Doctoral School of Materials Sciences and Technologies
Óbuda University
HUN-REN Centre for Energy Research

Report of Second Semester

Hydroxyapatite-based natural biopolymer composite for biomedical applications

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Student: Wasan Abdullah Fadhil Alkaron
Neptun code: J4UCRU
Supervisor: Dr. Csaba Balázsi and Dr. Katalin Balázsi

Content

Introduction

Hydroxyapatite

is classified as a highly bioactive and biocompatible inorganic calcium phosphate material naturally occurring in human bone and teeth compounds. Therefore, it is widely used in tissue engineering and bone replacement.

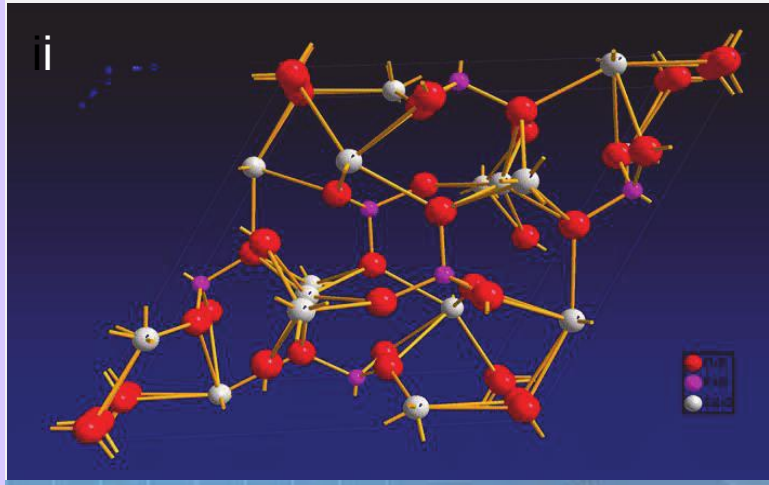
The chemical composition and structure of hydroxyapatite is similar to mineral constituent of natural teeth and human bones.

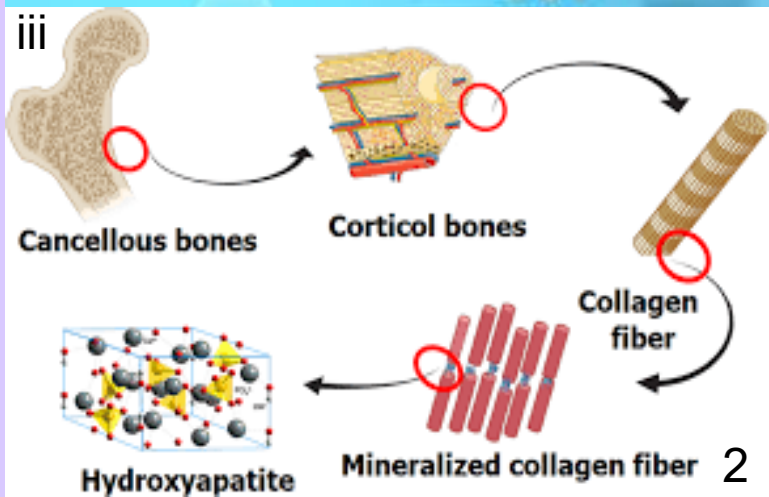
Chemical fourmula Ca10(PO4)6(OH)2

Human bones And teeth

Human bones
70% HAp, an inorganic compound + 30% organic materials like collagen fibers and bone marrow.

human teeth consist mostly of calcium (approximately 80%)

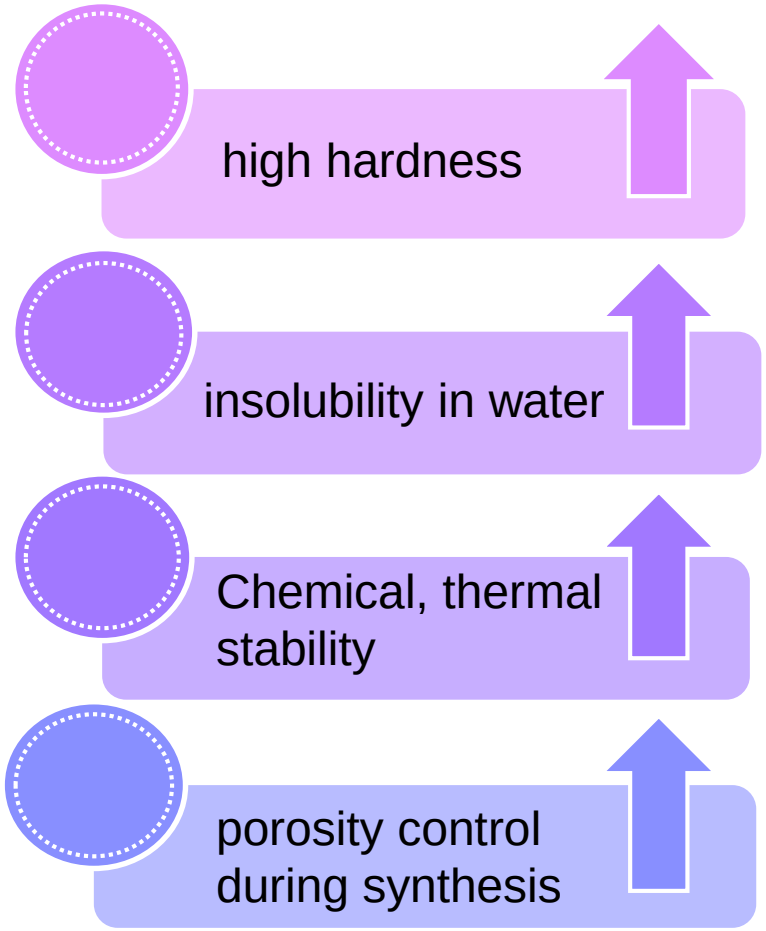




I. E.M. Rivera-Munoz, Hydroxyapatite-based Materials: Synthesis and Characterization, Biomedical Engineering-Frontiers and Challenges, 2011, pp. 75–98.
II. https://www.todaysrdh.com/a-dental-hygienists-overview-of-nano-vs-micro-hydroxyapatite/
III. J.Antia et.al, Recent advances in natural polymer-based hydroxyapatite scaffolds: Properties and applications, European Polymer Journal, 2021.

HAp properties

most thermally and chemically stable phase among the CaPs with molar ratio of 1.67



The chemical composition, crystallinity, size, and morphology of the HAp crystals and their aggregates play critical roles in determining their properties and potential applications.

Compound Name	Chemical Formula	Ca/P ratio	Solubility at 25 °C (g/l)	pH stability range at 25 C
Monobasic calcium phosphate anhydrate (MCP or MCPA)	$Ca(H_2PO_4)$	0.5	~ 18	0.0 – 2.0
monobasic calcium phosphate monohydrate (MCPM)	$Ca(H_2PO_4)_2{\cdot}H2O$	0.5	~ 17	a
Dicalcium phosphate dihydrate (DCPD), mineral brushite	$CaHPO_4 2H2O$	1.0	~ 0.0088	2.0–6.0
Dicalcium phosphate anhydrous (DCPA or DCP), mineral monetite	$CaHPO_4$	1.0	~ 0.048	a
octacalcium phosphate (OCP)	$Ca_8(HPO_4)_2(PO_4)_4 5H2O$	1.33	~ 0.0081	5.5 – 7.0
a-Tricalcium phosphate (a-TCP)	$\alpha\text{-}Ca_3(PO_4)_2$	1.5	~ 0.0025	c
b-Tricalcium phosphate (b-TCP)	$\beta\text{-}Ca_3(PO_4)_2$	1.5	~ 0.0005	c
Amorphous calcium phosphates (ACP)	$Ca_xH_y(PO_4)_z{\cdot}nH_2O$, n =3–4.5, 15–20 % H2O	1.2- 2.2	b	~ 5- 12
Calcium-deficient hydroxyapatite (CDHA)	$Ca_{10-x}(HPO4)_x(PO4)_{6-x}(OH)_{2-x}$ (0 < x < 2)	1.5 – 1.67	~ 0.0094	6.5 – 9.52
Hydroxyapatite (HA, HAp)	$Ca10(PO_4)_6(OH)_2$	1.67	~ 0.0003	9.5 - 12
Fluorapatite (FA or FAp)	$Ca10(PO_4)_6F_2$	1.67	~ 0.0002	b
Tetracalcium phosphate (TTCP or TCP)	$Ca4(PO_4)_2O$	2.0	~ 0.0007	b

i

a Steady at temperatures above 100 ◦C., b aqueous solutions cannot precipitate these compounds. c the solubility cannot be estimated.

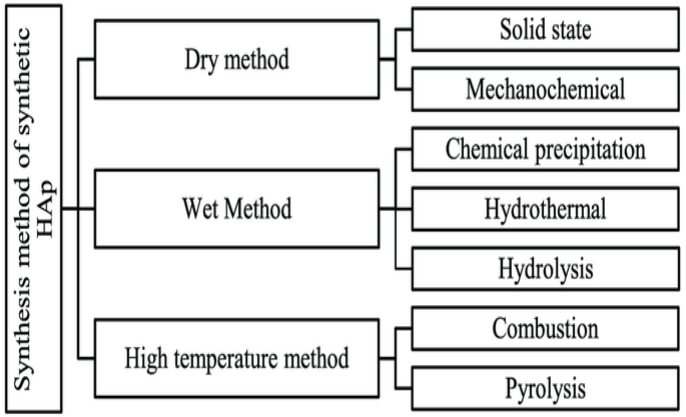
I. S. V. Dorozhkin, “Calcium orthophosphates (CaPO4): occurrence and properties,” *Prog Biomater*, vol. 5, no. 1, pp. 9–70, Mar. 2016, doi: 10.1007/s40204-015-0045-z.

Sources and preparation of HAp

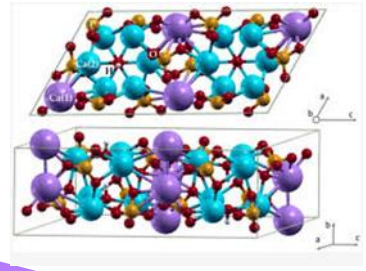
1. Wet methods
2. Dry methods
3. High-temperature processes

Synthesis HAp

i

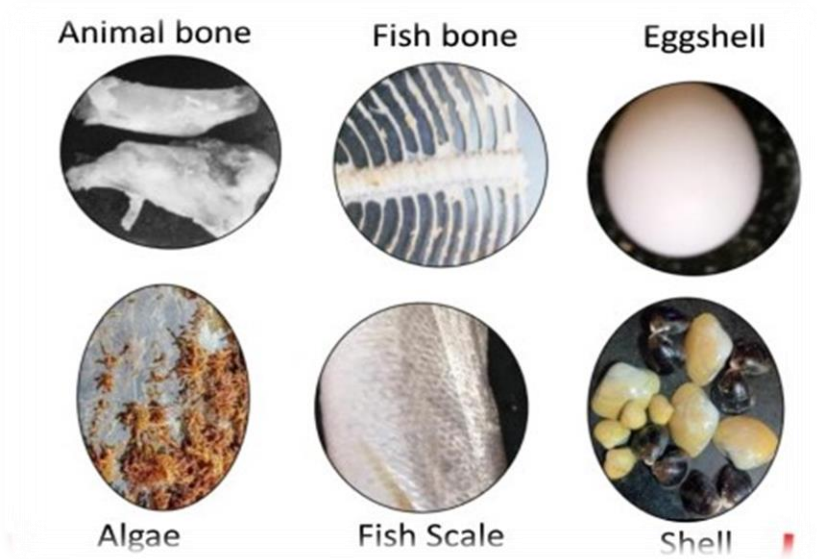


iii



Hydroxyapatite

ii



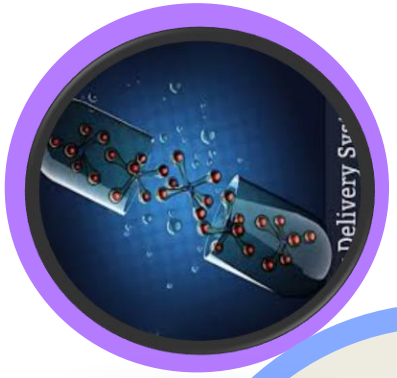
Natural Source HAp

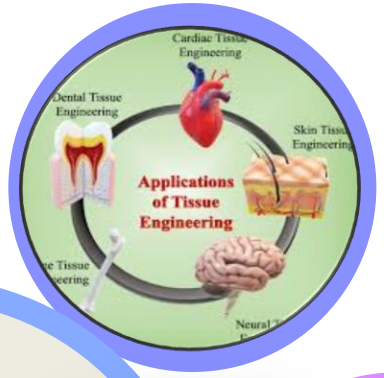
1. Eggshells
2. Mammalian Bones (Horse, Pig, Bovine)
3. Marian Source (Mollusk,

I. N.A.S. Mohd Pu'ad et.al, Synthesis method of hydroxyapatite: A review, Materials Today: Proceedings, Pages 233-239, 2020.
II. S. Pai et.al, A review on the synthesis of hydroxyapatite, its composites and adsorptive removal of pollutants from wastewater, Journal of Water Process Engineering, Journal of Water Process Engineering, 2020.
III. O. Nikolaeyna et.al, Incorporation of Iron(II) and (III) in Hydroxyapatite—A Theoretical Study, MDPI, 2021

Hydroxyapatite Application

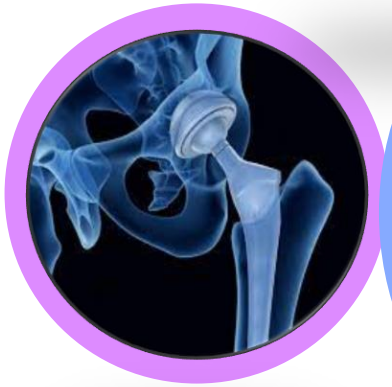
Drag delivery





Tissue engineering

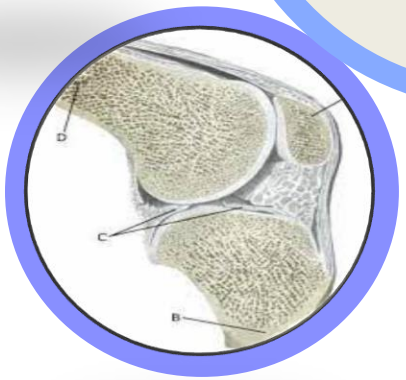
Implants

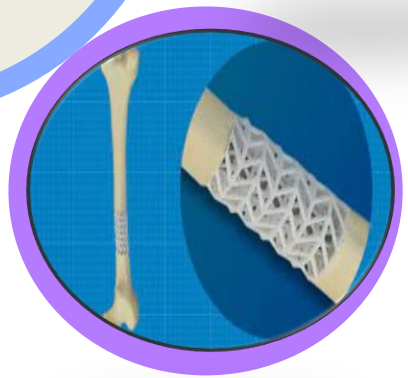


Hydroxyapatite

Water treatment

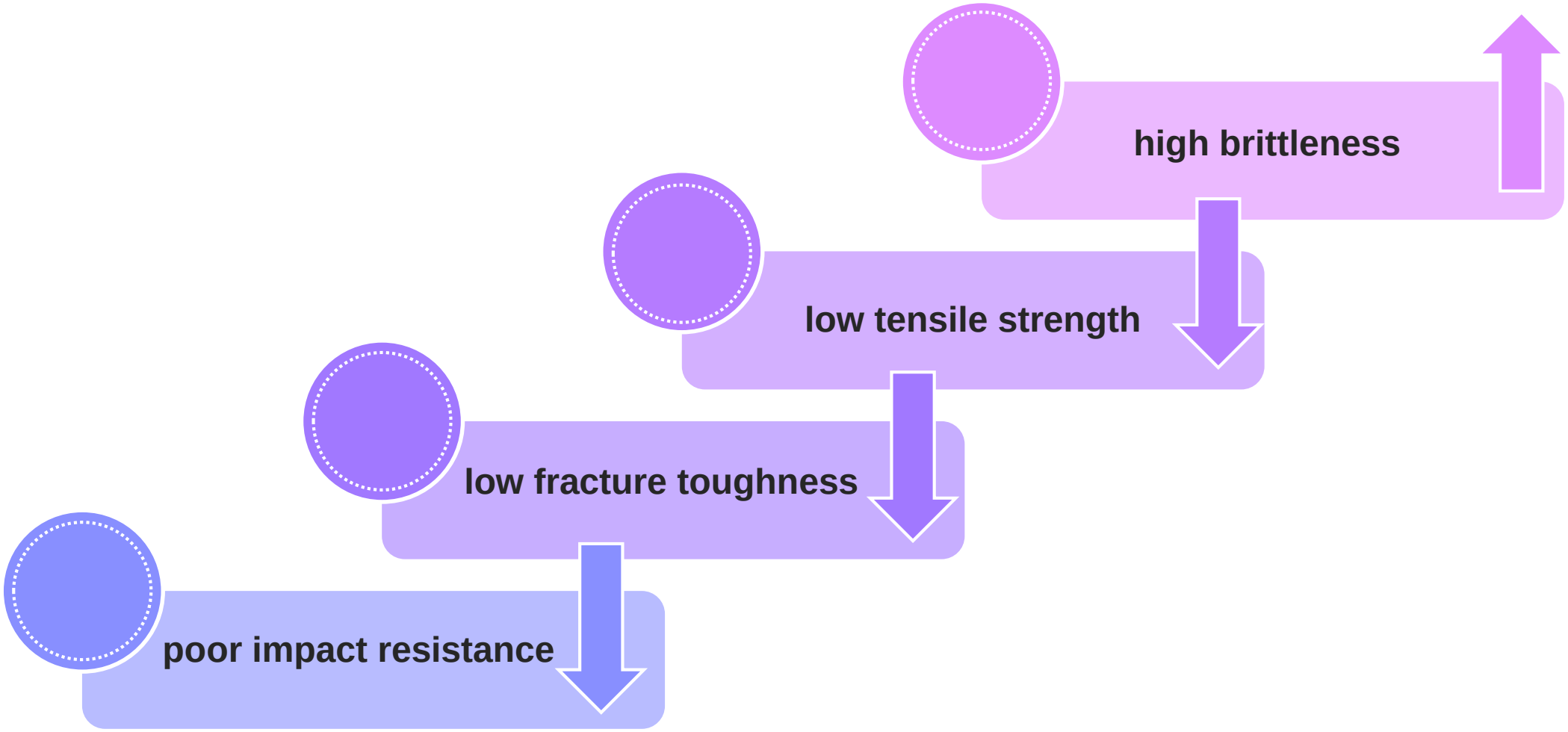
Membrane





Scaffold

Mechanical properties



HAp/polymer composites

Collagen

Gelatine

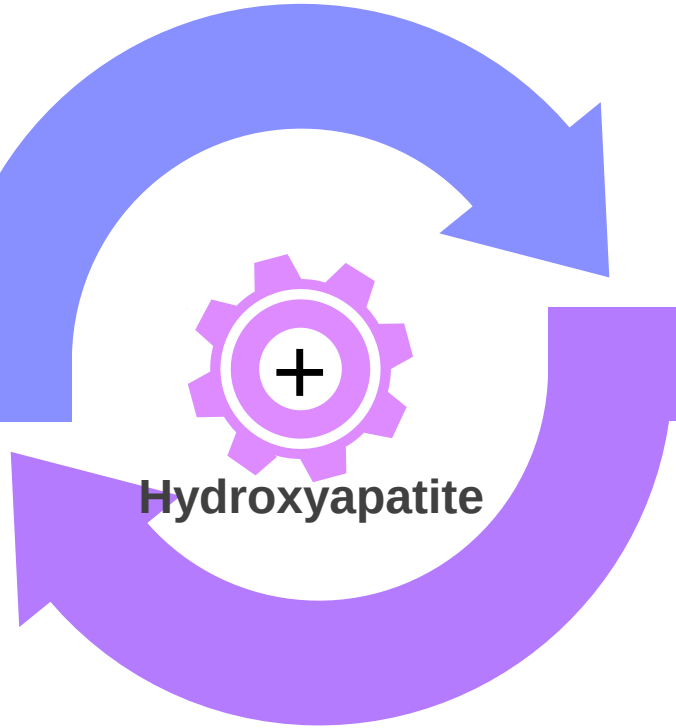
Chitosan

Cellulose

Alginate

Natural Polymer

hydrophilic tendency due to the presence of hydroxyl groups on their polymer chain.



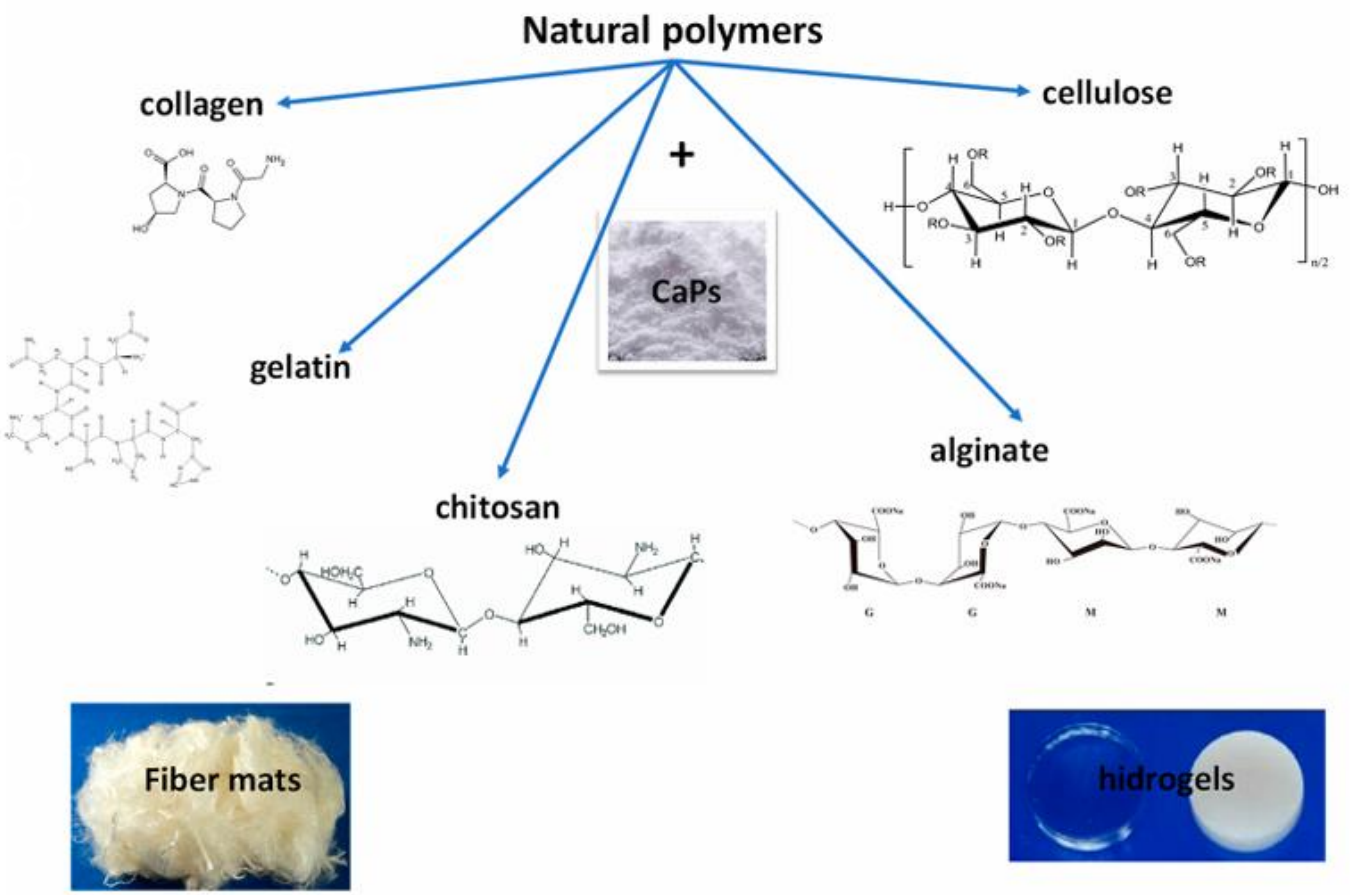
hydrophobic nature which restricts the homogenization and distribution of the inorganic phase

Synthetic Polymer

Polylactic acid (PLA)

Polyvinylpyrrolidone (PVP)

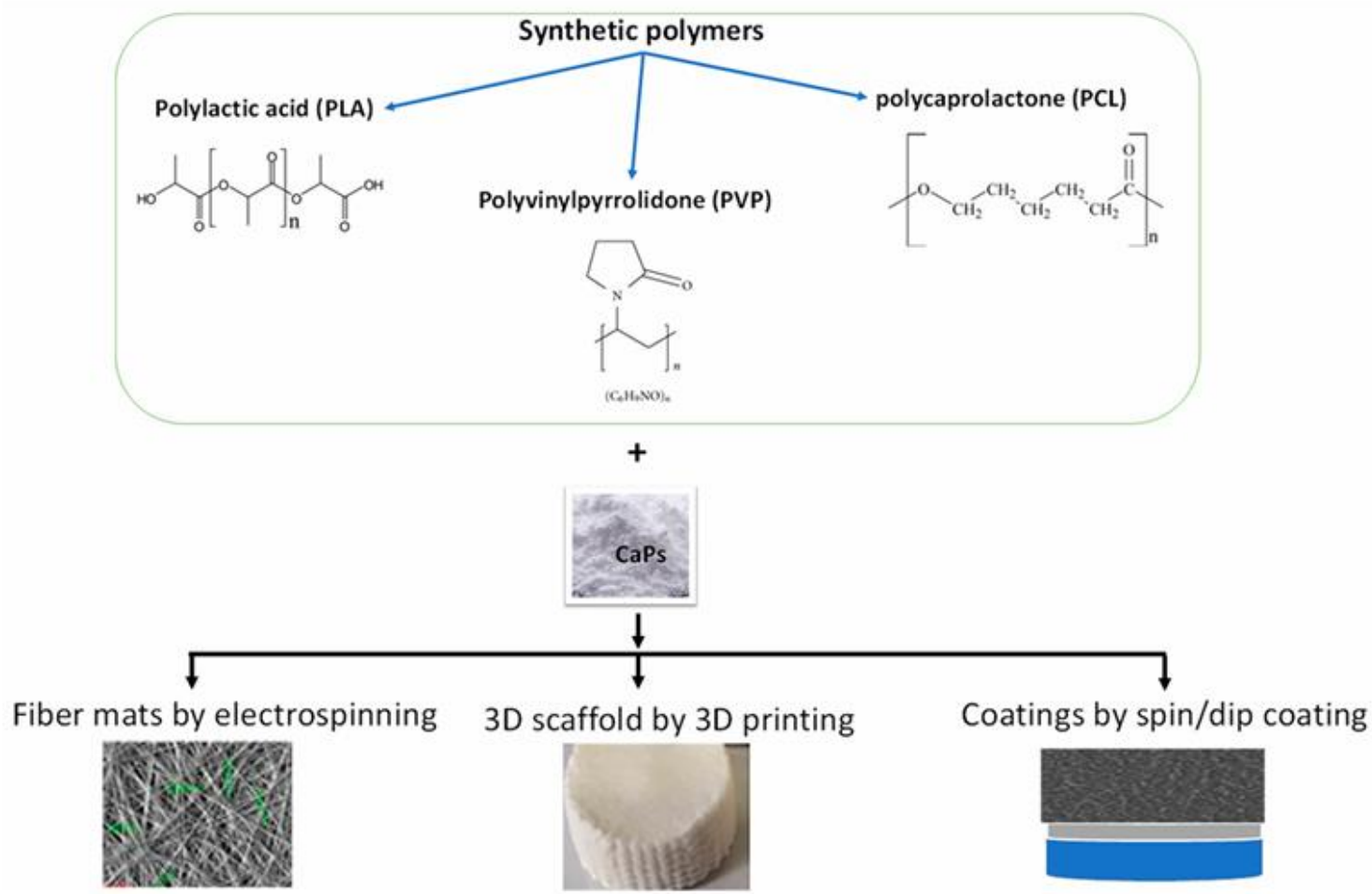
Polycaprolactone (PCL)



Graphical illustration of the most common natural polymers that can be used as CaP-containing composites. The applications of these materials are comprehensive since they can be produced as hydrogels or fiber mats.

I. M. Furkó, K. Balázsi, and C. Balázsi, “COMPARATIVE STUDY ON PREPARATION AND CHARACTERIZATION OF BIOACTIVE COATINGS FOR BIOMEDICAL APPLICATIONS-A REVIEW ON RECENT PATENTS AND LITERATURE,” 2017.

conventional fabrication approaches



Graphical illustration of the most frequently used synthetic polymers that can be used as CaP-containing composites, their possible application forms, and preparation

I. M. Furkó, K. Balázsi, and C. Balázsi, “COMPARATIVE STUDY ON PREPARATION AND CHARACTERIZATION OF BIOACTIVE COATINGS FOR BIOMEDICAL APPLICATIONS-A REVIEW ON RECENT PATENTS AND LITERATURE,” 2017.

Characterize the hydroxyapatite and its composites

1. Surface morphology and compositional analysis

2. Improved mechanical properties

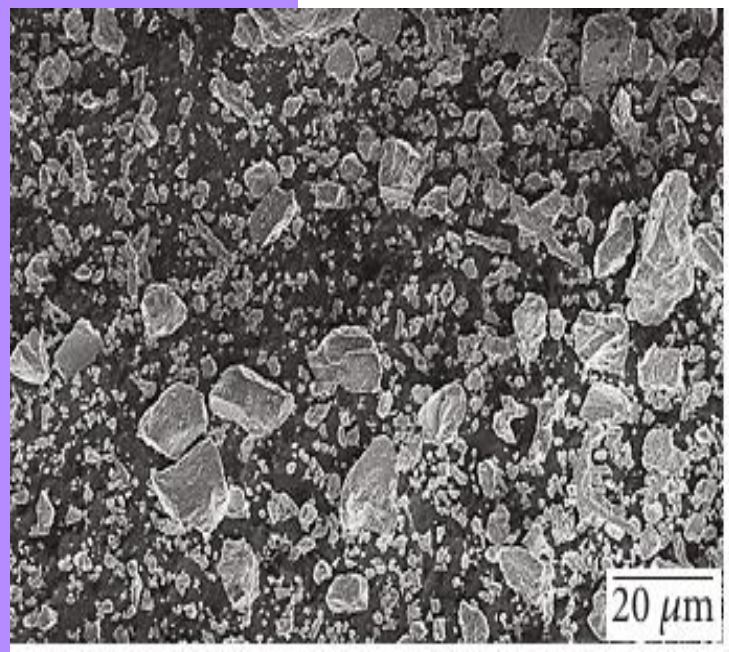
Aims and planning research

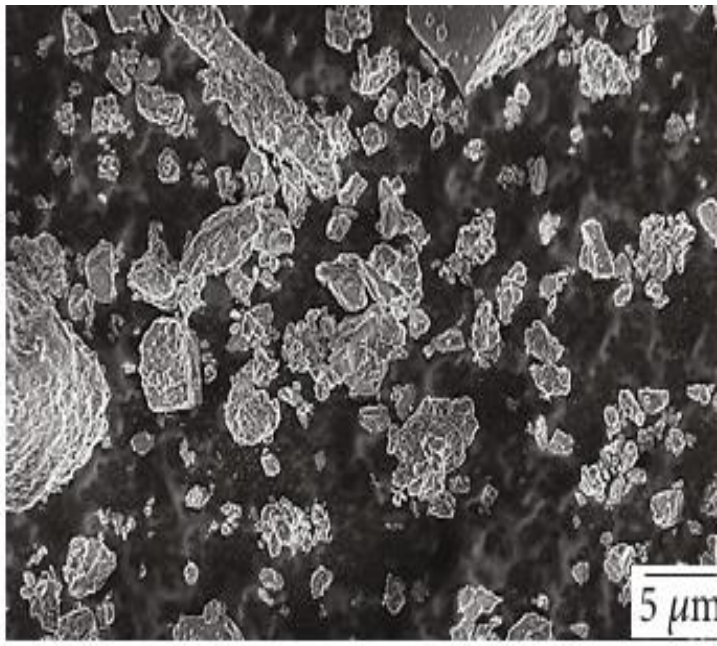
- ❖ preparation of HAp from natural sources (Eggshells) and study the characteristics of prepared HAp.
- ❖ Study the feasibility of using HAp as a filling material in its nano or micro-sized polymer composites by electrospinning method.
- ❖The mechanical properties of the obtained composites are important to be studied. The polymer matrix will be chosen according to its needs in industry, favorable properties like thermal properties, and its biodegradability.
- ❖The prepared and investigated HAp/composite materials are aimed to satisfy the requirements for biomedical applications.

Experimental Work

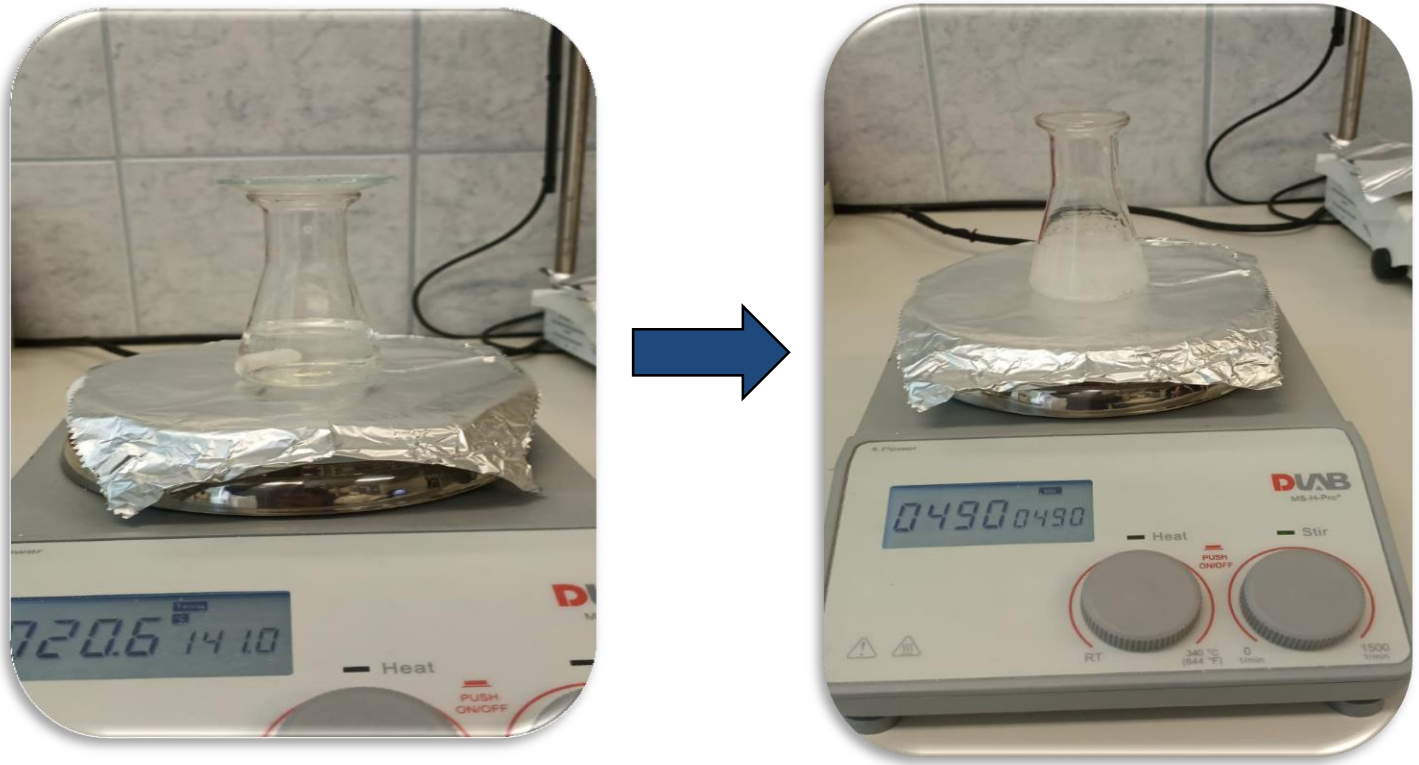
Preparation Eggshells powder

- ES is a source of Ca about 95% of inorganic (calcium carbonate).
- ES were initially washed and cleaned with tap water.
- Next, boiling water removed any biological impurities stuck on the shells.
- dried at 50 °C for 12 hours using an electric oven.
- broken by hand into small pieces then ground to powder using a mixer, followed by the microsieving process.



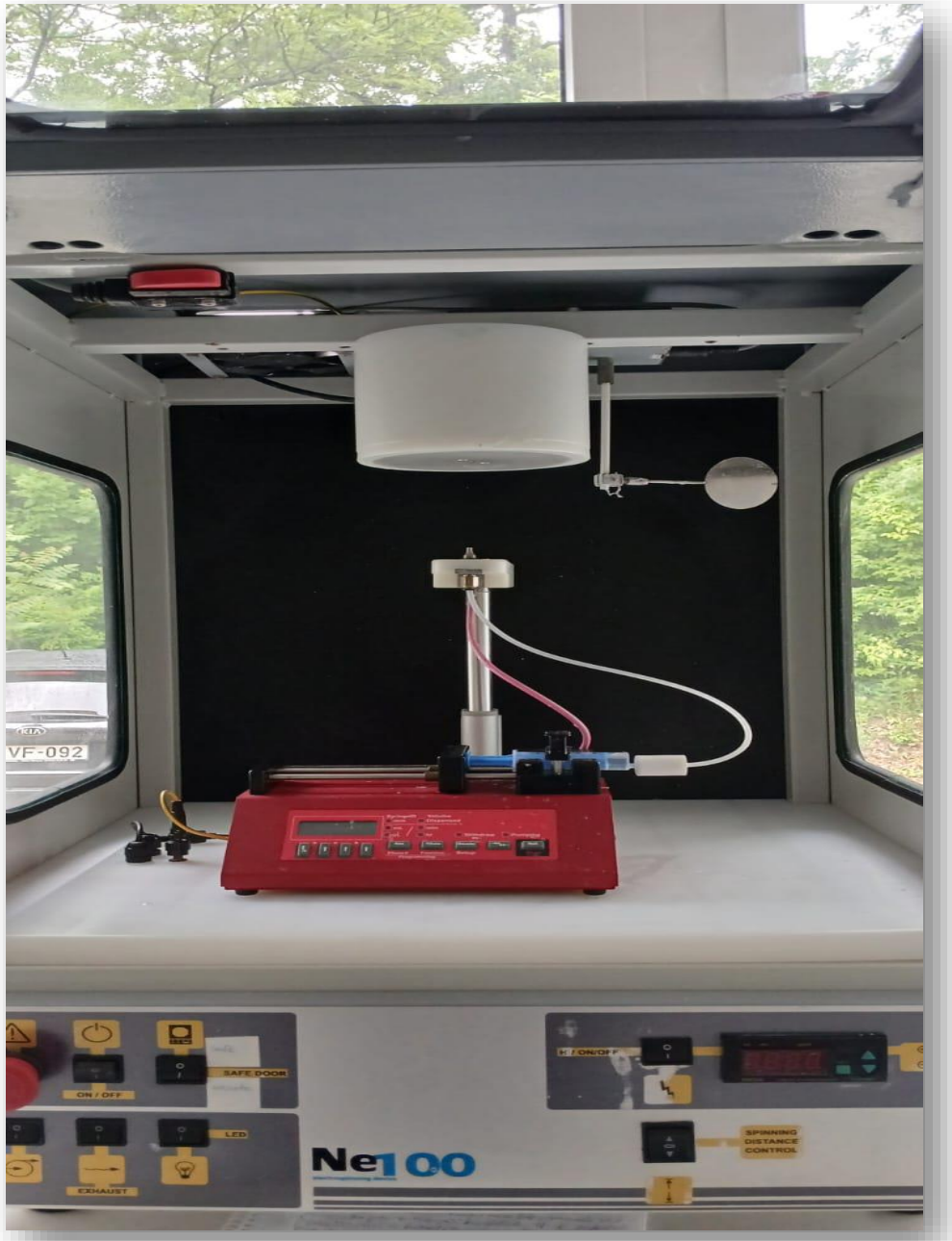


SEM images of ES particles: (a) an overview and (b) a detailed view of the surface morphology

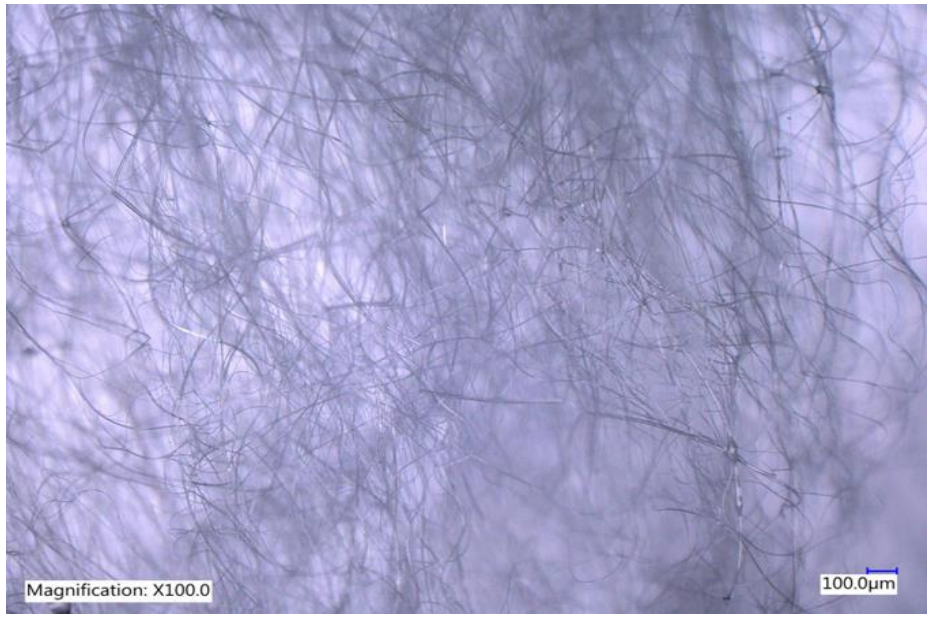


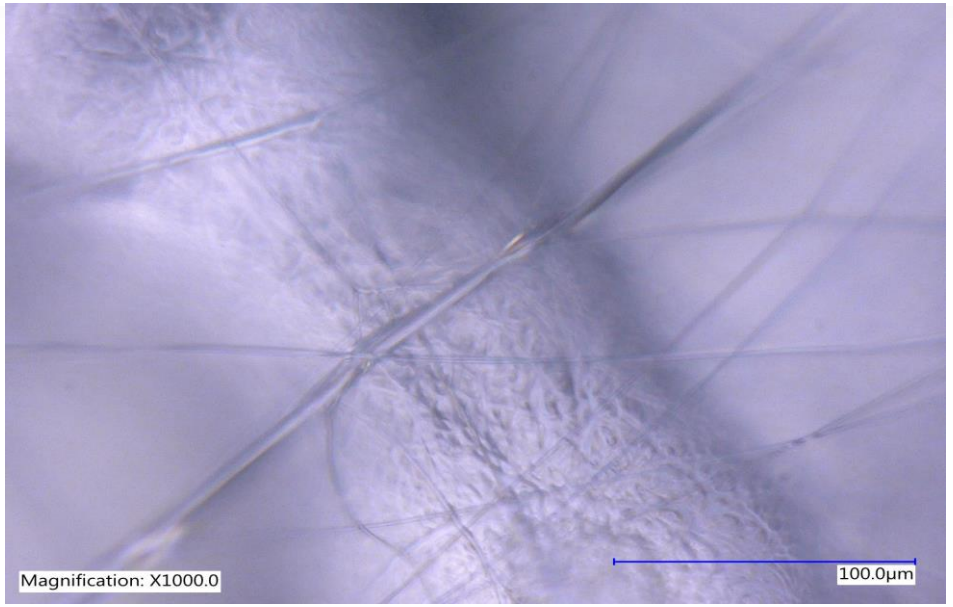
Magnetic stirrer

Preparation of PVP polymer



Electrospinning machine





Microscopic examination of generated fiber with different magnification

Courses and Credits

First semester

During the first semester, I've taken the following courses

Subject	Supervisor	Credit
Fundamentals of material science	Professor Maria Berkes	6
Biomaterials for medical applications	Professor Balázsi	6

Second semester

During the second semester, I've taken the following courses

Subject	Supervisor	Credit
Powder technology	Professor Csaba Balázsi	6
Transmission Electron microscopy (TEM)	Professor Katalin Balázsi	6

Publication Papers

	TITTLE	IF	%	Total credit
01	Effect of low-pressure plasma treatment on the thermal behavior of organo-modified montmorillonite nanoclay.	1.55	100	**36**
02	The effects of black tea extracts on the corrosion inhibition of mild steel in acidic solution.	-	100	**24**

Reviewing Paper

I assessed an article paper for a Journal, the manuscript title is "Analytical Study and Amelioration of Plastic Pavement Material Quality" and I have a certificate for reviewing the paper with https://doi.org/10.32388/07IS7V

THANK YOU

Köszönöm Szépen