Green Synthesys of Si and Al nanoparticles by pulsed laser ablation in water for *Spartium junceum L.* fibres modification

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Topic is funded by project:

Design of Advanced Biocomposites from Sustainable Energy Sources

Project's aim is to:

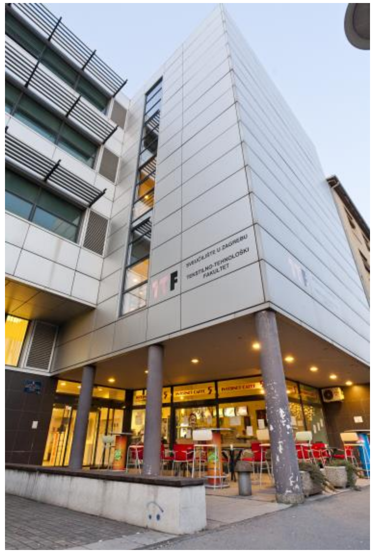
design and manufacture advanced biocomposite materials with improved properties for a wide range of applications

complete utilization of lignocellulosic biomass through biofuel production based on development and application of new technological solutions.

transfer innovations and developed technologies to the scientific and business society while respecting the principles of green chemistry & the circular economy.

Partners & Associates

1. Project coordinator:
University of Zagreb
Faculty of Textile Technology
Prof. Sandra Bischof, PhD



2. Project partner: University of Zagreb Faculty of Agriculture, Prof. Tajana Kricka, PhD

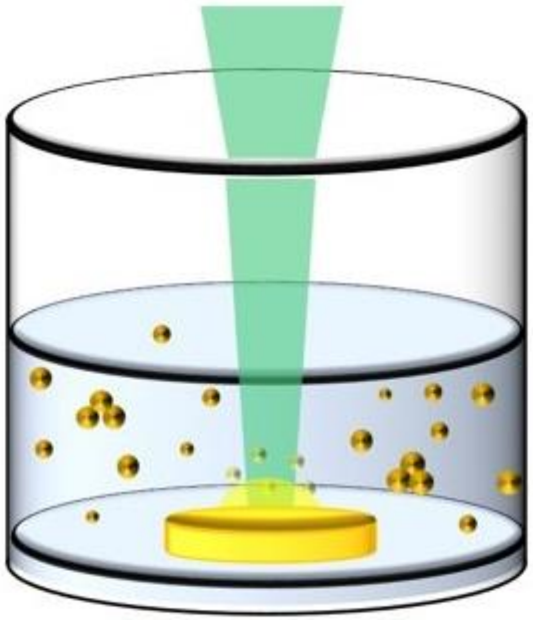
Project associates:

Institute of Physics
Nikša Krstulović, PhD

Institute Ruđer Bošković
Division of Physical Chemistry,
Laboratory for Biocolloids and Surface Chemistry
Maja Dutour Sikirić, PhD

Institute Ruđer Bošković
Division of Materials Chemistry,
Laboratory for Synthesis of new Materials
Tatjana Antonić Jelić, PhD

Green Synthesis of NPs: Advantages

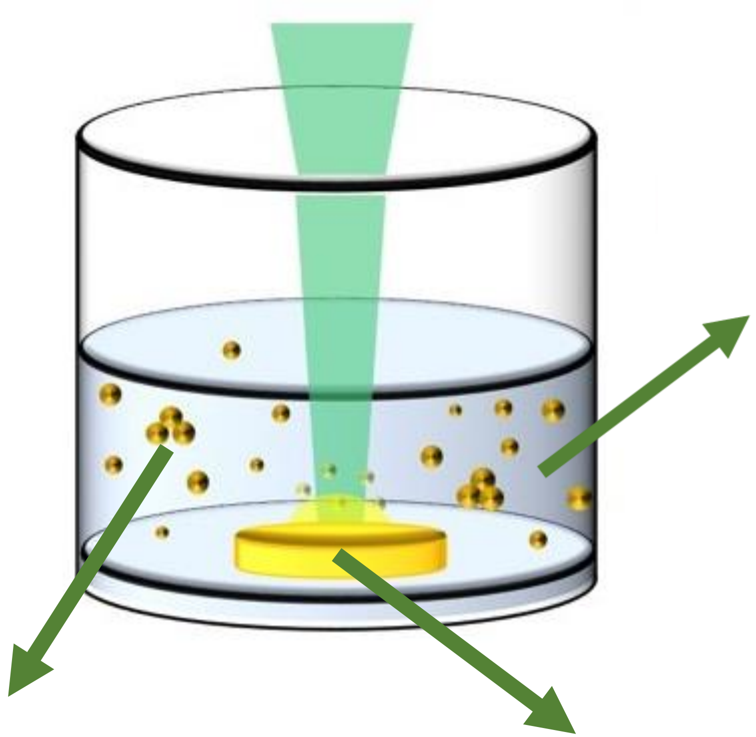


Laser synthesis of NPs in liquids is a versatile top-down technique for the production of colloidal nanoparticles

No by-products or residues of chemical reactions.

Further purification is not required

Green Synthesis of NPs



- Targets were irradiated by Nd:YAG laser (Quantell, Brilliant, Les Ulis, France)
- Operating wavelength: 1064 nm
- 5 Hz repetition rate
- Pulse durations of 5 ns for Al and 10 ns for Si target for 320 and 100 mJ of output energy
- The laser beam was focused by a 10 cm lens onto the target surface.

Green feedstock: Biomass

Our goals → **European bioeconomy** → **Sustainability & circularity**

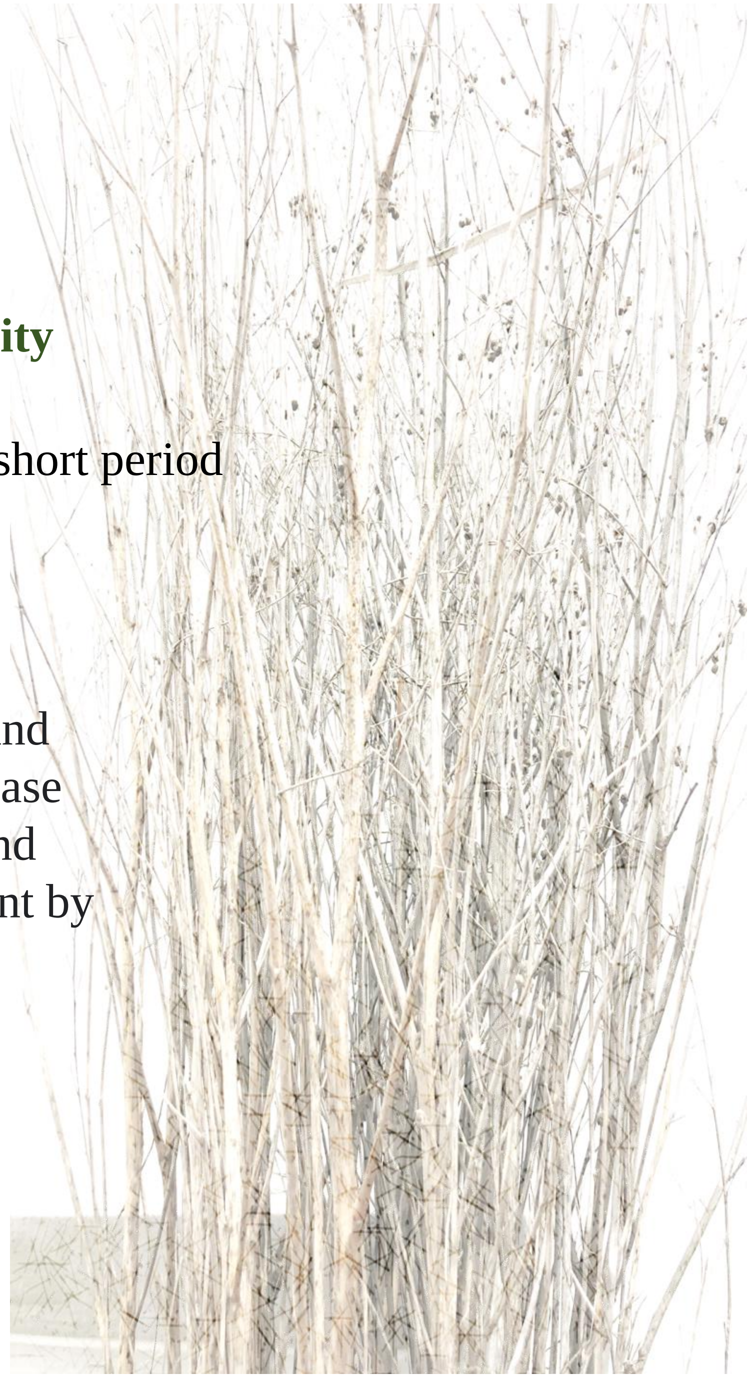
Biomass includes biodegradable parts products, waste or residues from agriculture, forest waste and waste from related industries as well biodegradable parts of industrial and municipal waste.
(Directive 2009/28/EZ)

- Sustainable within the short period
- Widely available
- CO_2 neutral

It can improve resource and waste management, increase agricultural production and enhance rural development by creating jobs and income

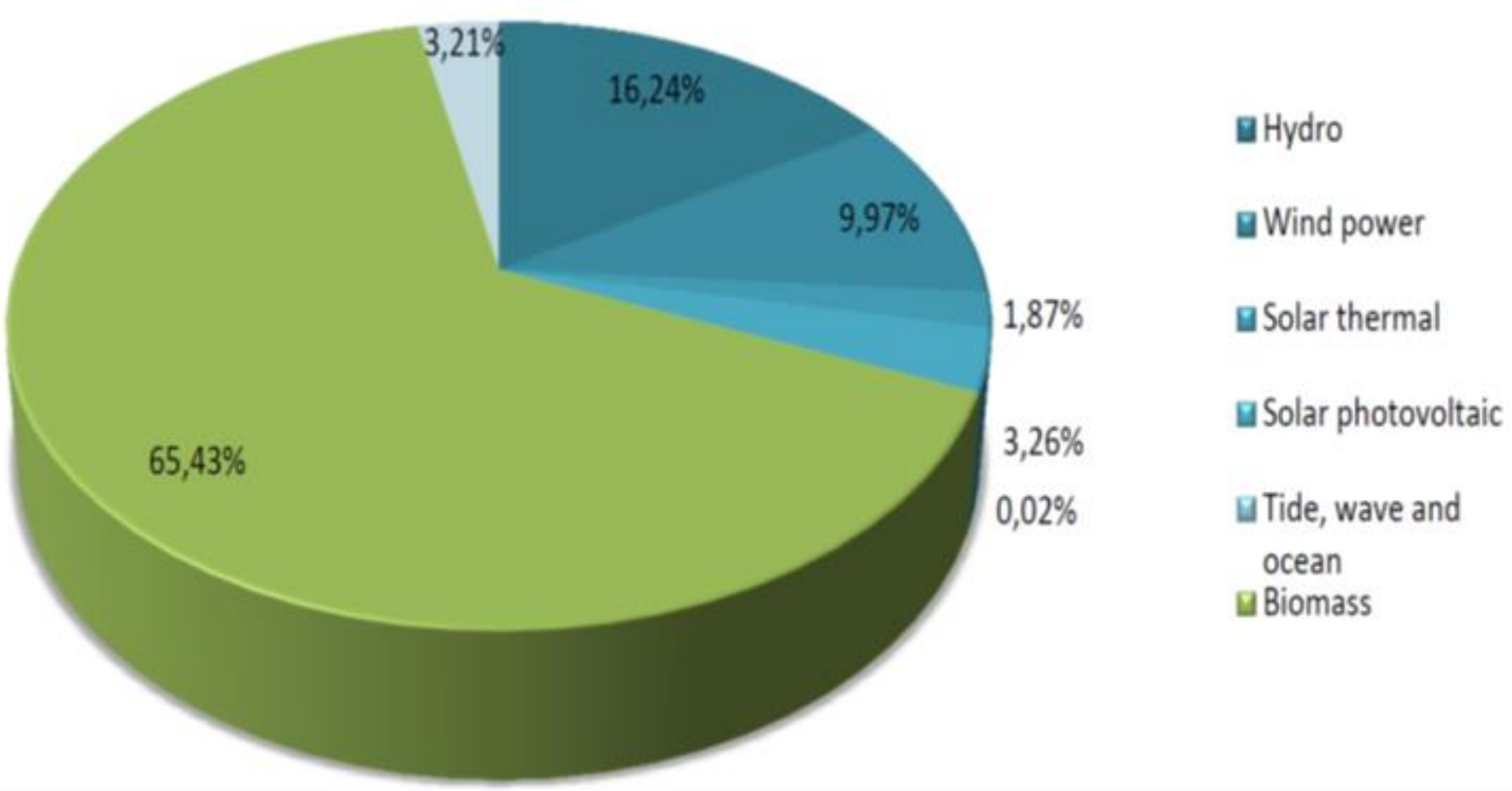
Composition:

cellulose	hemicellulose	lignin	other
38-50%	23-32%	15-25%	5-13%



Energy consumption in EU

- Biomass, a renewable energy source:
- biological material derived from living, or recently living organisms (wood and herbaceous materials)



Spartium junceum L. plant

Natural fibres → Bast fibres → flax, hemp, kenaf, ramie, jute, ***Spartium junceum* L.,** etc.

One of the most widespread plant species of the Mediterranean karst.

Throughout history it had wide range of applications:

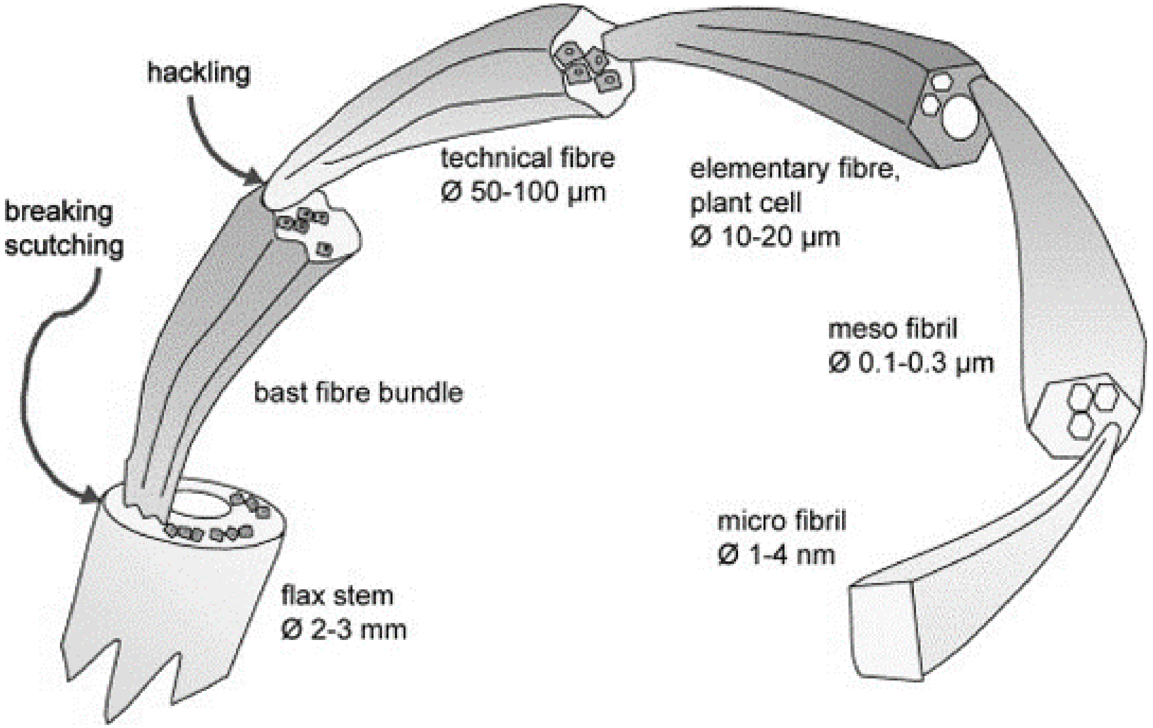
Perfume and dyes from the **flowers**

Baskets from the **stems**

Textile materials from the **fibres**

- Sustainable within the short period
- Widely available
- CO_2 neutral

Architecture of bast fibres: From stem to the fibrils



	Spanish broom	Virginia mallow	Flax	Hemp
Cellulose (%)	43	45	71	72
Hemicellulose (%)	19	27	19	19
Lignin (%)	30	25	3	5

Harvesting and fibre production in ancient time

The process begins by cleaning Spanish broom branches and tying them together in bundles.

People did this individually in front of their houses.

In the next phase stems are processed mechanically. They are rubbed against rough stone and rinsed in the sea. In this way the fibers are separated from the outer bark and inner portion of the stem is softened.

Spartium stems after rubbing process and isolated fibres.

Harvesting and fibre production nowadays

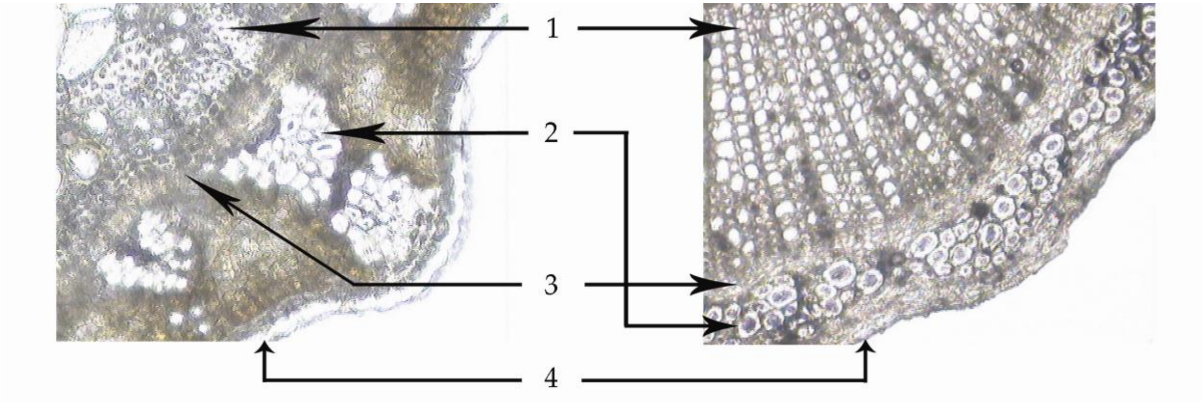
After microwave treatment fibre yield is approx. 15%

85% of residue revealed increase in lignin content

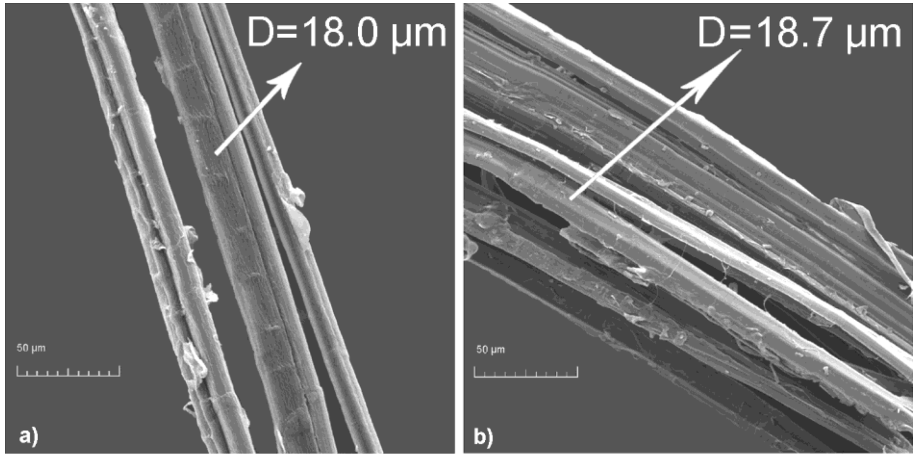
↓

Raw material for biofuel production

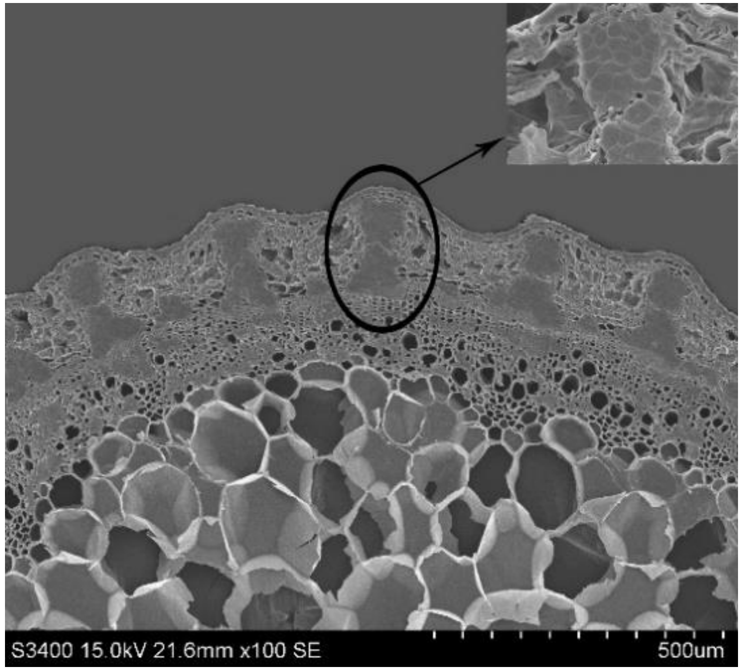
Comparison of flax and Spanish broom

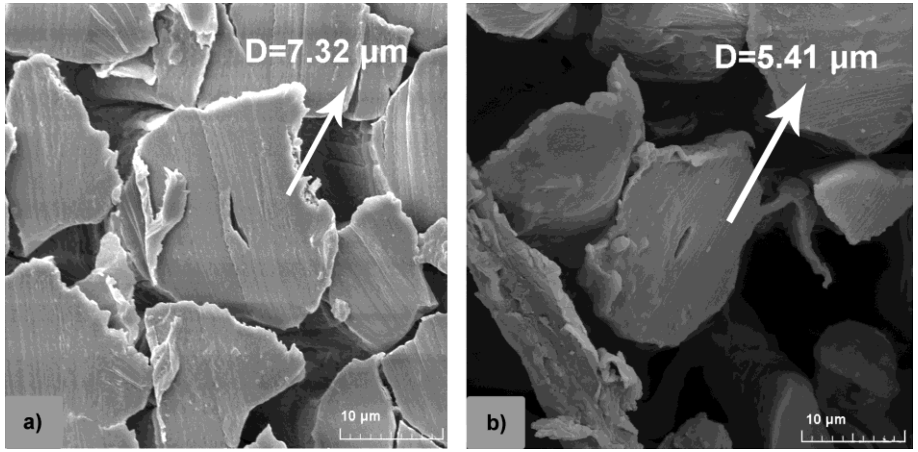


Cross section of Spanish broom (left) and flax (right) plant:
1- xylem, 2- sclerenchyma (bast fibers), 3- phloem, 4- epidermis.



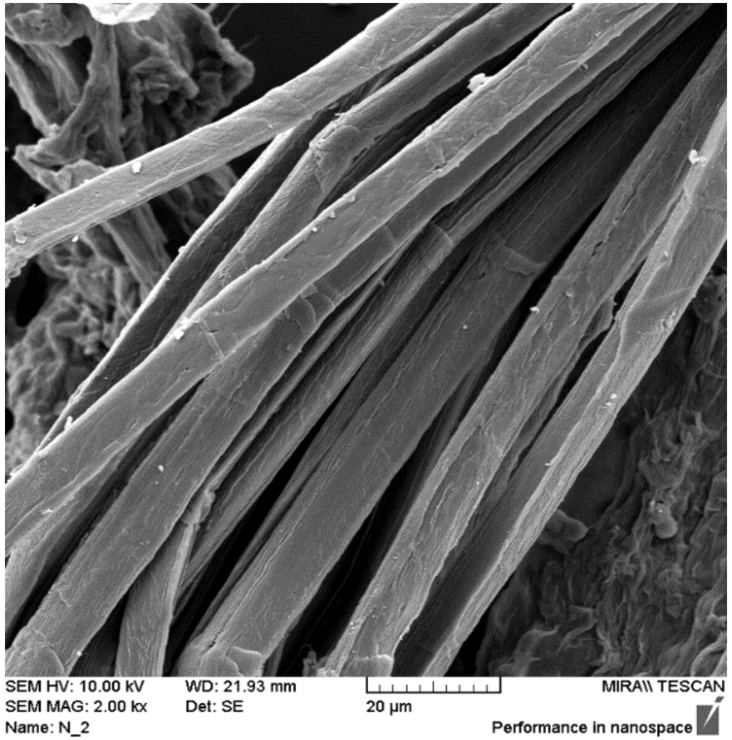
Longitudinal SEM image of (a) Spanish broom, (b) flax - elementary fibre as part of technical fibre.





Cross section SEM image of (a) Spanish broom, (b) flax - elementary fibre.

Natural fibre drawbacks



- Higher flammability
- Nonuniformity in dimensions and mechanical properties
- Higher moisture absorption

MODIFICATION AGENTS →

alkali

nanoparticle

peroxide

silane

isocyanate

acetyl

coupling agents

benzoyl

Most frequent nano agent

MONTMORILLONITE (MMT) for hydrophobic/pyrophobic treatments on textiles

<u>Previous research:</u> Modified MMT was used in doctoral thesis:

Kovačević, Z.: Development of advanced polylactide nanobiocomposite reinforced with Spartium junceum L. fibres, University of Zagreb Faculty of Textile Technology, Zagreb, (2019)

<u>Current research:</u> NPs with targeted purpose was synthesized since it was concluded in our previous research that Al and Si elements show satisfactory results

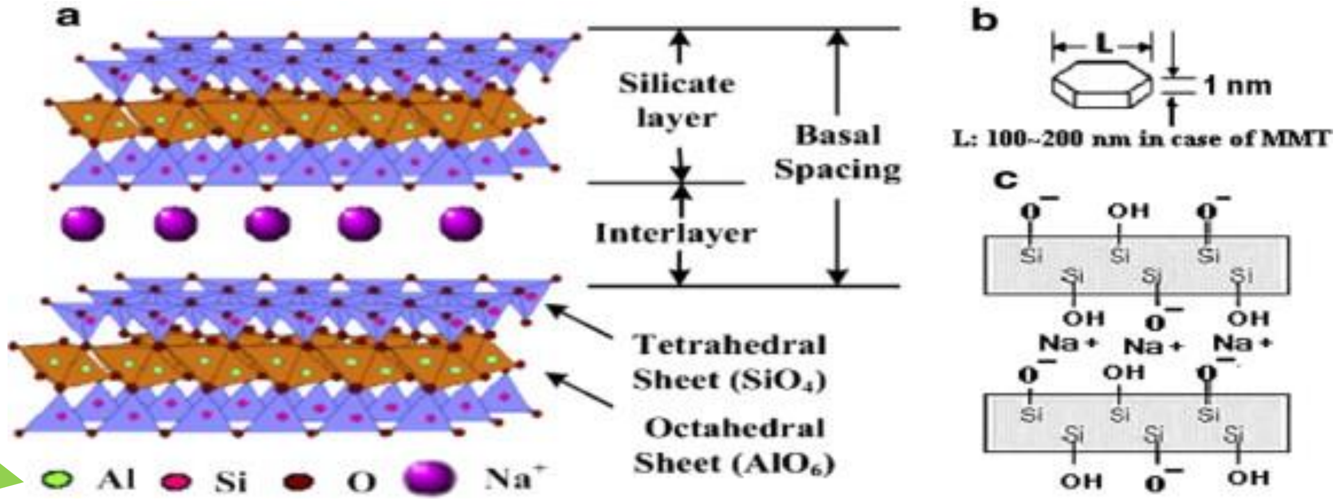
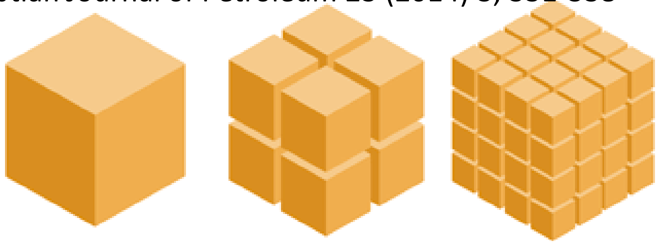


Figure 1. (a) Molecular structure of MMT containing exchangeable sodium ion (MMT-Na+), (b) high aspect ratio clay platelet, and (c) schematic representation of side view between layers

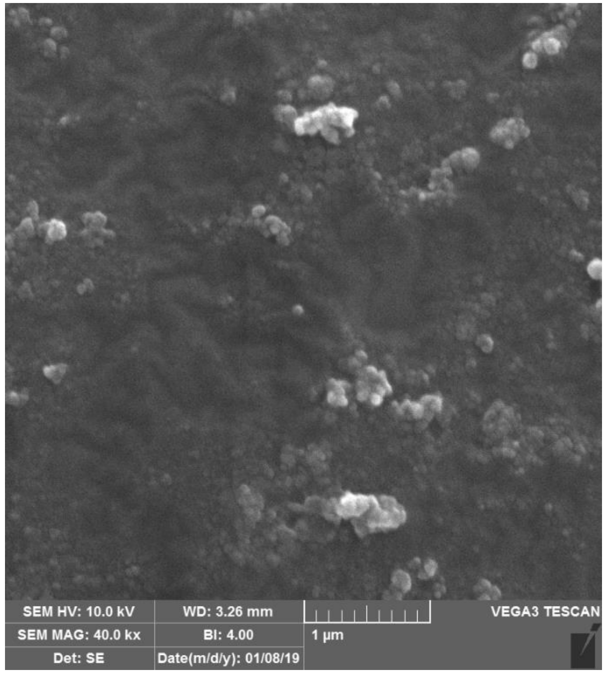
A.M. Motawie et al.: Physico-chemical characteristics of nano-organo bentonite prepared using different organo-modifiers, Egyptian Journal of Petroleum 23 (2014) 3, 331-338



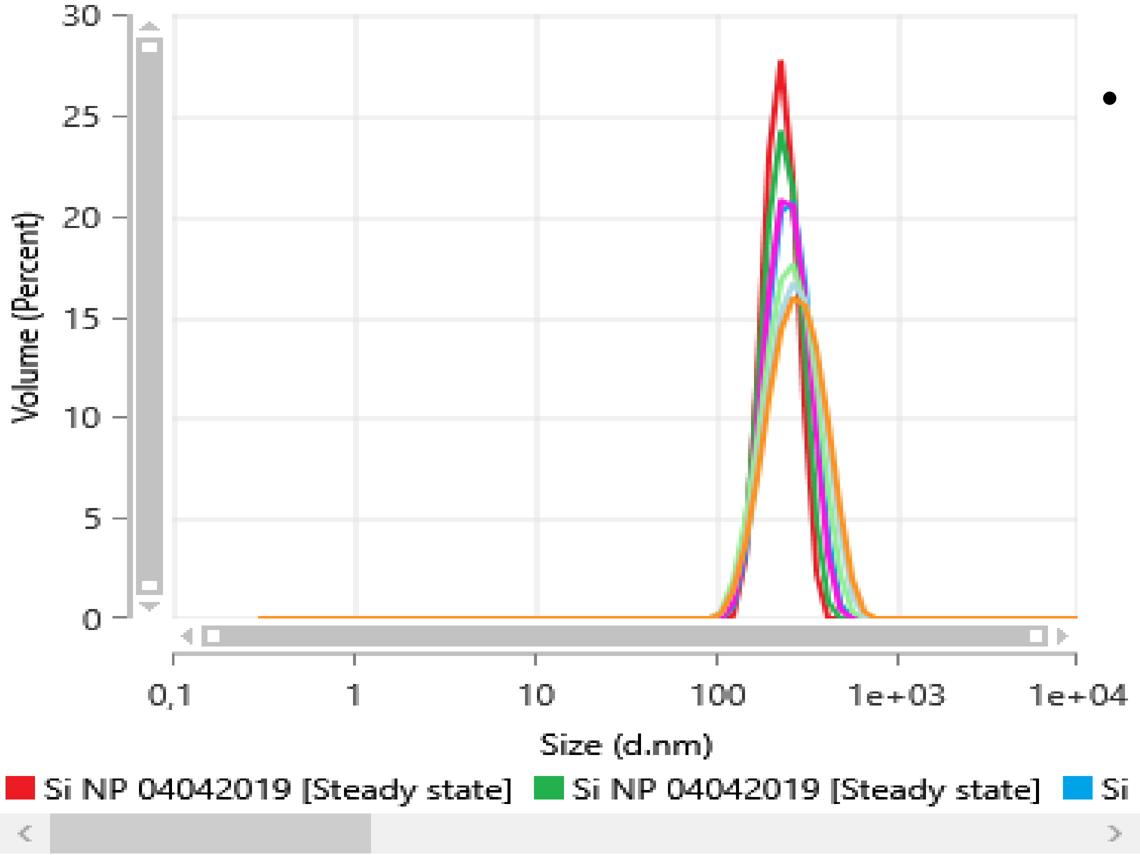
Edge length	4	2	1
Total surface area	96	192	384
Total volume	64	64	64
Surface-to-volume ratio	1.5	3	6

Baglioni P., Chelazzi D., Giorgi R. (2015) Innovative Nanomaterials: Principles, Availability and Scopes. In: Nanotechnologies in the Conservation of Cultural Heritage. Springer, Dordrecht

Si nanoparticles synthesized by laser ablation

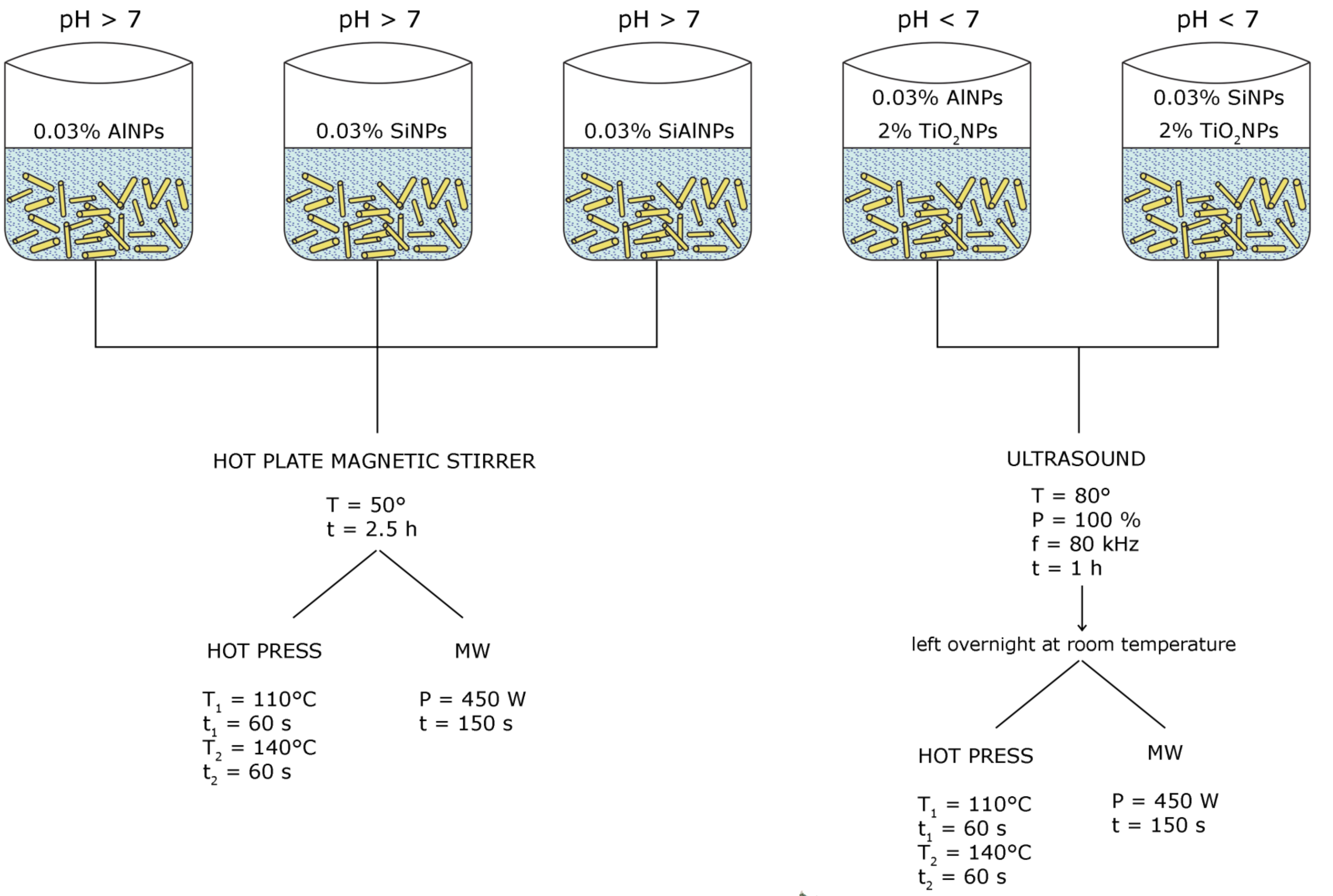


SEM micrograph of Si NPs

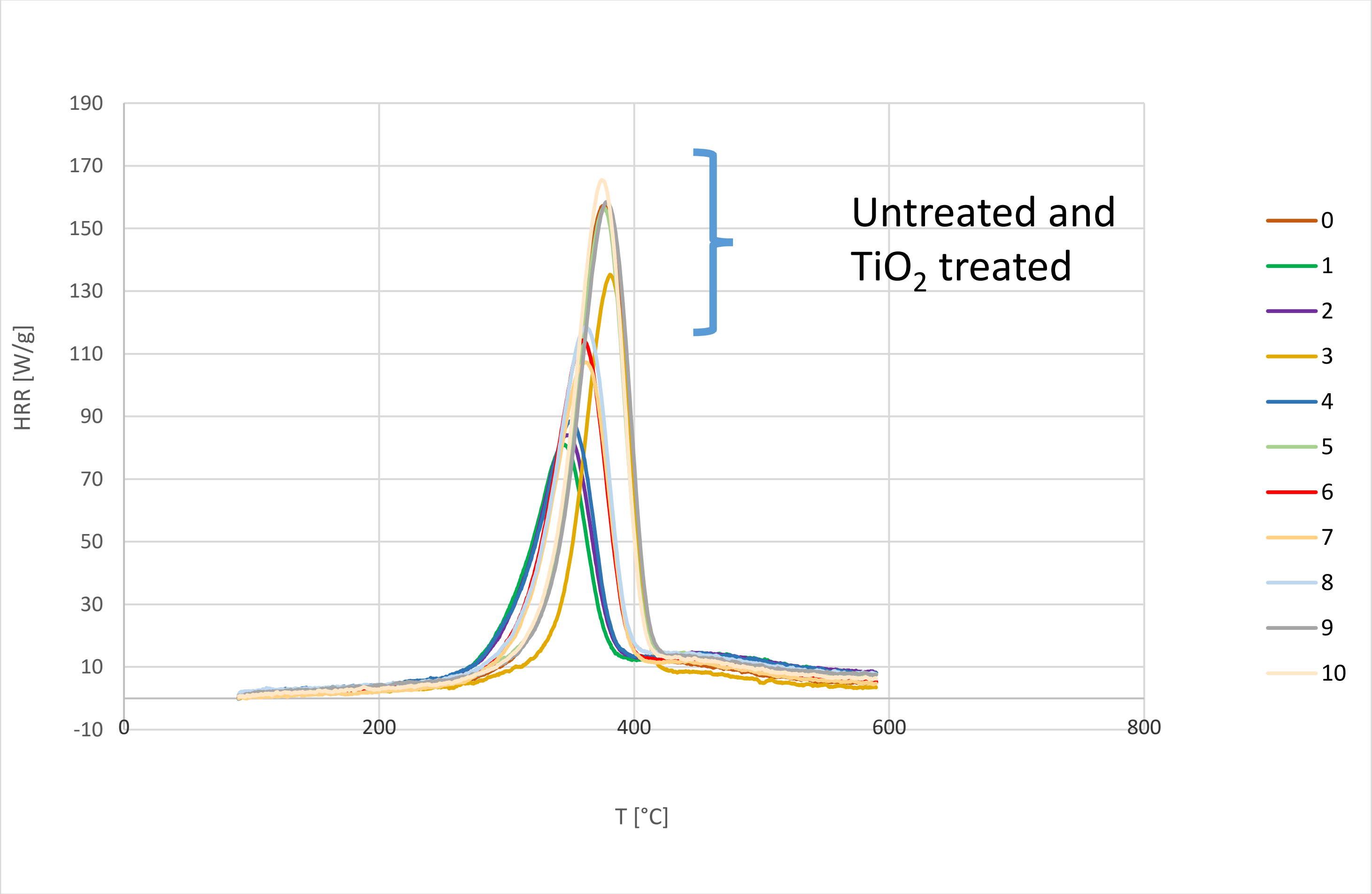


- The targets were irradiated by Nd:YAG laser (Quantell, Brilliant, Les Ulis, France) operating at wavelength of 1064 nm, 5 Hz of repetition rate and pulse durations of 10 ns for Si target and 100 mJ of output energy.

Spanish broom fibres + NPs

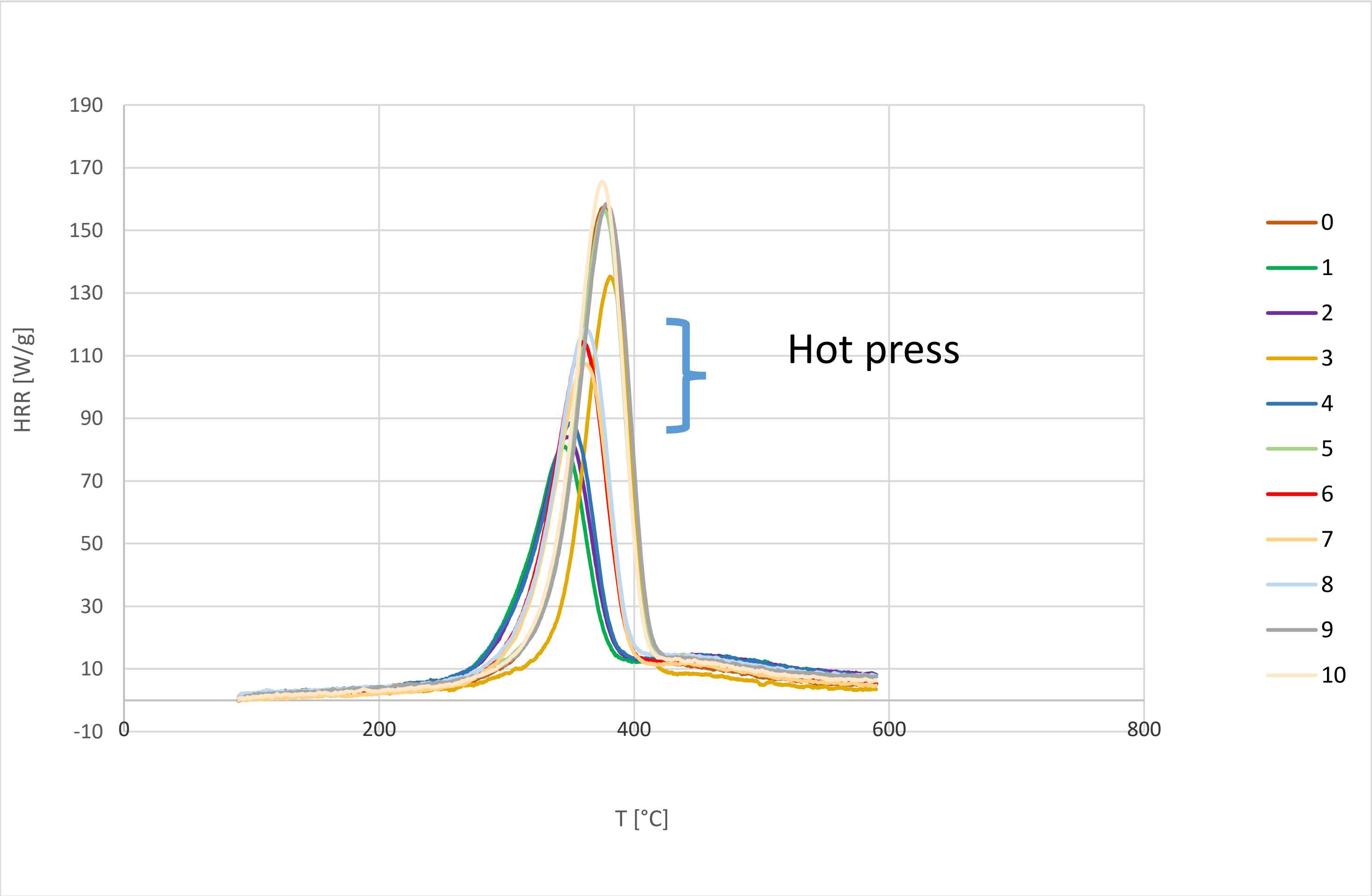


MICROSCALE COMBUSTION CALORIMETRY – TiO_2



- 0 – Untreated fiber
- 1 – Fiber treated with SiNPs + MW
- 2 – Fiber treated with AlNPs + MW
- 3 – Fiber treated with AlNPs + TiO2 + MW
- 4 – Fiber treated with SiAlNPs + MW
- 5 – Fiber treated with SiNPs + TiO2 + MW
- 6 – Fiber treated with SiNPs + hot press
- 7 – Fiber treated with SiAlNPs + hot press
- 8 – Fiber treated with AlNPs + hot press
- 9 - Fiber treated with SiNPs + TiO2 + hot press
- 10 - Fiber treated with AlNPs + TiO2 + hot press

MICROSCALE COMBUSTION CALORIMETRY – Hot press



- 0 – Untreated fiber
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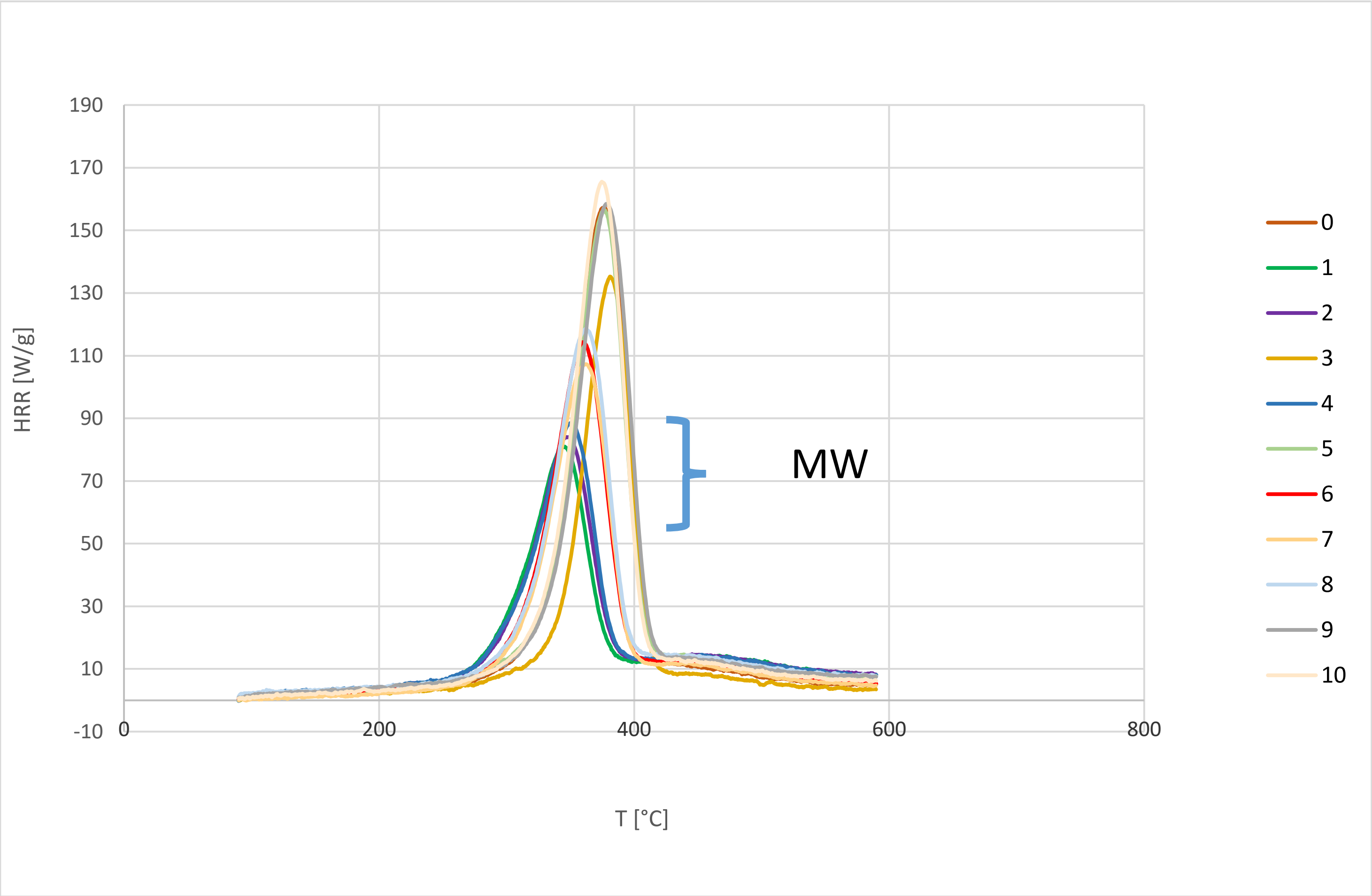
- 8 – Fiber treated with AlNPs + hot press
- 9 - Fiber treated with SiNPs + TiO_2 + hot press
- 10 - Fiber treated with AlNPs + TiO_2 + hot press

MICROSCALE COMBUSTION CALORIMETRY - MW



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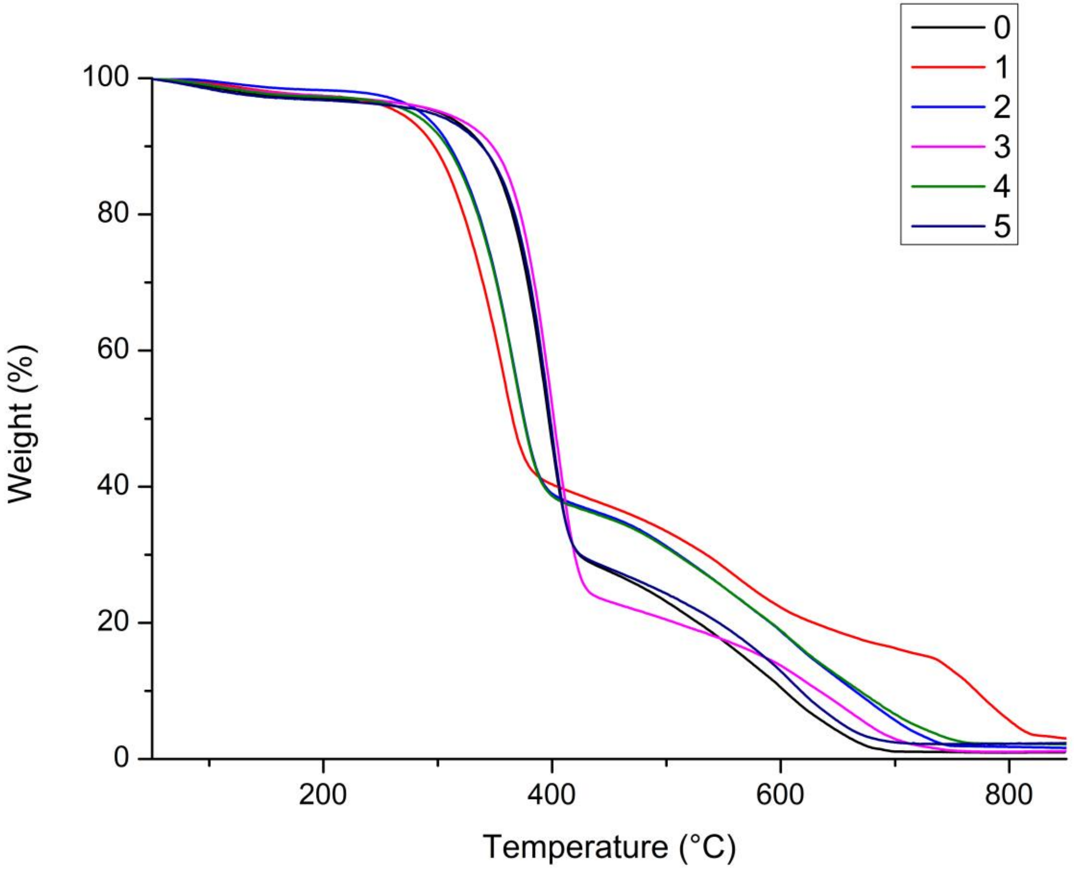
THERMOGRAVIMETRIC ANALYSIS



0 – Untreated fiber

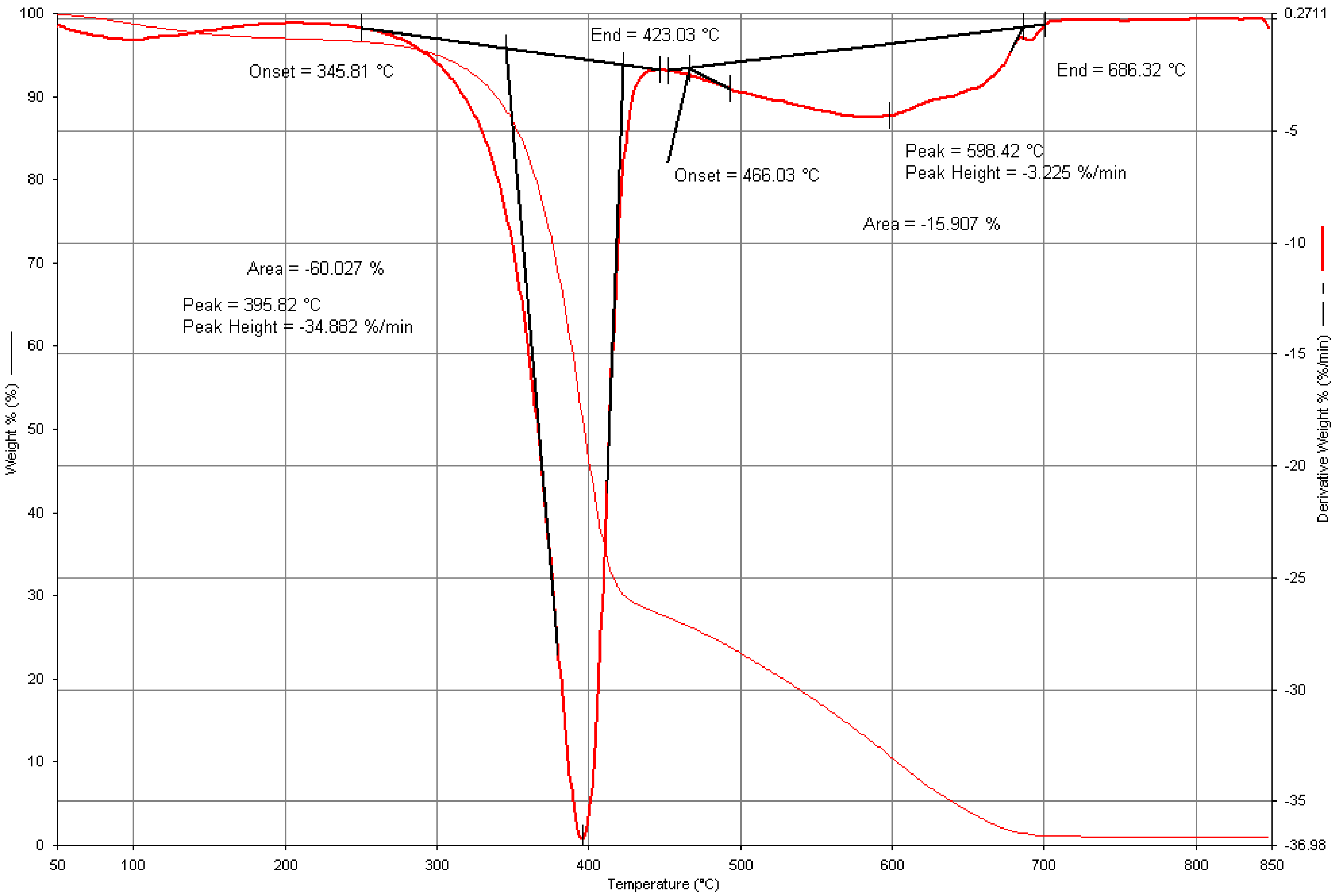
1 – Fiber treated with SiNPs + MW

2 – Fiber treated with AlNPs + MW

3 – Fiber treated with AlNPs + TiO2 + MW

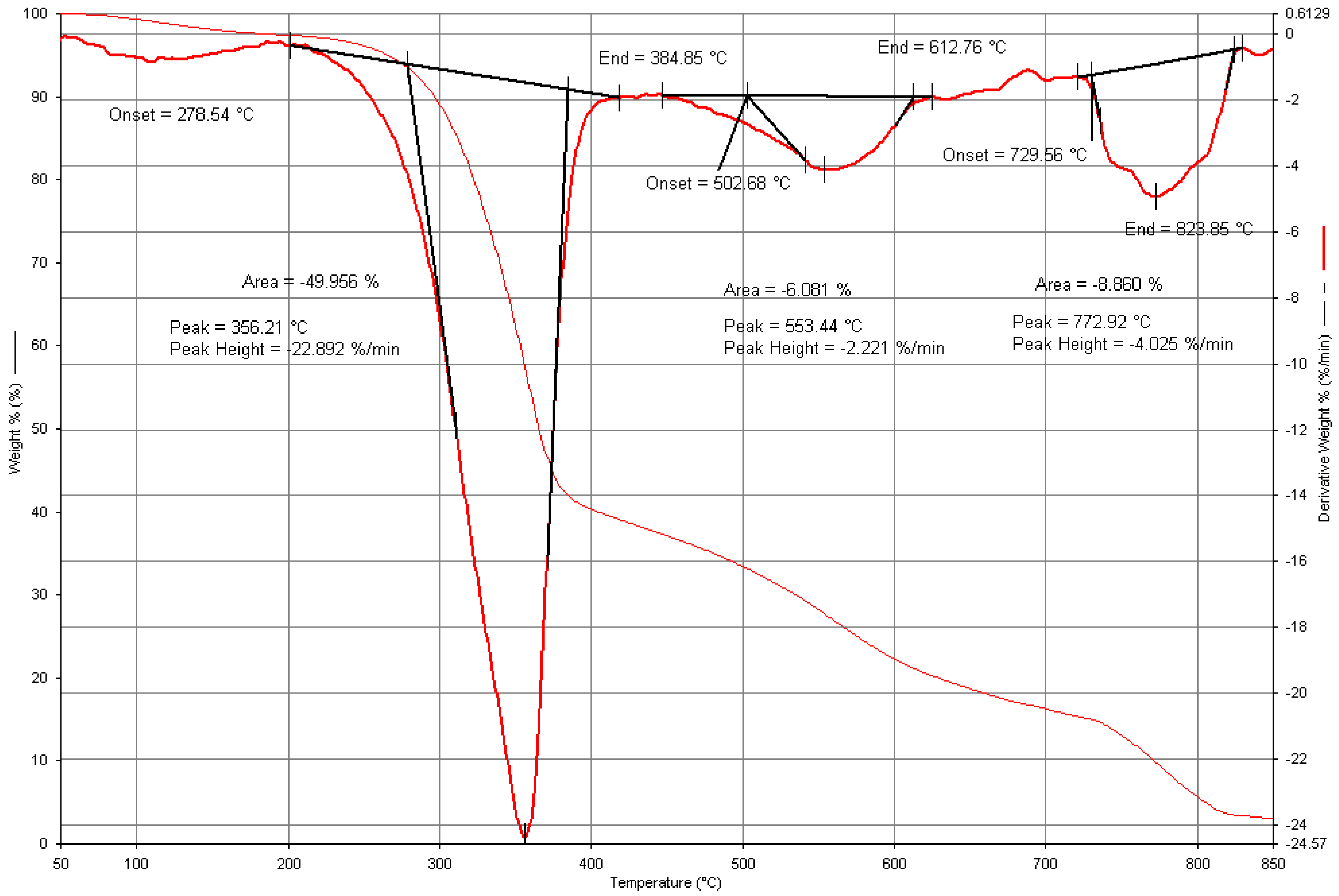
4 – Fiber treated with SiAlNPs + MW

5 – Fiber treated with SiNPs + TiO2 + MW

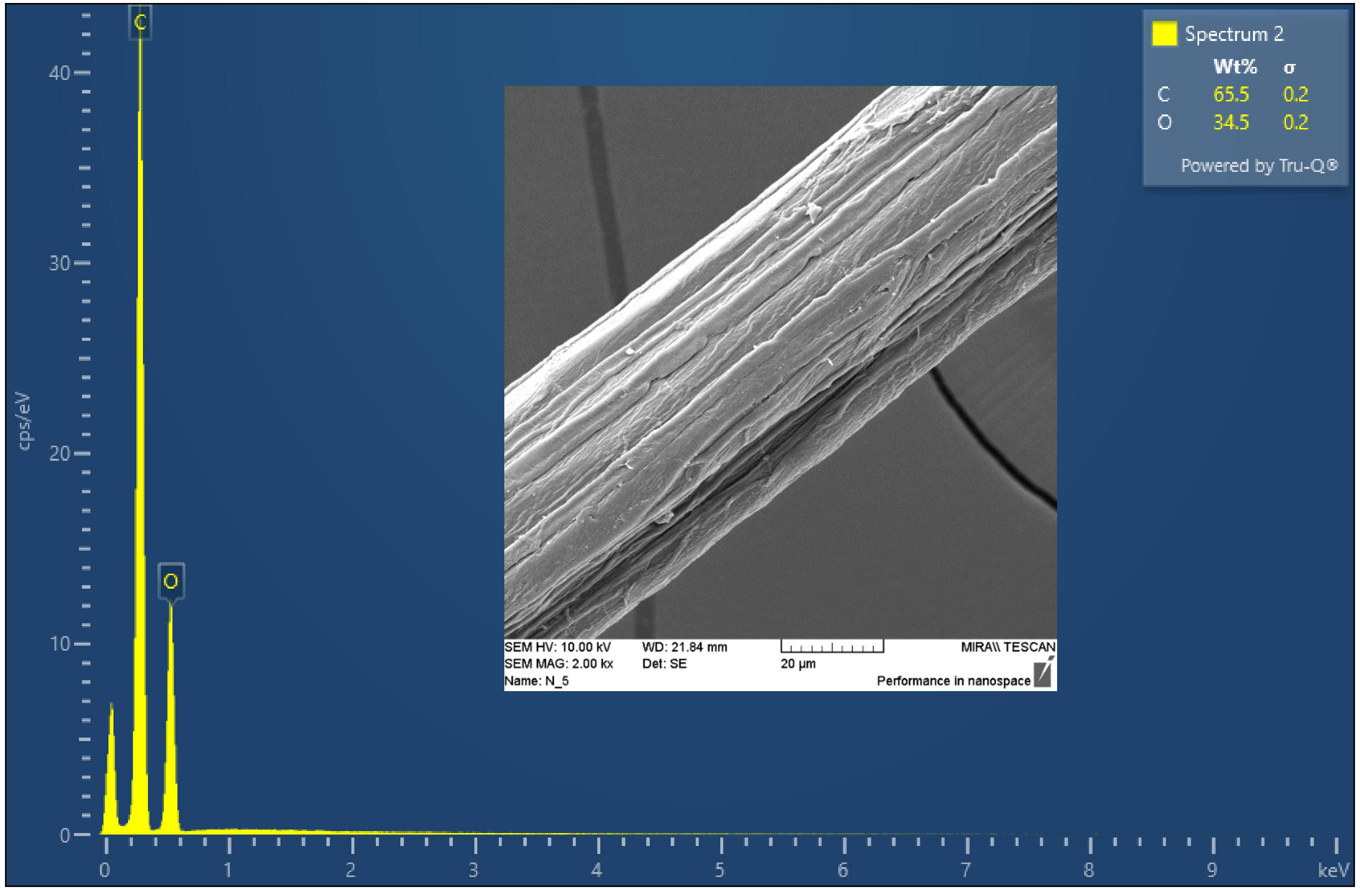


Sample 0
Untreated fiber

Sample 1
Fiber treated with SiNPs + MW

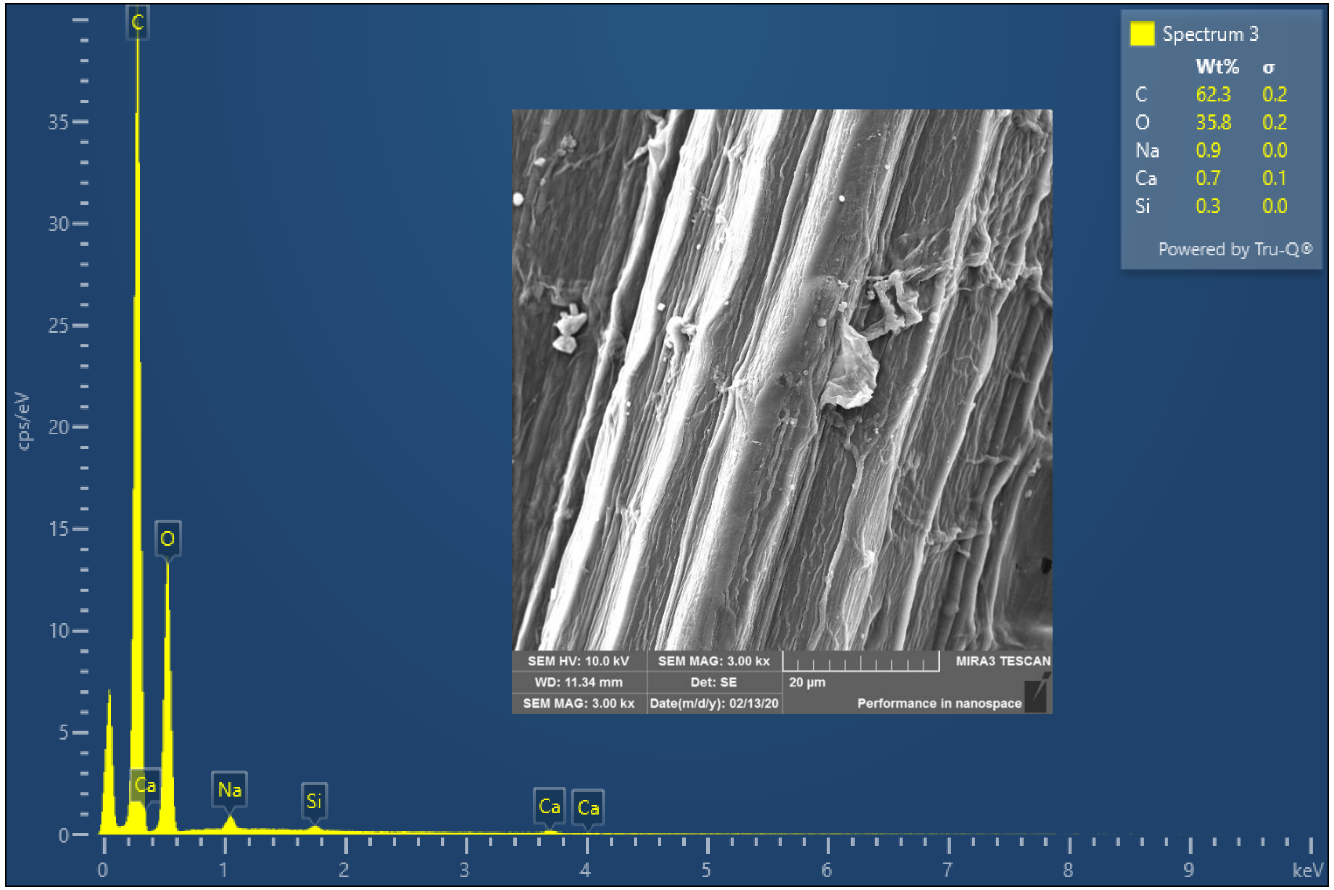


SCANNING ELECTRON MICROSCOPY



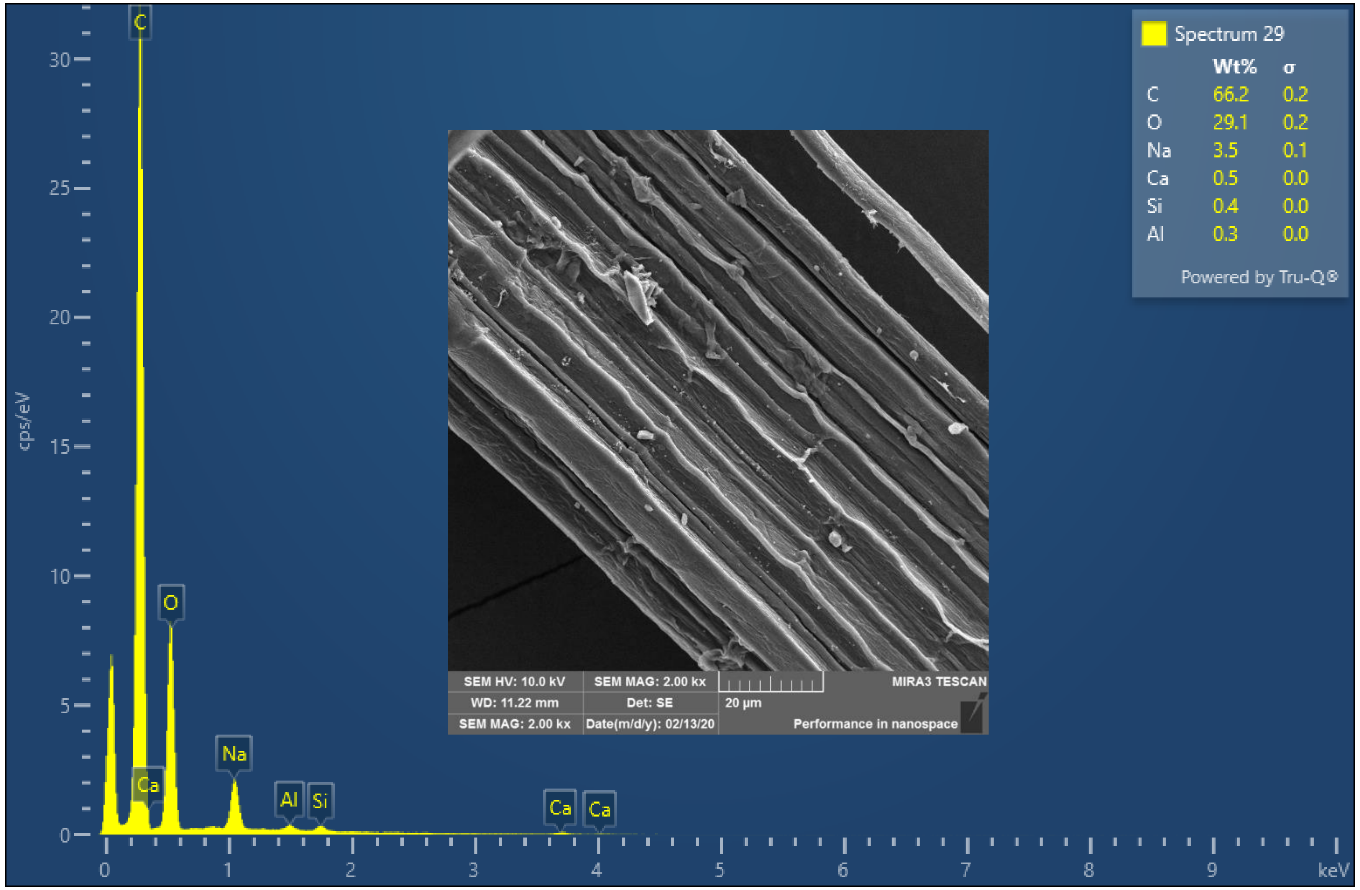
0 – Untreated fiber

SCANNING ELECTRON MICROSCOPY



1 – Fiber treated with SiNPs + MW

SCANNING ELECTRON MICROSCOPY



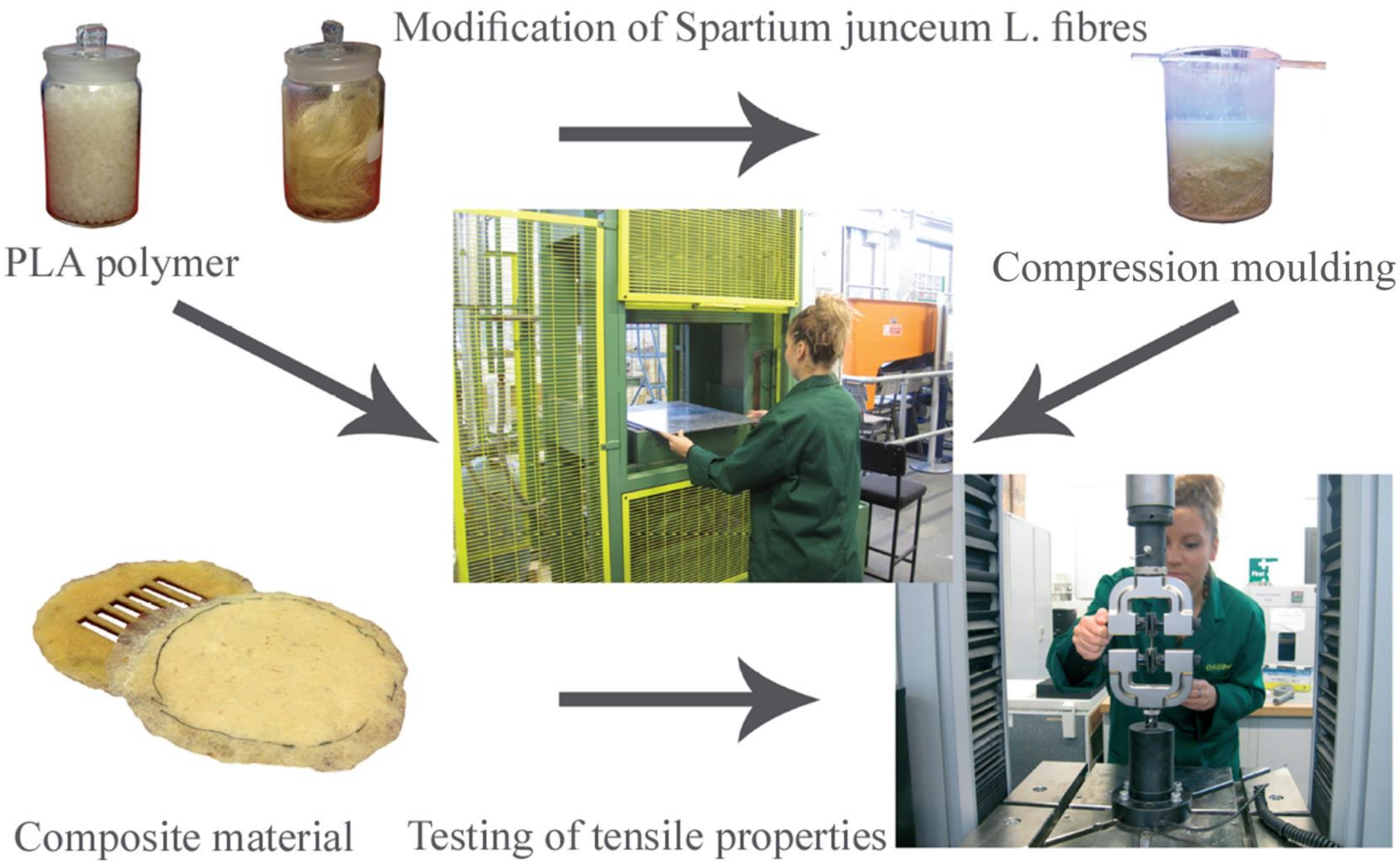
4 – Fiber treated with SiAlNPs + MW

POSSIBLE APPLICATION

of fibres functionalized with NPs for composites for automotive industry

Incompatibility with hydrophobic polymers

Lack of FR properties



POSSIBLE APPLICATIONS

FR functionalization for wide purposes




DIRECTIVE 2000/53/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

Biodegradable matrix + Natural reinforcement → Green composite

(b) no later than 1 January 2015, for all end-of life vehicles, the reuse and recovery shall be increased to a minimum of 95 % by an average weight per vehicle and year. Within the same time limit, the re-use and recycling shall be increased to a minimum of 85 % by an average weight per vehicle and year.

- European car makers are already testing natural products because of the increasing pressure of European Commision criteria to meet requirement that:

  70 % of car parts are made from recyclable material.

1. Underfloor protection trim
2. Instrumental panel
3. Door panels
4. Seat backs
5. Rear deck trays
6. Pillars
7. Headliners
8. Bumpers
9. Engine shield
10. Trunk trim

http://www.quattroworld.com/wpcontent/uploads/2011/02/A6110007_medium2.jpg

CONCLUSIONS

NPs ablated from Si target and incorporated into natural fibers of Spartium Junceum using microwave (MW) energy shows less aglomeration, compared with results obtained by heated¸contact press

Usage of NPs influenced improvement of FR properties of natural fibers

Textile reinforced composites are being increasingly employed in vehicles because of their low weight and low cost, so the increase of their consumption is in line with the increased sustainability demand.

Achieving decoupling between economy and environment is the key issue for implementing green economic development and ultimate achievement of industry's sustainable development.

THANK YOU!!!!

Acknowledgement

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Design of Advanced Biocomposites from Renewable Energy Sources (BIOCOMPOSITES)
https://biokompoziti.eu/

BIOCOMPOSITES

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