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SAPIENZA UNIVERSITÀ DI ROMA

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Nanocellulose based materials for Cultural Heritage:

Wood and textile applications

What is *Cellulose*?[1,2]

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It is the most abundant **natural biopolymer** in the world.

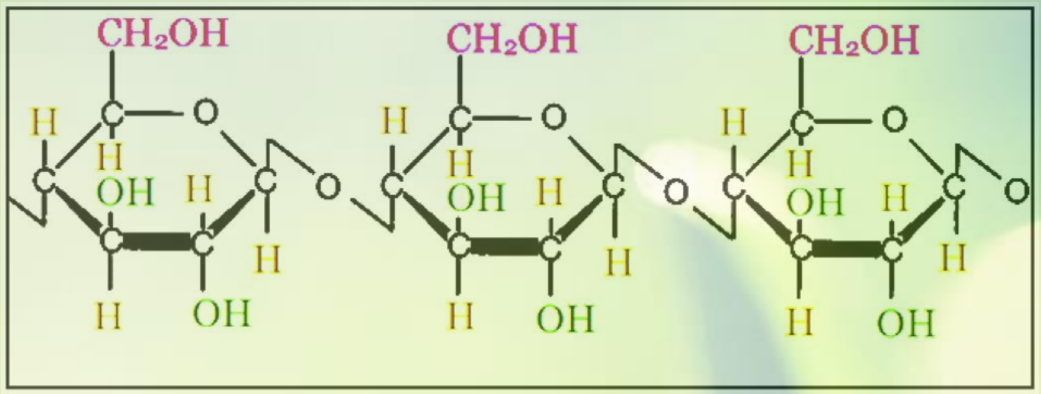

Fig.1 Structural chemical formula of cellulose.

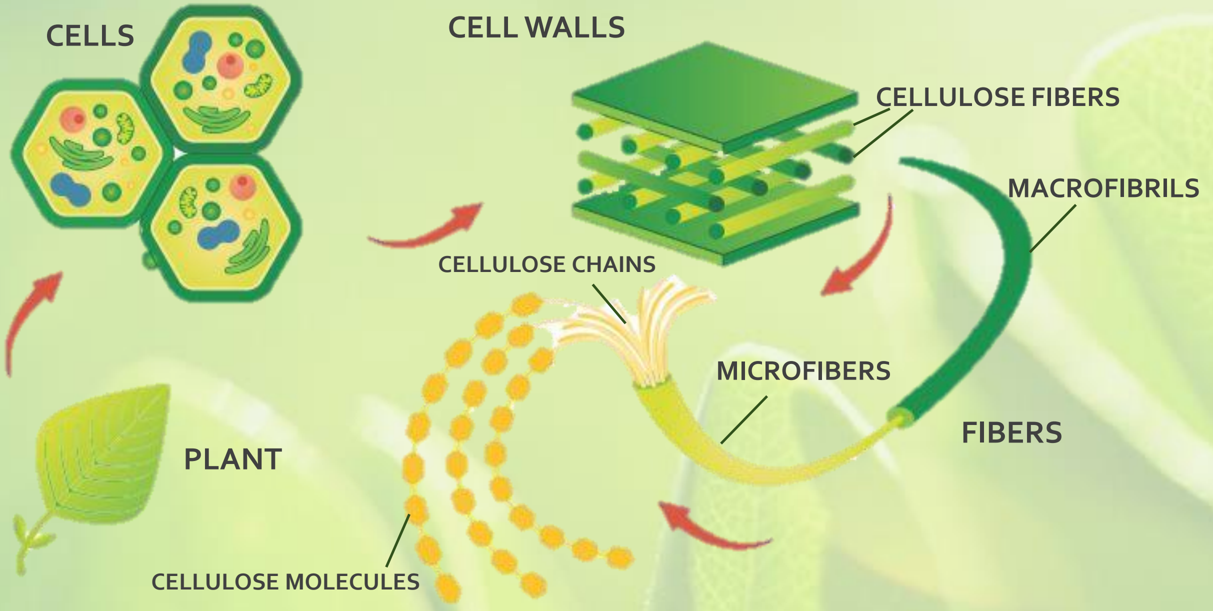

Fig.2 Illustration of plant cell structure.

Advantages of *Cellulose*:

- Renewable biomass;
- nontoxicity;
- biodegradability;
- stability;
- low cost;
- a good substitute to synthetic products.

And *Nanocellulose*?[2,3]

Nanocellulose is obtained from renewable polymers via **acid hydrolysis**[2]

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The cellulose fibril or crystallite containing at least **one dimension** in the **nanoscale** range.

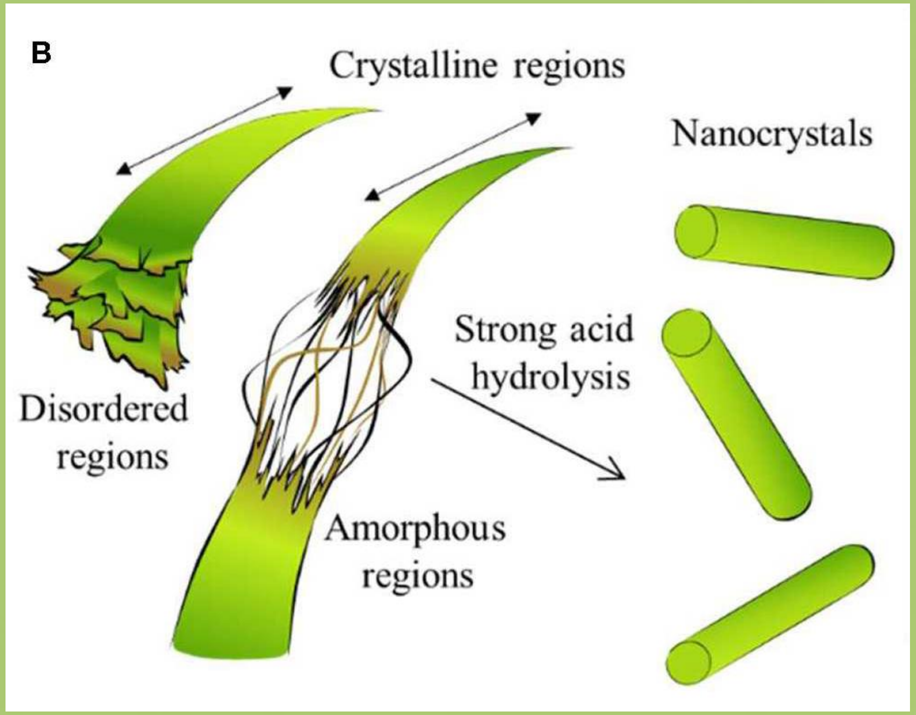

Fig.4 A schematic diagram of the reaction between cellulose and strong acid to obtain Nanocellulose[3].

Fig.3 Cellulose nanocrystals.

There are **three** fundamental **classes** of nanocellulose[2]:

Nano-fibrillated cellulose (NFC)

Cellulose nanocrystals (CNC)

Bacterial nanocellulose (BNC)

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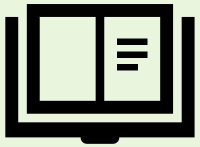
rod-like nanocrystal configuration

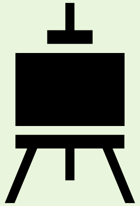
N.B.: Cellulose nanocrystal possesses **typical dimension** 3–30 nm in diameter as well as 100 nm to 1–2 lm in length.

Why is *Nanocellulose* important for the recovery and conservation of *Cultural Heritage*?[4]



Historical papers

Ancient woods



Painting canvases

Advantages of *Nanocellulose*:[2,3,4]

- High surface area;
- hydrophilicity;
- high elastic modulus (140–150 GPa);
- outstanding mechanical strength;
- lightweight (1.5 g/cm^3);
- good possibility for chemical modification;
- inexpensive.

How to use *Nanocellulose* for Cultural Heritage?[4,5,6]

Historical papers

Deacidification and consolidation of strongly degraded cellulosic artworks.

Ancient woods

Recovery and consolidation of decayed wood.

Painting canvases

Structural reinforcement for canvases degraded by aging.

Historical papers:

Grafted nanocellulose and alkaline nanoparticles for the strengthening and deacidification of cellulosic artworks[4]

WORK'S AIM: To create **"hybrid system"** formed by nanocellulose, useful for the **consolidation** of damaged paper, and alkaline nanoparticles necessary for the **neutralization of acidity**.

MATERIALS:

- Oleic acid-grafted cellulose nanocrystals **(GC)**;
- Ethanol;
- Calcium hydroxide **(OH3)** and calcium carbonate **(CO3)** nanoparticles;
- Aged paper samples **(AP)**;
- Unaged filter paper **(P)**.

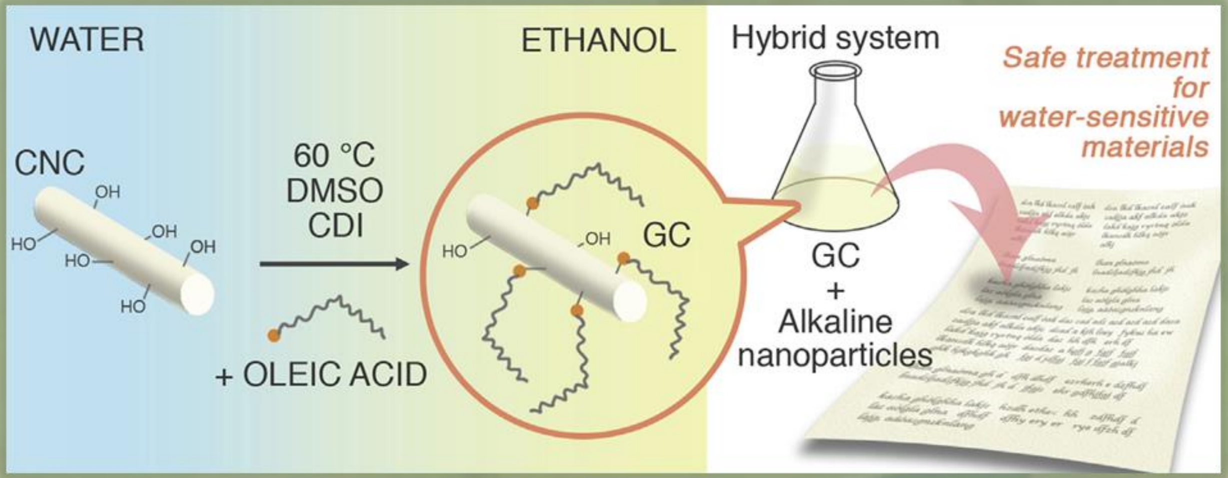


Fig.5 Graphical abstract.

TESTS:

- Evaluation of **pH**;
- Ultimate Tensile Strength measurements **(UTS)**;
- Three-interval thixotropy tests **(3ITT)**.

Fig.7 Three interval thixotropy tests (3ITT) of GC (A), GC-OH3 (B) and GC-CO3 (C) ; the visual aspect of the samples: GC (D), GC-OH3 (E) and GC-CO3 (F).

RESULTS:

- **Acidity neutralized** by GC-CO3 and GC-OH3;
- **Increase in UTS** only due to **nanocellulose**;
- **Thixotropic** dispersions;
- No alterations in the visual aspect.

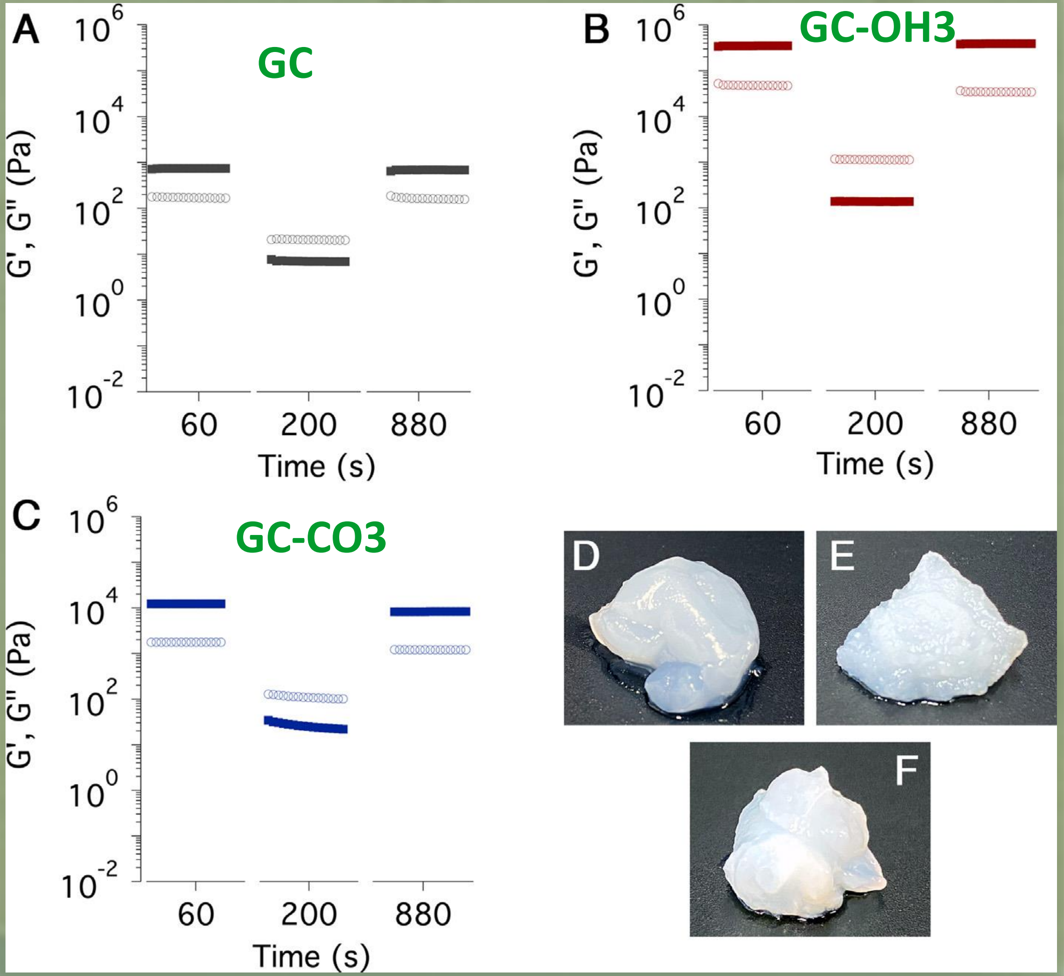
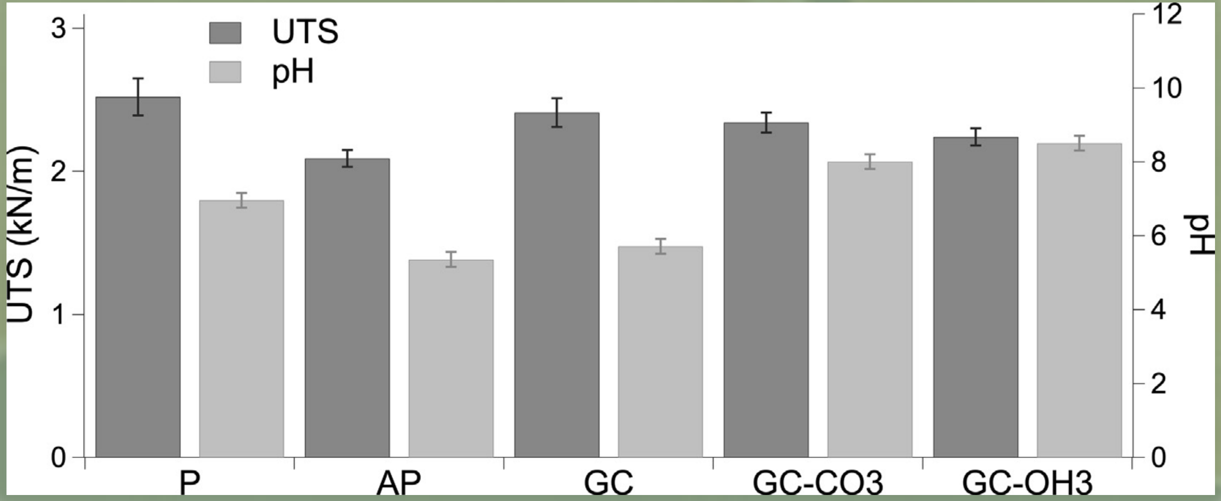


Fig.6 Ultimate tensile strength (dark bars), and pH (light bars) of paper samples.

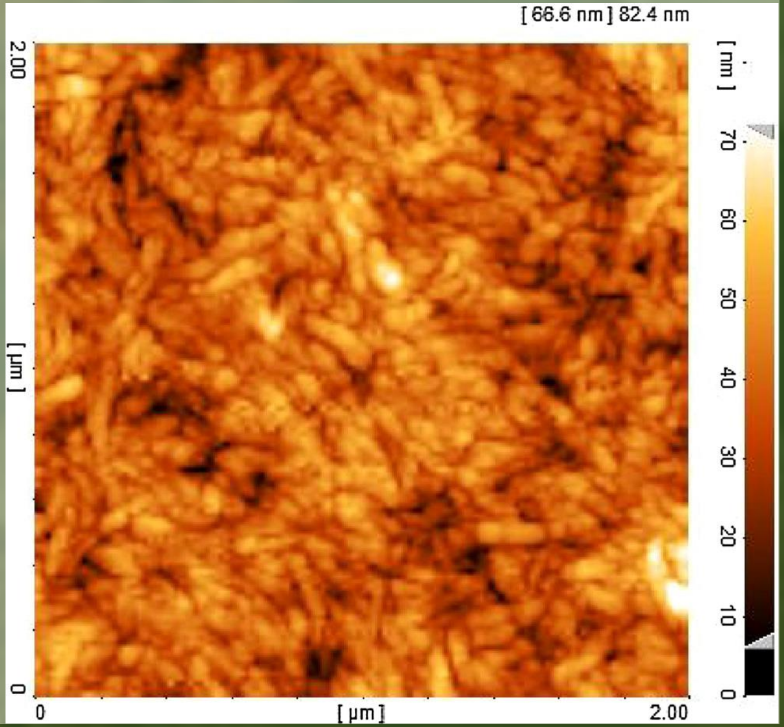


Ancient wood:

Bio-inspired consolidants derived from crystalline nanocellulose for decayed wood[5]

WORK'S AIM: Evaluation of the **consolidant efficacy** of the CNC-based products on rotted wood samples in terms of **stiffness increase** after treatments.

Fig.8 AFM image of CNC sol.



MATERIALS:

- Composite sol of CNC and PDMS-NH **(CP)**;
- Composite sol of CNC and lignin sol **(CL)**;
- Composite sol of CNC and PDMS-lignin **(CPL)**;
- Three classes of wood samples from old beams of **Norway spruce**: **A** (high degradation level); **B** (intermediate degradation level); **C** (low degradation level).

TESTS:

- Dynamic mechanical analysis **(DMA)** with different stresses depending on the decay class (class A, 0.5 MPa; class B, 1 MPa; class C, 2 MPa.);
- Static contact angle **(CA)** measurements.

Fig.9 Average values of the consolidant uptake (Y) for the various tested combinations (consolidant, decay class, impregnation cycles). The values are expressed as %.

	Decay class	number of impregnation cycles			
		5	10	20	30
CNC	A	20.2 ± 9.1	44.2 ± 15.5	64.9 ± 18.7	107.7 ± 27.4
	B	11.2 ± 10.0	20.2 ± 8.9	34.0 ± 12.5	34.2 ± 1.3
	C	na	8.5 ± 2.7	15.2 ± 2.0	24.2 ± 1.3
CPL	A	17.0 ± 6.7	28.8 ± 4.9	46.1 ± 6.4	98.5 ± 6.0
	B	8.7 ± 1.1	15.1 ± 6.4	28.4 ± 7.0	46.6 ± 2.8
	C	3.1 ± 1.5	5.4 ± 3.6	10.2 ± 5.1	12.5 ± 1.9
CP	A	11.0 ± 6.6	23.5 ± 2.0	42.4 ± 25.9	na
	B	5.3 ± 4.0	8.4 ± 4.9	13.9 ± 5.4	na
	C	1.2 ± 1.4	3.8 ± 2.2	7.7 ± 7.0	na
CL	A	20.6 ± 8.5	40.1 ± 17.7	na	na
	B	7.6 ± 3.9	14.0 ± 7.4	na	na
	C	2.7 ± 1.2	4.6 ± 2.0	na	na

"na": not assessed.

RESULTS (1):

- The amount of penetrated consolidant is a function of the **number of impregnation cycles** and it depends on the **degradation level** of sample;

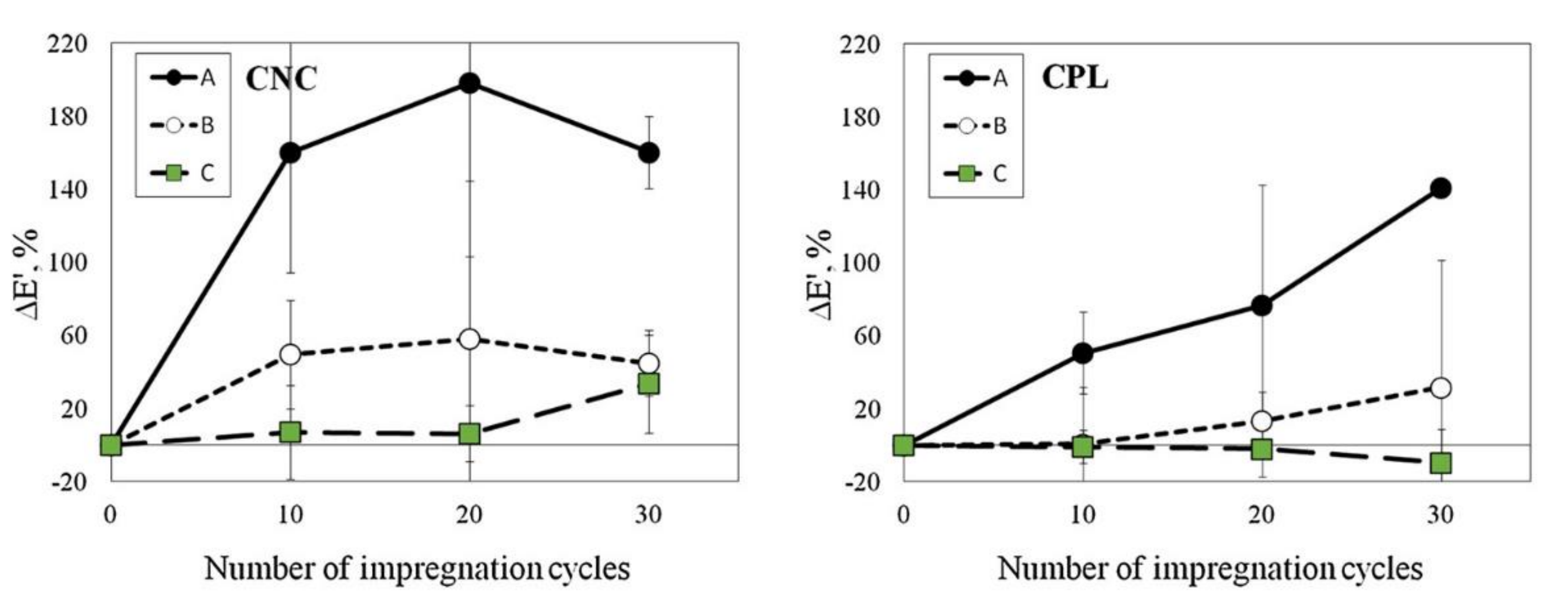
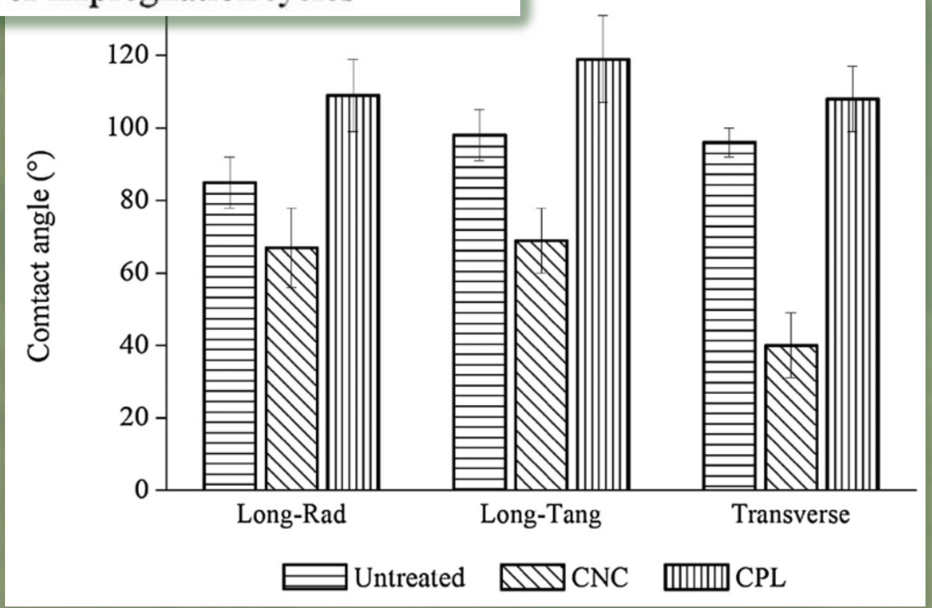


Fig.10 ΔE' vs. number of impregnation cycles for the two consolidants CNC and CPL on wood samples of different decay classes.

Fig.11 Static contact angle of water measured on surfaces of treated and untreated wood samples.



RESULTS (2):

- With the same number of impregnation cycles, the **storage modulus E'** increases more for **CNC** because it has **smaller crystals** that penetrate better inside the nanopores of the wood;
- **CNC** increases **wettability** of the wood surface;
- **CPL** makes the wood surface more **hydrophobic**.

Painting canvases:

On the potential of using nanocellulose for consolidation of painting canvases[6,7]

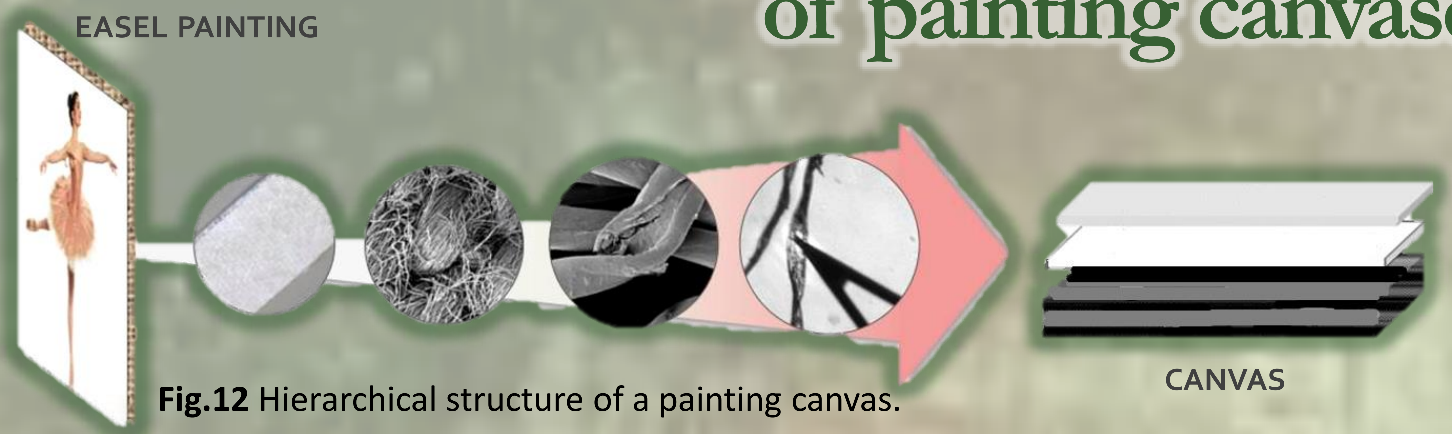


Fig.12 Hierarchical structure of a painting canvas.

WORK'S AIM:

To use **nanocellulose** materials as a **mechanical reinforcement** in a consolidation process for modern easel paintings.

MATERIALS:

- Mechanically isolated cellulose nanofibrils **(CNF)**;
- Carboxymethylated cellulose nanofibrils **(CCNF)**;
- Cellulose nanocrystals **(CNC)**;
- **Conventional consolidants** (animal glue, Klucel G, Paraloid B72, Beva 371);
- Samples: **painting canvases** made for the experiment and a **real painting**.

TESTS:

- Mechanical test according to **ASTM method**;
- Controlled relative humidity Dynamic mechanical analysis **(DMA-RH)**.

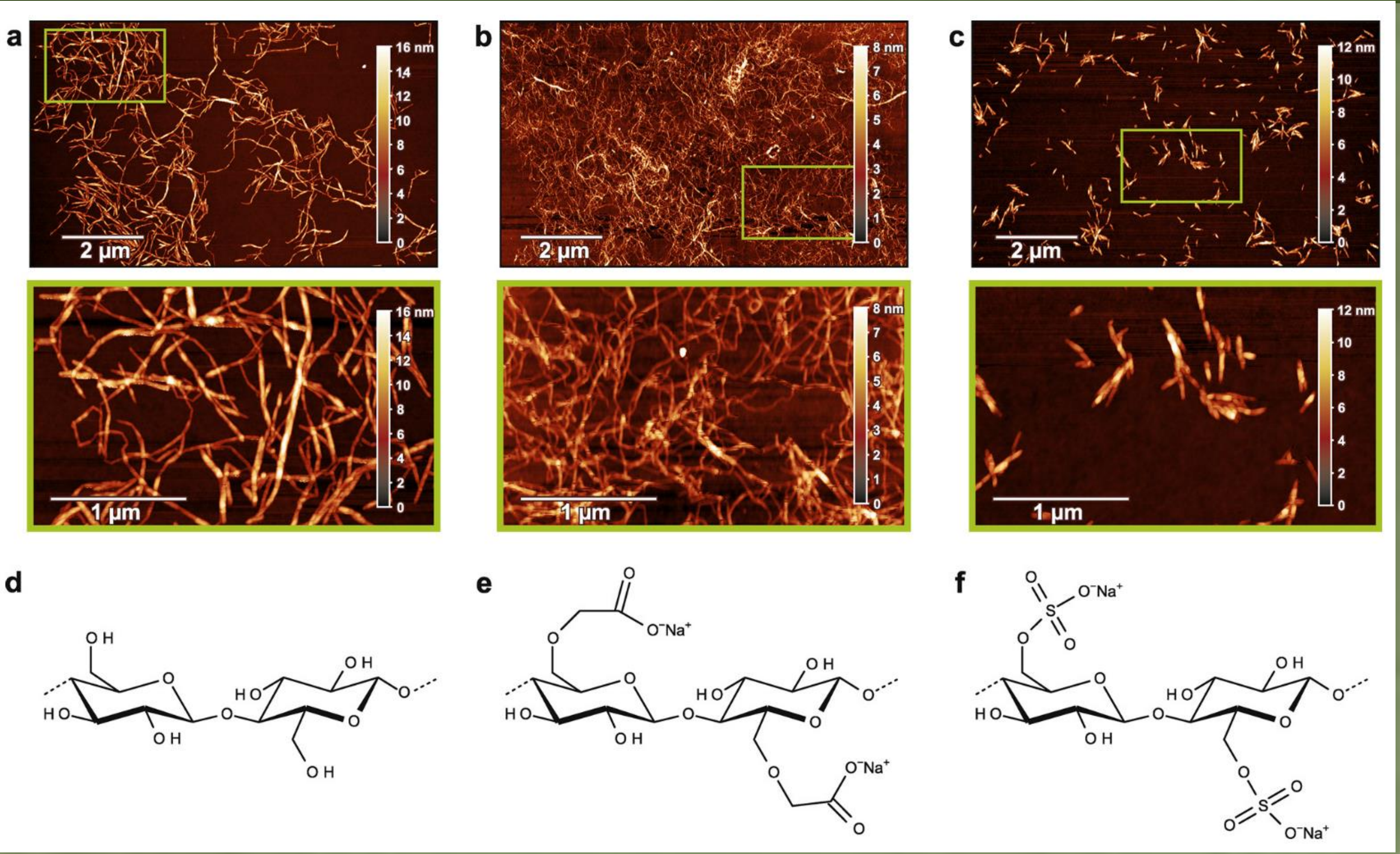
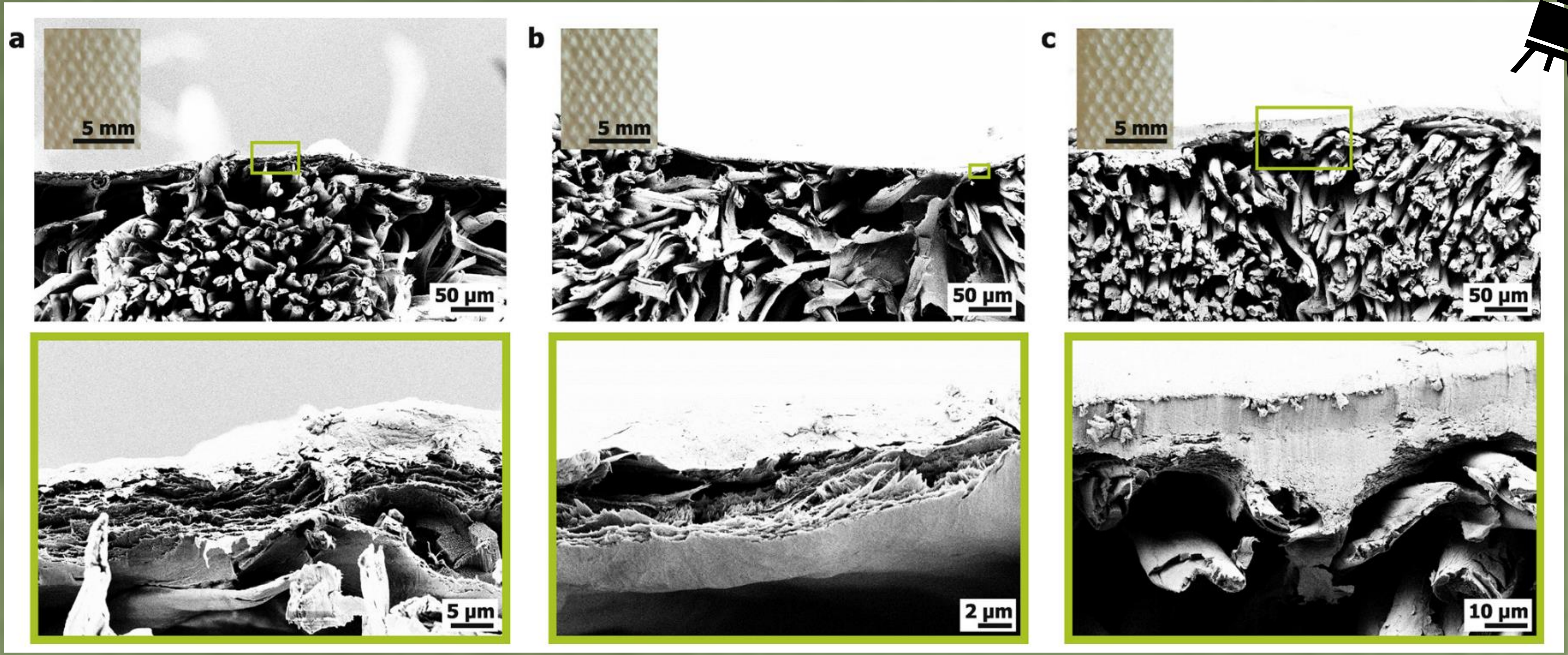


Fig.13 Atomic force microscopy images of: (a)(CNF); (b)(CCNF); (c)(CNC)) and the corresponding simplified surface chemistries (d–f).

RESULTS (1):

- The **surface functionalization** for CCNF and CNC improves **dispersibility**, which may enhance the **penetration** into the canvas;

Fig.14 Scanning electron microscopy images of aged cotton canvases coated 3 times with: (a) CNF; (b) CCNF and (c) CNC, with optical microscopy images as insets (left top).



RESULTS (2):

- Nanocelluloses form a **film** on the **canvas surface** → **reversible** consolidation treatment;
- No modification of the **visual appearance** of the canvases;

RESULTS (3):

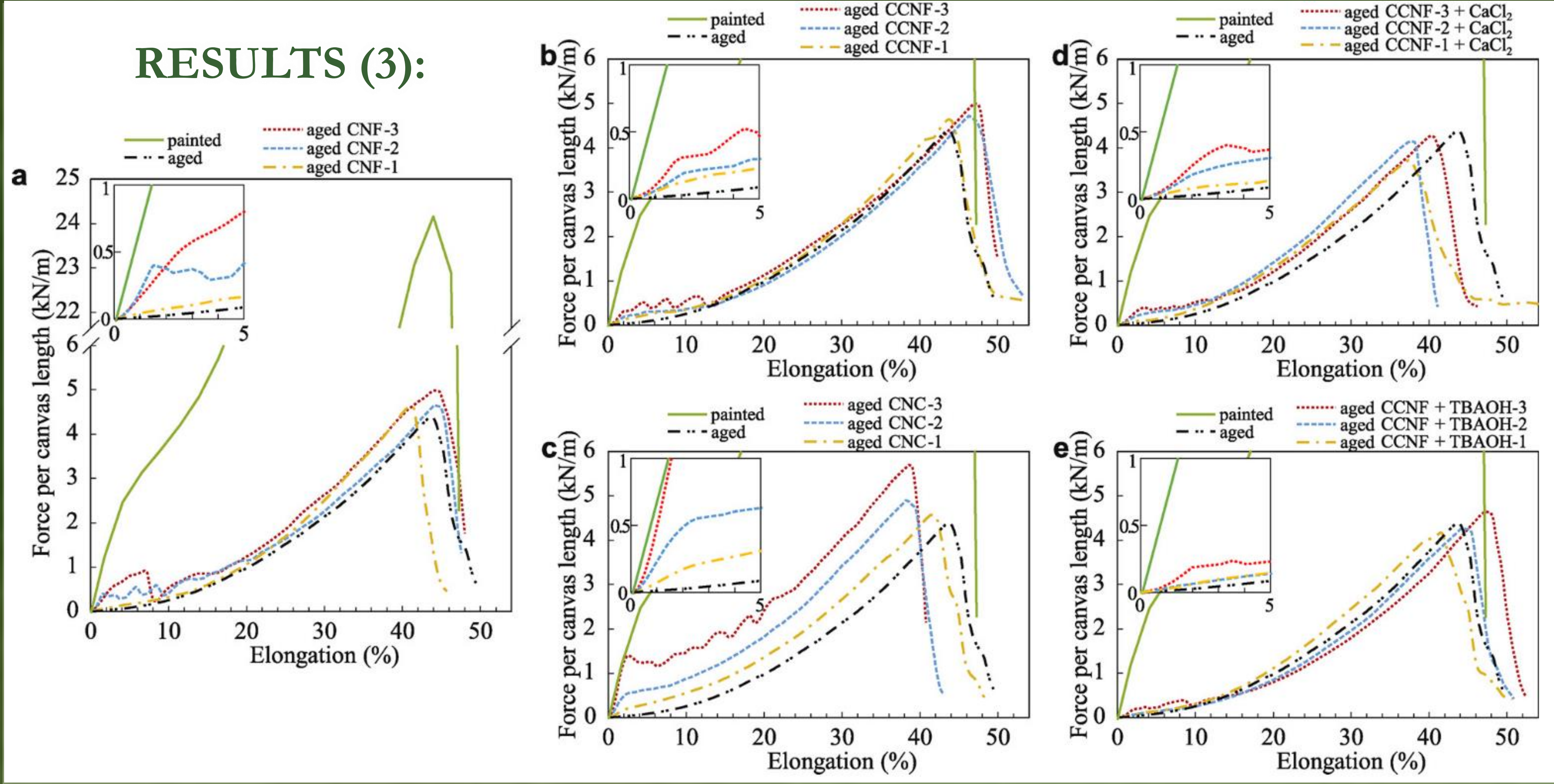


Fig.15 Mechanical properties of the aged canvases coated with different number of coatings of: (a) CNF, (b) CCNF, (c) CNC, (d) CCNF+$CaCl_2$ and (e) CCNF+TBAOH.

- Nanocellulose can provide a **substantial reinforcement** in the **low elongation region** (< 3%);
- CNC showed the **smallest reinforcement** per gained **weight** but the **highest reinforcement** per equivalent **number of coatings**;

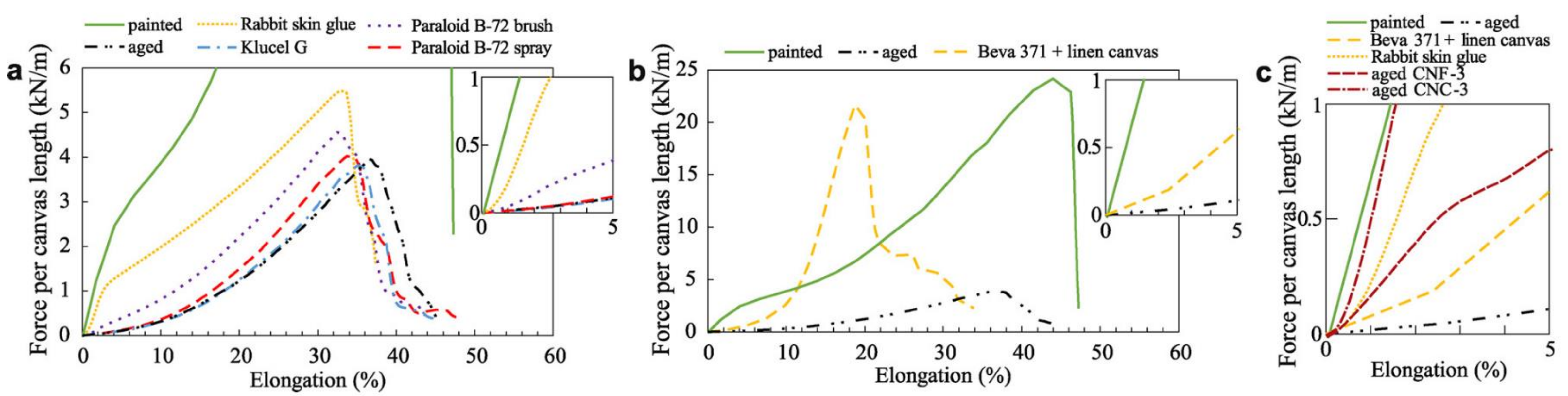
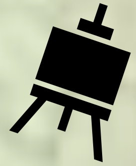


Fig.16 Mechanical properties of aged canvases after various consolidation treatments.



RESULTS (4):

- Compared to the conventional consolidants, **CNC** showed the **highest level of consolidation**;
- All the samples exhibited **higher stiffness** at **low RH** (20%) and **lower stiffness** at **high RH** (60%) → **plasticizing action** of water molecules on the cellulosic chains.

The research continues…

Thank you for your attention!

Anastasia Fornari

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