9th International Conference of the
European Industrial Hemp Association (EIHA)

May 23th – 24th 2012, Wesseling

"Hemp Fibers Surface Treatments for the Development of biocomposites and composites reinforcing agents"

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VE.LI.CA. Project

"Products for the future from ancient cultivation materials"

- **Total amount of R & D Programme: € 5,000,000**
- **Total Financial Intervention required: € 2,500,000**
- **Total time of realization of the R & D Program: 30 months**

Nr.	Research Institutes Involved
1	ISTITUTO DI BIOLOGIA E BIOTECNOLOGIA AGRARIA (IBBA)
2	ISTITUTO PER LO STUDIO DELLE MACROMOLECOLE (ISMAC)
3	ISTITUTO DI SCIENZE E TECNOLOGIE MOLECOLARI (ISTM)
4	ISTITUTO DI CHIMICA DEL RICONOSCIMENTO MOLECOLARE (ICRM)
5	ITALIAN BIOCATALYSIS CENTER (IBC)

Main targets

» Reintroduction of traditional crops

» Valorisation of agricultural residues and wastes

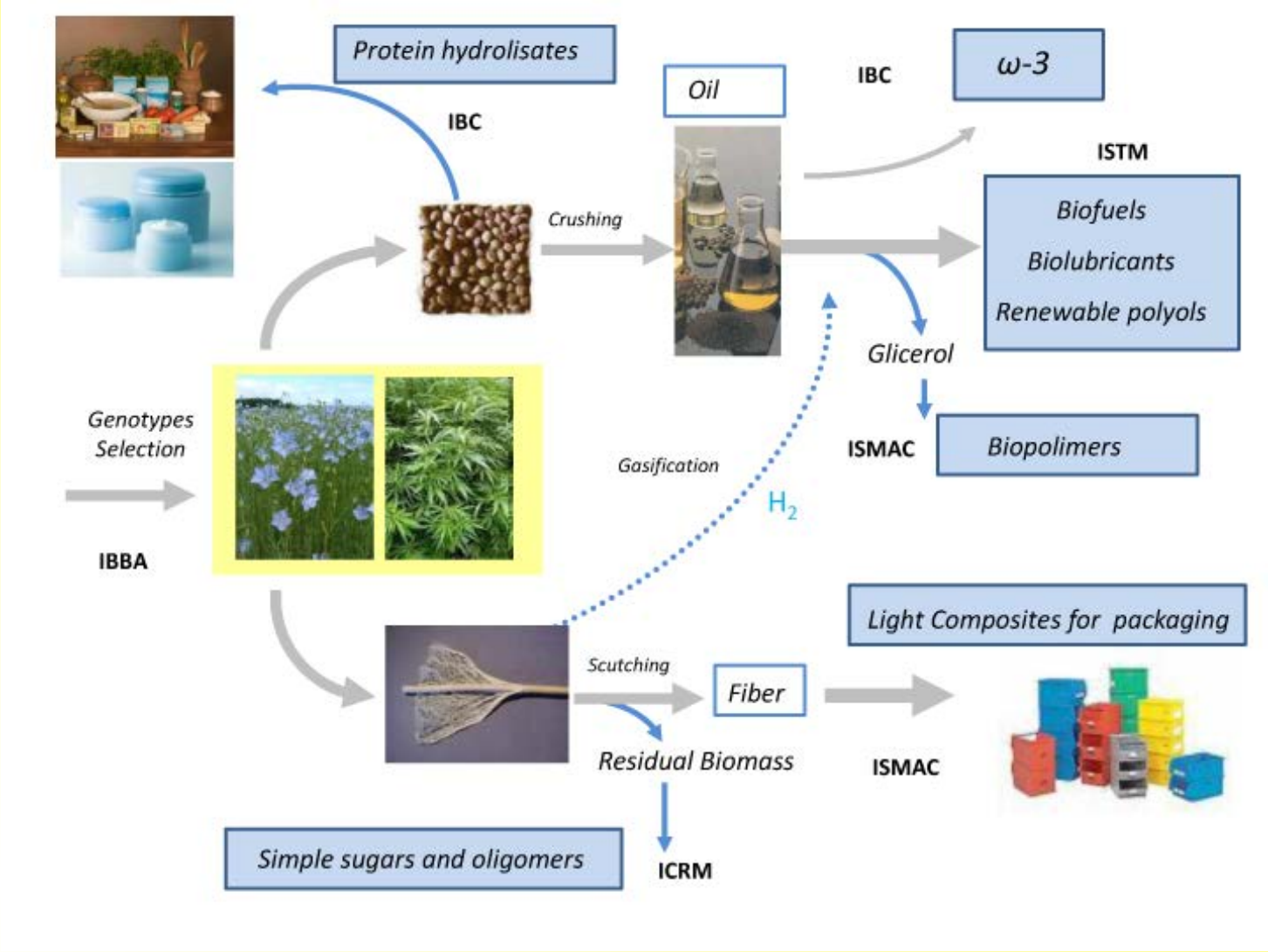
» Setting up of new productive chains

» Establishment of a network of expertises

» Establishment of a bioproducts portfolio

» New professionals formation

Ve.Li.Ca. Project Scheme



Hemp in Italy

- **Italian hemp is of very good quality for fabrics and it was exported worldwide.**

- **Before the last world war there were more than 100,000 hectares in cultivation, whereas in the last few years there are only a few hundred of hectares.**

- **In the last ten years the hemp cultivation has been making a comeback in Italy and the rest of Europe. There has been a rediscovery of the potential of hemp that has led to the establishment of many enterprises in the field of hemp and its applications. In Italy Assocanapa and other organisations, like Fibranova and Consorzio Canapa Italia, are now sponsoring the spreading of hemp.**

- **This new interest is due to peculiarities of hemp and to the present requirement of ecocompatibility and sustainable development.**

- **In Italy and in Europe (EC European Community) it is now legal to cultivate hemp for industrial purpose. The varieties allowed are only those with a content in THC (that is the substance with narcotic effect) lower than 0.2 %.**

CNR - ISMAC (BIELLA DEPARTMENT) FIELDS OF RESEARCH

The Institute for Macromolecular Studies (ISMAC) is an internationally recognised centre of polymer science and an institute of the Italian National Research Council (CNR).

- Recovery of the amino acids, proteins and istological components of animal fibres
- Exploitation of textile sub-products and wastes
- Synthesis and deposition of electro-conducting polymers on textiles
- Textile materials with biodegradability and biocompatibility properties for biomedical applications: tissue engineering, wound dressing, controlled release of drugs
- Functionalization of textile materials
- Enzymatic treatments for textile applications
- Biotechnology processes for the production of polymers from biomasses
- Treatments on polymer-based filters for efficiency improvement
- Thermal, physiological and tactile comfort
- Objective measurements of textile handle properties
- Surface morphology investigation
- Analysis and labelling of textile materials

RESEARCH WORK

Production of hemp micro and nanofibrils for reinforcement of biocomposites

- **Obtaining micro and nanofibrils is useful as they have better mechanical properties compared to the starting fibers.**

- **They contain within their structure more crystalline cellulose, which gives them, with respect to the starting fiber, an higher elastic modulus that contributes to increase the resistance.**

Experimental

Hemp Fibres

Chemical Treatments

Chemical-purified cellulose fibers

(Cryo-crushing)

Ultrasonication

Micro and Nanofibrils

Chemical treatments

The pre-treatment of hemp fibers is necessary to release the fibrils from the matrix in which they are embedded, mainly composed by hemicellulose, lignin, pectin.

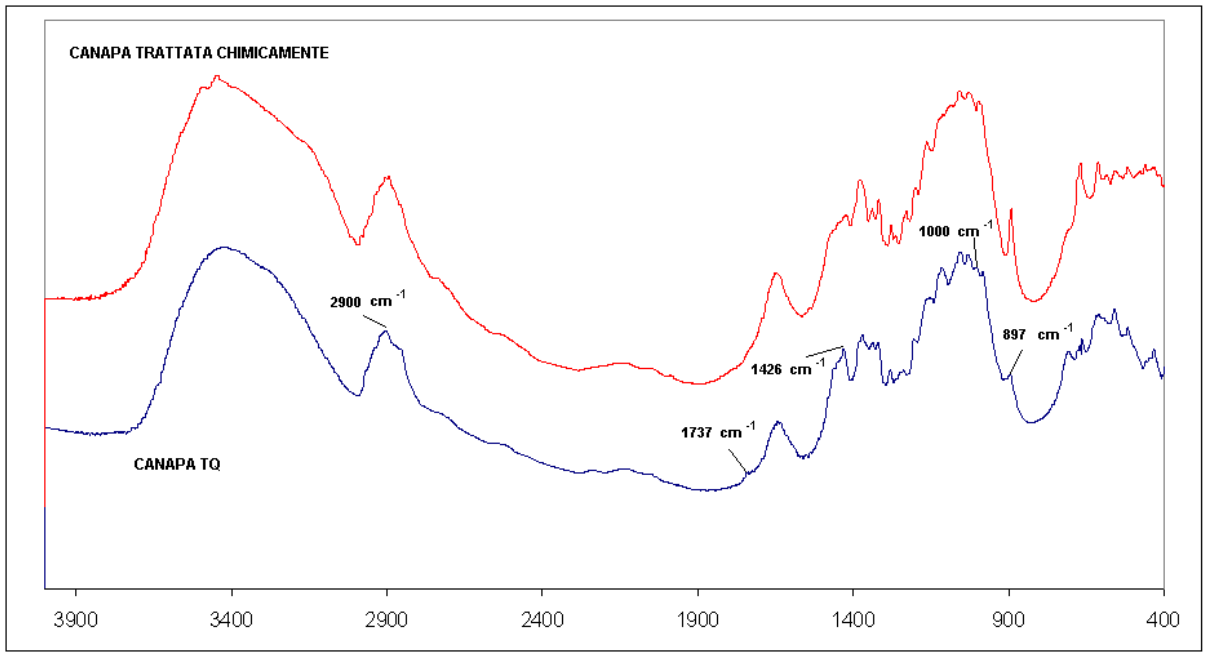
Hemp fibers were chopped to increase the contact surface area. Then, a 3 steps chemical treatment was carried out :

- **17,5% w/w NaOH for 2h, room temperature**
- **Acid Hydrolysis 1M HCl, 80^0 C , 2 h**
- **2% w/w NaOH,80^0 C, 1h**

After each chemical treatment the samples were filtered and rinsed with distilled water until neutral pH

Chemically treated fibers were analyzed by means of FT-IR spectroscopy in transmission mode (KBr pellets)

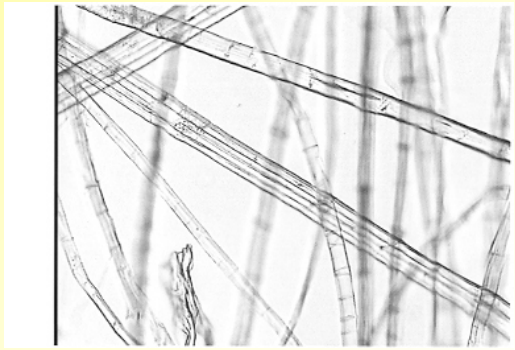
Hemicellulose and pectine removal and lignin partial removal	
C=O stretching	1737
Aromatic C=C stretching	1436
From Cellulose I to Cellulose II	
C-H stretching	2900
C-O stretching	1000
β-glucosidic linkage	897

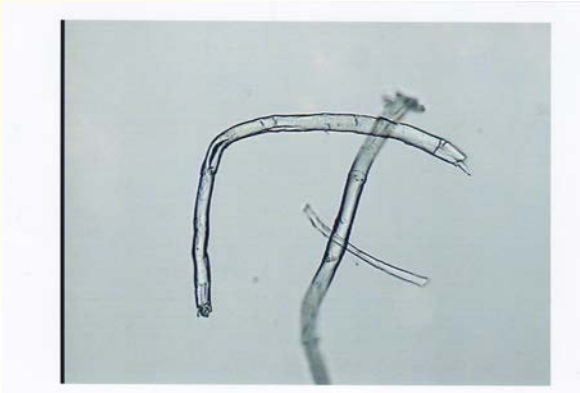


It was possible to highlight both the mercerization of fibers (transformation from native cellulose I to cellulose II) and the removal of the matrix embedding cellulose fibrils

Light and Electron Microscopy

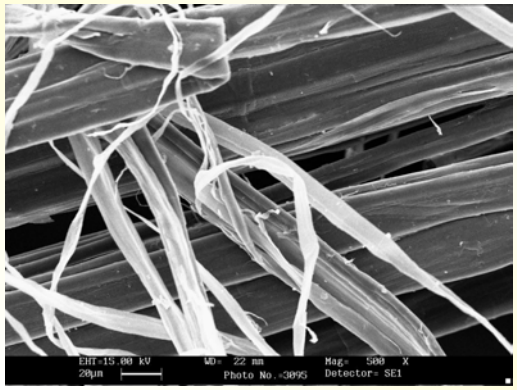
Untreated Hemp (100x)

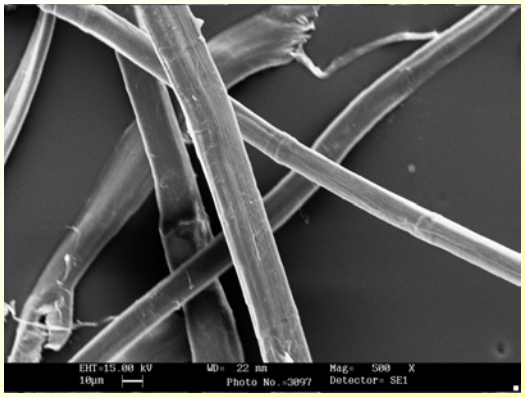




Chemically Treated Hemp (100x)

Untreated Hemp (500x)





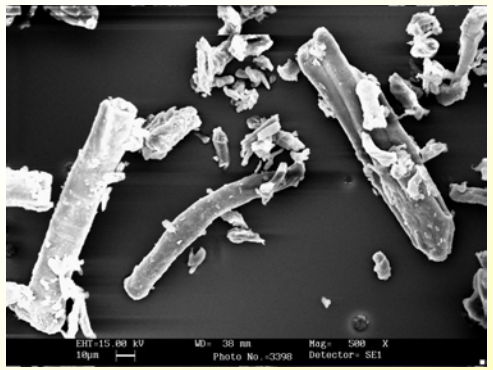
Chemically Treated Hemp (500x)

The untreated hemp is characterized by bundle of fibers bound together (around 100 µm). The chemical treatment reduces the bundle size and the surface roughness and lead to the fibre swelling .

Cryo-crushing

To further increase the separation of fibrils from cell wall, chemically treated fibers were subjected to a cryo-crushing process with liquid nitrogen in a mortar.

Chemically treated hemp + Cryo-crushing (100x)



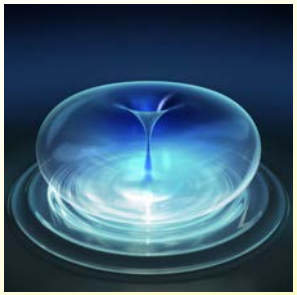
Chemically treated hemp + Cryo-crushing (500x)

Cryo-crushing causes the reduction of fibre lenght and size. Moreover, the formation of ice crystals within the fiber cell wall may cause the fibrils release when high impact are applied.

Ultrasonic treatment

Ultrasound are generated by a transducer that converts mechanical or electrical energy into high frequency acoustical energy.

Ultrasonication waves can produce a very strong oscillating power due to cavitation.

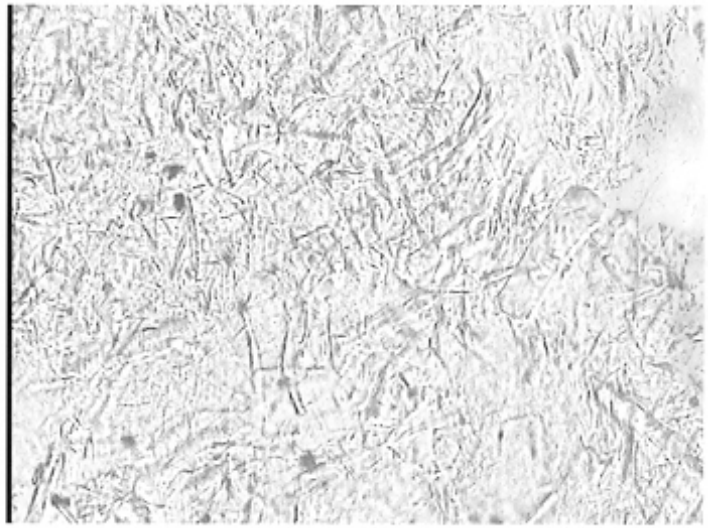


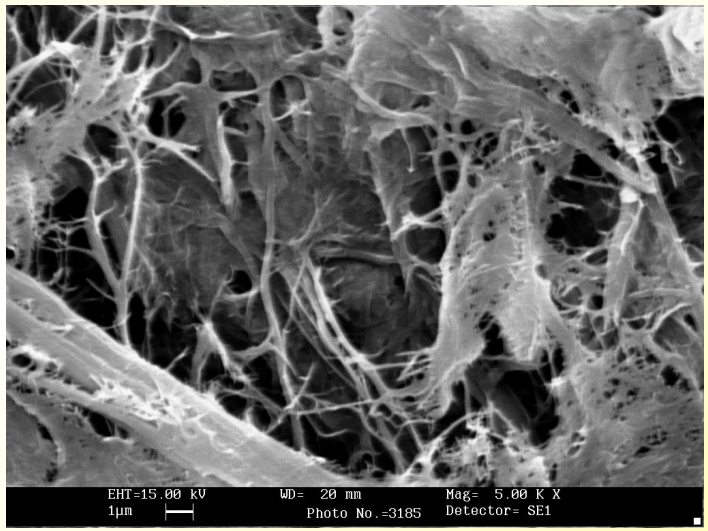
Cavitation creates millions of shock waves in the liquid, as well as elevated pressures and temperatures at the implosion sites.
Ultrasound can be used to separate micro and nanofibrils from cellulosic fibers.

Pre-treated hemp fibers were dispersed in deionized water and subjected to the ultarsonic treatment in a ice bath.

Output power: 750W
Treatment time10-30-60 minutes

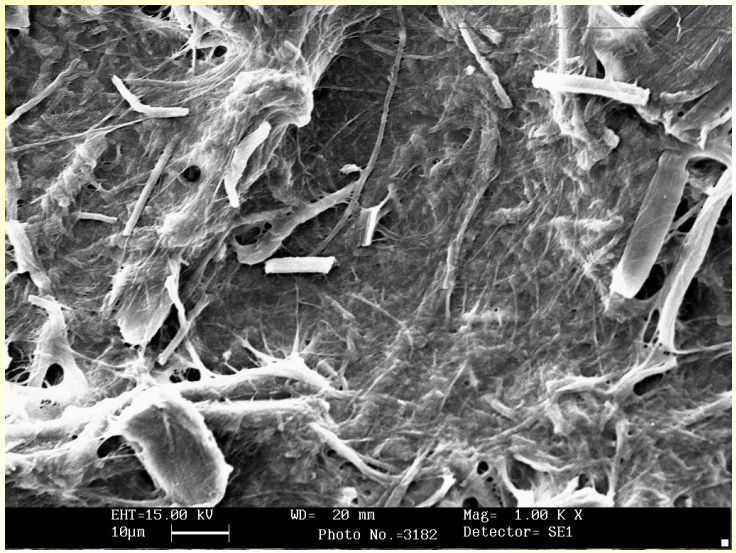
Light microscope (400x)





SEM 5000x (film by casting)

Problem to solve: hornification



Possible solutions:

- **Esterification**
- **Silanization**

This processes can allow to obtain individualized fibrils and enhance compatibility with polimer matrix

New Application

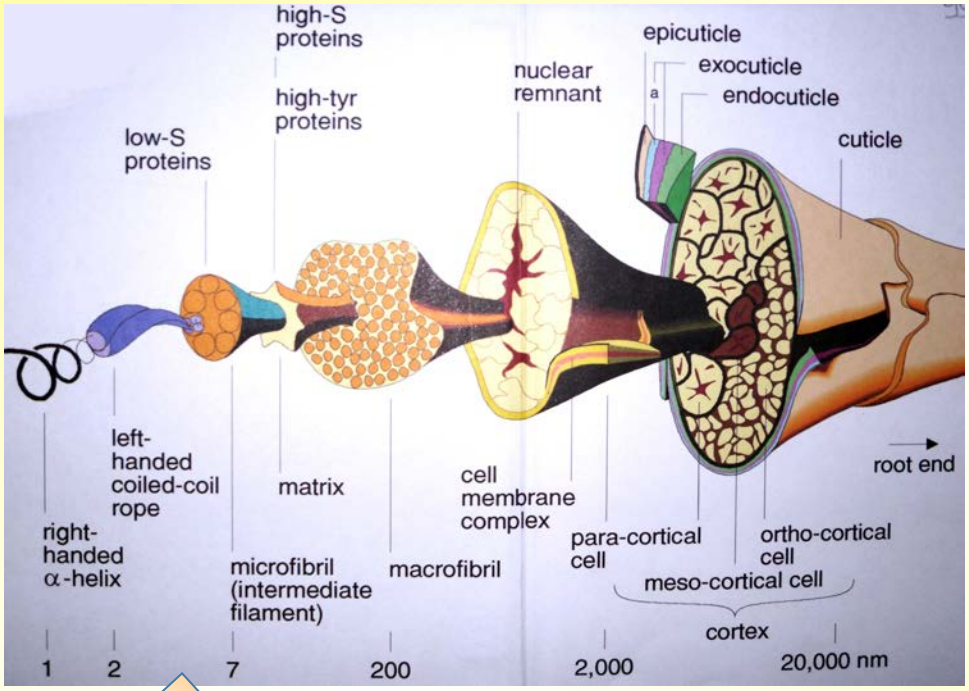
- Natural biocomposites:

  Wool Cortical cells / Hemp fibrils

The interest for the exploitation of biomasses for the development of new bio-products with high added value is growing over the years. Bio-materials prepared from the protein waste stream have been recently proposed for packaging, active filtration of air and water and biomedical applications. In particular, keratin-based wastes, made of low quality wools from stock-farming, fiber by-products from the wool textile industry, hairs, feathers, horns and nails from butchery, currently disposed in landfills have been estimated worldwide in more than 5 million tonnes per year.

WOOL

- 82% keratin proteins
- 17% non keratin proteins
- 1% lipids and polysaccharides

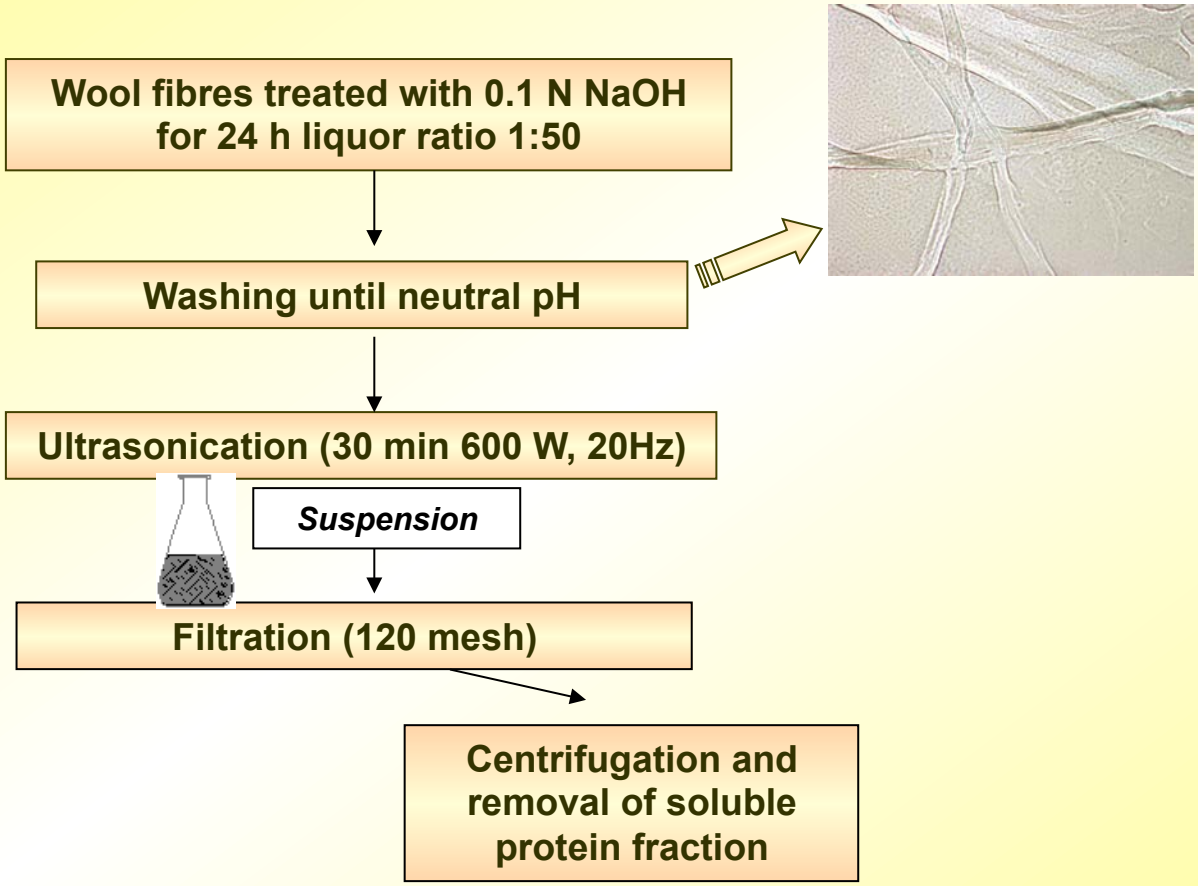


Cortical cells (fibrils)

The wool fiber is made up of three major morphological components, namely the cuticle, the cortex and the cell membrane complex.

The cortex is made up of elongated "cortical cells" oriented parallel to the fiber axis.

Cortical Cell extraction from wool



Usually the processes to produce keratin films, or other keratin based materials require the use of **toxic compounds**, for example reducing agents such as **thiols** and a **dialysis step** to remove them.

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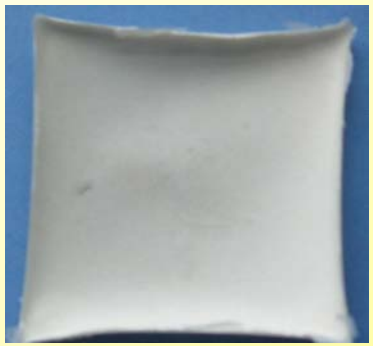
Composite Films

- **Hemp fibrils suspension and wool cortical cell suspension were concentrated by centrifugation and then both diluted with water to 0,01 g/ml.**

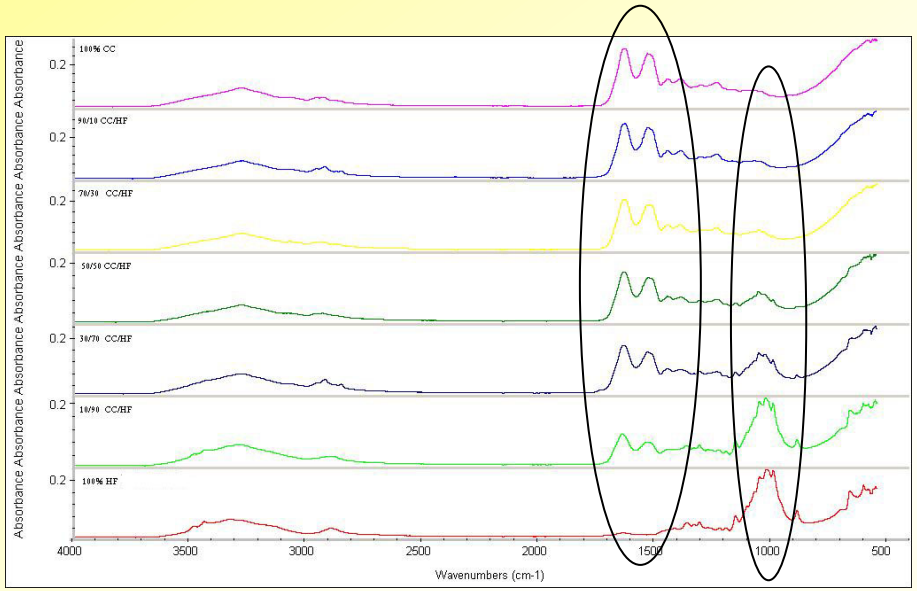
Different hemp fibrils(Hf)/cortical cell (CC) blends were prepared :

100% Hf/CC
90/10
70/30
50/50
30/70
90/10
100%

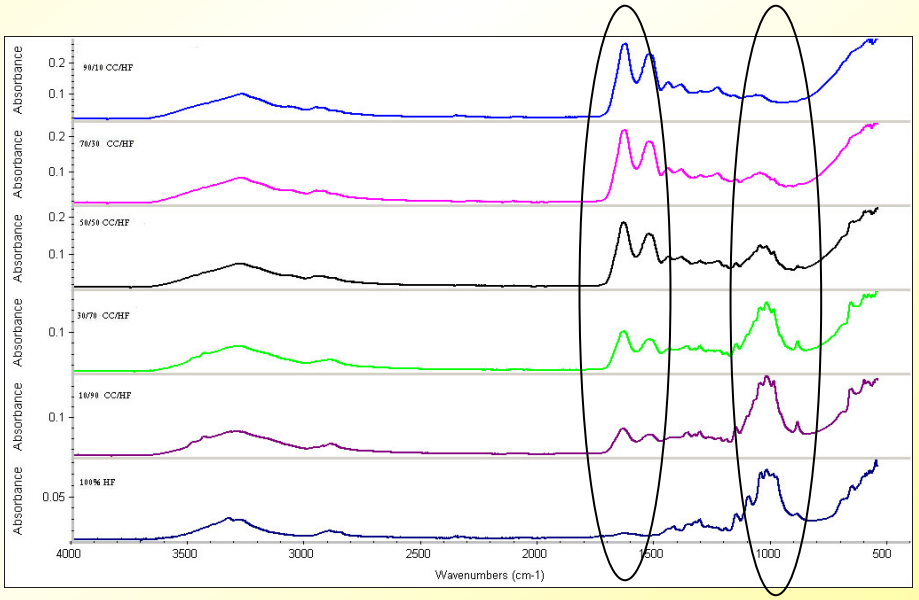


•5 ml of each blend were cast in polyester plates (20X20 mm). Water was removed in a ventilated oven at 50 °C.

IR spectroscopy



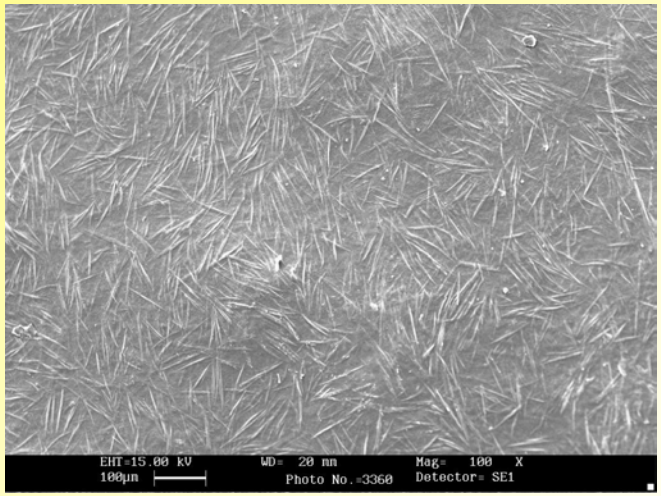
UPPER SIDE



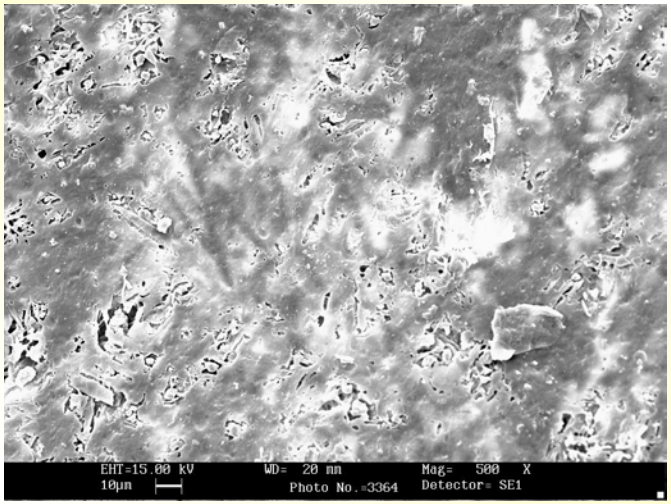
LOWER SIDE

FT-IR spectra show some typical absorptions bands of both cellulosic and wool protein material. Moreover, due to difference of density, there is a little prevalence of cellulose fibrils in the lower side of films

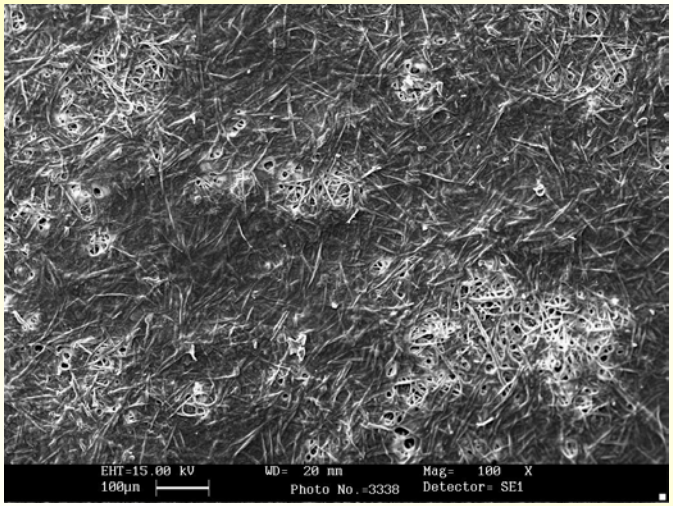
SEM



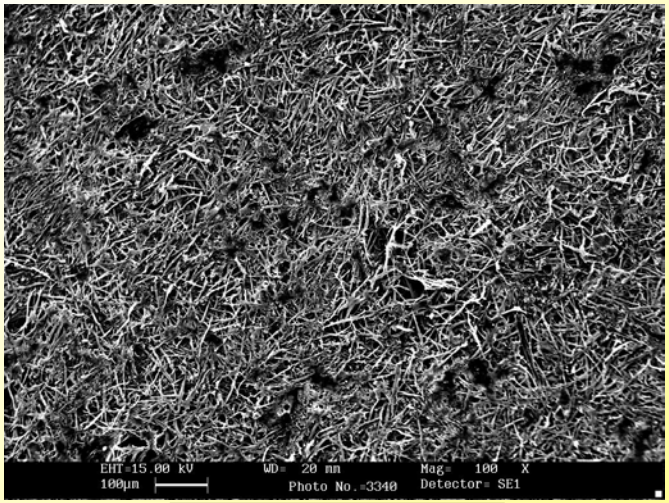
100% CC UP



100% CC DOWN

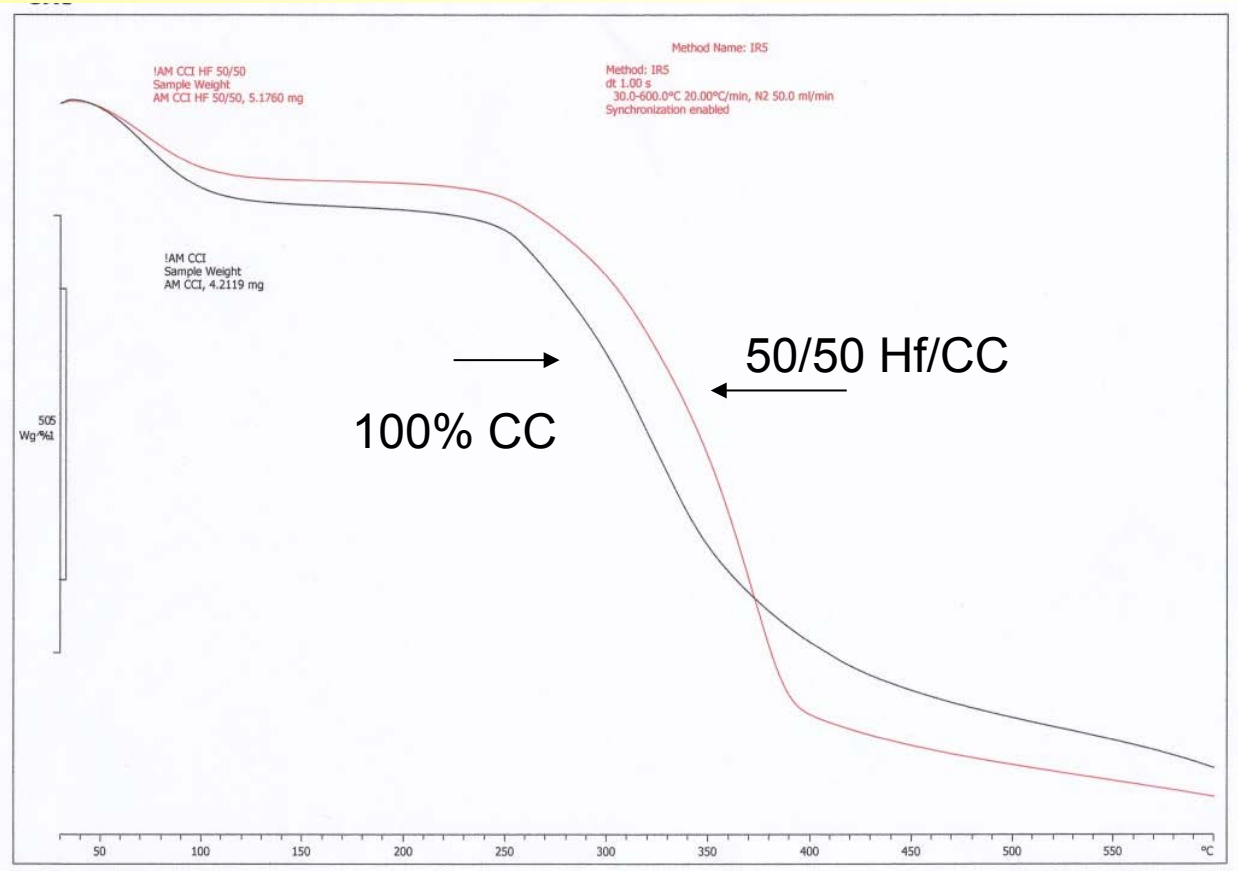


50% CC/HF UP



50% CC/HF DOWN

Thermal Behaviour



Thermal properties of the composites film were examined. The comparison between TGA curve of the 100% CC film and 50/50 Hf/CC shows the enhancement of thermal stability due to the presence of hemp fibrils

Mechanical characterization

Samples	Tensile strength (MPa)	S.D.	Elongation at break %	S.D.	Young Modulus (MPa)	S.D.
Film CC	8.27	2.15	3.02	0.54	330.36	31.64
Film CC 90+CA 10	12.78	1.70	3.11	0.42	479.95	28.58
Film CC 70+CA 30	16.51	2.43	3.11	0.42	667.94	27.36
Film CC 50+CA 50	12.63	3.30	2.34	0.65	788.47	150.44
Film CC 30+CA 70	2.58	2.52	1.18	0.47	354.85	266.41

The tensile strenght and modulus of films increase with the increase of hemp fibrils content till 50:50 Hf/CC ratio, confirming their role as reinforcing agents.

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THANK YOU
FOR YOUR ATTENTION