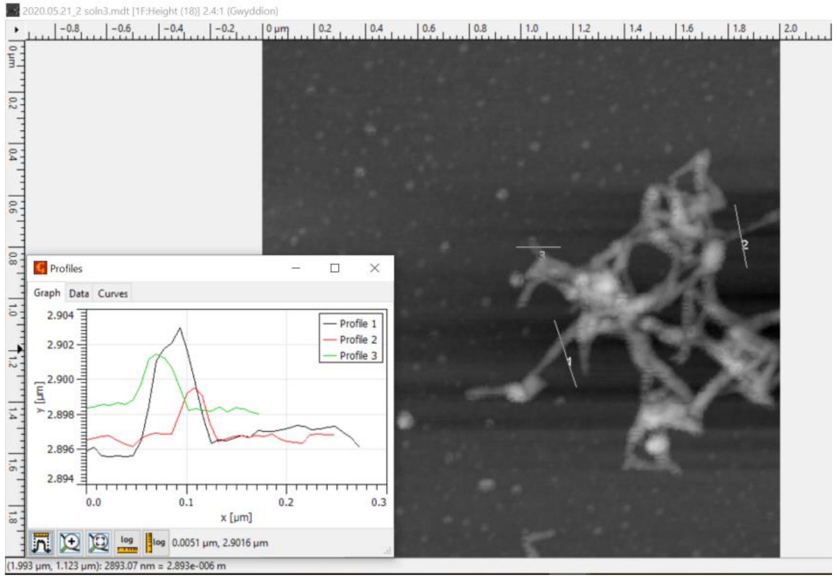




Results – Periodate Oxidation

- Farina di Agrumi

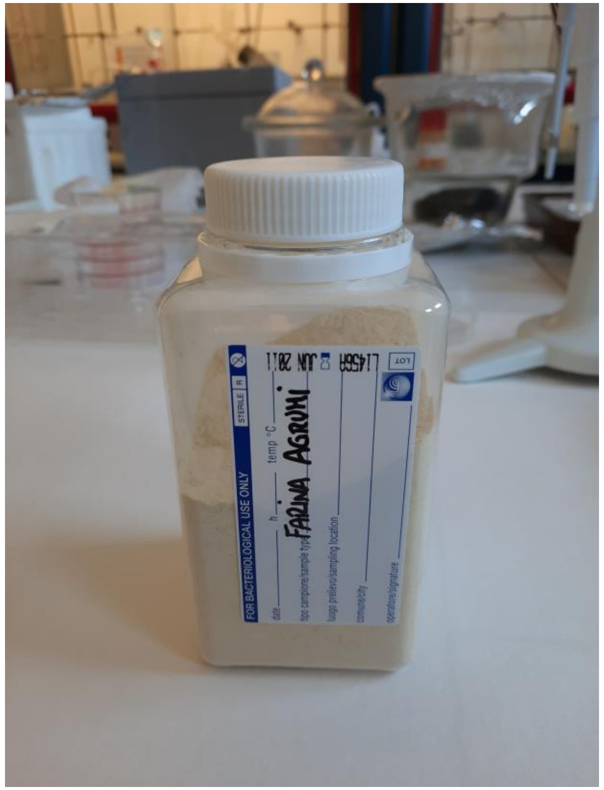


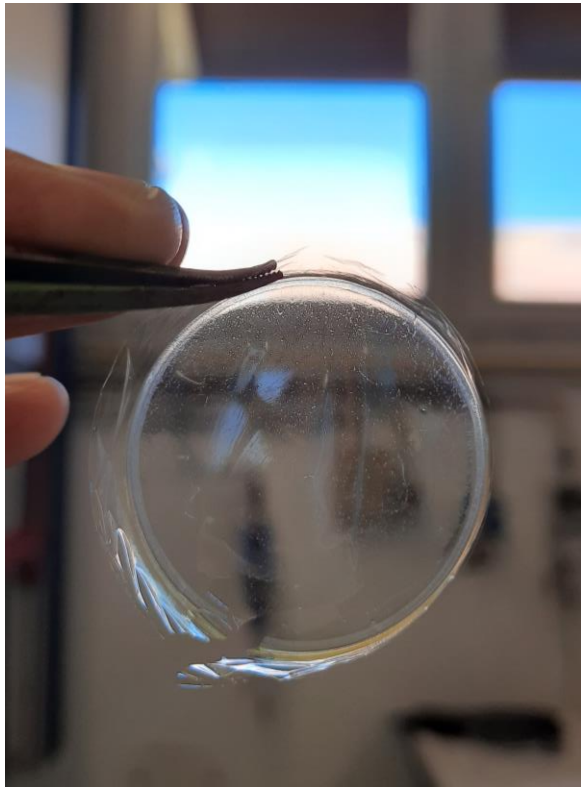


Curve	Height (nm)	SD	variance
1	6.19	0.3269	0.1069
2	3.19	0.4202	0.1766
3	3.13	0.1837	0.1837

Results – Periodate Oxidation

- Farina di Agrumi

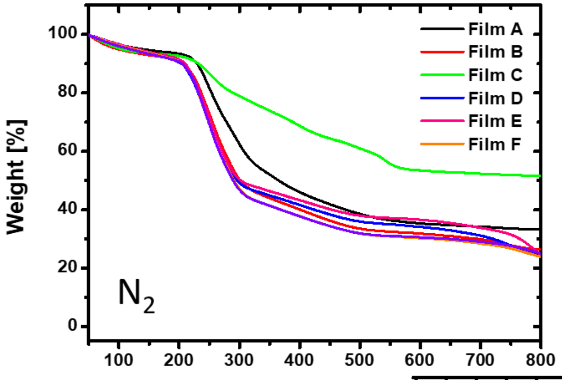


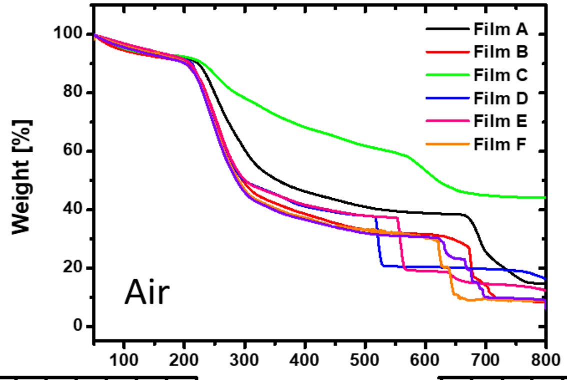


Results – Silanization (Thermal Stability)

TGA

Samples: A (5 wt%)and B (1 wt%)MPTS functionalized, C (1 wt%) TPMP functionalization, D Celeste 85, E Celeste 85 + 5% EtOH, F Celeste 90+5%EtOH, G Celeste 90

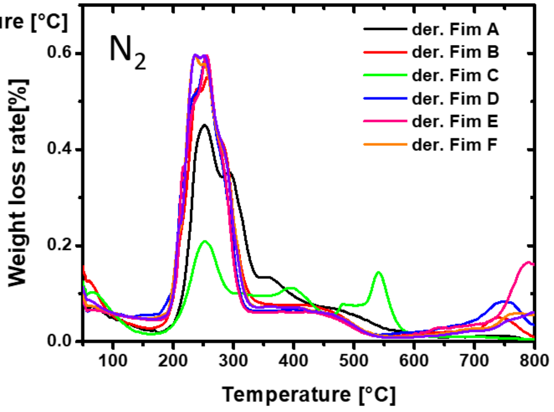


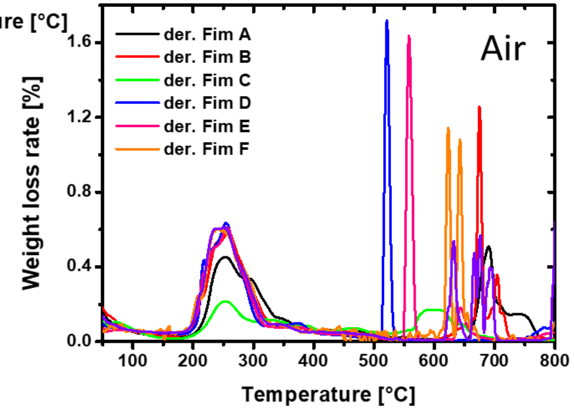


Sample	Res.N2 [%]	Res. Air [%]
A	33	14
B	26	8
C	52	44
D	25	16
E	25	12
F	24	8
G	25	9

High char forming yield

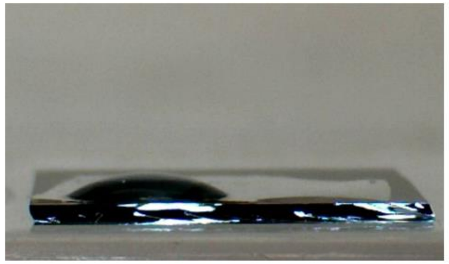
Burning during degradation in air



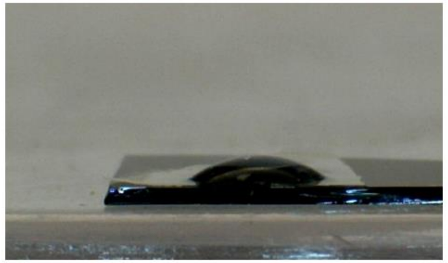


- Images from Dr. Federico Carosio (Politecnico di Torino)

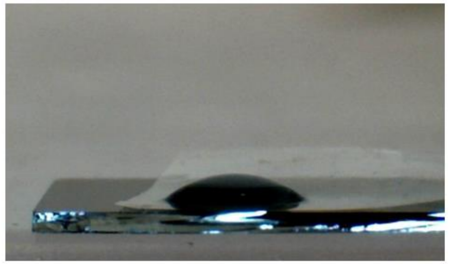
Results – Silanization (Hydrophobicity)



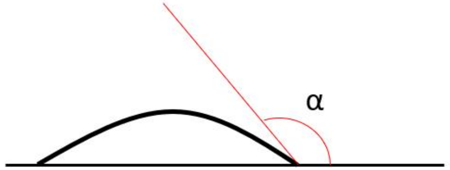
Blank Celeste 85
α =152.31°, SD: 0.4625,
variance: 0.21395

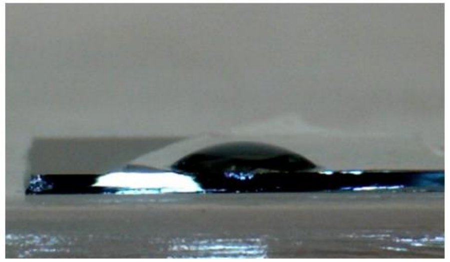


C85 + n-octyl 1
α =139.79 °, SD: 0.6832
variance: 0.46673

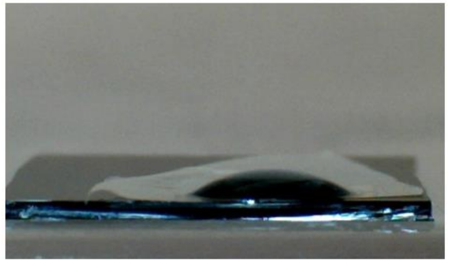


C85 + n-octyl 2
α =135.764 °, SD: 0.8508
variance: 0.72393





C85 + octadecyl 1
α = 132.492°; SD: 0.3696
variance: 0.13657



C85 + octadecyl 2
α = 142.05 °; SD: 0.7394
variance: 0.54665

Conclusions

- We are able to demonstrate the following:
  - Extraction of nanocellulose from the coarse materials (cellulose fibers and farina di agrumi) through periodate oxidation;
  - Silanizations (both liquid and gas phase) were successfully performed using silanes with phosphonate, thiol, and hydrophobic groups

Recommendations/Other Explorations

- Optimize chemical processes used (i.e. periodate oxidation for higher yield; silanization for better performing functionalized nanocellulose)
- Extend nanocellulose thermal stability functionalization techniques to make cotton fabrics that are flame retardant

Thank you very much!