„PETRU PONI" INSTITUTE OF MACROMOLECULAR CHEMISTRY - INTERDISCIPLINARY POLE FOR SMART SPECIALIZATION THROUGH RESEARCH-INNOVATION AND TECHNOLOGY FOR POLYMERIC (BIO/NANO) MATERIALS AND (ECO)TECHNOLOGIES

- INOMATPOL -

GENERAL INFORMATION

- Contract no. 142/10.10.2016, ID P_36_570, My SMIS 107464
- Beneficiary „Petru Poni" Institute of Macromolecular Chemistry Iasi (PPIMC)
- Project co-financed by European Regional Development Fund under the Competitiveness Operational Program 2014-2020
- Priority Axis 1 – Research, Technological Development and Innovation to Support Economic Competitiveness and Business Development
- Action 1.1.1 Large R&D Infrastructure, type "Investment projects for public R & D institutions/universities"
- Period: 42 months

CONTACT

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MANAGEMENT TEAM

- Project director – Dr. Narcisa Laura MARANGOCI
- Technic Coordinator – Dr. Anton AIRINEI
- Technical Expert (I) – Dr. Marcela MIHAI
- Technical Expert (II) – Dr. Ion BUNIA
- Acquisition Coordinator – Daniel CONDREA
- Legal Responsible – Jr. Dr. Raluca ANDONE
- Financial Responsible – Roxana MATACHE
- Assistant Manager – Diana ENCIU
- Monitor Responsible - Cătălina BALAN

GENERAL OBJECTIVE

Enhancing the capacity, quality and efficiency of the RDI activity by opening new research directions and by diversifying the range of research services targeted for industry – in accordance with the particular innovation needs of economic agents belonging to cluster-type organizations, with the purpose of stimulating the competitiveness of the Romanian scientific research at European level and enhancing the national/regional economic competitiveness of the Institute and its industrial partners in the field of smart specialisation in eco-nano-technologies and advanced materials.

SPECIFIC OBJECTIVES / EXPECTED RESULTS

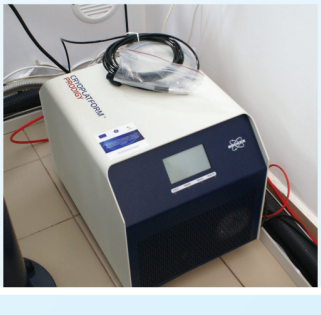
- **OS 1 – Reorganization and upgrading of the PPIMC RDI areas, in order to increase the capacity for innovative research services, by**
    - *creating new RDI laboratories: 20 synthesis laboratories and 1 support laboratory;*
    - *upgrading of existing RDI laboratories: 10 synthesis laboratories and 5 support laboratories.*
- **OS 2 – Development and upgrading the PPIMC RDI infrastructure to the EU advanced standards** by purchasing *62 RDI equipments (including a pilot one), of which 19 with values above 100.000 euro, 87 chemical niches, 87 special laboratory tables, 23 IT equipment and 4 intangible assets.*
- **OS 3 – Improving the quality and diversifying the offer of RDI services especially for the business media and the cluster structures,** during the project and within a minimum of 5 years from the completion of its implementation.
- **OS 4 – Development of eco-nano-technologies and industrial production of (bio-nano) polymeric materials in Romania and in N-E Region** by creating minimum *10 technologies* or new products and publication of *minimum 70 scientific papers* with authors from public and private sector, based on the protocols of collaboration with the economic agents, during the project duration and at least 5 years after its completion.
- **OS 5 – Increasing the competiveness of the cluster members and internationalization of their activity/performance by answering to the request of innovation, ensuring the transfer of knowledge and innovative services for the private companies from clusters or innovative parks,** upon request and based on public-private contracts, for traditional and new economic partners, members of the technological clusters / parks at least 5 years after the completion of the project.
- **OS 6 – Increasing the human resources quality by creating optimum conditions for the RDI activities and creating a number of** *30 new job positions* **up to the end of the project implementation period.**

- **OS 7 – Increasing the international visibility and PPIMC involvement in the European projects -** at least *35 project proposals for Horizon 2020* will be submitted within 5 years from the completion of the project implementation.

RESEARCH EQUIPMENT PURCHASED

1. Combined system NMR liquid 600 MHz - LC – MS, Bruker MaXis II

- NMR-LC-MS spectrometer optimized for applications in organic chemistry, organometallic, macromolecular chemistry and food chemistry as well as in medicine.
- the main modules (NMR, LC, MS, Sample preparation system) operate in both coupled and independent mode.



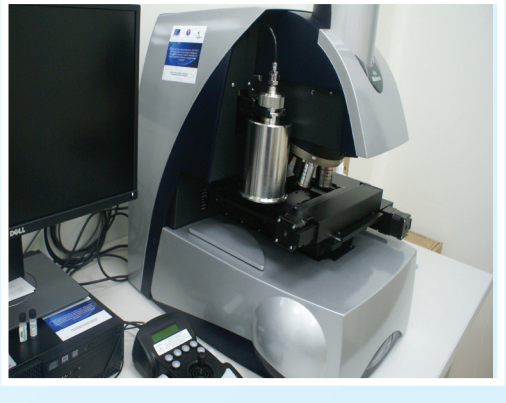
2. Lasers for Raman spectroscopy, Renishaw

- lasers with wavelengths of 785 nm (300 mW) and 442 nm (30 mW) allow Raman analysis (microspectroscopic analysis addressed especially to proteins, cells or organs) of a range of polymeric samples, including biological samples.

3. MALDI TOF Mass spectrometer, Bruker - Rapiflex

- system with collision cell for fragmentation (MS / MS) with collision gas (CID) at high pressure and post-source fragmentation (PSD) and possibility of delayed extraction (PIE).
- TOF / TOF type analyzer with reflector, operating capacity in linear detection mode, MS / MS reflector (tandem mass spectrometry) with precursor selection, using collision gases such as Ar or N_2.
- matrix assisted laser desorption ionization (MALDI) in vacuum.
- laser source capable of producing the MALDI type ionization effect up to a working frequency up to 10000 Hz, pulse power of at least 100 µJ / pulse and laser beam size adjustable in the minimum range 5 - maximum 100 µm.

4. Analysis system for determining the shape, concentration and size of the particles, Malvern Instruments Ltd UK Morphology G3 series



- size measuring range: 0.1 µm - 6000 µm.
- determines the size, shape (diameter, circularity, length, width, perimeter, area, solidity, elongation, etc.), transparency, concentration.
- allows the analysis of samples in the form of dry dispersions, particles on surfaces, dispersions in liquid, emulsions.

5. Microbalance with quartz crystal (QCM-D), Biolin Scientific Suedia Q-SENSE

- monitors the molecular interactions in real time.
- measures the mass and thickness of the molecular layer. Monitors the formation of layers, with a sensitivity in order of nanograms.
- ensures the structural analysis of the properties of molecular layers. Detects changes in the hardness of the molecular layer. Quantifies the viscoelastic properties of the films.
- works on maximum parameters on flexible surfaces, including metal, polymeric and chemical surfaces.
- can perform *in-situ* measurements in real time.

6. Equipment for mechanical testing of elastomers, Instron 3365

- two-column system - two force cells: 100 N and 500 N.
- videoextensometer; automatic calibration and recognition with the mechanical testing machine.
- climatic chamber functionally adapted for the mechanical testing machine.
- temperature range: -100 - +300 °C.
- specimen cutting system.

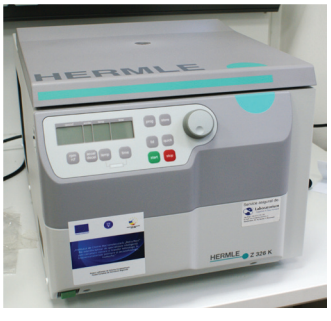
7-11. Vacuum ovens, Memmert VO-200

- pressure adjustment range: 10 - 1100 mbar
- temperature range: 20 - 220 °C

12. Digestion system in the microwave oven, Berghof, SPEEDWAVE XPERT

- high pressure reaction chamber made of stainless steel
- room volume 990 mL
- microwave power 1500 W

13-16. Laboratory centrifuges, Hermle Z326K



- *1 fixed angular* rotor with a maximum rotational speed of at least 6000 rpm, with 6 positions, each position of at least 50 mL
- 2 sets of tube adapters (tubes) for volumes of 2 and 15 mL
- *1 fixed angular rotor* with a maximum rotational speed of at least 12000 rpm, with 12 positions, each position of at least *2* mL
- 2 sets of tube and tube adapters for volumes of 0.2 and 0.5 mL
- temperature range between -20 ^{0}C si +40 ^{0}C

17. Respirometer, ECHO d.o.o - ERS 12

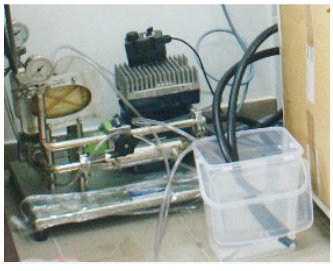
- 12 reactors with volume of 2 l
- thermostatic chamber + 5 - 60 ^{0}C
- flow regulator for each reactor (0-1 L/min)
- CO_2 infrared sensor (0 - 5000 ppm)
- oxygen sensor (range: 0-25%)
- data acquisition system
- process control software (temperature, gas, process parameters, flow data storage)

18. Multipotentiostat, Epi Sistem Stat 8000P

- simultaneous or separate analysis using 4 independent potentiostats
- MultiTrace software
- amperometric and voltammetric measurements
- range: 1 nA -10 mA / 100 mA with a resolution of 1 pA

19. Membrane separation module, Alfa Laval M10 LabUnit

- flat Cross Flow / Flat dead-end membrane system
- volume of food tank: 2 L
- maximum pressure: 7 bars
- flow rate 10-70 L/h
- by-pass pressure: 0-100 L/h



20. Fully equipped photoreactor, Peschl Ultra violet - MPDS Basic

- for liquids with molar extinction coefficient >30 m^{-1}
- magnetic drive pump
- UV sensor port
- process volume: 250-400 mL
- optical range <2 cm

21-22. Calcination furnaces, Nabertherm R80/ 500/12

- working capacity: 5 L
- max. power: 2kW / 220V
- max. speed heating: 1000 ^{0}C/h
- max. temperature: 1100 ^{0}C

23. Hydraulic press, Carver Auto-CH PL

- capacity 15 t
- 6”x6” heated trays
- opening between plates 0”- 14”
- programmable control system for force, temperature, time
- test cylinders and filters

24-25. Refrigerator-freezer, Artiko Model LFF 660 – 2 buc

- temperature range (^{0}C): refrigerator +1/+10 ^{0}C; freezer -30 / -10 ^{0}C
- manual/automatic defrosting system
- controller - visual and acoustic alarm system
- alarms for accidental voltage drops
- adjustment of alarm limit

26. Microbiological hood, Telstar Spania Bio II Advance 6

- Class II A with motorized control
- control panel
- UV lamp interconnected
- descending air velocity: 0.35 ± 0.025 m/s
- ascending speed: 0.53 ± 0.025 m/s

27. Spin coater, MIT Corporation - VTC-100PA

- max rotation speed: 12000 rpm
- teflon surface
- max. rotation time: 3000 sec/step

28-32. Analytical balances, Precisa - LX 220A SCS

- capacity: 220 g
- accuracy: 0.0001 g
- repeatability: 0.08 mg
- automatic calibration
- graphic display with lighting

33-35. Equipments for ice flakes, EVERMED - CAA900

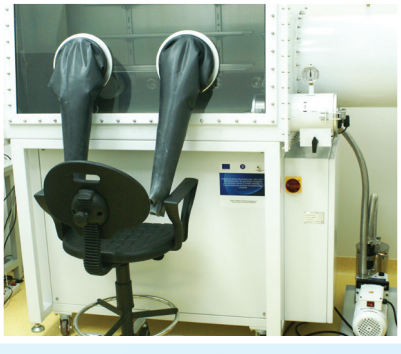
- ice shape: flat flakes
- cooled to - 5 ^{0}C
- layer thickness (approx.): 1.5 - 2 mm
- capacity: 90 kg / 24 hours
- tank capacity: 20 kg

36-40. Vacuum pump rotary evaporators, Buchi Labortechnik AG R 300 EL

- heating bath temperature up to 180 ^{0}C
- precise temperature control with adjustable protection system
- programmable timer in the range of 1-99 minutes

41-43. Glove boxes, Changshu Tongrun Electronic Torun 2GBS

- stainless steel construction, with 3 height adjustable interior shelves
- vacuum transfer chamber with access hatch and pressure relief valve, including mini transfer chamber
- automatic pressure controller
- fluorescent and UV germicidal lamps
- humidity and oxygen sensors



44. Freeze-dryer, Labconco FreeZone

- 6 liters with Teflon collector and freeze chamber
- allows the lyophilization of the samples of moderate and high volume from various types of containers, at a temperature up to -84 ^{0}C, suitable for samples with small eutectic point, resistant to organic solvents

45. Equipment for mechanical analysis in dynamic regime – DMA

- used for the viscoelastic characterization of polymers and polymeric materials, in dynamic regime
- evaluation of relaxations in polymers and their activation energies, recording the variation of the modulus of elasticity (E') according to temperature, determining the glass transition temperature, obtaining information on the presence of other phenomena (crystallization, melting)

IN PROGRESS ACQUISITIONS

Tangible assets

- Spin electronic resonance spectrometer
- UHR-SEM high resolution scanning electron microscope with STEM detector
- Cryo-ultramicrotome
- Sputter device
- Apparatus for analyzing the specific surface and porosity
- Real-time spectrometry system with pulsed laser photolysis
- Flow cytometry system for immunophenotypic analysis of cells
- EGA system (evolved gas analysis) for thermogravimetric analysis
- Vibrating sample magnetometer (VSM) with temperature chamber
- GPC / SEC multidetector system
- Multifunctional plant for complex exploitation of plant biomass type microscale
- Real Time PCR
- Profilometer

- Atomic absorption spectrometer
- Total organic carbon and total nitrogen determination analyzer
- Extruder for elastomers
- Climate chamber with humidity control
- Ultra-pure water system

Intangible assets

- Molecular modeling software package
- Software for molecular dynamics
- Software for numerical calculation, statistical analysis and optimization
- Molecular modeling software for materials and biomaterials

CREATION AND MODERNIZATION OF RDI LABORATORIES

AREAS OF RESEARCH

I. Nanostructured polymer biomaterials for the pharmaceutical industry and medicine

II. Electro- and opto-active nanomaterials

III. Composite polymeric materials and organic / inorganic hybrids for environmental protection and catalysis

IV. Polymers and advanced materials for energy conversion and storage

V. Biodegradable polymeric materials and eco-technologies for polymer waste recovery

VI. Multifunctional polymeric materials and eco-technologies for films, coatings, adhesives

VII. Eco-technologies for the complex valorization of plant biomass

Modernization of 3 building bodies in order to develop the 7 research directions:

- **Modernization / reconfiguration of laboratories / halls** to accommodate **20 new synthesis laboratories including pilot equipment / installations and a support laboratory;**
- **Modernization of spaces** to accommodate **other 10 synthesis laboratories and 5 support laboratories;**
- **Rehabilitation** of the spaces for processing/interpreting results, dissemination of results, technical spaces.

ACQUISITIONS:

- Large aerodynamic professional chemical niche - 42 pcs; Wesemann GmbH Laboreinrichtungen - Deltaguard
- Small aerodynamic professional chemical niche - 45 pcs; Wesemann GmbH Laboreinrichtungen - Deltaguard and ASECOS
- Double laboratory table (central) island type with console on metal structure with ceramic countertop and sink - 42 pcs. Wesemann GmbH Laboreinrichtungen - Delta 30
- Side laboratory table with console on metal structure with ceramic countertop and sink - 45 pcs. Wesemann GmbH Laboreinrichtungen
- Safety cabinets / cabinets for storage and handling of hazardous materials - 35 pcs; ASECOS - LaCont Germany
- Special chairs for laboratories, with and without backrest - 150 pcs
- 35 spaces equipped for RDI results processing

MAIN BUILDING

HALL FOR STRIPS MICROPRODUCTION

After rehabilitation / reconfiguration will host the ***Laboratories and the pilot for the complex recovery of the plant biomass and the fine and small tonnage synthesis***.










HALL FOR PREFABRICATED

After rehabilitation will host the ***Laboratory of Modeling and in-silico design of (nano) functional materials***.

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MISSION

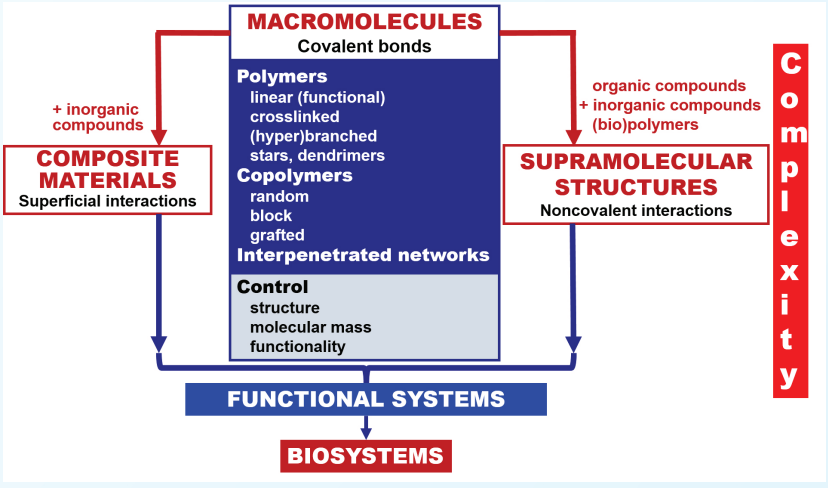
"Petru Poni" Institute of Macromolecular Chemistry is an Institute of excellence of the Romanian Academy. Established in February 1949, the Institute has a long tradition of over seventy years in fundamental and applied research in organic and inorganic chemistry, polymer chemistry and physics, materials science.

The main mission of the "Petru Poni" Institute of Macromolecular Chemistry consists in the accumulation, dissemination and valorization of knowledge obtained through fundamental and applied research in areas of national, European and international interest.

To achieve the desired excellence in research, the strategic objectives of the Institute aim at performance in human resource education and specialization (PhD, post-doctoral) or are oriented towards the application of scientific results through the transfer of knowledge and technologies or to provide services and consultancy for economic agents.

The Institute's research program, focusing on the main field of research - polymers and polymer materials science – has been periodically reconsidered both by implementing an internal call system for project proposals and by promoting areas considered to be strategic for the Institute. A rigorous selection of the human resources by professional category has led to a balanced staff structure by age category (about 30% of researchers younger than 35 years old) and experience.

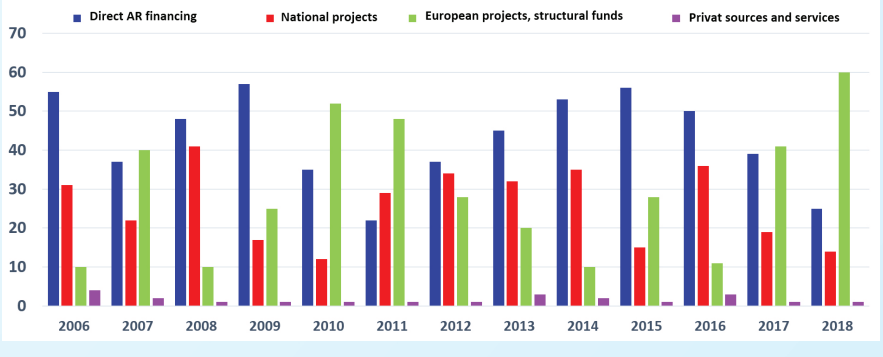
VISION



RESEARCH DOMAINS

The main research areas of the institute include research on biomaterials (controlled drug delivery systems, non-viral vectors for nucleic acid transport, hydrogels for tissue engineering), electro- and optoactive micro- and nano-materials for micro/ nanoelectronics (composites, organic-inorganic hybrids, semiconducting polyrotaxanes), materials for environmental protection or complex exploitation of plant biomass and are reflected in the annual research directions proposals approved by the Romanian Academy.

The need to develop and maintain the research infrastructure in operation has required important efforts by the Institute's researchers to access competitive funding resulting in a significant increase in funding coming from alternative sources in Institute's total revenues, in a few years the funding from competitive funding exceeding the direct funding from the budget of the Romanian Academy. It is still desirable to access private resources - insufficient on a national scale - which during the last 15 years did not exceed 3-4% of Institute's revenues.



BASIC RESEARCH

- over 300 scientific papers, books, book chapters / year
- an average of 150 presentations at scientific events / year
- organizing national and international scientific events (e.g. *„Cristofor Simionescu" Symposia - Frontiers in Macromolecular and Supramolecular Science* (10th ed. in 2018), *French-Romanian Seminars on Polymers* (12th ed. in 2016), *Progress in the science of organic and macromolecular compounds* (27th ed. in 2019)

APPLIED RESEARCH, TECHNOLOGY TRANSFER, MICROPRODUCTION

- industrial technologies
  - silicones: oils, elastomers, resins, adhesives, pastes, lubricants
  - polyurethanes: synthetic leather, adhesives, blocking greases
  - anionic and cationic ion exchangers
- special purpose materials
  - microparticles (e.g. skin wound treatment)
  - bioresorbable thermosensitive hydrogels (treatment of minor myocardial infarction)
- certification of (nano) polymeric materials

EDUCATION

- on average 10 doctoral theses sustained yearly
- 14 PhD theses promoters

SERVICES, CONSULTING

- consultancy for polymers / polymer materials preparation and processing
- knowledge and technology transfer

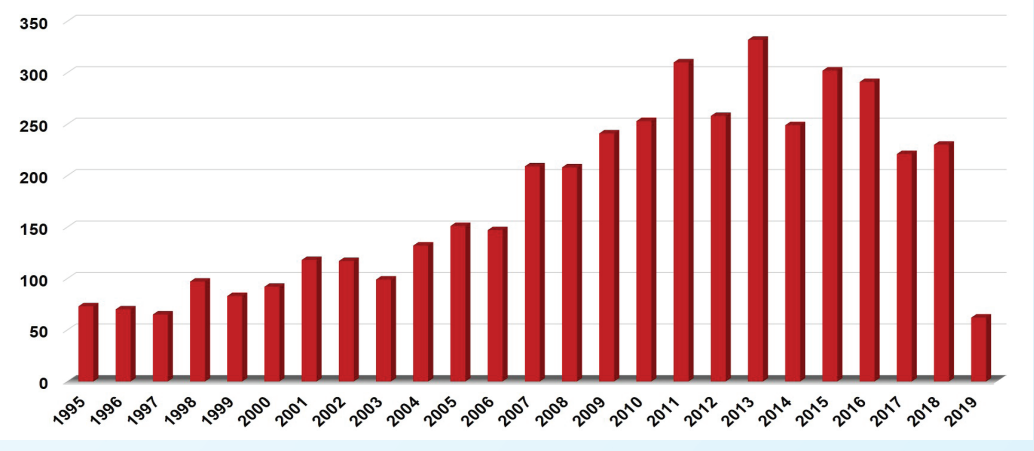
RESEARCH INFRASTRUCTURE

ICMPP has a valuable research infrastructure that allows researchers and PhD students as well as Institute's partners to carry out the full range of studies required to evaluate the structure (NMR, FTIR, XRD monocrystal, UV-Vis, HPLC-MS), morphology (AFM, SEM, TEM, XRD, SAXS) and properties (DSC, ATG, DMA, rheometry, and others) of the investigated materials.

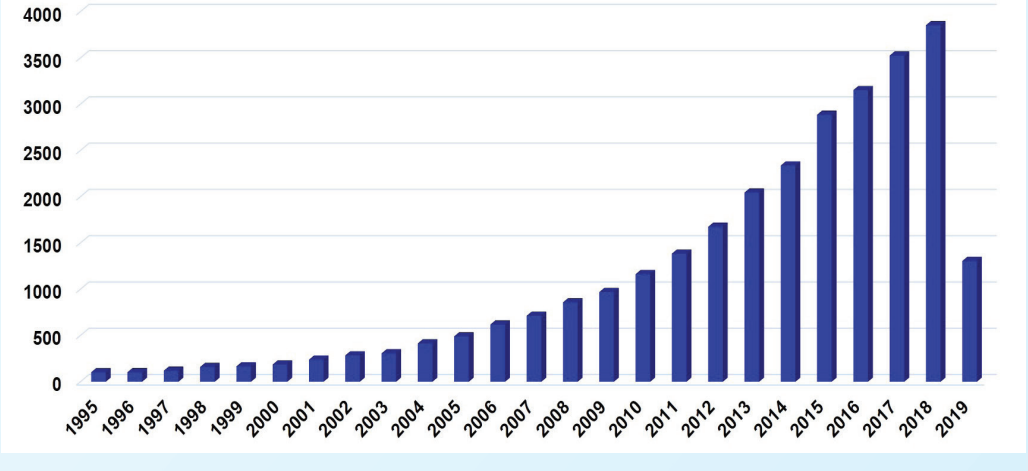
The equipment available in the institute is detailed at
https://erris.gov.ro/ICMPP.

PERFORMANCE AND INTERNATIONAL VISIBILITY

„Publish or perish" has been continuously the Institute's motto. Without over-emphasizing the importance of bibliometric values in assessing excellence in research, we can say that a first indication of the quality of the work comes from the number of papers and the interest they reach in the academic community. After 1990, the Institute's researchers are authors or co-authors of over 4600 papers published in ISI rated journals, which have over 33,000 citations (excluding self-citations), according to apps.webofknowledge.com. More than 50 researchers from PPIMC (out of 140) have Hirsch indices greater than or equal to 15.



Scientific papers published in ISI rated journals (1995-2019)
(webofknowledge.com, 01.05.2019)



Citations of published papers (1995-2019)
(webofknowledge.com, 01.05.2019)

The international visibility of the Institute can also be highlighted by scientific papers on the cover of prestigious journals, invited lectures at international symposia or international partnerships in Europe, China, Japan, Russia and the USA.

RESEARCH LABORATORIES

The scientific activity of the Institute is carried out in nine research laboratories:

Laboratory 1. Center of Advanced Research for Nanobioconjugates and Biopolymers

Laboratory 2. Polyaddition and Photochemistry

Laboratory 3. Polycondensation and Thermostable Polymers

Laboratory 4. Functional Polymers

Laboratory 5. Natural Polymers, Bioactive and Biocompatible Materials

Laboratory 6. Inorganic Polymers, Hybrid and Complex Systems

Laboratory 7. Electroactive Polymers and Plasmachemistry

Laboratory 8. Physical Chemistry of Polymers

Laboratory 9. Physics of Polymers and Polymeric Materials

LABORATORY 1

CENTRE OF ADVANCED RESEARCH IN BIONANOCONJUGATES AND BIOPOLYMERS

HEAD OF LABORATORY: DR. MARIANA PINTEALĂ

www.intelcentru.ro

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- Ing. Paul ZLATE / zlate.paul@icmpp.ro / engineer / chemistry
- Tudor ARDELEANU / Technician
- Livia ALBU / Technician 1

Temporary employed Senior Researchers/Post-Doctoral Researchers/ PhD Students:

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- Prof. Aatto LAAKSONEN / 5D-NatoP / aatto@mmk.su.se / chemistry
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- Dr. Anda-Mihaela CRĂCIUN (OLARU)/ SupraChem Lab / olaru.anda@icmpp.ro / chemistry
- PhD Student Bogdan Florin CRĂCIUN / TERADOT / craciun.bogdan@icmpp.ro / chemistry
- PhD Student Tudor VASILIU / TERADOT / vasiliu.tudor@icmpp.ro / chemistry
- PhD Student Radu ZONDA / SupraChem Lab / zonda.radu@icmpp.ro / chemistry
- PhD Student Monica SARDARU / POCPOLIG / monicasardaru@gmail.com / chemistry
- PhD Student Bogdan BRATANOVICI / POCPOLIG / ionelbratanovici@yahoo.com / chemistry

DESCRIPTION

The Centre of Advanced Research in Bionanoconjugates and Biopolymers (IntelCentre - www.intelcentru.ro) is a newly build (2010) infrastructure that. Has been implemented by a strategic project of 5 M Euro supported by the Romanian Sectorial Operational Program for Increasing the Economic Competitively.

IntelCentre is a truly interdisciplinary centre of excellence with the main focus on the design, preparation and characterization of biologically inspired nano-structures as potential drug carriers and the interaction of such artificial structures with living systems. The priority thematic areas of ***IntelCentre*** are focused on materials, products and innovative processes and health. The Centre was finalised in 2012 and since then one of the priorities of the development strategy in PPIMC was to make this centre a fully functional research department of the Institute.

IntelCentre is divided into **four research groups** consisting of chemists, biologists and physicists, working in **14 research laboratories** fully equipped through the project with **more than 100 modern equipments** (the organisation and the main resources of the ***IntelCentre*** are summarised in the table below). With the existing interdisciplinary combination of researchers with different scientific backgrounds – chemistry and chemical engineering, biology, biochemistry, molecular biology, materials science, physics, medicine and informatics – ***IntelCentre*** represents an unique opportunity to extend the recent structural advances into truly functional materials for a wide range of important applications.

PROJECT 1. NANO-SIZED MATERIALS FOR BIOAPPLICATIONS
PROJECT DIRECTOR: DR. MARIANA PINTEALĂ

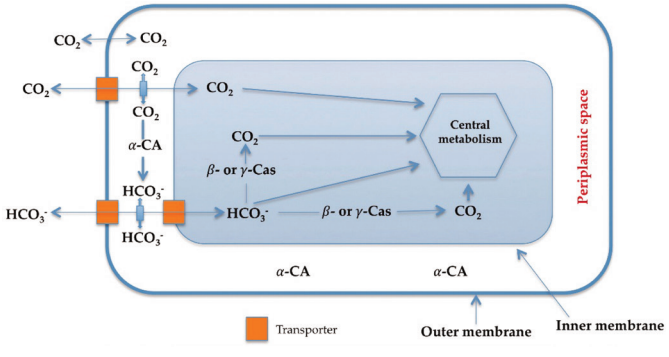
- Mimicking living matter mechanisms by five-dimensional chemistry.
- Constitutional systems for DNA transfection and drug delivery.
- Dynameric networks and gels for delivery, cell recognition and cell growth.
- Modelling and theoretical chemistry of constitutional systems.
- Electrochemical sensors.

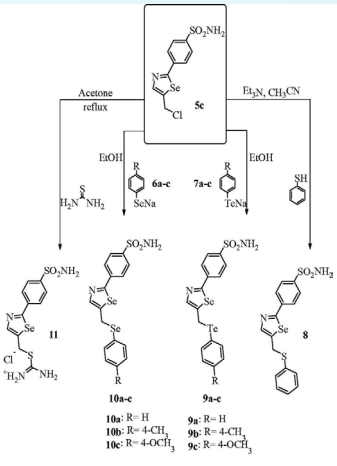
The PPIMC ***IntelCentre*** represents an **unique facility in Romania** for research in bionanoconjugates and biopolymers. **The infrastructure and the equipment are top level from the point of view of European standards of quality and performance.**

IMPORTANT RESULTS

- *Mimicking Living Matter Mechanisms by Five-dimensional Chemistry*

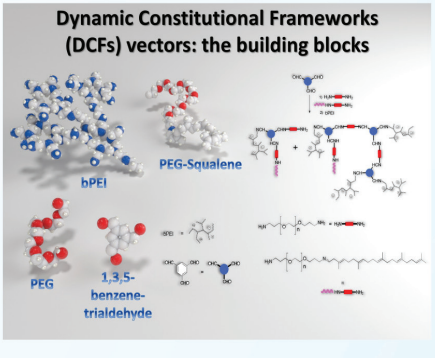
The obtained results showed that selenazoles are effective as inhibitors, which makes this class of AC inhibitors attractive as the top compounds for designing antibacterial with a new mechanism of action, which could counteract the intense problem of resistance to antibiotics found in most commonly used medicines.

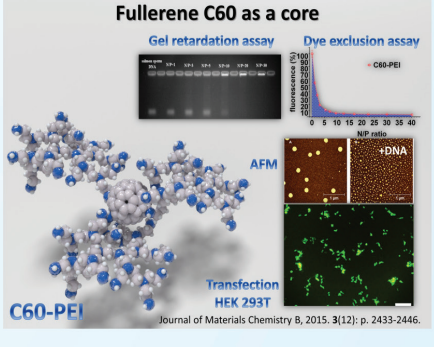


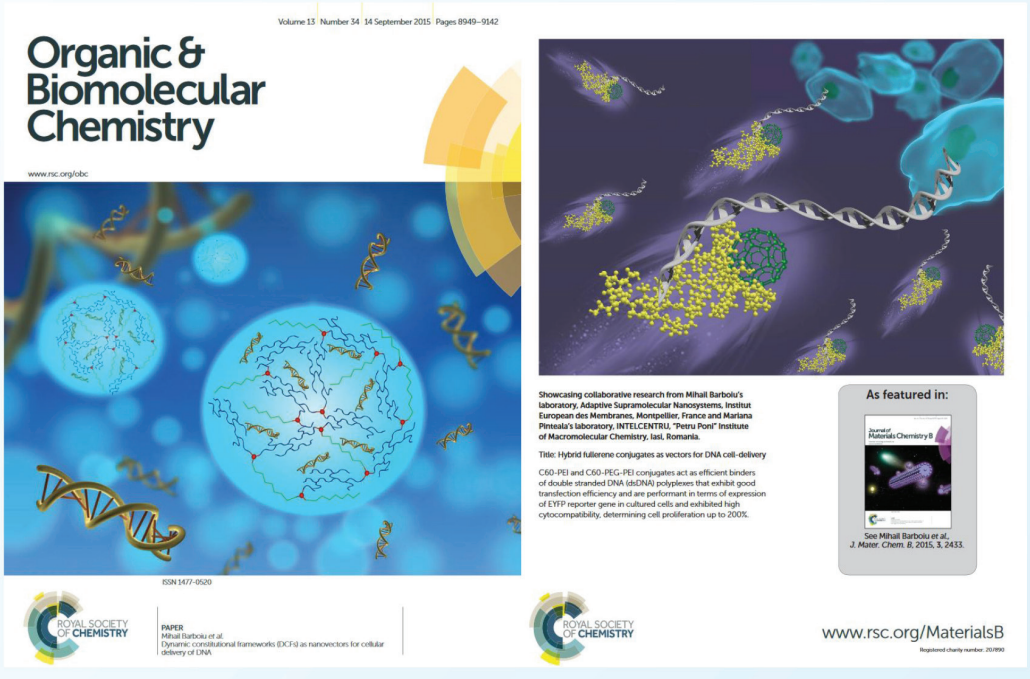


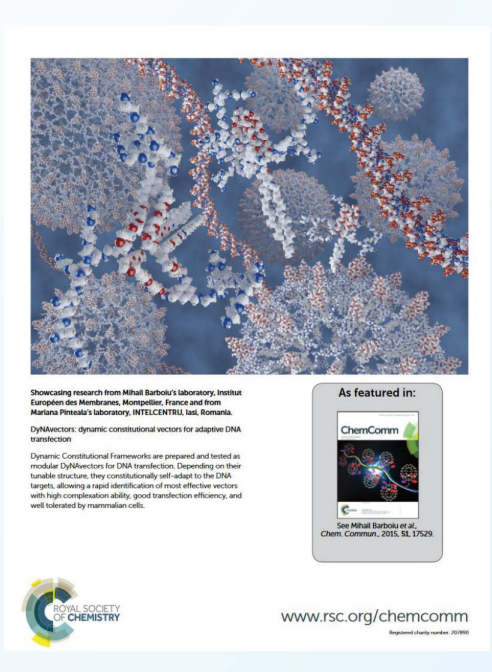
- *Constitutional Systems for DNA Transfection and Drug Delivery*

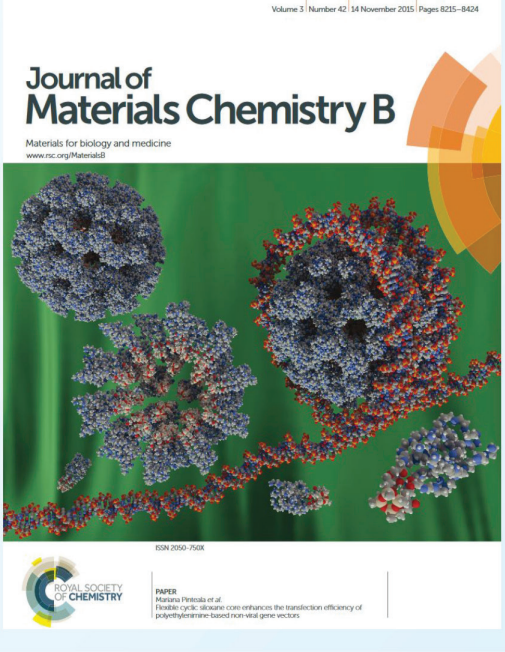
Dynamic Constitutional Framework (DCF) is a rapid screening method for obtaining a large library of compounds with desired properties, such as non-viral nanometric vectors capable of storing DNA and transporting it to the desired cells. Therefore, „libraries" of non-viral vectors were obtained by reversible covalent bonds, using a core (benzene-tricarboxialdehyde, squalene, fullerene, siloxane, polyrotaxanes and ß-cyclodextrin) modified with PEG and branched PEI in order to achieve DCFs for DNA packing and cell recognition. The components and their ratio in DCFs have been optimized to create the most efficient non-viral vectors.

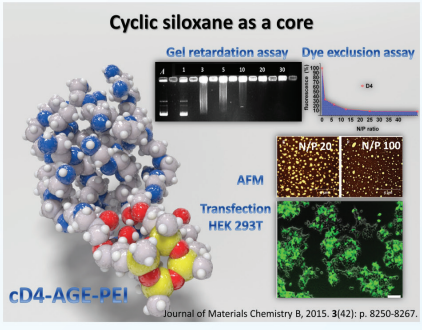


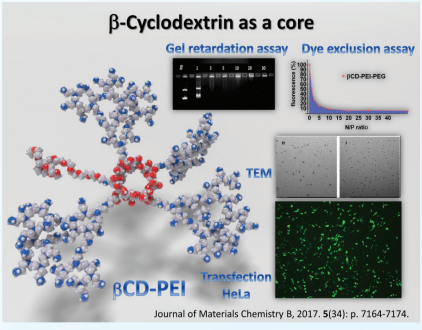


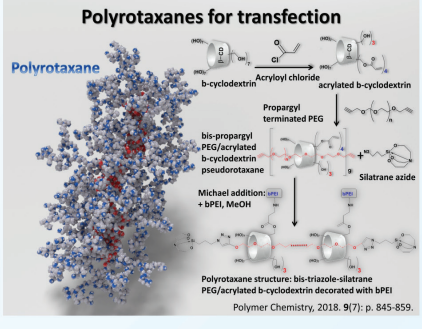

Volume 13 | Number 34 | 14 September 2015 | Pages 8949–9142
Organic & Biomolecular Chemistry
www.rsc.org/obc
ISSN 1477-0520
ROYAL SOCIETY OF CHEMISTRY
PAPER
Mihail Barboiu et al.
Dynamic constitutional frameworks (DCFs) as nanovectors for cellular delivery of DNA
Showcasing collaborative research from Mihail Barboiu's laboratory, Adaptive Supramolecular Nanosystems, Institut European des Membranes, Montpellier, France and Mariana Pinteala's laboratory, INTELCENTRU, "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania.
Title: Hybrid fullerene conjugates as vectors for DNA cell-delivery
C60-PEI and C60-PEG-PEI conjugates act as efficient binders of double stranded DNA (dsDNA) polyplexes that exhibit good transfection efficiency and are performant in terms of expression of EYFP reporter gene in cultured cells and exhibited high cytocompatibility, determining cell proliferation up to 200%.
As featured in:
See Mihail Barboiu et al., J. Mater. Chem. B, 2015, 3, 2433.
ROYAL SOCIETY OF CHEMISTRY
www.rsc.org/MaterialsB

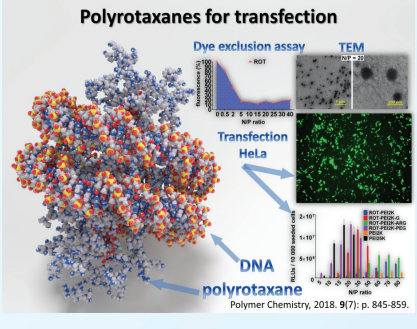

Showcasing research from Mihail Barboiu's laboratory, Institut Europeen des Membranes, Montpellier, France and from Mariana Pinteala's laboratory, INTELCENTRU, Iasi, Romania.
DyNAvectors: dynamic constitutional vectors for adaptive DNA transfection
Dynamic Constitutional Frameworks are prepared and tested as modular DyNAvectors for DNA transfection. Depending on their tunable structure, they constitutionally self-adapt to the DNA targets, allowing a rapid identification of most effective vectors with high complexation ability, good transfection efficiency, and well tolerated by mammalian cells.
As featured in:
ChemComm
See Mihail Barboiu et al., Chem. Commun., 2015, 51, 17529.
ROYAL SOCIETY OF CHEMISTRY
www.rsc.org/chemcomm


Volume 3 | Number 42 | 14 November 2015 | Pages 8215–8424
Journal of Materials Chemistry B
Materials for biology and medicine
www.rsc.org/MaterialsB
ISSN 2050-750X
ROYAL SOCIETY OF CHEMISTRY
PAPER
Mariana Pinteala et al.
Flexible cyclic siloxane core enhances the transfection efficiency of polyethylenimine-based non-viral gene vectors



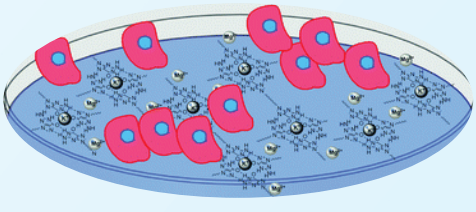


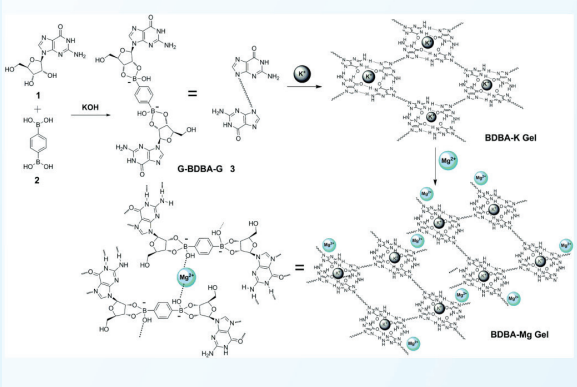


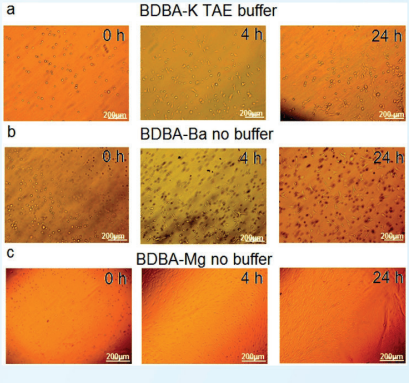


- Dynameric Networks and Gels for Delivery, Cell Recognition and Cell Growth

Functional G-quartet hydrogels were obtained based on natural guanosine and benzene-1,4-diboronic acid and Mg2+, which support cell growth without any visible signs of gel degradation.

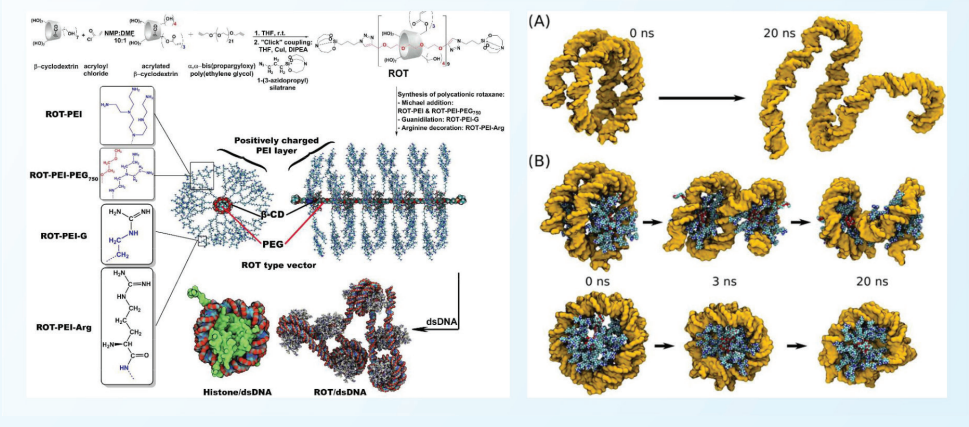






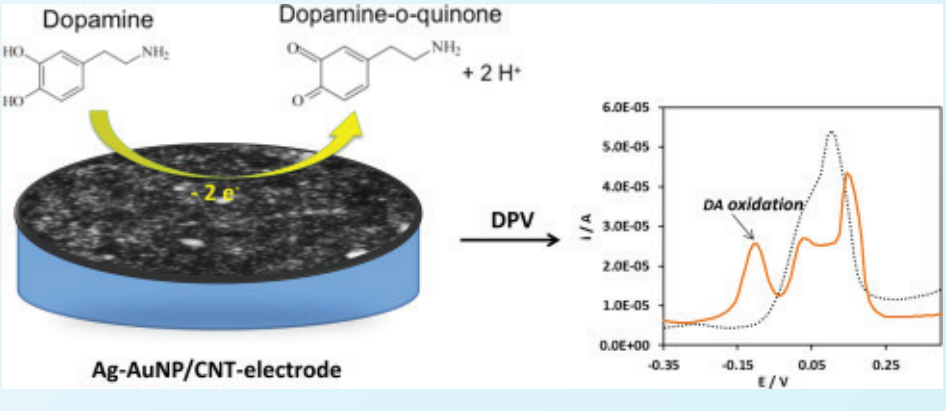
- Modelling and Theoretical Chemistry of Constitutional Systems

In silico chemical modelling of constitutional systems was performed in order to evaluate the conformational changes of dsDNA during its complexation/compaction with different non-viral vectors.



- Electrochemical Sensors

The development and optimization of an electrochemical process for synthesis of bimetallic silver-gold nanoparticles was performed in respect with their efficiency for oxidation of dopamine. Electrochemical methods confer the ability to control the formation of nanoparticles at the very early stage of growth, which is essential for tailoring their properties such size, composition and redox activity, reflected then in the electrocatalytic effect toward dopamine neurotransmitter oxidation. Considering the physiological and pathological implications of dopamine, the development of a sensor for accurate and selective determination of this neurotransmitter at low levels characteristic for living system can bring a great contribution to disease diagnosis.



PROJECT 2. POLYMER AND BIOPOLYMER MATERIALS. MODIFICATION, DEGRADATION, STABILIZATION

PROJECT DIRECTOR: DR. DAN ROȘU

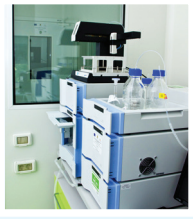
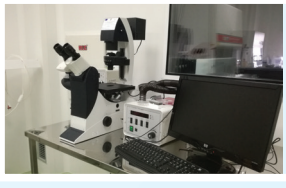
- Polymer and biopolymer materials. Modification, degradation, stabilization
- Biocomposite materials based on synthetic polymers/biopolymers
- Kinetics of crosslinking processes
- Thermal behaviour of polymers and polymer mixtures
- Photochemical behaviour and photodegradation of polymer materials.

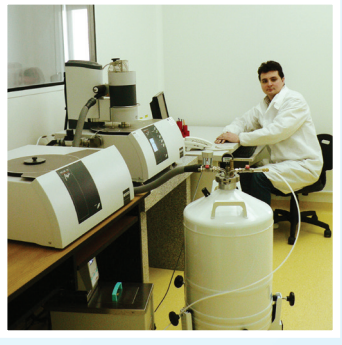
IMPORTANT RESULTS

- Preparation of biocomposite materials based on synthetic polymers / biopolymers
- Physico-chemical and structural characterization
- Stabilization of composite materials, synthetic polymers/biopolymers with coatings from natural resources
- Monitoring the behaviour of polymeric/biopolymer systems under thermal degradation conditions
- Establish specific mechanisms and kinetics of thermal degradation reactions
- Study of the stability of light and/or UV radiation depending on the irradiation dose, the wavelength and the photostabilizer
- Testing the resistance to microbiological attack of polymeric materials based on polymers/biopolymers

INFRASTRUCTURE

IntelCentre **Department**	**Facilities**	**Equipments**
Chemical Synthesis and Biosynthesis Department	Three fully equipped laboratories with specific equipment for organic and macromolecular synthesis at micro-, mini- and large-scale; synthesis monitoring and instrumental control.	Particle size and Zeta potential measurements by DLS - DelsaNano C analyser coupled with an Autotitrator module 

		Flexar HPLC system, Perkin Elmer 
Tissue Engineering and Non-viral Gene Department	Four fully equipped laboratories as ISO 7 and ISO 8 level clean rooms; - low temperatures storage equipment (-45, -86, -150 ^{0}C); - ultrapure water preparing system; - microbiological hoods; - freeze-dryer; - gas systems for N_2, O_2, CO_2, Ar, compressed dry air; - class II, type A biosafety cabinets working within an ISO 7 level clean room; - class III biosafety cabinet with N_2 and CO_2 controlled atmosphere; sterilization systems; - autoclaves for cell culture destruction at the end of experiments	DMI3000 B inverted microscope with incubation system, Leica Microsystems  DS-11 + Nanodrop Spectrophotometer, DeNovix 
Molecular Modelling Department	The cluster contains 9 servers Dell PowerEdge R510, each of them in configuration: - 9 Intel Xeon Processor E5645 (2 CPU; 6 cores, 2.4 GHz); - 8 GB RAM in each server; - 10x 300GB SAS 15K hard drives configured in 2 x 300GB in RAID1 the rest for storage.	Gaussian 09 version with TCP Linda Single Machine. Open source software applications (GROMACS v4.5.4, GAMESS) 
Instrumental analysis, scientific imaging and electrochemical characterization Department	The highly sensitive equipment are working in ISO 6 and ISO 7 level clean rooms; - an extended gas delivery system ensures the necessary volumes of N_2, O_2, CO_2, Ar at precise regulated parameters;	Axis Nova XPS Spectrophotometer, Kratos Analytical 

	- antivibration tables are used to sustain SEM, AFM and Raman confocal microscopes; - all rooms are connected to a HVAC (heating, ventilation, air conditioning) system, doubled by a high flow air filtering unit; - in all rooms the air composition is monitored, to prevent toxicants accumulation and explosion; - non-hazardous avoiding systems are used in investigation laboratories.	Simultaneous TG/DTG/DSC thermal analysis system STA 449 F1 Jupiter, Netzsch DSC system 200 F3 Maia, Netzsch 
	LVEM5 Benchtop Electron Microscope (TEM, STEM, SEM, ED), Delong America Inc.	
	- FluoroMax-4 spectrofluorometer, HORIBA	
	- NT-MDT NTEGRA Spectra AFM coupled with Raman confocal microscope, Renishaw	
	- LAMBDA 35 UV/Vis System, Perkin Elmer - LEICA EM CPD300 Automated Critical Point Dryer, Leica Microsystems	
	- Chirascan™ CD Spectrometer (Applied Photophysics Limited, UK) - AUTOLAB PGSTAT302N (ECO CHEMIE Utrecht, The Netherlands	

REPRESENTATIVE PROJECTS

- ***SUPRACHEM LAB*** - Laboratory of supramolecular chemistry for adaptive delivery systems - a ERA chair initiative (Horizon 2020 WIDESPREAD 2-2014: ERA Chairs, nr. 667387) – ERA CHAIR - Prof. Emeritus Marc J. M. ABADIE, Coordinators - Dr. Mariana PINTEALĂ / Dr. Teodora RUSU - The objective of the SupraChem Lab Project is to unlock and foster excellent research in PPIMC IntelCentre by setting up a strong research group in the field of hybrid materials for adaptive self-organized supramolecular structures. http://www.intelcentru.ro/suprachem_lab/
- ***5D-nanoP*** - Mimicking living matter mechanisms by five-dimensional chemistry (PN-III-P4-ID-PCCF-2016-0050) – Coordinator Prof. Aatto LAAKSONEN. The objective of the 5D-nanoP project is to contribute to the emerging field of biomimetics, by supramolecular chemistry advanced approaches, in a strong multi- and inter-disciplinary context. As main objective, the project intends to develop a strategy to synthesize and test (macro)molecular entities of dynamic (re)organizing type, able to act as nanoplatforms of biologic and biomedical relevance. http://www.intelcentru.ro/5D-nanoP/ro /index.php
- ***POCPOLIG*** - New porous coordinating polymers with variable dimensions organic ligands for gas storage (POC E; P_37_707/31.08.2016) – Coordinator - Dr. Vasile LOZAN, Project Manager - Dr. Narcisa Laura MARANGOCI - The objective of the project is to increase the capacity and quality of the research and innovation development activity by attracting specialists with advanced skills, opening a new research direction in the field of metal-organic networks (MOF) and diversifying the range of research services and transferring them to industrial partners, in order to stimulate the competitiveness of the Romanian scientific research at European level and of the national/regional economic competitiveness of the Institute and of the economic actors in the field of intelligent specialization of eco-nano-technologies and advanced materials. http://pocpolig.icmpp.ro/
- ***Biologically Inspired Systems for Engineered Structural and Functional Entities*** (PN-II-ID-PCCE-2011-2-0028) – Coordinator - Dr. Mariana PINTEALĂ The objective of the project is to feature the nano-entities with at least the following parameters: (i) the general structure of a polyplex, either stable or dynamic modular as composition, (ii) the functionality of a cargo-complex that chemomimic the histones, morphomimic the nucleosome, and biomimic virus like gene vectors, (iii) the ability to include or to reversibly bind and transport (bio)chemical species necessary to assist the nucleic acids during their extracellular transport and intracellular trafficking, and (iv) the ability to physical-chemical associate to artificial extracellular matrices, in order to generate delivery systems with transfection abilities, for *ex vivo* applications. http://www.intelcentru.ro/Biomimetics_ PCCE/ro/index.html

REPRESENTATIVE PUBLICATIONS

- A. L. Lungoci, I.A. Turin-Moleavin, A. Corciova, C. Mircea, A. Arvinte, A. Fifere, N.L. Marangoci, M. Pinteala, Multifunctional magnetic cargo-complexes with

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- L.G. Bahrin, L. Clima, S. Shova, I. Rosca, C. Cojocaru, D. Bejan, M.C. Sardaru, N. Marangoci, V. Lozan, A. Rotaru, Synthesis, structure, computational modeling, and biological activity of two novel bimesitylene derivatives, *Research on Chemical Intermediates* 45, 453, 2019
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LABORATORY 2

POLYADDITION AND PHOTOCHEMISTRY

HEAD OF LABORATORY: DR. TINCA BURUIANĂ, SR I

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- Mihaela GHEORGHIU, A1/technician

GENERAL TOPIC: INNOVATIVE POLYMERIC MATERIALS, HYBRID NANOCOMPOSITES AND FUNCTIONALIZED NANOSTRUCTURES

The research activity of the **Polyaddition and Photochemistry Laboratory** is mainly focused on chemical synthesis, with the following directions:

- Synthesis of new functional monomers for polymers, photopolymers, copolymers, block copolymers and hybrid nanocomposites for applications in optics, catalysis, or biomedical field
- Obtaining of polymeric materials using different photopolymerization techniques, microwave-assisted polymerization, ATRP/RAFT, etc.
- Preparation of new polymers for membranes through the reactions of maleimide groups with suitable reactants, functionalization of some synthetic polymers by "click" chemistry or chemical modification by thermoreversible reactions
- Preparation of self-healing composite membranes based on (bis)maleimide-monomers and nanocomposite membranes based on synthetic polymers and inorganic fillers with gas permselectivity
- Development of polyurethane materials and high performance polymer composites by using of renewable materials/vegetable materials; achievement of materials with superior properties based on polyurethane hydrogels for bioapplications.

PROJECT 1. POLYMERIC MATERIALS AND HYBRID NANOCOMPOSITES BASED ON NEW MONOMERS AND COMBINATIONS OF NANOPARTICLES

PROJECT DIRECTOR: DR. TINCA BURUIANA

- Organic synthesis/polymers/polymer nanocomposites of polyurethane acrylates, polyurethane ionomers, acrylic/urethane-acrylic copolymers and block copolymers class
- Urethane acrylic monomers/oligomers and modified acrylate copolymers; photopolymers with variable structure/composition
- Obtaining of inorganic nanoparticles (metals, metal oxides)
- Structural and morphological characterizations
- Photochemistry studies in solution/polymeric films, testing in targeted applications.

IMPORTANT RESULTS

- Obtaining of acrylic and urethane acrylic (silyl-urethane) monomers employed in the achievement of photopolymers, copolymers, block copolymers and tridimensional polymeric networks

- Photochemical behaviour studies in solutions and polymeric films under UV/Vis irradiation or under laser pulses (femtoseconds)
- Obtaining of polymer/inorganic nanoparticles (Au, Ag, ZnO, TiO2, graphene) hybrid composites
- Testing of urethane oligomers and modified acrylic copolymers in the attaining of adhesives and dental composites, thin polymer films, fluorescent sensors
- Realization of scaffold for cell growth using biphotonic polymerization (2PP) of some urethane/silyl-urethane monomers
- Testing of hybrid composites in photocatalysis, antimicrobial coatings

PROJECT 2. POLYMERIC (NANO)MATERIALS FOR MULTIFUNCTIONAL MEMBRANES WITH TARGETED SELECTIVITY

PROJECT DIRECTOR: DR. GAINA CONSTANTIN

- Heterocyclic polymers and polymer composites
- Thermostable polyesters, aliphatic copolyamides, micro-/nanometric composites
- Self-healing crosslinked polymers

PROJECT 3. BIOCOMPATIBLE AND BIODEGRADABLE POLYURETANE MATERIALS

PROJECT DIRECTOR: DR. STEFAN OPREA

- Polyurethanes based on renewable raw materials or vegetable materials
- Polyurethane hydrogels with biomedical applications, biopolyurethanes, polyurethanes with ionic metals
- Micro/nanoporous bioactive materials based on polyurethanes
- Spectral, thermal, mechanical characterization and biodegradation studies
- Electrospinning experiments of polymeric solutions

IMPORTANT RESULTS

- Obtaining of new polyurethanes, bioactive polyurethane hydrogels and polymer composites
- Physico-chemical, structural and morphological characterization of polyurethanes
- Evaluation of the stability, biodegradability and biological behaviour for the polymeric materials
- Obtaining of polyurethane nanofibers through electrospinning

INFRASTRUCTURE

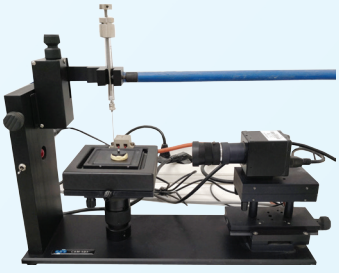
DISCOVER (CEM 500) microwave system - Represents a powerful microwave synthesizer for performing a wide range of organic and inorganic synthetic chemistry reactions. Performs atmospheric (up to 80 mL flask and pressurized 10 mL reactions) and the vials employ easy-to-use snap on caps - no need for crimping tools. Working temperature ranged from ambient to 300 ^{0}C, which can safely be reached in a matter of minutes. Variable speed of the magnetic stirring.

Leica DM 2500M microscope with phase contrast, polarized light, fluorescence and temperature control - The microscope is designed for the analysis of various materials and quality control. Its unique concept combines the intuitive operation with the achieving of high quality images, providing rapid and accurate results. It operates in transmitted light illumination furnished by a halogen lamp. Images are always high-contrast and full of detail. Additionally, the microscope is equipped with fluorescence contrast and temperature Mettler Toledo controller.

Cone Plate Viscometer RM 100 TOUCH CP 2000 - Represents a cone-plate rotating viscometer (with cone included) having rotation speeds between 0.3 and 1500 rpm and torque range from 0.05 to 30 mNm. Temperature can be varied between 5 to 80 ^{0}C through Peltier effect. Measure viscosity with a sample of less than 1 mL. Quick warming and cleaning. Save the measurement protocols directly on the viscometer. Can be connected to a computer or a printer by USB port. External control thanks to the optional VISCO RM software.

Shimadzu AGS-J, 1kN Universal Tester - Generally used for evaluating the mechanical characteristics of various polymeric samples. It displays high precision and reliability in material testing, with forces measured with a precision better than ±1% of indicated values. The digital LED displays show either actual force or stress and either elongation or strain. A large variety of convenient functions can be selected such as automatic detection of specimen breakdown point or automatic force calibration. Appropriate for tensile, compression, 3-point bending and 4-point bending tests.

KSV Cam 200 goniometer **-** The goniometer is equipped with a light source, camera, and flat horizontal support for test slides The CAM 200 device uses drop shape analysis for determining static or dynamic contact angles, absorption and surface or interfacial tensions of liquids. Contact angles on different substrates between 5° and 180° (accuracy 0.1°) and surface tension from 0.01 to 999 mN/m (accuracy 0.01 mN/m) can be accurately obtained after fitting the images with appropriate methods. Special algorithm searches drop profile with sub-pixel accuracy. Automatic baseline detection.



UV illumination chamber SHH-150ZP **-** The illumination chamber is operating at a 380 nm illumination wavelength and a lighting degree of approximately 7000 lx. Can be used for plant, material and drug testing. It can operate continuously and has 2 illumination modes - UV and fluorescence.

Shimadzu EZ Test, 5kN Mechanical Tester **-** The instrument is used to evaluate the mechanical properties of polymeric materials and is characterized by high precision and reliability. It has a digital display based on LED indicating the applied force/stress and samples elongation degree. With a 5 kN maximum capacity, this device is perfect for tensile testing of plastics, being used for testing rubber, polymer films or other materials with long elongation.

REPRESENTATIVE PUBLICATIONS

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- S. Oprea, V.O. Potolinca, V. Oprea, Influence of the hydroquinone ether moieties and Bisphenol A glycerolate diacrylate on the UV stability behavior of new polyurethane materials, J. *Polym*. Res. 25, 79, 2018
- S. Oprea, V.O. Potolinca, Thermomechanical and dielectric properties of novel pyridine-based polyurethane urea elastomers, *J. Elast. Plastics* 50, 276-292, 2018
- S. Oprea, V.O. Potolinca, V. Oprea, Biodegradation of pyridine-based polyether polyurethanes by the Alternaria tenuissima fungus, J. Appl. *Polym. Sci*. 135, 46096, 2018
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- T. Buruiana, V. Melinte, H. Aldea, I.M. Pelin, E.C. Buruiana, A new fluorinated urethane dimethacrylate with carboxylic groups for use in dental adhesive compositions, *Mater. Sci. Eng. C. Mater. Biol. Appl*. 62, 96-104, 2016
- C. Gaina, V. Gaina, D. Ionita, Functional modification of PVA with maleimide compounds, *Polym. Bull*. 73, 2019-2038, 2016
- Y. Mamunya, V. Levchenko, G. Boiteux, G. Seytre, M. Zanoaga, F. Tanasa, E. Lebedev, Controlling morphology, electrical, and mechanical properties of polymer blends by heterogeneous distribution of carbon nanotubes, *Polym. Compos*. 37, 2467-2477, 2016
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- O. Ursache, V. Gaina, C. Gaina, Poly(vinyl alcohol)-inorganic hybrid materials with thermocleavable groups, *Polym. Plast. Technol. Eng.* 52, 546-552, 2013

REPRESENTATIVE PROJECTS

- Conception and achievement of hybrid nanocomposites based on novel polymer structures for biomedical and optical applications in nanotechnology; Project coordinator PN-II-ID: Dr. Emil C. Buruiana; Project value (2011-2016): 1,500,000 lei
- Design and preparation under mild “green” conditions of UV-cured polymer - metal/metal oxide nanoparticles hybrid coatings with predictable antimicrobial or sealing features; Project coordinator TE: Dr. Violeta Melinte; Project value (2018-2020): 450,000 lei
- Hybrid composites based on doped ZnO micro-/nanoparticles for enhanced UV and visible light photocatalysis; Project coordinator PD: Dr. Viorica Elena Podașca; Project value (2018-2020): 250,000 lei
- Novel advanced smart biomaterials of giomer type with applications in

dentistry; Contact person: Dr. Tinca Buruiana; Project value (2012-2016): 600,000 lei

- Electrically stimulated three-dimensional structures for tissue engineering; Contact person: Dr. Emil Buruiana; Project value (2012-2014): 70,454 Euro
- Direct laser writing of polymer - graphene composites; Contact person: Dr. Tinca Buruiana; Project value (2012-2015): 90,909 Euro
- Composite structures made of biopolyurethane matrix resins synthesized from vegetable oils reinforced with liberian fibers; Partner responsible: Dr. S. Oprea; Project value (2012-2016): 700,000 lei
- BIOactive highly porous and injectable Scaffolds controlling stem cell recruitment, proliferation and differentiation and enabling angiogenesis for Cardiovascular ENgineered Tissues (BIOSCENT-FP7); Contact person: Dr. C. Ciobanu; Project value (2009-2013): 209,600 Euro

LABORATORY 3

POLYCONDENSATION AND THERMOSTABLE POLYMERS

HEAD OF LABORATORY: DR. HABIL. CORNELIU HAMCIUC

TEAM

- Dr. habil. Corneliu HAMCIUC, SR I, chamciuc@icmpp.ro, chemical engineer
- Dr. Maria BRUMĂ, SR I, mbruma@icmpp.ro, chemist
- Dr. Ion SAVA, SR I, isava@icmpp.ro, chemical engineer
- Dr. habil. Mariana-Dana DĂMĂCEANU, SR II, damaceanu@icmpp.ro, chemist
- Dr. habil. Luminița MARIN, SR II, lmarin@icmpp.ro, chemist
- Dr. Elena HAMCIUC, SR II, ehamciuc@icmpp.ro, chemical engineer
- Dr. Camelia HULUBEI, SR II, hulubei@icmpp.ro, chemical engineer
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- Alexandru ANISIEI, Master student, anisiei.alexandru@icmpp.ro, chemist
- Iulian BERLADEAN, Master student, iulian.berladean@gmail.com, chemical engineer

GENERAL TOPIC /RESEARCH FIELDS

The research activity carried out within the laboratory is focused on the synthesis and characterization of heterocyclic/heterochain polymers and modified natural polymers with the aim to obtain advanced materials with high performance properties for specific applications.

The laboratory has expertise in:

- Organic compounds functionalized with suitable building blocks for applying as sensors, actuators, solar cells, opto-electronic devices, membranes for gas separation
- Flame retardant phosphorus-containing organic compounds with potential applications in increasing the flame resistance of traditional polymeric materials
- Polymeric nanocomposite materials with special properties: electrical, optical and magnetic
- Biopolymers and materials based thereon for bio-applications.

The principal concern of the laboratory is to transfer the accumulated skills and experience to the production of materials and devices based on polymers impacting the economic sector, namely materials for micro- and nanoelectronics, medicine, gas and liquid separation technologies, environmental protection, alternative energy resources, as well as flame resistance materials with improved properties.

The laboratory consists of three research groups focused on three projects and comprises a total of 28 members.

PROJECT 1. HIGH PERFORMANCE HETEROCYCLIC POLYMERS FOR THIN FILMS, SEPARATION MEMBRANES, COMPOSITES AND PROTECTING COATINGS

PROJECT DIRECTOR: DR. HABIL. MARIANA-DANA DAMACEANU

The Project team consists of 3 experienced researchers (2 SR I, 1 SR II), 4 young postdoctoral researchers (1 SR III, 2 SR, 1 YR), 2 PhD students and 1 Master student, all creative and competitive, with strong knowledge in the field of

low-molecular compounds and aromatic and heteroaromatic polymers for advanced applications. The group aims mainly at developing innovative materials by addressing new structural concepts and proving through high-tech scientific methods the reported characteristics and the applicative potential that constantly meets the contemporary technological requirements.

MAIN ACTIVITIES

- Fine organic synthesis of heterocyclic compounds
- Synthesis of heterocyclic oligomers and polymers
- Preparation of free-standing films (foils) and coatings on various supports
- Preparation of composite materials
- Study of physicochemical properties of monomers and polymers
- Characterization of materials

IMPORTANT RESULTS

- **Polyimide materials for applications in electronics and optoelectronics:** developing porous polyimide materials with a dielectric constant < 2.5 and polymers with different degrees of polarity, with low / high dielectric constants for use as dielectric layers in capacitors or various electronic and optoelectronic devices.
- **Semiconducting materials:** developing oligomers or polymers containing various aromatic/heteroaromatic moieties, such as thiophene, imide, phenoxazine, triphenylamine etc. with electrical charge transporting capability for use in field-effect organic transistors (OFETs) or memory devices.
- **Development of new active materials for electroluminescent devices** with high efficiency by combining multiple luminophores in the same molecular architecture or by generating light emission from the intramolecular charge transfer complex with the aim to vary the color of the emitted light.
- **Developing flexible and transparent polymeric supports for plastic electronics.**
- **Membranes based on thermostable heterocyclic polymers for the separation of hot gases:** CO_2 capture and H_2 separation from the gas mixtures resulted from combustion or industrial processes; new PIM type polymer architectures based on polyimides or other heterocyclic polymers such as polyoxadiazoles or polybenzoxazoles.
- **Materials based on low molecular or macromolecular heterocyclic compounds for alternative energies applications:** synthesis of oligomers containing aromatic/heteroaromatic units such as phenoxazine, peryleneimide, thiophene or triphenylamine for use in dyes-sensitized solar cells (DSSCs) and of polymers with „p-n" heterojunction for use in polymeric solar cells; developing membranes based on sulfonated polymers of various

structures (polynaphthylimides, polybenzimidazoles) for fuel cells.

- **Heterocyclic polymers for biomedical applications:** biocompatible and/or biodegradable polymers functionalized with various heterocycles as active principles for controlled release systems; polyimide supports for cell growth usable in biomedical implants.
- **The development of aromatic and heteroaromatic polymers for application in sensors and „micro-array" platforms.**
- **The development of smart materials based on heterocyclic polymers with chromic response to external stimuli:** photochromic polymers with azo groups, electrochromic polymers, ionochromic or halochromic polymers.
- **Obtaining heterocyclic polymers by electrochemical polymerization:** electrochemical polymerization of some heterocyclic monomers in order to obtain polymeric films with a completely or partially conjugated structure for electronic and optoelectronic applications.

PROJECT 2. MULTIFUNCTIONAL COMPOUNDS AND HETEROCATENAR POLYMERS WITH LIQUID CRYSTAL CHARACTERISTICS OR BIOLOGICAL PROPERTIES. HYBRID COMPOSITE MATERIALS BASED ON THEM
PROJECT DIRECTOR: DR. HABIL. LUMINITA MARIN

The project team consists of eleven members. It is a quite young and enthusiastic group, with the average age of 35 years, with various professional degrees, from Senior Scientist II to Master students. While the primary scientific interest of the group was mainly focused on the synthesis and characterization of new polysulfones and thermotropic liquid crystals based on azomethine linkage, the scientific expertise of the group continuously evolved in line with the new requirements of the contemporary world.

IMPORTANT RESULTS

I. Eco-materials based on chitosan. This research direction meets the new eco-design requirements of the contemporary world, in accordance with the new directives of the European Commission, which aims to protect non-renewable resources and prevent pollution. In this respect, the group develops chitosan-based organic materials, a linear polysaccharide derived from abundant renewable resources (e.g. crustaceans, insects, fungi and seaweed), which has superior bioactive properties, being safe for consumers and low cost.

- **I.1. Chitosan based hydrogels** with controlled properties under the synthetic conditions. Biocompatible hydrogels are synthesized, suitable for *in vivo* applications (controlled drug release systems, scaffolds for tissue regeneration): with antifungal activity, luminescent hydrogels as metal chemosensors, superabsorbent hydrogels for application as soil conditioners and hygiene products, chiral hydrogels for enantiomeric separation.

- **I.2. Nanoporous imino-chitosan fibers.** The fibers are obtained by electrospinning and are further functionalized with different bioactive agents, function on the targeted application: antifungal materials for wound healing, especially for the treatment of burns, controlled drug delivery systems, luminescent chemosensors, capture and sequestration of CO_2 in the atmosphere.
- **I.3. Imino-chitosan films.** Obtaining imino-chitosan films with high conversion degree of the amine groups of chitosan in imine units. Due to the reversible character of the imine units, the films have dynamic properties, which are activated in a humid environment.

II. Phenothiazine based materials for opto-electronic applications. This research direction is dedicated to the obtaining of materials with efficient light emission in solid state, for organic light emission diodes (OLEDs). It consists in design and synthesis of new compounds and their materials preparation.

- **II.1. Synthesis of low molecular weight compounds with aggregation induced emission (AIE),** based on phenothiazine and heavy halogen atoms, with a RIR (restricted intramolecular rotation) design.
- **II.2. Grow of single crystals.** Experience in growing single crystals, important aspect in understanding the structure/properties relationship, for the development of materials with increased efficiency.
- **II.3. Preparation of nanocrystals.** Preparation of nanocrystals by the reprecipitation method, solvent induced phase separation, temperature induced phase separation, emulsion phase separation. The materials obtained are appropriate for application as OLEDs or bio-applications.
- **II.4. Grow of cocrystals** based on the synthetized compounds. In order to enhance the luminescent properties, the synthetized compounds are grown in form of cocrystals, as single crystals and films.
- **II.5. Preparation of luminescent nano- and microfibers** from small molecular compounds by reprecipitation method.

III. Liquids crystals

- **III.1.Synthesis of new liquid crystals.** Our group has experience in synthesis and characterization of liquid crystalline compounds. Therefore, the main concern is directed to the synthesis of new liquid crystals with luminescent mesogens and the improvement of their opto-electronic properties by controlling the ordering degree of the films manufactured from the mesophase state.
- **III.2. Preparation of liquid crystal composite systems dispersed in polymeric matrices (PDLC).** This direction is aimed to the preparation of new PDLC systems for bio-applications, using as matrix biopolymers or biocompatible synthetic polymers: chitosan, polyvinyl borate, polysulfone.

IV. Non-viral vectors for DNA transfection. Synthesis of non-viral vectors based on imine bonds, with dendrimeric structures, obtained by dynamic covalent chemistry.

PPROJECT 3. FUNCTIONAL POLYMERS CONTAINING PHOSPHORUS OR NITROGEN IN THE MAIN CHAIN AND/ OR IN THE SIDE CHAIN FOR APPLICATIONS IN INDUSTRY, MEDICINE OR ENVIRONMENTAL PROTECTION

PROJECT DIRECTOR: DR. HABIL. CORNELIU HAMCIUC

The team of the project consists of 7 members (1 SRI, 2 SRII, 1 SRIII, 1 SR, 2 YR) and aims to obtain multifunctional polymeric materials with applications in high performance technologies. The research aims at the development of heterocyclic/heterochain polymers containing phosphorus and/or nitrogen atoms, with potential uses in the biomedical field or in the production of flame retardant materials as well as polymeric composites/nanocomposites with thermal, electrical, magnetic and optical properties.

IMPORTANT RESULTS

I. Flame retardant systems containing phosphorus

- **I.1. Functional polymers: polyesters, polyphosphates and polyphosphonates,** having phosphorus and/or nitrogen atoms in the main chain, respectively in the side chain, with flame resistance, high thermal stability and/or liquid crystal properties. The aim is to obtain polymers with high phosphorus content and low toxicity to the environment, for use as flame retardants with increased efficiency in increasing the flame resistance of traditional polymers.
- **I.2. Epoxy resins containing polymers with phosphorus,** preserving initial resin performance and improved fire resistance, with potential uses as adhesives, coatings, polymeric materials for electronics and electrotechnics.

II. Biomedical systems with complex structures

- **II.1. Polymeric nanofibres membranes** (obtained through electrofilation process) with applicative potential in the cutting edge areas of modern technology.
- **II.2. Hydrogels** for controlled drug release systems. New systems are envisaged using biodegradable polymers as organic component (polyvinyl alcohol, pullulan, polyvinylpyrrolidone, polyphosphazenes etc.) and zeolite as inorganic material. The effect of polymer type as well as the proportion and combination of components on the effectiveness of incorporation, release rate and drug release kinetics are studied.
- **II.3. Polymer composite materials for biomedical applications.** Polymeric composites with improved antimicrobial activity and low cytotoxicity by incorporating zeolite containing silver ions into a biocompatible organic matrix are developed.

III. Materials for micro- and optoelectronics

- **III.1. Polymer composites and nanocomposites** based on inorganic compounds (silica, zeolites, barium titanate, barium and titanium oxides, titanium dioxide nanotubes, carbon nanotubes) with electroactive properties, low/high dielectric constant, for capacitors, actuators or systems to produce energy.
- **III.2. Polymers with photoluminescent properties** based on nitrogen-containing heterocycles, showing fluorescence in the blue range, excellent thermal and mechanical properties, chemical stability and high glass transition temperatures.
- **III.3. Imidic polymers of partially alicyclic structure,** processable in flexible and transparent films, with varying refractive indices and/or dielectric constant specific to the application.

INFRASTRUCTURE

Polarized light microscope

- sistem temperature controlled system in the range 25- 400 ^{0}C
- magnifications 4 ×, 20 ×, 40 ×
- lenses for adjusting the polarization of the light
- automatic image capture system

Electrochemical system (potentiostat - galvanostat)

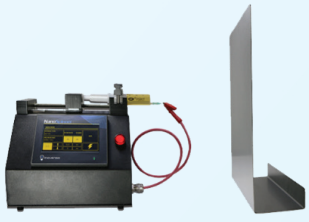
- electrochemical cell with 5-nack cap
- reference electrode: SCE, Ag/Ag+
- potential range: -2V ÷ +2V
- scanning rate: 1 μV/s - 1V/s
- minimum pulse duration: 125 μs

Labconco freeze dryer FreeZone Freeze Dry System

Freeze drying system for aqueous samples, under pressure. It is equipped with digital display and is acid resistant. Minimum pressure: 0.01 mbar. It is particularly suitable for lyophilization of hydrogels.

Electrospinning system NS Starter Kit Inovenso

The system is dedicated to preparation of nanofibers at small-scale. It has a compact configuration, and offers the possibility of controlling the collection distance, flow rate and applied voltage.



Glove Box System

System for conducting experiments in a controlled inert atmosphere, of high purity. It is provided with a cooling chamber at -20 ^{0}C, two transfer chambers, two glove ports, fluorescent and UV germicidal lamps and a microprocessor control system with display for controlling the working and handling parameters.

REPREZENTATIVE PROJECTS

- **Dye-sensitized solar cells by molecular engineering of phenoxazine- or phenothiazine-based sensitizers,** acronym EngDSSC; Code: PN-III-P2-2.1-PED-2016-0510, Ctr. 59PED/2017, Project Director: M.-D. Damaceanu; Budget: 600000 lei.

EngDSSC project fully addressed the main objective - Secure, Clean and Efficient Energy of ENERGY Theme in Horizon 2020. In this multidisciplinary project, related to the solar energy conversion, two partners worked on the development of dye-sensitized solar cell (DSSC) based on organic dyes. The aim of the project was to obtain a competitive DSSC prototype by molecular engineering of new sensitizers. In this project, besides the synthesis of new sensitizers, the cell design and the prototype manufacturing technology were developed. The new sensitizers combined some structural features such as: a phenothiazine- or phenoxazine-substituted triarylamine as donor moiety, a π-linker, and the cyanoacrylic acid used as both anchoring group and electron acceptor. Further, the synthesized compounds were structurally characterized and investigated in detail with respect to the thermal, optical and electrochemical properties. Based on the obtained results, structure-property relations were established, DSSC testing conditions were selected and DSSC prototype technology was developed, thus reaching the technological maturity level TRL4.

- **Smart materials with versatile chromic response to external stimuli developed by macromolecular engineering,** acronym SMARTCrom; Code:PN-III-P4-ID-PCE-2016-0708, Ctr 66/2017, Project Director: Dr. M.-D. Damaceanu; Budget: 850000 lei.

Subscribing to HORIZON 2020 «Innovation» area, SMARTCrom project aims at working on a multidisciplinary and extremely new topic – smart materials by introducing the «smart» concept in the field of heterocyclic polymers. The basic project idea is the development of smart materials with chromic response to

external stimuli, such as electrical potential, metal ions, or light radiation. The heterocyclic polymers will be mainly high performance polyimides that will be modified as to carry various receptors. The new macromolecular architectures will include an optimum combination of heteroaromatic, aromatic or aliphatic units in the same structural unit of the polymer receptor, so as to provide the desired chromic response to a particular stimulus, or even to more stimuli.

- **Chitosan based hydrogels as luminescent chemosensors for detection and removal of heavy metals;** Romanian-Chinese bilateral Project: PN-III-P3-3.1-PM-RO-CN-2018-0098, Project Director: L. Marin

The main objective of the project is to obtain luminescent chemosensors with ecological design, based on luminescent hydrogels. This research topic comes to meet the need for materials originating from renewable resources to ensure a friendlier environment. The necessity of building such sensors is argued by the increasing contamination with heavy metal pollutants along with technological development, which prompted the European and Asian organizations for protection of Health and Environment to include them as priority substances to be monitored. To achieve this objective, the two team work together sharing knowledge from complementary areas: synthesis of luminescent hydrogels with ecological design (Romanian team) and investigation and optimization of their properties in order to make luminescent chemosensors (Chinese team). Luminescent hydrogels are synthesized from renewable materials, chitosan and natural aldehydes, based on a hydrogelation method developed in our group.

- **Hybrid visible light communications and augmented reality platform for the development of smart driver assistance and vehicle active safety systems;** PN-III-P1-1.2-PCCDI-2017-0917, 2018-2020, Project Director ICMPP: L. Marin.

The project aims to develop a hybrid visible light comunication and augumented reality platform for smart driver assistance and vehicle active safety systems. The project ideea started from the necesisity of improving the safe and efficiency of transportation on the Romanian roads, taking into consideration than over 1.3 milions of beings per year are vulnerable to road accidents. To achieve this goal, 7 institutions of excellence in the country, with complementary expertise and geographically positioned in 5 different development regions are employed. The specific objective of the ICMPP partner is to develop new OLED devices, with improved switching speed to make them suitable for use in visible light communication systems.

- **Phosphorous-containing polymers for high performance materials used in advanced technologies and/or biomedical applications.** Contract number: PNII-RU-TE-2012-3-0123, Project Director: Dr. Diana Serbezanu; Period: 2013-2016; Value: 615833 lei.

The main goal of the project was the development of new polymeric structures containing phosphorus in the main and/or side chain, recommended for applications in the cutting edge fields of modern technology and nanotechnology (electronics and optoelectronics) as well as biomedicine (biosensors, controlled drug release, tissue engineering). The structure of the polymers led to products with high thermal stability, good solubility, wide range between glass transition

temperature and thermal decomposition temperature, ability to form films, exceptional physical-mechanical properties, liquid crystal behavior, optical properties, flame resistance, biodegradability, biocompatibility, etc.

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LABORATORY 4

FUNCTIONAL POLYMERS

HEAD OF LABORATORY: DR. HABIL. MARCELA MIHAI

TEAM

- Dr. Marcela MIHAI/marcelas@icmpp.ro/SR II/
Multicomponent complex systems based on synthetic and natural polymers: polyelectrolyte complexes, multilayers, composites with $CaCO_3$
- Dr. Ecaterina Stela DRĂGAN/SR I/sdragan@icmpp.ro/
Synthesis and characterization of ionic polymers, smart composite hydrogels (cryogels), organic/inorganic ionic hybrids, ion exchangers, applications in controlled drug delivery, separation and environmental protection, surface modification by polyelectrolytes (layer-by-layer) for biomedical applications
- Dr. Maria Valentina DINU /SR II/vdinu@icmpp.ro/
Macro- and nanostructurated multicomponent cross-linked polymeric systems: hydrogels/cryogels synthesized by conventional methods, ice-templating processes and/or leaching techniques, organic sorbents (ion exchangers) and ionic composites, polymer-filled nanoreactors, polymer vesicles
- Dr. Ion BUNIA/SR III/ibunia@icmpp.ro/
Synthesis and characterization of ion exchangers crosslinked with functional groups able for ionic exchange; applications in separations and environment protection
- Dr. Florin BUCĂTARIU/SR III/fbucatariu@icmpp.ro/
Organic / inorganic composites obtained by layer-by-layer deposition of synthetic and natural polyelectrolytes on various solid surfaces
- Dr. Silvia VASILIU/SR/msilvia@icmpp.ro/
Crosslinked systems based on synthetic polymers and polysaccharides: controlled/ sustained drug delivery systems, adsorbents
- Dr. Ștefania RACOVIȚĂ/SR/stefania.racovita@icmpp.ro/
Crosslinked systems based on synthetic polymers and polysaccharides: controlled/ sustained drug delivery systems, adsorbents
- Dr. Claudiu Augustin GHIORGHIȚĂ/SR/claudiu.ghiorghita@icmpp.ro/
Functionalization of solid surfaces with polyelectrolytic multilayers used in the retaining / release of different chemical species

- Dr. Ionel Adrian DINU/SR/adinu@icmpp.ro/
  Stimuli-responsive (co)polymers and amphiphilic block copolymers synthesized by ionic and controlled radical polymerization; chemical modification of polymers by post-polymerization reactions on pre-existing functional groups; polymer-based nanocarriers with stimuli-triggered activit.
- Dr. Maria Marinela LAZĂR/YR/mariperju@icmpp.ro/
  Synthesis, characterization and environmental applications of ionic composite hydrogels based on synthetic and natural polymers
- Dr. Diana Felicia LOGHIN/YR/dfelicia@icmpp.ro/
  Functionalization of starch by grafting or oxidation to obtain corresponding polyanions; preparation of macroporous semi-interpenetrating polymer network composites based on starch or anionically modified starch with applications in controlled drug delivery and environmental protection.
- Dr. Ana Irina COCÂRȚĂ/YR/irina.cocarta@icmpp.ro/
  Synthesis, characterization and applications of hydrogels based on synthetic and natural polymers
- Technical staff: Ioan TEȘCU; Martha MARCU; Angela PELIN

GENERAL TOPIC: SYNTHETIC AND NATURAL IONIC POLYMERS

- Ionic matrices with morphologies and external stimuli responsiveness triggered by the synthesis conditions to adsorb and release in a controlled manner bioactive ionic species such as: enzymes, proteins, drugs, cells, etc.
- Macroporous composite interpenetrating polymer networks based on polysaccharides or their derivatives
- Cross-linked microparticule systems based on synthetic and natural polymers; kinetic studies of loading and release
- Ion exchangers with complexing properties
- Nanostructured composites based on calcium carbonate and linear and / or cross-linked ionic polymers

PROJECT 1: ION MATRIXS SENSITIVE TO EXTERNAL STIMULI, WITH SORPTION / RELEASE PROPERTIES OF BIOACTIVE SPECIES

PROJECT DIRECTOR DR. ECATERINA STELA DRĂGAN

Development of the field regarding the immobilization/release of bioactive ionic species such as: enzymes, proteins, drugs, cells in/from porous matrices responsive to the external stimuli and a systematic research on the synthesis,

properties and specific applications of the porous ionic matrices by:

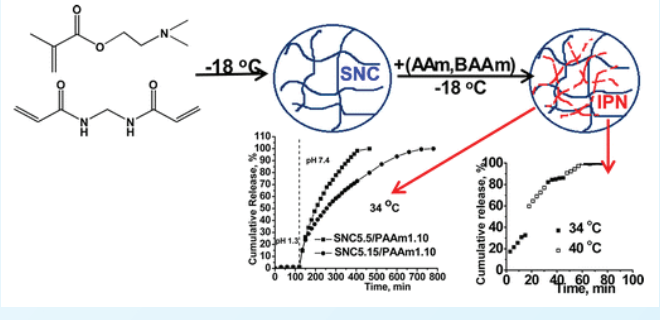
(1) Construction of novel porous matrices, either as thin films, or as macroporous monoliths, with tailored functionalities and porosity;

(2) Study of the specific interactions of the porous matrices with various ionic species to identify their specific biomedical applications.

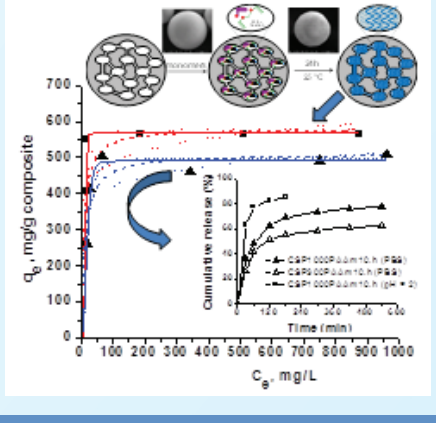
Both the construction of the multilayer films and the synthesis of porous matrices by cryogelation are performed by very flexible and ecofriendly techniques; therefore, they are recommended for the preparation of materials with biomedical applications.

IMPORTANT RESULTS

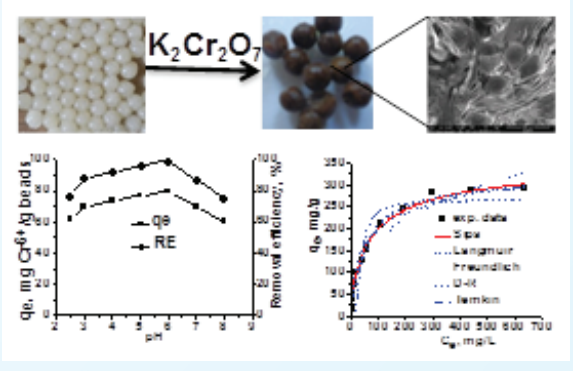
- **Fast responsive macroporous interpenetrating polymer network (IPN) hydrogels fabricated by a sequential strategy.** The 1st network is consisting of poly(N,N-dimethylaminoethyl methacrylate) cross-linked with N,N'-methylenebisacrylamide (BAAm), and the 2nd network is formed by cross-linking of poly(acrylamide) with BAAm, both networks being generated by cryogelation technique. Sorption and release upon/from the SNCs and IPN cryogels of small drugs was triggered by pH, temperature, and ionic strength.



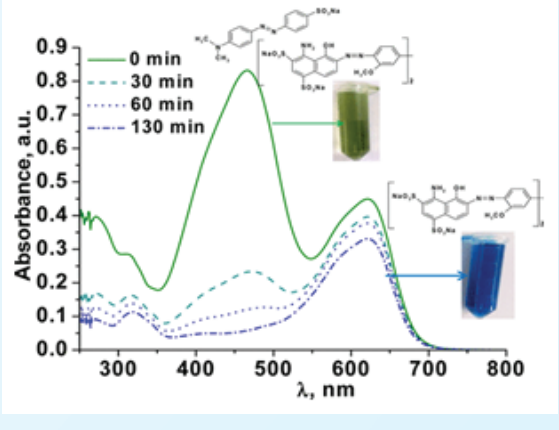
- **Composite sorbents** synthetized by impregnation and cross-linking copolymerization of acrylamide in the pores of Daisogel silica. The obtained composites were efficient in the loading/release of lysozyme as model macromolecular drug.



- **Composite sorbents consisting of chitosan and poly(vinyl amine)**, cross-linked with glutaraldehyde and ethylene glycol diglycidyl ether, designed by uniform dispersion of some microspheres of porous strong base anion exchangers having (vinylbenzyl diethyl 2-hydroxyethyl)ammonium chloride functional groups, and sizes in the range 90-200 μm. Macroporous composites as cryobeads or monoliths were successfully applied to the sorption of Cr(VI).



- **Composite anion exchangers (CANEX)** fabricated by an innovative approach consisting of using silica Daisogel as host for an anion exchanger bearing vinylbenzyl N,N-diethyl 2-hydroxyethyl ammonium moieties. CANEX microspheres were able to selectively capture Methyl Orange, in binary mixtures with either methylene blue, as cationic dye, or Chicago Sky Blue 6B as competing anionic dye.



PPROJECT 2: NANOSTRUCTURED COMPOSITE MATERIALS BASED ON LINEAR AND CROSSLINKED ION POLYMERS

PROJECT DIRECTOR DR. MARCELA MIHAI

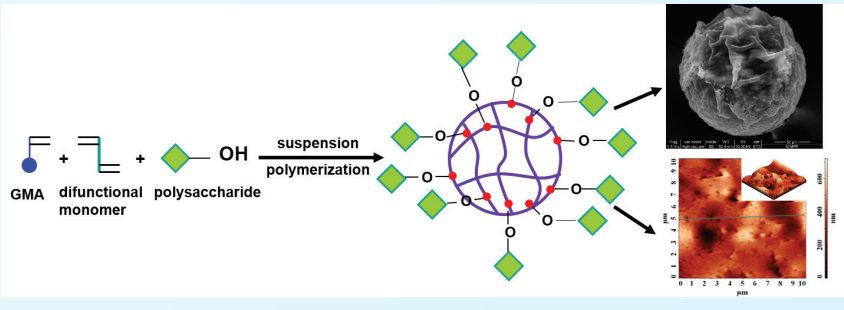
Use of linear and / or cross-linked, natural or synthetic ionic polymers - synthesized especially within the project research group -, in the development of nanostructured composite materials by different methods:

- polymerization in suspension
- self-assembly through physical interactions
- *in vitro* mineralization of calcium carbonate and various supporting ionic materials
- testing the new materials in applications such as environmental protection and medicine.

IMPORTANT RESULTS

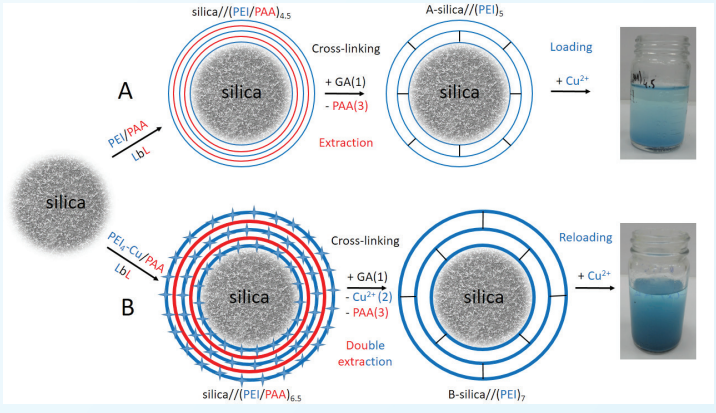
- Porous materials obtained by grafting of polysaccharides (xanthan, gellan, chitosan, sodium hyaluronan) onto crosslinked networks based on glycidyl methacrylate

The aqueous suspension polymerization is one of the most common techniques used for the preparation of porous microparticles due to some advantages, such as: small number of reagents in comparison with emulsion polymerization or other techniques; ability to control the size and size distribution of microparticles; simple purification method (filtration, centrifugation) for the final product; lower cost compared to a broad spectrum of properties acquired by the microparticles; excellent heat transfer during the process. A combination between synthetic (glycidyl metacrylate and dimethacrylic monomers) and natural polymers (xanthan, gellan, chitosan, sodium hyaluronan) could lead to the new polymeric materials that can combine the specific properties of synthetic polymers like: chemical stability and resistance at different values of pH and temperature with the special properties of natural polymers such as bioadhesion, biocompatibility and biodegradability.

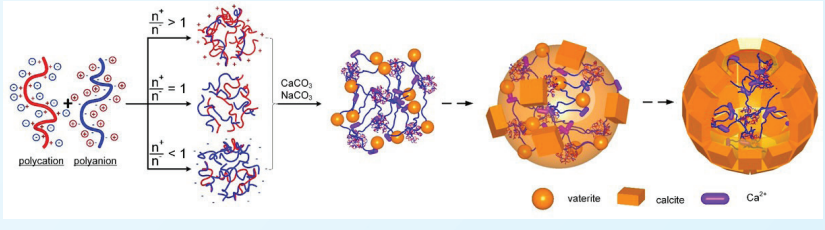


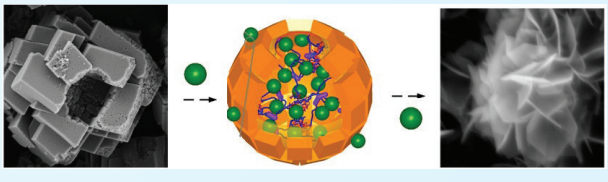
Grafting of polysaccharides on macromolecular chains led to the preparation of polymeric materials with larger specific surfaces, smaller particle sizes (due to better suspension stabilization in the presence of polysaccharides) and higher swelling capacities compared to the microaprticles based on glycidyl methacrylate. Also, the presence of polysaccharides in the structure of microparticles increases the biocompatibility of these systems. Due to their properties, the microparticulate systems can be used in medical fields as possible controlled/sustained drug delivery systems or in water purification as adsorbents.

- **Silica / polyelectrolyte multilayer composites obtained by layer-by-layer technique followed by extraction of polyanion from multilayer and subsequent interaction with heavy metal ions (eg Cu^{2+}).**



- **Morphogenesis of calcium carbonate** in the presence of macromolecular compounds, depending on different parameters: nature, concentration and type of functional groups of polymers, concentration of inorganic part, pH of the environment, reaction time.





- **Obtaining of ion exchangers in two phases:**

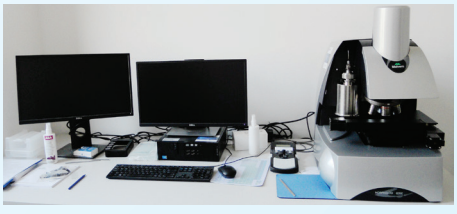
(1) obtaining cross-linked acrylic precursors by the technique of aqueous suspension copolymerization of vinyl monomers (ethyl acrylate, acrylonitrile, vinyl acetate, etc.) in the presence of a cross-linking agent (divinylbenzene) and an inert medium (toluene, extraction gasoline, etc.)

(2) chemical modification of precursors by polymer-analogous reactions of aminolysis, hydrolysis and carboxymethylation in order to obtain weak basic, weak acid and amphoteric ion exchangers.

INFRASTRUCTURE

- ***Particle charge detector Mütek PCD-03, GmbH, Herrsching, Germany,*** used to determine the concentration of water-soluble ionic polymer solutions, the zero charge point in the case of micro- and composite nanoparticles.

- ***Morphologi G3,*** equipment for obtaining complete information on the shape, size, transparency and concentration of particles in various media (suspensions, emulsions, dry powders), real-time image capture and processing of recorded data.



- ***Rotary coater Nadetech tip NDR*** used for multilayer films construction on flat surfaces.

- ***UV-Vis Spectrophotometers (SPECORD 200 and SPEKOL 1300, Analytik Jena)*** for measurements of the concentration of bioactive compounds (drugs, metal ions, proteins, model dyes etc.).

- ***M- Shimadzu Testing Machine EZTest (EZ-LX/EZ-SX Series):*** tensile, compression and bending tests for soft materials, max load capacity 500 N

- ***Glove box MODEL: 2GBS, Changshu Tongrun Electronic „TORUN”*** for handling in high-purity controlled atmosphere, samples with high sensitivity to humidity and oxygen.

- ***CC1-K6 Huber Cryostat, -25 ^{0}C ÷ +200 ^{0}C,*** for the syntyesis of hydrogels below the freezing temperature of water (cryogels)
- ***Digital camera microscopes*** for recording optical images of cryogels and composites
- ***Vacuum ovens*** - used in drying, sterilizing and heat treatment of materials
- ***Rotary evaporators*** - distillation units with laboratory applications, such as concentrating solutions, removing solvents, vacuum drying wet solids, degassing liquids
- ***pH-meters***
- ***TKA Microlab equipment for water purification***

REPRESENTATIVE PROJECTS

- **Lego-style approach for problematic water streams treatment (WaterLego)**
  224-ERA.Net RUS Plus, 2018-2020, project director Dr. S. Schwarz
  Director partner PPIMC – Dr. Marcela MIHAI

The objective of the WATER-LEGO project is to generate innovative, accessible and environmentally friendly materials, which can be assembled in a „lego" style in the form of sequential sorption filters, for decontamination of waters containing mixtures of toxic or unconventional pollutants.

- **Intelligent Sorption Materials for Water Treatment (ISOMAT)**
  IB-RA-172 – Germany, 2018-2020, project director Dr. S. Schwarz
  Director partner PPIMC – Dr. Marcela MIHAI

The objective of the project is to develop inexpensive complex sorbents based on inorganic materials and renewable biopolymers (for example, pectin, chitin, etc.) and to perform adsorption tests in real waters, collected from the river Spree.

- **Integrated and sustainable processes of environmental pollution, wastewater reuse and waste recovery (SUSTENVPRO)**
  contract no. 26PCCDI/1.03.2018, 2018-2020, project director Prof. C. Teodosiu
  Director partner ICMPP – Dr. Marcela MIHAI
  Component project 2 (PC2). Efficiency of water treatment processes and development of innovative materials for the elimination of priority pollutants, PC2 Director Dr. Marcela MIHAI

The objective of PC2 is to improve some technologies in advanced drinking water treatment, objective that at European level represents a challenge for drinking water suppliers. Therefore, during the project, innovative polymeric materials or composites will be designed, with properties (porosity, shape, size, sorption capacity, selectivity) adapted to the characteristics of the treated waters (types and concentrations of pollutants), with high efficiency for eliminating priorities model pollutants studied in the SUSTENVPRO project.

- **Stimuli responsive nanostructured (bio)composites**
  Project code: UEFISCSU - ID 981, Project Manager Dr. Ecaterina Stela DRĂGAN

The project objectives have followed to design novel types of nonionic/ionic composites, such as: (I) fast-responsive composite hydrogels, with potential for the retention and separation of biological micro- and nanoparticles; (II)

organic/inorganic ionic hybrids stabilized by covalent bonds responsive to more stimuli (solvent, ionic strength, pH, temperature); (III) stimuli-responsive interpenetrated networks composite hydrogels based on biocompatible polymers with adsorption properties of model dyes and metal ions; (IV) organic/inorganic ionic hybrids based on silica with high mechanical strength to be used at high pressure.

- **Porous ionic matrices with tailored architectures and responsiveness to host bioactive compounds**
  Project code: PN-II-ID-PCE-2011-3-0300; 2012-2016, Project Manager Dr. Ecaterina Stela DRĂGAN

The project objectives were (I) to develop new macroporous multicomponent hydrogels based on synthetic and natural ionic polymers under freezing conditions, (II) to obtain biocompatible porous ionic thin films by the LbL technique, and (III) to evaluate their potential for the sorption/immobilization and controlled release of bioactive species.

- **Engineered eco-friendly biocomposites with selective chelating properties for removal and recovery of heavy metal ions from contaminated waters (Biocomp4MetIRem)**
  Project code: PN-III-P1-1.1-TE-2016-1697; 2018-2020, Project Manager: Dr. Maria Valentina DINU

The project objective is to design novel ligand-functionalized biocomposites and to evaluate their performance and feasibility as selective sorbents for removal/recovery of heavy metal ions. The results obtained from modeling and optimization procedures using tools of artificial intelligence will provide very useful information for the experimental and industrial practice, in the sense of (i) substitution/prediction of experiments in order to save materials, energy, and time, as well as for a better planning of research activities, and (ii) emphasizing the maximum expected performance of a selected system and the conditions necessary to achieve it.

REPRESENTATIVE PUBLICATIONS

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- S. Racovita, M. A. Lungan, I. Bunia, M. Popa, S. Vasiliu, Adsorption and release studies of cefuroxime sodium from acrylic ion exchange resin microparticles coated with gellan, *React. Funct. Polym.* 105, 103-113, 2016
- I. Bunia, V. Socoliuc, L. Vekas, F. Doroftei, C. Varganici, A. Coroaba, B.C. Simionescu, M. Mihai, Superparamagnetic Composites Based on Ionic Resin Beads/$CaCO_3$/Magnetite, *Chem. Eur. J* 22, 18036-18044, 2016
- M.V. Dinu, A.I. Cocarta, E.S. Dragan, Synthesis, characterization and drug release properties of 3D chitosan/clinoptilolite biocomposite cryogels, *Carbohydr. Polym.* 153, 203-211, 2016
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LABORATORY 5

NATURAL POLYMERS, BIOACTIVE AND BIOCOMPATIBLE MATERIALS

HEAD OF LABORATORY: DR. GHEORGHE FUNDUEANU-CONSTANTIN

TEAM

- Dr. Gheorghe FUNDUEANU-CONSTANTIN / ghefun@icmpp.ro/SR I/ Biomedical applications of natural and synthetic polymers (intelligent polymers)
- Dr. Marieta NICHIFOR / nichifor@icmpp.ro/ SR I/Synthesis, characterization and biomedical applications of natural and synthetic polymers
- Dr. Georgeta MOCANU / gmocanu@icmpp.ro/ SR I/ Synthesis, characterization and biomedical applications of natural and synthetic polymers
- Dr. Iuliana SPIRIDON / spiridon@icmpp.ro/ SR I/ Biomass, natural polymers, biorefinery, composites
- Dr. Nicolae OLARU / nolaru@icmpp.ro/ SR I/ Polysaccharide derivatives, nanostructured materials based on polymers and organic oxides
- Dr. Sergiu COȘERI/ coseris@icmpp.ro/ SR I/ Natural polymers: functionalization and applications
- Dr. Luminița GHIMICI / lghimici@icmpp.ro/ SR II/ Characterization and applications of ionic polymers
- Dr. Marieta FUNDUEANU-CONSTANTIN / marieta@icmpp.ro/ SR II/ Chemical modifications of natural polymers, micro- and nano-gels for biomedical applications
- Dr. Dana Mihaela SUFLET / dsuflet@icmpp.ro/ SR III/ Polysaccharides functionalization, biomedical applications of polymers
- Dr. Irina POPESCU / ipopescu@icmpp.ro/ SR III/ Polyelectrolytes: synthesis and characterization
- Dr. Magdalena Cristina STANCIU / cstanciu@icmpp.ro/SR/ Synthesis and characterization of natural and synthetic polymers
- Dr. Anca GRIGORAȘ / angrig@icmpp.ro/ SR/ Polymer physics
- Dr. Narcis Catalin ANGHEL / anghel.narcis@icmpp.ro/ SR/ Biomass, natural compounds

- Dr. Gabriela BILIUȚĂ /gabriela.nistor@icmpp.ro/ SR/ Natural polymers: functionalization and applications
- Dr. Irina Mihaela PELIN / impelin@icmpp.ro/ SR/ Polymer/hydroxyapatite composites
- Dr. Sanda Maria BUCĂTARIU / sanda.bucatariu@icmpp.ro/ AC/ Polymeric composites for biomedical applications
- Tinca BUNIA / gtinca@icmpp.ro/ technician
- Sorin LAZĂR / doctorand/ Biomass, natural polymers
- Raluca Ioana BARON / PhD student/ Natural polymers: functionalization and applications
- Madalina Elena CULICĂ / PhD student/ Natural polymers: functionalization and applications
- Ioana Alexandra DUCEAC / PhD student/ Natural polymers: functionalization and applications

GENERAL TOPIC

Complex, multifunctional polymeric structures for biomedical and biotechnological applications

RESEARCH FIELDS

- Design, manufacture and testing of new polymers / polymeric matrices with complex structures used for biomedical and biotechnological applications.
- Synthetic and natural polymers chemically modified, with complex architectures, for the controlled release of medicines, for the "targeted" delivery of medicines, as biomimetic supports for the engineering (regeneration) of different tissues (bone, muscle, epithelial, etc.) or for others biomedical and biotechnological applications (flocculations, purifications, enzyme immobilization, etc.).
- Self-regulated drug delivery systems based on polymers sensitive to external stimuli able to release the drug when normal physiological conditions are disturbed. Obtaining from synthesized polymers of micro and nanoparticles in suspension or in colloidal solutions.
- Derivatives of natural or synthetic polymers with variable amphiphilicity and / or sensitive to external stimuli, for biotechnological or biomedical applications.
- New polymers with antimicrobial activity based on natural products (polysaccharides, bile acids).
- The use of gentle, environmentally friendly methods for the selective functionalization of natural polymers, in particular cellulose, starch and pullulan. The proposed functionalization methods are applied in particular

for the oxidation reaction of the various OH groups (primary or secondary) in the anhydroglycoside unit of the polysaccharides. The synthesized oxidation products are then used as matrices for the incorporation of nanoparticles (silver, magnetic), the preparation of hydrogels or adsorbent materials for removing dyes and heavy metals from wastewater.

- Identification of innovative concepts for the development of new materials based on natural compounds with applications in environmental protection, medicine, cosmetics, food industry.
- Functionalization of natural polymers and use of new biodegradable and biocompatible matrices to diversify the architecture of composites.
- Cellulose nanofibers and magnetic nanoparticles for the treatment of tumor by hyperthermia.
- Hybrid nanostructured materials, carbon nanofibers from natural polymers with antimicrobial activity.

PROJECT 1: DERIVATIVES OF NATURAL OR SYNTHETIC POLYMERS WITH VARIABLE AMPHIPHILICITY AND/OR SENSITIVE TO EXTERNAL STIMULI FOR BIOTECHNOLOGICAL OR BIOMEDICAL APPLICATIONS

PROJECT DIRECTOR: DR. MARIETA NICHIFOR

- Synthesis of new ionic or non-ionic polymers, linear or cross-linked, with variable amphiphilicity, in the form of micro- or nano-particles
- Study of the interaction of synthesized polymers with biologically active substances, surfactants or other model molecules, in order to identify new areas of use (flocculants, purifications / separations / immobilization biomolecules or systems with controlled release of: drugs, enzymes, vaccines, etc.).

PROJECT 2: POLYMERIC STRUCTURES WITH COMPLEX ARCHITECTURES (MICRO- AND NANOPARTICLES, SEMI- AND INTERPENETRATED NETWORKS, BIOMIMETIC SUPPORTS, INTELLIGENT HYDROGELS) FOR BIOMEDICAL AND BIOTEHNOLOGICAL APPLICATIONS

PROJECT DIRECTOR: DR. GHEORGHE FUNDUEANU-CONSTANTIN

- Design and development of new natural and synthetic polymers chemically modified with ionic and / or hydrophobic groups for biomedical and biotechnological applications
- Design and development of intelligent drug delivery systems based on hydrogels, micro- and nano-particles

- Use of oxidized cellulose / oxidized pululan - polyvinyl alcohol hydrogels for the removal of metal ions and organic dyes from wastewater

PROJECT 3: NATURAL COMPOUNDS - NON-CONVENTIONAL FUNCTIONALIZATION AND VALUATION STRATEGIES

PROJECT DIRECTOR: DR. IULIANA SPIRIDON

- Separation of natural polymers from biomass by non-conventional processes. Chemical modification of polysaccharides and lignin for increased biocompatibility with various matrices
- Synthesis of composite materials based on natural polymers and functionalized natural polymers
- Study of the stability of materials under the combined action of humidity, temperature and UV radiation
- Mechanical characterization of biocomposite materials
- Evaluation of the antimicrobial and antioxidant activity of materials
- Preparation of cellulose acetophthalate nanofibers in the form of ammonium salt
- Preparation of nanocomposites based on chitosan and metallic oxides, by electrospinning from acetic acid solutions, in the presence of polyethylene oxide

INFRASTRUCTURE

- ***Zetasizer Nano ZS (Malvern):*** for the measurements of the particles size in the range of 1-8000 nm (by dynamic light scattering at an angle of 90°, using a He-Ne laser at λ = 633 nm) and Zeta potential of the nanoparticles. The device allows the temperature control in the range of 3-80 ^{0}C

- ***Freeze dryer Martin Christ, ALPHA 1-2LD*** - allows drying of the samples from aqueous solution by sublimation of water at low temperature and pressure.

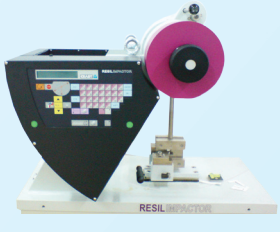
- ***SHPLC modular system (Shimadzu)*** equipped with a quaternary pump working in isocratic regimen or with low pressure gradient, at 0.1-10 mL/min elution rate, RID and UV-Vis detectors (with simultaneous recording at two different wavelength), oven for column temperature control (30-85 ^{0}C), HPLC reverse phase column (silica particles covered with C18) used for qualitative detection and quantitative analysis of low molecular weight compounds (<1000 Da), mixed bed GPC columns for molecular weight measurements of hydrophilic neutral and ionic polymers (5000 - 500000 Da).

- ***Brabender station for polymer processing***. It is the basic unit that drives different processing devices (mixer, extruder), the parts being connected in a network with permanent exchange of information between the individual components of the system, allowing the recording, control and preset of the nominal values of the system parameters.

- ***The climate chamber Angelantoni Industrie (Italy), model CH 250 E*** allows the study of the aging phenomena of polymeric materials under the influence of humidity, temperature and UV radiation.

- ***Tensile strength tester*** (Tester 53482 series, measuring range 1-5 kN, accuracy class 1) allows the evaluation of tensile strength. The control, recording and analysis of the test system data is carried out through an INSTRON (Bluehill Lite) software program specially designed for this type of testing.

- ***Impact resistance testing device (CEAST Italia)*** allows the impact test to be carried out using the IZOD method, respectively CHARPY. The impact test using the Charpy method is performed according to ISO 179-1: 2010.



- ***Abrasion resistance tester*** produced by Bareiss company (Germany) allows the measurement of abrasion resistance of elastomers.

REPRESENTATIVE PROJECTS

- **Nanosized micelles and vesicles from amphiphilic block copolymers with polysaccharides as hydrophilic blocks. A versatile route to new biomaterials. Project PN-II-ID-PCE-2011-3-0622; Project director Marieta Nichifor; 2011-2016; Budget: 1,500,000 Lei.**

The aim of the project was to synthesize amphiphilic block copolymers with chemical structures controlled by synthesis, from polysaccharides (dextran, pullulan) as hydrophilic blocks and biodegradable polyesters of bile acids (cholic, deoxycholic or litocolic acids) as hydrophobic blocks. Double hydrophilic block copolymers of polysaccharides and poly(isopropylacrylamide) with capacity to self-assembly only above their low critical solution temperature were also been prepared. Polymer properties (blocks composition and length) determining the formation of nanosized organized structures (micelles, vesicles) were identified and these structures properties (size, shape, morphology, stability, ability to encapsulate hydrophobic and /or hydrophilic compounds) were studied. In order to improve the properties and applicability as drug carrier with time and specific site controlled activity, the synthesized nanoparticles were functionalized by crosslinking, attachment of ionic and hydrophobic groups, or binding of site specific vectors (folic acid). Biological activity including encapsulation capacity for one or two drugs, their release, biocompatibility and interaction with specific cells was evaluated.

- **Intelligent therapies for non-communicable diseases, based on the controlled release of pharmacological compounds from cells encapsulated after genetic manipulation or vectorized bionanoparticles; Project PN-III P1-1.2-PCCDI-2017-0697; Acronym: INTERA; Responsible partner (ICMPP) Gheorghe Fundueanu; 2018-2020; Budget: 1,380,000 Lei.**

The INTERA complex project aims to develop innovative therapeutic methods that, by reducing the inflammatory process, will improve the pathological processes. INTERA includes multidisciplinary studies that only together can create and define new medical nano- or micro-devices that can be used for intelligent and innovative anti-inflammatory therapies. INTERA includes 4 projects: (1) Encapsulation of genetically manipulated eukaryotic cells for the controlled release of some pharmacologically active products (2) Creating a 3D platform designed for pre-clinical drug testing consisting of cells incorporated into three-dimensional bio-matrices; (3) Intelligent nanobioparticles designed for vectoring bioactive compounds to pathological sites for the therapy of vascular inflammation (4) Polymer conjugates for the efficient induction of expression of genes of interest with applicability in cell therapy. The consortium consists of 4 partner research units - two institutes of the Romanian Academy (IBPCNS, ICMPP), a university (UPB) and a national CD institute (INCDFM) with good territorial coverage (Bucharest-Ilfov-Iași).

- **Mimicking living matter mechanisms by five-dimensional chemistry approaches; Project: PN-III-P4-ID PCCF-2016-0050; Acronym: 5D-nanoP; Responsible partner Gheorghe Fundueanu; 2018-2022; Budget: 945,000 Lei.**

The 5D-nanoP project aims to interface the fundamental scientific field of constitutional dynamic chemistry with the practical approaches of medical chemistry and biomedical applications. In the spirit of the metaphor launched by Jean-Marie Lehn (Nobel Prize for Chemistry, 1987), the project proposes to materialize the concept of 5D chemistry by designing, synthesizing, characterizing and using molecules with conditioned affinity, for the development of supramolecular nanoplatforms, useful as pharmacological and genetic vectors implicated in physiological or pathological processes at the cellular and tissue level.

- **New amphiphilic cationic oligomers as synthetic alternatives for antimicrobial peptides and/or as external biocides. Proiect PN-III-P4-ID-PCE-2016-0519; Project director Marieta Nichifor; 2017-2019, Budget: 850.000 Lei.**

The main objective of the project is to design, synthesize and evaluate new more biocompatible materials with enhanced antimicrobial activity against a wide number of Gram-positive and Gram-negative bacteria, yeasts and fungi, with application both as antibiotics alternatives and external powerful biocides. Synthesis of selective antimicrobial polymers designed as antibiotic replacements uses bile acids as starting materials. Bile acids are natural compounds with facial amphipilicity and reactive groups (OH, COOH), which can be modified by appropriate synthesis strategies to obtain oligomers with amino groups. Amphiphilic polymers with quaternary ammonium groups attached to a polysaccharide (dextran, chitosan) backbone can be used as external biocides. Hydrophobic component (alkyl, alkene, steroid) of these amphiphiles is attached at the end of the polysaccharide chain. Oligomer membrane activity is tested on model lipid membranes (liposomes) having the same lipid components as bacteria and red blood cell outer walls. Antimicrobial activity is evaluated by minimum inhibitory and bactericidal concentrations, and selectivity towards bacteria is quantified by comparison of toxicity against bacteria and red blood cells.

- **Natural raw materials engineering: cellulose based biointerfaces for protein detection; Project: PN-III-P4-ID-PCE-2016-0349; (Acronym: ERAW); Project Director: Sergiu Coșeri; 2017-2019; Budget: 825,000 lei.**

This project proposes a new approach for the manufacture of devices for detecting proteins, by using cellulose substrates functionalized by oxidation and activation reactions of carboxylic groups.

REPRESENTATIVE PUBLICATIONS

- G. Biliuta, S. Coseri, Cellulose: A ubiquitous platform for ecofriendly metal nanoparticles preparation, *Coordination Chemistry Reviews* 383, 155-173, 2019
- S. Coseri, Cellulose: To depolymerize… or not to?, *Biotechnology Advances* 35, 251-266, 2017

- G. Fundueanu, M. Constantin, I. Oanea, V. Harabagiu, P. Ascenzi, B.C. Simionescu, Entrapment and release of drugs by a strict „on-off" mechanism in pullulan microspheres with pendant thermosensitive groups, *Biomaterials* 31, 9544-9553, 2010
- G. Fundueanu, M. Constantin, P. Ascenzi, Preparation and characterization of pH- and temperature-sensitive pullulan microspheres for controlled release of drugs, *Biomaterials* 29, 2767-2775, 2008
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- G. Fundueanu, M. Constantin, I. Oanea, V. Harabagiu, P. Ascenzi, B.C. Simionescu , Prediction of the appropriate size of drug molecules that could be released by a pulsatile mechanism from pH/thermoresponsive microspheres obtained from preformed polymers, *Acta Biomaterialia* 8, 1281-1289, 2012
- I. Spiridon, R. N. Darie-Nita, A. Bele, New opportunities to valorize biomass wastes into green materials. II. Behaviour to accelerated weathering, *Journal of Cleaner Production* 172 2567-2575, 2018
- M. Nichifor, G. Mocanu, M.C. Stanciu, Micelle-like association of polysaccharides with hydrophobic end groups, *Carbohydrate Polymers* 110, 209-218, 2014
- L. Ghimici, M. Nichifor, Dextran derivatives application as flocculants. *Carbohydrate Polymers* 190, 162–174, 2018
- D.M. Suflet, I. Popescu, I.M. Pelin, A. Nicolescu, G. Hitruc, Cationic curdlan: Synthesis, characterization and application of quaternary ammonium salts of curdlan, *Carbohydrate Polymers* 123, 396-405, 2015

LABORATORY 6

INORGANIC POLYMERS, HYBRID AND COMPLEX SYSTEMS

HEAD OF LABORATORY: DR. MARIA CAZACU

TEAM

- Dr. Maria CAZACU, SR I, mcazacu@icmpp.ro/ polymer chemistry and physics; silicone chemistry and technology; metal-containing compounds and materials: micro-molecular compounds and coordination polymers, metal clusters and nanoparticles; compounds and materials for applications in energy, environment, medicine, biology, catalysis
- Dr. Valeria HARABAGIU, SR I, hvaleria@icmpp.ro/ chemistry and physico-chemistry of polymers and polymeric materials; supramolecular chemistry; (nano)composites
- Ph.D. Aurica P. CHIRIAC, SR I, achiriac@icmpp.ro/ synthesis of macromolecular structures assisted by an electromagnetic field; design and preparation of composites and hybrid polymeric materials and their characterization by specific techniques
- Dr. Carmen RACLEȘ, SR I, raclesc@icmpp.ro / functionalized siloxane compounds, polysiloxanes, chemical modification; organic precursors, ligands and metal complexes; metallic and polymeric nanoparticles and composite materials; liquid crystals with siloxane spacer; surfactants; dielectric elastomers
- Dr. Liviu SĂCĂRESCU, SR I, livius@icmpp.ro/ polysilane synthesis, organic synthesis using microwaves and ultrasound irradiation, synthesis of polysilane-metal nanocomposites, molecular modelling, electron transfer and optical processes in polysilanes and nanocomposites, methods for materials characterization
- Dr. Sergiu SHOVA, SR II, shova@icmpp.ro / metal-containing compounds and materials: small-molecular compounds and coordination polymers, metal clusters and nanoparticles; compounds and materials for applications in energy, environment, medicine, biology, catalysis; structural characterization by single-crystal X-ray diffraction
- Dr. Rodinel ARDELEANU, SR II, rodar@icmpp.ro/ silicone chemistry, chemical modification of polisilanes, synthesis of ligands and metal complexes, supramolecular chemistry, macrocyclic nanostructures with photocontroled conformations, phytosynthesis of metalic nanoparticles

- Dr. Aurica FARCAȘ, SR II, afarcas@icmpp.ro/ organic and polymer chemistry, supramolecular chemistry and material science in the domain of conjugated polyrotaxanes applications.
- Dr. Gheorghe ROMAN, SR II, gheorghe.roman@icmpp.ro / organic synthesis, heterocyclic chemistry, development of novel synthetic methods, structural characterization of organic compounds, synthesis and characterization of coordination polymers, medicinal chemistry, structure-activity relationship in chemical libraries
- Dr. Corneliu COJOCARU, SR II, ccojoc@gmail.com / computer-aided modelling and optimization of physical-chemical processes, computational chemistry for molecular modeling, adsorbents and adsorption processes, polymeric membranes for separation, polymer assisted ultrafiltration; polymeric and composite materials for environmental applications
- Ph.D. Tudorachi NITA, SR II, ntudor@icmpp.ro / synthesis of polymers and composite materials; simultaneous thermal analysis (thermogravimetry/ IR spectrometry/mass spectrometry), determination of kinetic parameters and decomposition mechanisms
- Ph.D. Loredana E. NITA, SR II, lnazare@icmpp.ro / macromolecular compounds synthesized by classical methods and in the presence of a magnetic field for biomedical applications; dimensional analysis and spatial distribution in polymeric structures using Mastersizer, Nanosizer ZS and NIR-CI equipment
- Dr. Lucia PRICOP, SR III, lpricop@icmpp.ro/ inorganic chemistry; silicones
- Dr. Mihaela SIMIONESCU, SR III, msimionescu@icmpp.ro / synthesis of organo-silicon polymers, organic synthesis using microwaves and ultrasound irradiation, polisiloxane copolimers with dipolar molecular segments, synthesis of polysiloxane-imides with piezoelectric response, methods for materials characterization
- Dr. Gabriela SĂCĂRESCU, SR III, gsacarescu@icmpp.ro / polysilane synthesis in heterogeneous and homogeneous systems, synthesis of macromolecular precursors for preparation of silicon-carbide ceramics at low temperature, synthesis of silicon quantum dots (SiQD) and polymeric transporters , methods for materials characterization
- Dr. Maria IGNAT, SR III, ignat.maria@icmpp/ inorganic materials and porous composites; photocatalysis; applications in environmental pollution processes
- Dr. Petrișor SAMOILĂ, SR III, samoila.petrisor@icmpp.ro / synthesis of magnetic oxides by wet chemical methods, synthesis of metallic catalysts by surface redox reactions, preparation of magnetic composites, methods for materials characterization: XRD, FTIR, TEM, SEM, TPR, TPO, VSM, thermogravimetry
- Dr. Mihaela DASCĂLU, SR III, amihaela@icmpp.ro / synthesis of siloxane monomers and oligomers; polymerization techniques; nanostructured organic-inorganic hybrid materials; synthesis of Ag nanoparticles; metal complexes of Schiff bases with siloxane units; silicone materials for actuation and energy harvesting; structural characterization

- Ph.D. Iordana NEAMTU, SR III, neamtui@icmpp.ro / synthesis of macromolecular compounds by classical polymerization techniques and in non-equilibrium plasma; (hydro)gels; polymeric nanocomposites for biomedical applications and characterization of materials by specific techniques
- Dr. Ana-Maria RESMERIȚĂ, SR III, resmerita.ana@icmpp.ro / synthesis and physico-chemical characterizations of complex supramolecular architectures and supramolecular networks.
- Dr. Mirela-Fernanda ZALTARIOV, SR, zaltariov.mirela@icmpp.ro/ synthesis of siloxane/silane derivatives with different functional groups; siloxane/silane ligands; metal complexes, coordination polymers and metal-organic networks; thiosemicarbazone-type ligands and their metal complexes, characterization of the compounds by spectroscopic methods
- Dr. Xenia PATRAȘ, SR, xenia.patras@gmail.com/ pharmacology; controlled release drugs
- Dr. Cristian PEPTU, SR, cristian_peptu@yahoo.com/ bioengineering; chemical modification of polymers; biomaterials
- Dr. Maria Emiliana FORTUNA, SR, fortuna.maria@icmpp.ro/ organic chemistry; chemical modification of polymers
- Dr. Alina G. RUSU, SR, rusu.alina@icmpp.ro / synthesis of polysaccharide derivatives and their characterization; preparation and characterization of hybrid polymeric structures for biomedical applications
- Dr. Alexandra BARGAN, YR, anistor@icmpp.ro/synthesis of polysiloxanes, heterocyclic structures with N — Si bond to pentacoordinated silicon; polycyclic siloxane compounds; siloxane ligands and their metal complexes; characterization of the compounds by X-ray diffraction on the monocrystal; evaluation of surface properties (DVS, contact angle, etc.)
- Dr. George ȘTIUBIANU, YR, george.stiubianu@icmpp.ro / synthesis of polysiloxanes; preparation of nanocomposite materials; infrared light imaging applied in the analysis of nanocomposite materials; modeling of energy transfer in thin films; complex characterization of polymer-based materials
- Dr. Alina SOROCEANU, YR, lazar.alina@icmpp.ro / ligands and metal complexes; single-crystal X-ray diffraction; methods of characterization of materials; preparation of composites and their characterization; evaluation of potential applications
- Dr. Mihail IACOB, YR, iacob.mihai@icmpp.ro / functionalized siloxane compounds, polysiloxanes, organic precursors, ligands and metal complexes; metallic and polymeric nanoparticles and composite materials; surfactants
- Dr. Codrin ȚUGUI, YR, tugui.codrin@icmpp.ro / siloxane polymers; dielectric elastomers based on crosslinked silicones and interpenetrated networks; electromechanical characterization of dielectric elastomers (mechanical, dielectrics, breakdown voltage, actuation and energy harvesting tests); electromechanical transducers used in energy conversion

- Dr. Adrian BELE, YR, bele.adrian@icmpp.ro / polysiloxane synthesis and homogeneous and heterogeneous system; additions of polar entities by hydrosilylation and UV-activated reactions; polymer nanocomposites; polymeric capacitors and sensors; characterization methods of materials; dynamic sorption of vapors, mechanical properties of elastomers
- Dr. Alina Ghilan, YR, diaconu.alina@icmpp.ro / synthesis of composite materials and hydrogels for biomedical applications, dimensional analysis, and spatial distribution in polymeric structures using Mastersizer, Nanosizer ZS, and NIR-CI equipment
- Dr. Razvan ROTARU, YR, rotaru.razvan@icmpp.ro/ composites; ultrasound; electrical and magnetic properties
- Dr. Marius SOROCEANU, YR, soroceanu.marius@icmpp.ro/ semiconductor polymers; electro-optical propertie
- Angelica VLAD, YR, avlad@icmpp.ro / functionalized siloxane compounds, polysiloxanes, ligands and metal complexes; composite materials; surfactants
- Angela ROTARU, eng. gr.1A, arotaru@icmpp.ro / manager of security and healthy department of PPIMC
- Georgiana-Oana ȚURCAN-TROFIN, PhD student, turcan-trofin.georgiana@icmpp.ro
- Andra-Cristina HUMELNICU, PhD student, humelnicu.andra@icmpp.ro
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- Alexandru STOICA, masterand, stoica.alexandru@icmpp.ro
- Constanța Munteanu, assistant, constantarodica@yahoo.com
- Roxana SOLOMON, technician, solomon.roxana@icmpp.ro

GENERAL TOPIC

- Development of frontier research leading to innovative materials, advanced (multifunctional materials, smart materials, metamaterials, biomaterials) in response to current societal challenges (related to medicine, environmental protection, energy, optoelectronics, etc.) and in accordance with the thematic priorities of the Horizon 2020 Program, thus creating the basis for accessing European funds;
- The theoretical and practical foundation of the proposed researches for obtaining new functional and sustainable materials and developing an in-depth knowledge of the key parameters underlying these processes;
- Using the existing expertise in the subprogramme team, strengthening and developing it through close collaboration between project team members and by attracting young people to the team;

- Development of interdisciplinary competences for identifying the applicative potential of the prepared materials;
- Development of the research infrastructure of the laboratory/institute by attracting alternative sources of financing (participation in complex national/international projects);
- Specialization of young people in the subprogramme field by promoting doctoral training programs and accessing national and international research programs for human resources.

PROJECT 6.1. ORGANIC-ANORGANIC HYBRIDS FOR BIOMEDICAL AND HIGH TECHNICAL USES

PROJECT DIRECTOR: DR. VALERIA HARABAGIU

OBJECTIVES

Preparation, structural/morphological characterization of the following materials and investigation of interactions in multicomponent systems, including biological media and tissues:

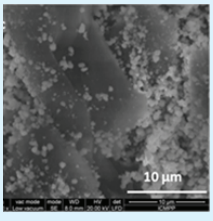
- Hybrid membranes for skin tissue treatment and regeneration;
- Composites with polysaccharide-based electro-magnetic properties;
- Hybrid materials with adsorbent properties.

The group has expertise in the development of clean methods for obtaining sustainable composites based on polysaccharide-inorganic compound, with high-tech uses and materials for biomedical applications or environmental protection.

THEME OF INTEREST

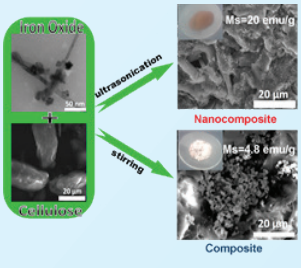
Viscose - barium titanate composites obtained by ultrasound and electric field treatment

Electromagnetic shielding: penetration depth: 250 μm la 50-55 Hz, the shielding effectiveness: 9 dB at 10^4-10^5 Hz



Ferromagnetic composites. Micronized cellulose - maghemite / goethite - obtained by ultrasonication and heat treatment in the microwave field.

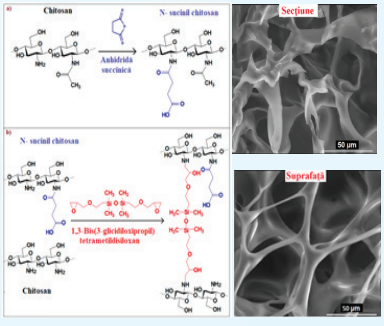
Ultrasound allows a more even distribution of inorganic nanoparticles in cellulose matrix and a significantly higher saturation magnetization compared to mechanical mixing.



Porous membranes for transdermal drug delivery

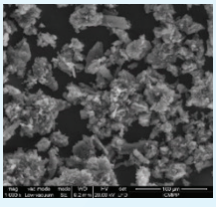
Hydrophilic-hydrophobic membrane of chitosan modified with succinic anhydride and cross-linked with bisglycidoxypropyldisiloxane

- biocompatible
- water swelling capacity: 600%; loaded with lidocaine provides analgesic effect, similar or superior to the commercial EMLA product



Adsorbent materials for industrial water purification of heavy metals or organic pollutants

Mesoporous carbon composites modified with bis(aminopropyl)polydimethylsiloxane; adsorption capacity for Cs ions: 48.1 mg/g.



PROJECT 6.2. SILICONES AND DERIVED MATERIALS
DPROJECT DIRECTOR: DR. MARIA CAZACU

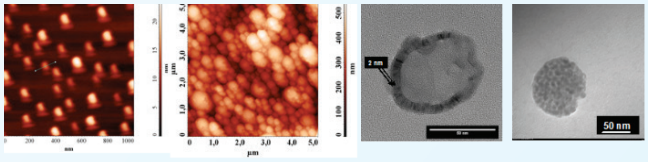
OBJECTIVES

- Siloxane polymers and compounds common and modified by attachment of polar or functional groups
- Homo- or heteronuclear complex combinations based on hybrid ligands
- Metal clusters and nanoparticles
- Silicone nanocomposites with inorganic or organic dispersed phases stimuli responsive
- Advanced polymers and materials for energy conversion and storage; silicone-based energy conversion units obtained by “green chemistry”

MAIN RESEARCH DIRECTIONS ADDRESSED IN THE LAST EIGHT YEARS

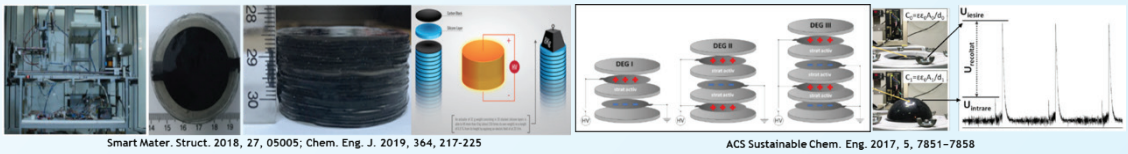
I. Amphiphilic organo-siloxane compounds. By chemical modification of the small-molecular or polymeric siloxanes with different hydrophilic functional

groups, new materials are obtained, capable of self-assembly, a phenomenon that directs the final properties and applications. In particular, siloxane surfactants with synthetically adjustable surface properties are studied, capable of acting as nanoparticle stabilizers, micellar solubilizing agents, phase transfer agents, ligands for self-assembled metal complexes, etc.



I. Nanopart. Res. 2010 12, 2163-2177; Colloids Surf., A 2014, 443, 233-239; Colloids Surf., A 2014, 448, 160.

II. Dielectric elastomers for application as active elements in electromechanical devices: sensors, actuators, electricity generators (33 articles published in the last 8 years occupying an important position among the research groups in this field worldwide).

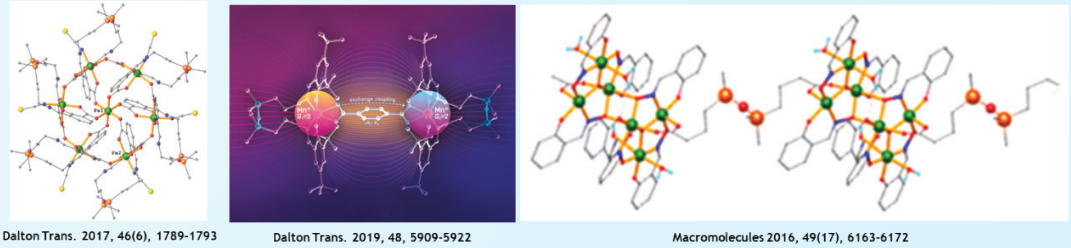


Smart Mater. Struct. 2018, 27, 05005; Chem. Eng. J. 2019, 364, 217-225

ACS Sustainable Chem. Eng. 2017, 5, 7851−7858

Electromechanical actuators and enery generators

III. Ligands and metal coordination structures by the use of siloxane and silane segments as highly flexible and hydrophobic substrates, spacers or terminations with strong impact especially on the conformation, surface, catalytic and biological properties of the resulting compounds. The number of such structures registered in the CCDC database is a modest one, being enriched with the over 100 structures registered by the team since 2011 (over 65 articles published by the team). For the advanced study of these compounds (magnetic, biological, catalytic properties) collaborations are established with groups from abroad (Austria, France, Slovakia, Serbia, Norway, USA, Spain, Portugal).



Dalton Trans. 2017, 46(6), 1789-1793

Dalton Trans. 2019, 48, 5909-5922

Macromolecules 2016, 49(17), 6163-6172

Metal complexes and coordination polymers with ligands having siloxane spacers

PROJECT 6.3. PHOTOACTIVE ANORGANIC POLYMERS
PROJECT DIRECTOR: DR. LIVIU SĂCĂRESCU

OBJECTIVES

- Hyperconjugated systems in polysilane matrix: inclusion of electronoactive compounds in polysilane matrix and study of the photo-electronic interactions;
- Hybrid polysilane/polymer composites: synthesis and study of materials obtained by including polysilanes in natural or synthetic polymers support

RESEARH INTERESTS

- Silicon-organic polymers with hyperconjugated polysilane segments
- Polysilane-based materials with applications in optics and molecular electronics
- Polysilane nanocomposite with applications in sensoristics and medical imaging
- Fluorescent polymeric composites and/or semiconductors in matrices of natural polymers
- Interactions between sigma-conjugated polymers and metal complexes
- Hyperconjugated supramolecular structures
- Polymeric transporters for silicon quantum dots (SiQD)
- Combined nanostructural analysis TEM/SAXS/GPC
- Materials for environment and energy
- Computational chemistry and processes optimization

PROJECT 6.4. COMPOSITE MATERIALS AND MULTIFUNCTIONAL HYBRID STRUCTURES BASED ON NATURAL AND SYNTHETIC POLYMERS
PROJECT DIRECTOR: DR. AURICA P. CHIRIAC

PROJECT OBJECTIVES

- Design and preparation of new macromolecular compounds and materials with structural characteristics specific to self-assembly processes (SA);
- Development and comprehension of SA processes at a molecular level of

various compounds and materials; understanding the interactions responsible for SA processes;

- Applying known analysis techniques, as well as developing new methods for in-depth characterization of the new SA systems;
- Physical and chemical investigation of various natural (albumin, hyaluronic acid, alginates, starch, etc.) and synthetic polymers (polyorthoesters, poly aspartic acid, polylactic acid, etc.) and analysis of surface properties and their activation possibilities by mechanical methods, infrared or UV radiation, or under a magnetic field, to obtain new hybrid nanostructures;
- Obtaining and investigating new structures and their properties for use in the biomedical field or in purification processes;
- Development of immobilization methods in correlation with the polymeric matrix, the nature of the bioactive agent, and the expected application of the new materials;
- Determination and implementation of the functionality of the obtained systems.

RESEARCH DIRECTIONS

I. Design and synthesis of new multifunctional macromolecular structures

We consider the design and synthesis of macromolecular compounds, along with natural polymers, for the development of (nano) hybrid materials for biomedical applications and materials science. The strategy pursued is based on the combination of macromolecular chemistry and synthesis processes to create new generations of adaptive hybrid materials.

The proposed approach covers the synthesis and modification of polymeric materials, characterization, and theoretical investigation and, finally, testing the applicability of the new compounds. Macromolecular functional structures are developed by precise adjustment of the architecture, functionality, self-assembly capacity and polymer nanostructuring through synthesis strategies, as well as by controlling physical interactions and interface properties for specific applications. Also, the aim is to achieve a better understanding of the molecular structure, nanomorphology, interface functionality of the obtained compounds and the properties required for the intended apllication.

II. Preparation of hybrid structures: synthetic/natural polymers, magnetic and biocomposites, in the form of nano- and microparticles, films or gels

We focus on developing customized macromolecular structures for hybrid materials, to improve the binding capacity of magnetic or bioactive compounds, thus offering greater opportunities for their use. At the same time, we are developing innovative synthesis methods under the influence of magnetic fields to prepare functional macromolecules through complex molecular design strategies and to solve future challenges in the field of biomedicine and materials science.

To achieve the proposed objectives we investigate the preparation of

macromolecular architectures with: high degree of structural precision, synergistic characteristics generated through multifunctionality, controlled assembly, adaptive characteristics (sensitive structures) that respond to the proposed nano- or micro-media.

III. Use of magnetic field effects to obtain macromolecular compounds and hybrid structures

We propose to benefit from magnetic interactions, which are of both theoretical and practical interest, using the magnetic field (continuous, alternative) in the design of materials with predefined properties. Many of these materials, magnetic in their basic states or susceptible to external disturbances, find their applicability as molecular switches, sensors, etc.

At the same time, the effects of the magnetic field have a dual character, exerted on one hand on the dynamics of molecular motion and, on the other hand, on the spin dynamics of the radicals. Although magnetic interactions are of a smaller order of magnitude than chemical interactions, they can induce specific effects on various properties.

Thus, magnetic fields can alter the speed and efficiency of chemical processes or even the topology of the reaction components. It is also known that by the action of the magnetic field the physical properties of the polar molecules, such as structure, density, surface tension, viscosity, etc., can be modified according to the magnetic susceptibility of the molecules, as well as by the presence of ions in the system. The modification of the properties of the synthesized polymers in the magnetic field is attributed to the catalytic effect, due to the distortions of the molecules, increased interactions and changes of bond angles.

PROJECT 6.5 POLYROTAXANES SUPRAMOLECULAR ARCHITECTURES

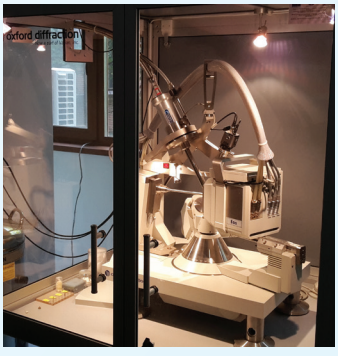
PROJECT DIRECTOR: DR. AURICA FARCAS

PROJECT OBJECTIVES

The research objectives are developed in the following directions:

- Synthesis of new macrocycle host structures (cucurbit[n]urils (CBs), crown ethers, calix[n]arene, permodified cyclodextrines derivaties
- Synthesis of new π-conjugated polyrotaxanes (based on polythiophene polyfluorene, poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrol, polyazomethines and study the photo-physical properties for optoelectronical applications
- Synthesys and characterization of new supramolecular networks based on polyrotaxanes and/or π-conjutated/ insulated polymers

INFRASTRUCTURE



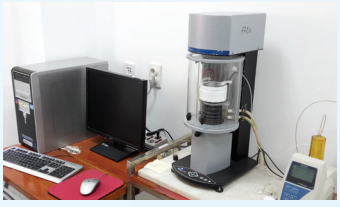
Oxford-Diffraction XCALIBUR E CCD X-ray Diffractometer for single-crystals used to determine the molecular and crystalline structures of different compounds with small molecular masses. The equipment includes: a Xcalibur platform (a Kappa goniometer with 4-circles configured for the X-ray source and generators), cooling units for the X-ray source and the CCD detector, the EOS CCD detector having a high sensitivity with a diagonal active area of 92 mm; the X-ray source (Mo Kα, λ = 0,71073 Å); a CrysAlis^{Pro} software for intelligence gathering and processing the experimental diffraction data needed for the crystallographic analysis of the compounds with small molecular masses and proteins; a Autochem^{TM} software package for solving and refining the structures; Cryojet system XL (90-300K): a Cryojet unit, a cooling system for making the diffraction experiment at variable temperatures, Dewar flask capacity of 75 l for liquid nitrogen

Bruker FTIR Spectrometer (VERTEX 70) equipped with a DLaTGS detector which covers a spectral range from 12.000 to 250 cm^{-1}, working at room temperature and having a sensitivity of D*>2x10^{8} cm $Hz^{1/2}W^{-1}$ and covers a spectral range from 7500 to 370 cm^{-1}. Operating modes: Transmittance MID-IR: 370-4000 cm^{-1}; Transmittance FAR-IR: 180-600 cm^{-1}; ATR with ZnSe crystal: 600-4000 cm^{-1}.

Spectrophotometer UV-Vis (SPECORD PLUS) with double beam for transmission, extinction, reflectance and energy measurements for solid and liquid samples in spectral range 190 - 1100 nm, equipped with a carrier for films and integrating sphere.

Moisture sorption analyser IGASORP (Hiden Analytical, Warrington, UK) compact, fully automated, for fast and accurate sorption measurements, in dynamic regime, for water and organic vapors. The equipment allows the measurement of water vapors or organic solvent sorption capacities and records the sorption/ desorption isotherms and kinetic curves, in normal or cyclic regime.

Sigma700 tensiometer (KSV Instruments, Finland) fully automated having a high precision microbalance which allows the determination of various properties of materials as: surface and interface tension, watering ability, dynamic contact angles and critical micellar concentration.



Device for mechanical tests Instron 3365 with a force cell of 500 N, used for testing the materials and products made by elastomers. The instrument for mechanical tests is equipped with a high precision video extensometer which allows the deformation measurements with a high accuracy without being in contact with the sample. Furthermore, the device has a climatic chamber which permits the sample testing in a temperature range of -100 ^{0}C and -350 ^{0}C. The materials can be exposed to different tests as: traction, traction in cyclic regime or compression. By making the traction and/or compression tests it is possible to determine the highest stretch, stretching stress, Young modulus, residual strain, impact bend strength, yield stress etc.

Discover LabMate monomodal microwave reactor performs reactions at temperatures up to -300 ^{0}C. It could be controlled by an infrared probe under integrated stirring. The IntelliVent system for pressure feedback and control allows a sensitive pressure monitoring when the reaction is done in closed vessel. The equipment is provided with Synergy™, a specially designed software package that is useful to design the experimental methods and store them on a PC.

Transmission electron microscope HITACHI - HT7700- This instrument belongs to a new class of TEM series launched in 2010. This is the first TEM that can easily switch from high resolution to high contrast mode owing to the double lens-gap system. The equipment works in broad daylight, without binoculars, the image being directly displayed on a PC monitor. Full configuration, with the following functions: TEM, S/TEM, EDX, TEM-tomography, TEM-low dose, cryoTEM and integrated panorama function.

Small angle X-ray scattering instrument: NanostarU - Bruker- it can be used to analyze any kind of samples in SAXS, WAXS, GISAXS mode using High Flux, High Resolution and Standard configurations. It is programmable for multiple samples, providing an accurate analysis within 1–125 nm. The temperature can be set within -30 and 120 ^{0}C. The X-rays are generated with a high class advanced microsource. Diffractograms are registered on a VANTEC 2000 detector.

Gel permeation chromatograph Brookhaven WGE SEC 3010 – the equipment provides absolute values for molar mass and intrinsic viscosity, no calibration being required. With this system, one can determine Mark-Houwink coefficients for a sample with a single injection, or can perform branching calculations without assumptions. The instrument is equipped with full multiple detection: RI, Visco, MALS (7 different angles), UV.

The STA 409 PC Luxx Simultaneous thermal analyzer conected to a FTIR and a mass spectrometer gas analysis systems allows one-step analysis on the same sample of mass changes, decomposition behavior, thermal stability, oxidation behavior, transition enthalpies, phase transition temperatures, glass transition temperature, crystallization behavior, phase diagrams and the influence of additives. The equipment is connected to FTIR and MS ensuring the evaluation and analysis of the gases resulting during the thermal decomposition of the investigated structures. The equipment performs measurements in a vacuum, oxidizing atmosphere or inert gas, from -110 ^{0}C to 700 ^{0}C.

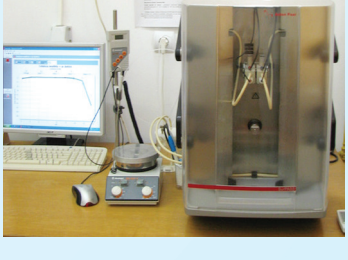
ZetaSizer Nano ZS – is a molecular size analyzer for the enhanced detection of aggregates and measurement of small or dilute samples, using dynamic light scattering with 'NIBS' optics. The equipment allows the evaluation of particle and molecule size, translational diffusion, electrophoretic mobility, Zeta potential of particles at high and low concentrations, and

molecular weight. The Zeta potential analyzer uses electrophoretic light scattering for particles, molecules and surfaces, and the molecular weight analyzer uses static light scattering. Measuring range for dimensions - 0.3 nm at 10 µm.

MasterSizer 2000 - is a laser diffraction testing instrument used to evaluate particle size distribution in a range between 0.02 µm and 2000 µm, with a precision of ± 1%. It is a flexible and modular, but fully integrated, particle sizing system with assured measurement performance from submicron to millimetre, wet or dry, from milligram quantities to the measurement of bulk chemicals and minerals. The dispersion medium is water, and depending on the samples and needs, surfactants - usually nonionic - or additives may or may not be used: trisodium phosphate, sodium oxalate, calcium chlorid.

SisuChema NIR-CI System - combines NIR spectroscopy with high resolution imaging. It provides detailed information on the chemical components, their quantities and distributions within the sample. It is invaluable information for the characterization and quality assurance of advanced materials, where the functionality of the material is dependent on its chemical and physical structure. The analyzer can be applied to a broad number of applications: non-destructive determinations on pharmaceutical tablets, distribution and concentration of the components within a sample; the study of the uniformity of pharmaceutical blends; particles size and distribution of the chemical components in heterogeneous mixtures; identification of polymorphic forms.

Electrokinetic Analyzer for Solid Surface Analysis: SurPASS is a high-end electrokinetic analyzer featuring fully automated Zeta potential analysis of macroscopic solids in real-life conditions. The Zeta potential is related to the surface charge at a solid/liquid interface and is a key parameter for understanding surface properties and developing new specialized materials.



Johnson Matthey Magnetic Susceptibility Balance determines the magnetic properties of paramagnetic and diamagnetic solids and liquids. The method is based on the principle of the stationary sample and a moving magnet. The volumetric susceptibility in c.g.s units can be measured in the range: 0.001 x 10^{-7} - 1.99 x 10^{-4}.

REPREZENTATIVE PROJECTS

- Innovative nanotechnologies based on polymer for obtaining new advanced materials (NAPOLI 19), PNIII-40PCCDI, 2018-2020/ V. Harabagiu.
- The engine of the hydrogen-based energy revolution. Fuel cells, on the road from research to production by minimizing technological barriers (ROFCC), PNIII-25PCCDI, 2018-2020/ V. Harabagiu.
- Sustainable biochemical method for air revitalisation in spacecrafts (BIO-MARS), STAR-157/2017, 2017-2019/ M. Ignat.
- Metal-organic networks with finely controlled hydrophobicity using silicone chemistry, SiMOFs, PN-III-P4-ID-PCE-2016-0642, Contract 114/2017, 2017-2019/ M. Cazacu.
- Eco-innovative technologies for recovering the platinum metal group from used catalytic converters (ECOTECH-GMP), Contract 76PCCDI/2018/2018-2020/ M. Cazacu.
- New scaffolds for extension of structure-activity relationship studies of metal-based anticancer drugs, PN-III-P1-1.1-PD-2016-1027, Contract: 5/02.05.2018, 2018-2020/Dr. M. Zaltariov.
- Multifunctional Spin Crossover Materials, H2020-MSCA-RISE-2016, SPINSWITCH,: 734322 SPINSWICH, 2016-2020/ S. Shova.
- Synthesis and study of polymeric metallosiloxanes - new materials of interest for catalysis and nanosciences, POLISILMET, POSCCE-A2-O2.1.2-2009-2, Contract no. 129/2010, 2010-2013/ M. Cazacu.
- New mechanisms and concepts for exploiting electroactive Polymers for Wave Energy, Conversion, PolyWEC, FP7-ENERGY-2012-1-2STAGE ENERGY.2012.10.2.1: FUTURE EMERGING TECHNOLOGIES, Project no. 309139, 2012-2017/Partner: M. Cazacu.
- Energy harvesting by dielectric elastomer generators, Romanian-Swiss Research Programme (RSRP) Joint research project Romania-Switzerland (RSRP), No: 10 / RO-CH/RSRP/01.01.2013, 2013-2015/Partner: C. Racles

REPREZENTATIVE PUBLICATIONS

- A Luca, C.-T Mihai, D.D. Stanciu, V. Bild, E. Cojocaru, R. Ancuceanu, V. Harabagiu, C. Peptu, C.A. Peptu, M.M. Leon-Constantin, T. Alexa-Stratulat,

In-vivo safety and efficacy evaluation of a novel polymeric based lidocaine formulation for topical analgesia, *Farmacia* 67, 117-125, 2019
- S. Sova, A. Vlad, M. Cazacu, J. Krzystek, A. Ozarowski, M. Malcek, L. Bucinsky, P. Rapta, J. Cano, J. Telser, V. Arion, Dinuclear manganese(III) complexes with bioinspired coordination and variable linkers showing weak exchange effects: a synthetic, structural, spectroscopic and computation study, *Dalton Trans*. 48, 5909–5922, 2019
- A.G. Rusu, A. P. Chiriac, L. E. Niță, M. Bercea, N. Tudorachi, A. Ghilan (Diaconu), D. Pamfil, D. Rusu, F. D. Cojocaru, Interpenetrated polymer network with modified chitosan in composition and self-healing properties, *Int J Biol Macromol*. 132, 374-384, 2019
- A. Farcas, K. I. Assaf, A.-M. Resmerita, L. Sacarescu, M. Asandulesa, P.-H. Aubert, W. M. Nau, Cucurbit[7]uril-threaded poly(3,4-ethylenedioxythiophene): A novel processable conjugated polyrotaxane, *Eur. J. Org. Chem*. 2019, http://dx.doi.org/10.1002/ejoc.201801724
- A.-M. Resmerita, M. Asandulesa, G. Bulai, A. Farcas, Novel supramolecular networks based on PEG and PEDOT cross-linked polyrotaxanes as electrical conductive materials, *Eur. Polym. J*. 114, 39-46, 2019
- R. Rotaru, M. Savin, N. Tudorachi, C. Peptu, P. Samoilă, L. Săcărescu, V. Harabagiu, Ferromagnetic iron oxide-cellulose nanocomposites prepared by ultrasonication, *Polym. Chem*. 9, 860-868, 2018
- C. Racles, M.-F. Zaltariov, M. Iacob, M. Silion, M. Avadanei, A. Bargan, Siloxane-based metal–organic frameworks with remarkable catalytic activity in mild environmental photodegradation of azo dyes, *Appl. Catal. B Environ*. 205, 78–92, 2017
- L. Săcărescu, M. Simionescu, G. Săcărescu, A. Quade, J. F. Kolb, C. Miron, Nanostructuration of polysilane-SiQDs composite by pulsed electrical discharges in water, *React. Funct. Polym*. 120, 38–45, 2017
- A. P. Chiriac, A. Ghilan (Diaconu), L. E. Niță, N. Tudorachi, L. Mititelu-Tarțău, A. Crețeanu, O. Dragostin, D. Rusu, G. Popa, The influence of excipients on physical and pharmaceutical properties of oral lyophilisates containing a pregabalin-acetaminophen combination, *Expert Opin Drug Deliv*. 14, 589-599, 2017

LABORATORY 7

ELECTROACTIVE POLYMERS AND PLASMOCHEMISTRY

HEAD OF LABORATORY: DR. MIRCEA GRIGORAS

TEAM

- Dr. Mircea GRIGORAȘ, grim@icmpp.ro, SR I, Oligomers and polymers containing conjugated bonds
- Dr. Maria BERCEA, bercea@icmpp.ro, SR I, Complex fluids
- Dr. Ioan CIANGA, ioanc@icmpp.ro, SR I, Multifunctional soft materials based on conjugated conducting polymers
- Dr. Simona MORARIU, smorariu@icmpp.ro, SR II, Complex fluids
- Dr. Luminița CIANGA, lcianga@icmpp.ro, SR III, Polymeric materials with controlled, complex topologies and various properties (chiral, mesogen, electroconducting, biocompatible and/or biodegradable)
- Dr. Anca-Dana BENDREA, anca.bendrea@icmpp.ro, SR, (Semi) conducting, conjugated polymers for tissue engineering, diagnosis and therapy
- Dr. Mihai ASĂNDULESA, asandulesa.mihai@icmpp.ro, SR, Oligomers and polymers containing conjugated bonds
- Dr. Cristina-Eliza BRUNCHI, brunchic@icmpp.ro, SR, Complex fluids
- Dr. Ana-Maria SOLONARU, solonaru.anamaria@icmpp.ro, SR, Oligomers and polymers containing conjugated bonds
- Dr. Loredana VĂCĂREANU, sloredana@icmpp.ro, SR, Oligomers and polymers containing conjugated bonds
- Dr. Mirela TEODORESCU, teodorescu.mirela@icmpp.ro, SR, Complex fluids
- Dr. Oana-Iuliana NEGRU, negru.oana@icmpp.ro, SR, Oligomers and polymers containing conjugated bonds
- Ioana-Alexandra PLUGARIU, plugariu.ioana@icmpp.ro, PhD student, Complex fluids

GENERAL TOPIC

1. Multifunctional materials based on conjugated polymers

- Conjugated oligomers and polymers of the polyarylene, polyarylenevinylene, polyarylenetylene, polythiophene, polyaniline, polyperylene, polybenzothiadiazole and polyimine class, synthesis, structure and properties;
- Hybrid materials based on organic polymer/ polycyclic aromatic

nanostructures (graphene and graphne oxid) for application in optoelectronic devices;

- Synthesis by polymerization initiated in the cold plasma of new copolymers and the study of influence of specific reaction parameters on their electrophisical properties;
- Deposition of films with specials properties by synthesis in cold plasma;
- Electrochemical and conductivity studies of the synthetized conductive polymers;
- Hybrid and polymeric materials for electrochromic, light-emitting and chemo-/biosensors devices;
- Biocompatible, conjugated polymers with controlled architecture designed for tissue engineering;
- "Hairy-rod" architecture and water self-dispersible conjugated polymers, able to self-assembly, for applications in cancer diagnosis and therapy;
- Conjugated polymers-based composites for applications as electronic textile („e-textiles") or bioapplications (biotextiles).

2. Thermodynamics and rheology of polymers and polymeric materials

- Preparation and characterization of organic/inorganic hybrid materials for cosmetic, pharmaceutical and biomimetic applications;
- Design and properties of physical or chemical gels based on natural and/or synthetic polymers for smart biomaterials with targeted applications;
- Investigation of thermodynamic and hydrodynamic interactions influencing the behavior of polymers of interest for advanced materials;
- Investigation of phase separation phenomena for hydrocolloids;
- The constitutive response of complex fluids under the action of external stimuli: temperature, pH, electric field, external forces, etc.

PROJECT 7.1: OLIGOMERS AND POLYMERS CONTAINING CONJUGATED BONDS

PROJECT DIRECTOR: DR. MIRCEA GRIGORAȘ

IMPORTANT RESULTS

- Synthesis of organic intermediates, monomers and/or heterocyclic or aromatic macromonomers for polymers with conjugated structure, as well as nanocomposite materials and conjugated polymers/inorganic dopant. The synthesized polymers were characterized both of point of view of the obtained structure and their properties (molecular mass, UV absorbtion, fluorescence, thermal stability, degree of cristallinity, anizoptopic optical properties, electrochemical properties). The electrochemical performances

of the nanocomposites materials based on conjugated polymers and graphene/ reduced graphene oxid were evaluated for energy strorege devices by various tehniques such cyclic voltametry and galvanostatic charge/discharge tehnique.

- Design and synthesis of conjugated, conducting polymers for biomedical applications (tissue engineering, fluorescence microscopy cell imaging, diagnosys and therapy, “non-labeled” soft biosensors for neurotransmitters or illict drugs detection)

PROJECT 7.2 COMPLEX FLUIDS
PROJECT DIRECTOR: DR. MARIA BERCEA

IMPORTANT RESULTS

- Elaboration and characterization of different biomaterials based on natural and synthetic polymers.
- Investigation by different methods of thermodynamic and hydrodynamic interactions that influence the behavior of the polymers used for obtaining advanced materials.
- The results obtained during the last 5 years have been published in more than 40 scientific papers, and the team members were involved in 7 research projects.

INFRASTRUCTURE

Potentiostat - Galvanostat Bioanalytical System (BAS 100B/W) - for determining the domains of potentials in which reduction or oxidation of the analytes processes take place, the intensity values reduction or oxidation currents from which it can be deduced the reversibility of the electrochemical processes as well as the number of electrons involved in the reactions at the electrode.

Spectrometer SEC2000- UV-Vis designed to investigate the mechanism of the electrochemical reactions at the electrode/ solution interface by recording the absorption spectrum together with the application of the working electrode potential.

Osmometer Osmomat 090 (Gonotec) allows the measurement of the average numerical molecular weight and of the second virial coefficient for water-soluble polymers and polymers dissolved in organic solvents.

Rheometers (Anton Paar and Bohlin) with con-plane and plane-plane geometries and Peltier systems for temperature control, used for the viscoelastic characterization of polymers and polymeric materials in continuous and sinusoidal shear regime.

HACH 2100 AN Turbidimeter (HACH-LANGE, USA) allows the monitoring of chemical reactions or physical phenomena and the control of systems at turbidity level up to 10.000 NTU.

REPRESENTATIVE PROJECTS

- **Novel conjugated structures for high efficiency all-organic solar cell,** Project IDEI, PN-II-ID-PCE-2011-3-0274, 2012-2016, Contract no. 148/2011, https://grigoras300.weebly.coml

Conjugated polymers with arylaminic structural units (carbazole, triphenylamine) are highly studied in recent years because they are good hole transporting materials, have photoconductivity, photorefractivity, fluorescence, redox and nonlinear optical properties, being interesting for applications in xerography, electroluminescence diodes, solar cells, etc. From this point of view, the use of these polymers for heterojunction solar cells (BHJ-bulk heterojunction configuration), where an arylamine polymer is intimately mixed with an acceptor and deposited sandwiched between an transparent anode ITO, modified with a PEDOT film/PSS and a cathode having low ionization potential (Ca , Al, Zn) is the most economical way to replace silicon-based solar cells. Within this project, according to the initial proposal, the diversification and optimization of these photoactive organic materials and their use as active layers in photovoltaic devices were addressed. The obtained results were published in 28 scientific papers, participation in 33 national and international scientific events with 14 oral communications and 19 posters.

- **Organic and hybrid nanostructured conductor materials for multifunctional applications,** Project IDEI, PNCDI, ID_993, contract 649/2009, 2009-2011, http://www.icmpp.ro/grants/Mircea%20Grigoras/Web_ro_2009.pdf

The main objective of this project was the synthesis of conductive polymers with improved solubility and processability that allow carrying out in depth studies of molecular and supramolecular structure to establish correlations between

structure and properties and to widen the range of possible applications. The topic of the proposal was mainly focused on two polymeric structures: polyarylenevinylene and polyaniline.

- **Polymer materials with smart properties,** Project IDEI, PN-II-ID-PCE-2011-3-0199, 2011-2016, http://bercea300.weebly.com

By combining new concepts concerning the formation of supramolecular structures under well-defined conditions, new polymeric materials with intelligent properties have been developed and characterized. Multicomponent polymer materials obtained by different physical, chemical or combined processes have been reported. Some materials are able to respond to the action of external stimuli in a predictable manner by sharp changes of the physico-chemical properties (viscoelastic or conformational characteristics, hydrophilic-hydrophobic balance, refractive index, permeability, etc.). The obtained results were published in 38 scientific papers, 1 book, one book chapter, and presented at 12 national and international scientific events with 11 oral communications and 22 posters.

- **Polymer gels based on clay,** Project IDEI, PNCDI, ID_980, contract nr. 516/22.01.2009, 2009-2011, http://www.icmpp.ro/claygel/index.html

The project aimed to develop and characterize hybrid polymer/clay materials with morphologies and structures controlled on a nanometric scale. A series of new gel nanocomposites based on clay and synthetic or natural polymer have been prepared and characterized, following the understanding of some scientific aspects regarding the complex phenomena occuring in these systems. Some materials exhibiting electrostrictive behavior under an electrical impulse were reported. The obtained results were published in 15 scientific papers, 2 book chapters and presented at 19 national and international scientific events.

- **Basics establishment of the directed synergy of integrated micro/nano components in textile composites, aimed for endowing with smart functions the safety equipments designed for aggressive environments (EPINTEL),** National Program of Excellence Research, CEEX, 2006-2008, Contract no. 105/19.09.2006, http://www.tex.tuiasi.ro/epintel/Page1621.html

Involving two scientific branches, namely the fundamental sciences (chemistry, physics, biology) and the technical sciences (textile engineering, microelectronics, mechanical engineering), the project aimed to create and develop a Romanian network of excellence for fundamental and applied research focusing on the design and production of smart individual safety equipment, integrated within a European thematic. The PPMIC team synthesized a series of 3D porous composites, based on conjugated polymers and cotton textile supports, hierarchically structured at both macro and nanoscopic levels. The obtained materials showed flexibility and conformability, remarkable photophysical, electrochemical and antibacterial properties, with application perspective in both portable bioelectronics devices (useful in telemedicine) as well as biotextiles.

- **Textile composites for electromagnetic interference shielding (SIR),** National Program PNCDI II-P4, 2007-2010, Contract 81050/18.09.2007

The overall objective of this project was to obtain and characterize textile

composites based on micro metallic wires or conducting polymers, with shielding properties of non-ionizing (radio-frequency) electromagnetic radiation. The novelty brought by this project consisted in combined exploitation of peculiar properties of both micro-ferromagnetic wires and conducting polymers by interfacing them with conventional textile materials. Complex structures of type *metallic yarn-conjugated polymer coated cotton yarn* were obtained by *„in situ"* photochemically induced polymerization technique.

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LABORATORY 8

POLYMERS PHYSICAL CHEMISTRY

HEAD OF LABORATORY: DR. ANTON AIRINEI

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- Dr. Fanica MUSTATA/fmustata@icmpp.ro/ SR I/Epoxy composites based on synthetic and natural resins
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- Dr. Maria Cristina POPESCU/cpopescu@icmpp.ro/ SR II/Characterization of polymer materials by spectral methods
- Dr. Carmen Mihaela POPESCU/mihapop@icmpp.ro/ SR II/Bionanocomposites
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- Constantin GARABET/technician/
- Dorel URSU/technician/
- Roxana IRIMIA/technician/
- Daniela ACATINCAI/technician/

GENERAL TOPIC

- Preparation of materials based on multicomponent systems: sensitive materials to external stimuli, having antimicrobial/antioxidant/bioactive properties, materials with special surface properties, bionanocomposites
- Physico-chemical and biological characterization and testing of the new obtained materials
- Biodegradation and artificial aging of polymer materials
- Incorporation of active compounds in polymer biocompatible matrices
- Thermal behavior of polymer materials
- Hydrogel preparation based on natural polymers, sensitive to external stimuli
- Special aspects regarding the obtaining of nanoparticles from natural polymers and their physico-chemical characterization
- Design of new multifunctional materials containing polymer nanoparticles
- Valorization of lignocellulosic wastes by their incorporporation in polymer multicomponent systems, taking into account improving the impact on the environment
- Natural and synthetic polymers modified with resinic acid derivatives, obtained by Diels-Alder reactions
- New crosslinked polymers based on epoxy resins from vegetal and/or synthetic oils
- Study of the mass transport processes (drugs, biocid agents, etc.) in biocompatible polymer systems
- Investigation of thermal transport processes in polymers containing inorganic and/or organic nanophases

- Preparation and synthesis conditions of some multicomponent systems with advanced optical properties
- Structural, morphological characterization and analysis of optical properties of obtained complex systems
- Photophysical and photochemical behavior of these systems in different media under influence of physical and chemical factors
- Investigation of quenching mechanisms of the fluorescence by steady state and dynamic spectral techniques

PPROJECT 8.1: INTERACTIONS IN COMPLEX SYSTEMS. PHOTOPHYSICAL AND PHOTOCHEMICAL EFFECTS
PROJECT DIRECTOR: DR. ANTON AIRINEI

- Ceramic nanofibers based on oxide semiconductors ZnO/(Sn, La, Sm, Er) and SnO_2/Ni, Zn by electrospinning method. These materials were characterized morphologically and structurally using different instrumental techniques (XRD, TEM, SEM, DSC, TG, FT-IR spectroscopy, UV-Vis and Raman, etc), and correlations between optical, thermal and electrical properties and the preparation conditions of these nanocomposites were determined in order to find new applications. Ceramic materials based on ZnO doped with Sn, La, Sm, Er present a high efficiency for the degradation of some organic dyes such as Rhodamine B and Congo Red. Electrical and humidity measurements proved that the nanofibers containing SnO_2 doped with NiO can be utilized in obtaining humidity sensors.
- Intra/inter-molecular interactions in solutions and in solvent mixtures (preferential solvation) and the effect of medium factors – polarity, acidity, bazicity - on the optical properties of some organic compounds containing aromatic rings: 1,3,4-oxadiazole, quinoxaline, phenolphthaleine, fluorene, bisphenol A. Chemosensor properties were analysed for some metal ions such as Cd^{2+}, Cu^{2+}, Mg^{2+}, Ag^{+}, Co^{2}+, Ni^{2+}, Sn^{2}+, Zn^{2+} si Mn^{2+}, which play an important role in living organisms and environment. Spectral studies were evidenced a high sensitivity for Cu^{2+}, Co^{2+} si Ag^{+} ions. Solvatochromic analysis of these chromophores was utilized to estimate the optical nonlinear properties and to determine the characteristics of intramolecular charge transfer.
- Quenching processes of the emission in indolizine, isoquinoline derivatives, analysis of sensor properties for nitroaromatics were analysed.
- Structural characterization of some composites based on EPDM/flax fibers and EPDM/butyl rubber.
- Solvatochromic behavior of some azomaleimide derivatives using density functional theory (DFT), charge transfer in azomaleimides by quantochemical calculations (DFT, TD-DFT, *ab initio*).
- Photochromic processes in azoaromatic compounds.
- Polymer composites containing metal oxide nanoparticles: polysulfone (PSF)/ nickel ferrite, polythiophene/nickel nanoparticles, PVFD/cobalt ferrite, polysulfone nanofibers/nickel, tin oxide nanoparticles.

- Obtaining and characterization of cerium oxide nanoparticles, zinc oxide doped with cerium oxide nanoparticles, the influence of dopant nature on the optical properties.

PROJECT 8.2: PHYSICAL CHEMISTRY OF MULTICOMPONENT SYSTEMS. MATERIALS WITH SPECIAL PROPERTIES AND APPLICATIONS
PROJECT DIRECTOR: DR. CORNELIA VASILE

- New innovative methods to obtain multifunctional materials, sensitive to external stimuli (temperature, pH) were developed based on bionanocomposites containing biodegradable polymers (collagen, chitosan, cellulose, alginates), poly(N-isopropylacrylamide) and nanoparticles, which present antibacterial, antifungal and antioxidant activity, low permeability to gases, low migration of components in packaged product, having special surface properties, and these materials are biodegradable. These materials are destined both to bioactive packaging of foods for their conservation and to extent the period of validity and to medical and pharmaceutical fields as matrices for incorporation of some bioactive compounds for their controlled and target release.
- Five laboratory technologies verified at pilot scale were developed in order to obtain food packaging and antimicrobial urinary catheters. Also, the effect of gamma radiations and of plasma on some polymer materials was studied for their functionalization. Special results (from 2015 - to present): ISI articles: over 70, cumulated FI: over 100, citations 2019 (ISI-WoS/Thomson): around 300, patents: 5 national and 1 international, books: Polymeric Nanomaterials in Nanoterapeutics, Elsevier, 2019 and Food Packaging Materials and Technologies/MDPI, CH, 2019.

PROJECT 8.3: MULTIPHASE POLYMER SYSTEMS
PROJECT DIRECTOR: DR. ANCA FILIMON

- The project is based on the idea of complex multiphase systems and combines the new physico-chemical and structural concepts for development and characterization of some multiphase composite polymeric materials with specific properties and superior to those of the conventional polymers required in biomedical and industrial applications. Due to the complexity of the aspects related to the chemistry, kinetics and thermodynamics of the physico-chemical processes involved in the multiphase polymeric systems study, there are many areas that generate extensive studies for establishing the relationship between structure-properties-new areas of use. In this context, the following research directions are considered:
- Obtaining multifunctional materials by using polymers with special architectures: functionalized polysulfones (chloromethylated, phosphorylated, quaternized) and natural derivatives (cellulose, cellulose derivatives, polyvinyl alcohol, chitosan) with improved physical and chemical properties

(stability and durability, elastic properties, degree of crystallinity, shear behavior, viscoelastic behavior over time and depending on the temperature) and different forms of organization for applications in the top fields of modern technology.

- Optimization of properties by viscometry/rheology as a function of different parameters: concentration, temperature, solvent, and composition.
- Ionic transport processes in solutions by conductometric study.
- Establishing compatibility of polyelectrolyte/neutral polymer mixtures from osmometric measurements.
- Elaboration of mathematical models for multicomponent systems (e.g., polymer/solvent/nonsolvent or polymer/polymer/solvent) in order to quantify the specific interactions.
- Processing of multicomponent solutions by electrospinning to create new fibrous materials that can modulate membrane properties and have sustainable in membrane technology with potential application as bactericidal coating layers.
- Testing the applicative potential of membranes in various fields (biomedical, industrial) by evaluation of the biocompatibility, antimicrobial activity and electrical performance imposed by membrane technology (ion exchange membranes for hemodialysis). Also, research focused on controlling the membrane performance in terms of the selectivity and separation accuracy for applications as ultrafiltration membranes in water treatment and gas separation.

PROJECT 8.4: MULTIFUNCTIONAL POLYMER MATERIALS FROM RENEWABLE RESOURCES

PROJECT DIRECTOR: DR. DIANA CIOLACU

- Project gives special attention to the isolation and purification of cellulose and lignin from renewable materials, chemical functionalization of these natural polymers, as well as to the incorporation of natural polymers into complex materials with special properties, research directions that have materialized in valuable and extremely interesting results.
- In this regard, the research team investigated the supramolecular structure of cellulose, such as the allomorphic forms of cellulose - cellulose I, II and III, and amorphous cellulose, through different instrumental techniques, study focused on intra- and intermolecular interactions, their configurations, conformations and orientations.
- Another research direction was the extraction and purification of cellulose from vegetable waste (orange peel) by sulfite process. The obtained physico-chemical characteristics of this cellulose recommend it to be used as filler, absorbent material or as a raw material for obtaining cellulose derivatives.
- Moreover, in this project, were carried out for the first-time the enzymatic hydrolysis reactions of the main allomorphic forms of cellulose, in the presence of Aspergillus niger and Trichoderma reesei. The results of this

study generated the hypothesis that the enzymatic hydrolysis process could be used as a possible method to synthesis new cellulosic materials with a controlled structure-properties-applications relationship.

- The chemical functionalization of cellulose was carried out following different research directions, such as: (i) homogeneous treatment of cellulose with organophosphorus products, in order to obtain cellulose derivatives with improved thermal resistance and with polyelectrolyte properties; (ii) grafting of acrylamide onto cellulose, in the presence of a magnetic field, in order to improve the hydrophilicity of the fibers; (iii) chemical functionalization of cellulose by esterification reactions (acetylation of cellulose allomorphs; synthesis of cellulose esters with adamantoyl groups; cellulose esters based on Diels-Alder adducts of resin acids and resin acids with acrylic acid).
- Lignin was functionalized by (i) polyaddition reaction of lignin with epichlorohydrin, in the presence of an alkaline environment, in order to obtain lignin-epoxy resins; (ii) the graft copolymerization reaction between lignin and vinyl monomers, or (iii) enzymatic esterification reactions with stearic acid, in medium of organic solvent, in order to obtain new lignin derivatives.
- Over the years, the scientific studies of this research group have been diversified and oriented towards finding modern solutions for using the main components of biomass in various applications, such as the incorporation of functional natural polymers into complex materials (insulating materials from lignin-epoxy resins, composite materials), obtaining of polymeric materials based on epoxidized vegetable oils (thermo-crosslinkable matrices, flexible coating films) and the preparation of three-dimensional polymeric networks with applications in tissue engineering (hydrogels, aerogels, xerogels).
- In this regard, the development of composites based on natural polymers (cellulose/cellulose derivatives or lignin/functionalized lignin) and synthetic polymers (polyolefins, polyesters, epoxy resins) allowed the obtaining of materials with improved physical, mechanical and dielectric properties, as well as biodegradation capacity.
- Manufacture of thermo-crosslinkable matrices based on bisphenol A diglycidyl ether and epoxidized vegetable oils (castor oil, maize germs, grape seeds, soybean, hemp, in) and of flexible films based on epoxidized oil or castor oil modified with maleic anhydride is a research direction developed over several years. The flexible films thus obtained were used to prepare composite materials made from epoxidized vegetable oils/synthetic epoxy resins.
- An important contribution of this research team is the obtaining of new hydrogels from cellulose, cellulose/natural polymers (lignin, xanthan, chondroitin sulphate, alginate, dextran, pullulan), as well as cellulose/ synthetic polymers (polyvinyl alcohol). Biocompatibility evaluation of hydrogels (studies on controlled release of active pharmaceutical ingredients, cell viability and cell growth) have shown the high potential of these materials to be used in the pharmaceutical and medical fields.
- One of the latest research directions is the synthesis of cellulose nanoparticles

by conventional and unconventional methods and their subsequent incorporation into the three-dimensional network of cellulose hydrogels, with the purpose to increase them degree of swelling and to improve the mechanical properties. In addition, the introduction of silver nanoparticles into these hydrogels has imprinted antimicrobial properties, demonstrated by processes of partial inhibition of bacterial development in the *Escherichia* coli and *Staphylococcus aureus* species.

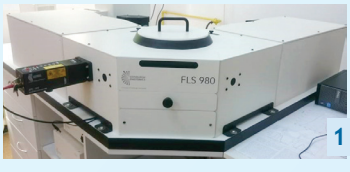
PROJECT 8.5: TRANSPORT PROCESSES IN MULTICOMPONENT POLYMER SYSTEMS

PROJECT DIRECTOR: DR. ANDREEA IRINA BARZIC

- Electric/thermal transport in polymer materials is improved depending on pendant groups and doping level.
- The shape of dispersion curves in transparent polymers is essential for evaluation of optical losses in opto-electronic devices.
- Development of anisotropic polymer supports by classical methods (rubbing) and innovative ones (texturing with lyotropic matrix) for liquid crystal displays.
- Preparation of some polymer/metal hybrid structures showing that interfacial adhesion is enhanced by plasma exposure in various conditions
- Rheologically evidenced that there is a correlation between polymer microstructure in solution and morphological features in solid phase (fibers, films, nanocomposites).

INFRASTRUCTURE

- ***UV/Vis 210Plus Analityk Jena spectrophotometer***
- ***Perkin Elmer LS55 luminescence spectrometer***
- ***FLS980 Edinburgh Instruments photoluminescence spectrometer (1)***
- ***Anton Paar Physica MCR301 rheometer (2)***
- ***Rheometer Bohlin CS50*** with cone-plate measuring system, Malvern, UK; conductometer Keithley (Keithley Instruments, SUA); light polarized microscope (Bresser, Germania)
- ***ECHO ER12 respirometer (3)***
- ***GC-MSD/FID gas-chromatograph*** with mass spectrometry and flame ionization detectors, Agilent 6890N Inert XL ***(4)***



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- ***Dissolution tester coupled with UV/Vis spectrometer,*** Agilent Technologies (Agilent 708-DS/Cary 60 UV/Vis) ***(5)***
- ***Optical microscope Leica DM 2500 M+DFC 290 (6)***
- apparatus for the determination of gas permeability
- Schott CT52 viscometer; electrospinning device Starter Kit V2


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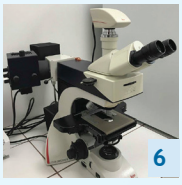
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REPRESENTATIVE PROJECTS

- **Improving food safety through the development and implementation of active and biodegradable food packaging systems,** ACTIBIOSAFE, Program EEA-JRP-RO-NO, Project 1SEE/30.06.2014, 2014 – 2017, 900,000 euro, Director: dr. C. Vasile

Biodegradable food packaging systems based on stratified composites or obtained by melt processing of the polylactic acid/chitosan/vegetal extracts/nanoparticles multicomponent system in collaboration with NOFIMA - Norge, USAMV Bucuresti, ICPAO Medias and RODAX SA Bucuresti - Romania were developed.

- **Antimicrobial bionanocomposites for medical applications,** Bionanomed, Program PN-II-PT-PCCA BIONANOMED no. 164/2012, 2012 - 2016, 2,500,000 RON, Director: dr. C. Vasile

The main objective of the project was to obtain antimicrobial urinary catheters, biocompatible and biodegradable. These were made at laboratory phase or pilot phase from complex formulations containing polylactic acid or polyurethane, hydrolyzed collagen, elastine, condroitin sulfate, hyaluronic acid and silver nanoparticles prepared *in situ*.

- **Ionizing radiation and plasma discharge mediating covalent linking of stratified composites materials for food packaging,** Proiect 17689/2014-2018, Director proiect: dr. C. Vasile, beneficiary IAEA- Vienna

New possibilities to obtain multifunctional nanocoverings and the effect of radiations on the polymer materials.

- **Composites based on nanoclay, nanocellulose and MIP for eco-friendly microbial formulations,** Project COFUND-M-ERA.NET II-COMPIO, 2017-2020, 180,000 euro, Director: dr. M. C. Popescu.

High performance composites incorporated in seed coverings or in spreading formulations, with improved barrier and mechanical properties were obtained.

- **New nanostructurated oxide materials prepared by spray pyrolysis applied in technologies of purification and generaration of regenerable energy,** PN-III-P1-1.1-MC-2017-0203, 2018, 22,000 RON, Director: dr. P. Pascariu

The project dealt with obtaining new oxide nanostructurated materials based on zinc oxide doped with Al, Sm, Fe, Cr and La, prepared by in spray pyrolysis.

- **New sensors for the detection of some heavy metals from industrial wastes. Characterization and investigation of some quenching processes of fluorescence,** PN-III-P1-1.1-MC-2018-1243, 2018, 21,708 RON, Director: dr. R.I. Tigoianu

Using absorption and emission spectroscopy, new synthesized compounds were characterized (lanthanide complexes with Schiff bases, indolizine derivatives) in order to obtain sensors for heavy metal detection: Cu, Fe, Pb, Cd, etc., from industrial wastes.

- **High performance polymeric biomaterials based on functionalized polysulfones with medical applications,** PN-II-RU-TE-2012-3-0143/2013-2016, Director: dr. A. Filimon

Project was aimed to achieve new composites/blends - functionalized polysulfones/natural polymers and functionalized polysulfones/synthetic polymers - in order to obtain semipermeable membranes with superior performance to those already known, suitable to biomedical applications.

- **Innovative hydrophilic matrices based on biopolymers with properties designed for medical applications (MATINOV),** PN-II-RU-TE-2014-4-0558, 2015-2017, 550,000 RON, Director: dr. D. Ciolacu.
- **Aero- and cryogels based on biopolymers - versatile materials for medical applications (BIOGELS),** PN-III-P3-3.1-PM-RO, 2017-2018, 28,755 RON, Director: dr. D. Ciolacu
- **New approaches in designing polymer surfaces with controllable pattern for applications in biomedicine and high technologies,** PNII-RU-TE-2014-4-2976, 2015-2017, 550,000 RON, Director: Dr. A.I. Barzic

REPRESENTATIVE PUBLICATIONS

- I. Bicu, F. Mustata, Novel cellulose esters derived from the levopimaric acid-maleic anhydride adduct: synthesis, characterization and properties, *Cellulose* 24, 2049-2057, 2017
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LABORATORY 9

POLYMERS AND POLYMERIC MATERIALS PHYSICS

HEAD OF LABORATORY: ACAD. BOGDAN C. SIMIONESCU

TEAM

- Acad. Bogdan C. SIMIONESCU/bcsimion@icmpp.ro/SR I/chemistry and physics of macromolecular compounds
- Dr. Călin DELEANU/calin.deleanu@yahoo.com/SR I/NMR applied to chemistry and life sciences
- Dr. Virgil BĂRBOIU/vbarboiu@icmpp.ro/SR I/ physics of macromolecular compounds
- Dr. Constanța IBĂNESCU/constanta.ibanescu@icmpp.ro/SR I/technology and rheology of polymeric materials
- Dr. Mariana CRISTEA/mcristea@icmpp.ro/SR II/thermo-mechanical investigations of polymers and processes
- Dr. Magdalena AFLORI/maflori@icmpp.ro/SR II/morphological characterization of polymeric materials, the obtaining of new materials through surface modifications
- Dr. Daniel ȚÎMPU/dtimpu@icmpp.ro/SR II/application of X-ray diffraction and atomic force microscopy in the study of polymers
- Dr. Emil-Ghiocel IOANID/ioanida@icmpp.ro/SR II/plasmochemistry, physico-mechanical properties of polymers
- Dr. Mihaela OLARU/olaruma@icmpp.ro/SR III/photochemistry, polyurethanes, hybrid nanocomposites, nanostructured materials, heritage and cultural identity
- Dr. Mihaela SILION/silion.mihaela@icmpp.ro/SR III/mass spectrometry in the characterization of low molecular weight compounds and polymers
- Dr. Alina NICOLESCU/alina@icmpp.ro/SR III/NMR applied to chemistry, medicine and agro-food sciences
- Dr. Mihaela AVĂDANEI/mavadanei@icmpp.ro/SR III/applications of FTIR spectroscopy in the study of polymers
- Prof. Xenia PATRAȘ/xenia.patras@gmail.com/SR/pharmacology, microbiochemistry
- Dr. Daniela IONIȚĂ/dgheorghiu@icmpp.ro/SR/thermo-mechanical investigations of polymers and processes

- Dr. Gabriela HITRUC/ghitruc@icmpp.ro/SR/applications of AFM in the study of polymers
- Dr. Mioara DROBOTĂ/miamiara@icmpp.ro/SR/functionalization of polymer surfaces by physical and chemical methods
- Dr. Cristian URSU/cristian.ursu@icmpp.ro/SR/materials science, surface science and nanotechnology, plasma physics
- Dr. Irina ANTOCHI/irina.bordianu@icmpp.ro/SR/hybrid nanocomposites, micro- and nanostructured materials, composite materials based on coordination polymers
- Dr. Gabriela AILIESEI/gdarvaru@icmpp.ro/YR/NMR applied to macromolecular and organic chemistry
- Dr. Mihaela BALAN-PORCĂRAȘU/mihaela.balan@icmpp.ro/YR/NMR applied to organic and supramolecular chemistry
- Dr. Iuliana STOICA/stoica_iuliana@icmpp.ro/SR/applications of AFM in the study of polymers
- Dr. Bogdan-George RUSU/rusu.george@icmpp.ro/YR/biomaterials, materials science, thin layers
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- Elena MARLICĂ/emarlica@icmpp.ro/chemist/WAXD for polymers
- Dorina ANGHEL/anghel@icmpp.ro/chromatographic techniques
- Irina TUDORACHI/irinatud@icmpp.ro/thermal degradation of polymers

GENERAL TOPICS/RESEARCH FIELDS

The department includes instruments and techniques whose manipulation and/or data interpretation require an in-depth understanding of a particular polymer characterization method. There are *structural characterization methods* (nuclear magnetic resonance spectrometry-NMR, Fourier-transform infrared spectrometry-FTIR), *methods for the investigation of morphology and surface properties* (scanning probe microscopy-SPM, wide angle X-ray diffraction analysis-WAXD, scanning electron microscopy-SEM, Raman microscopy), *methods for the investigation of molecular weights* (mass spectrometry, gel permeation chromatography-GPC) and *methods for the determination of viscoelastic properties* (dynamic mechanical analysis–DMA). Also, an *excimer laser laboratory* functions in the department. The teams of the department provide consultancy in the institute for polymer characterization and have their own research topics.

PROJECT 9.1 ORGANIC AND HYBRID STRUCTURES – A NEW STEP IN THE THERMO-RHEOLOGICAL PROCESSES CORRELATED WITH COMPLEMENTARY METHODS
PROJECT DIRECTOR: DR. MARIANA CRISTEA

Thermo-mechanical investigations (dynamic mechanical analysis–DMA) of polymer and processes have been preformed mainly on cellulose, high performance polymers (polyimides, polybismaleimides, polyvinyl chloride, polyvinyl alcohol, elastomers based on silicones and urethanes, EPDM, polyesters or sol-gel and imidization processes.

The data sheet of a polymer is a list of technical characteristics expressed by numbers that are valid in certain conditions, very often not mentioned. A thermo-rheological representation provides the big picture of polymer properties. First, this means the determination of the effects of temperature and time on the polymeric structure, e.g. the effect of these factors on the storage modulus associated with the rigidity of the polymer. The determination of the glass transition range is equally important, because outside this interval the polymer undergoes changes that entail severe consequences in practice. Second, the method gives information about the processing conditions. The polymeric material should be moldable, under the conditions that the structure remains intact. Molecular weight changes are checked through mass spectrometry. It is noteworthy that the DMA method is able to forecast the evolution of the polymeric material in time, under certain circumstances.

PROIECT 9.2 NATURAL ORIGIN OR NATURAL INSPIRED BIOACTIVE COMPOUNDS
PROJECT DIRECTOR: DR. CĂLIN DELEANU

Metabolites from complex biological and food matrices have been studied by NMR techniques. Natural inspired bioactive compounds have been synthesized and their structures have been fully characterized.

PROJECT 9.3 NON-CONVENTIONAL METHODS FOR NANOSTRUCTURING THE SURFACES OF POLYMERIC MATERIALS
PROJECT DIRECTOR: DR. MAGDALENA AFLORI

- Morphological and compositional study of polymeric materials.
- Obtaining multifunctional polymeric materials used in biomedical engineering.

PPROJECT 9.4 POLYMER COMPOSITES STUDIES BY X-RAY DIFFRACTION METHOD - WAXD, SPM MICROSCOPY, DIELECTRIC SPECTROSCOPY AND FTIR SPECTROSCOPY
PROJECT DIRECTOR: DR. DANIEL ŢÎMPU

- Study of 3D morphological modifications and local properties of complex polymeric surfaces (spherical microparticles, nano-wires)
- Determination of transient species with very short lifetime by real time fluorescence spectroscopy in the nano/microseconds domain
- Development of a new technique of broadband dielectric spectroscopy for submicron films

PROJECT 9.5 NANOSTRUCTURED MATERIALS – SYNTHESIS, PROCESSING AND TESTING FOR MULTIPLE APPLICATIONS
PROJECT DIRECTOR: DR. MIHAELA OLARU

- Development of functional hierarchical nanostructured materials (antimicrobial coatings, electroluminescent components)
- Development of hybrid materials for drug delivery
- Development of transparent and conductive thin layers through sequential laser ablation
- Induction of micro/nanostructures at the surface level through excimer laser processing
- Development of materials for the conservation/restoration of cultural heritage objects (monumental stone, ceramics, bone)
- Investigation of the molecular structure of the pigments and pictorial components used in the creation of old Romanian heritage paintings: the first use by a painter belonging to the Impressionist school (Nicolae Grigorescu) of the natural ultramarine pigment and the first mention of the use of indium oxide as a yellow pigment in a work of art (Stefan Luchian).

INFRASTRUCTURE

1. ***NMR Spectrometers***

1.1 NMR spectrometer, 600 MHz, for liquids, with MS couplings. Model Bruker Avance Neo 600

- Liquid nitrogen cooled cryoprobe with enhanced sensitivity
- Inverse detection probe optimized for metabolomics and bidimensional spectra
- Direct detection probe optimized carbon spectra
- Automatic sample changer
- MS coupling enabling association of the exact molecular weight of organic compounds with the NMR spectrum
- Vibration dumpers

1.2 NMR Spectrometer, 400 MHz, for soft solids. Model Bruker Avance Neo 400

- Direct detection 4 mm probe optimized for soft solids
- Inverse detection probe optimized for bidimensional spectra
- Direct detection probe optimized carbon spectra
- Vibration dumpers

1.3 NMR Spectrometrer, 400 MHz, for liquids. Model Bruker Avance Neo 400

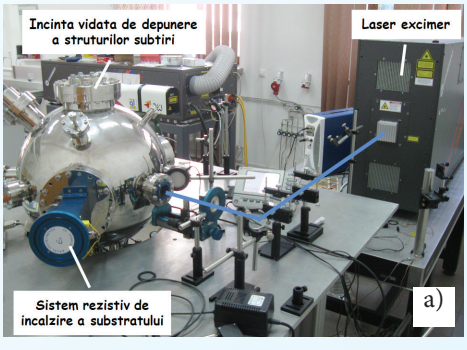
- Direct detection probe optimized for carbon, fluorine and silicon nuclei, used in open access
- Direct detection 10 mm probe for low soluble compounds
- Vibration dumper

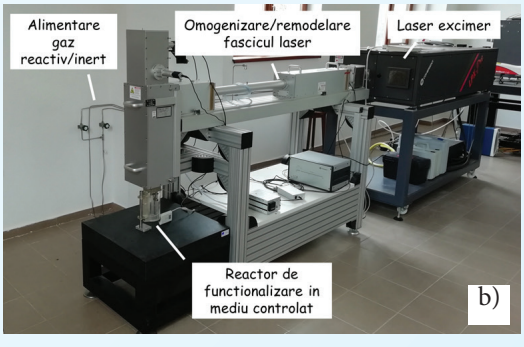
2. ***X-ray Diffractometer: D8 ADVANCE Bruker***

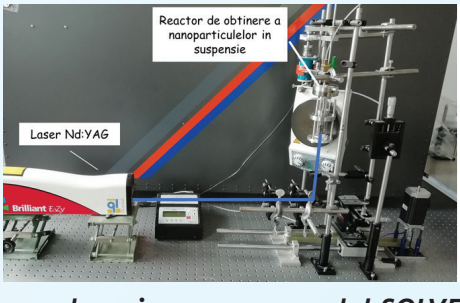
- WAXD analysis
- Studies with temperature variation
- X-ray reflectometry
- Thin films investigations
- Grazing incidence

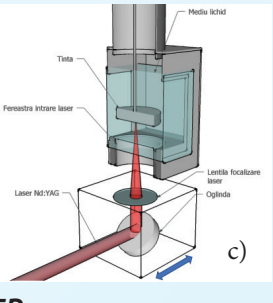
3. *Excimers lasers laboratory*

- System for thin film deposition through laser ablation (a)
- VarioLas laser lithography system (b)
- System for generation of nanoparticles in suspension through liquid laser ablation (c)









4. *Scanning probe microscope, model SOLVER PRO-M, NT-MDT*

- Techniques: AFM-Atomic Force Microscopy (contact mode, semi-contact mode, noncontact mode); EFM-Electric Force Microscopy; MFM-Magnetic Force Microscopy; STM-Scanning Tunneling Microscopy
- Scanning Tunneling Microscopy
- Surface morphology studies, micro/nanometric local physical properties (mechanical, electrical, thermal, magnetic properties), AFM nanolithography (AOL-Anodic Oxidation Lithography, SPL–Static Plowing Lithography (Scratching); DPL-Dynamic Plowing Lithography) and STM Lithography

5. *Scanning electron microscope QUANTA 200-FEI*

- Working procedures: High vacuum with secondary ED electron detector - obtaining

topography images; Low vacuum, scattered electron detector - BSD - compositional contrast images

- Resolution to 30 kV: 4nm
- EDX compositional analysis detector (both high vacuum and low vacuum)

6. ***Confocal microscope RAMAN (RENISHAW) IN VIA***

- Spectral domain: 100-5000 cm^{-1} from laser line
- Spectral resolution: less than 1 cm^{-1}
- Confocal microscope
- Image resolution: less than 10 μm
- Investigation of various materials from the point of view of the structure and morphology

7. ***Agilent 6520 Accurate-Mass Q-TOF LC/MS***

- Separation, identification and quantification of small organic/inorganic molecules and biomolecules
- Electrospray Ionization (ESI)
- Hybrid quadrupole – Time of Flight (Q-TOF) analyzer
- Resolution: up to 20000 mass resolution
- High sensitivity: up to 10-18 mol (scan mode)
- Mass accuracy: greater than 2 ppm
- Mass range: up to 20,000 Da
- Fast data acquisition (greater than or equal to 10 MS/MS spectra/sec) compatible with liquid chromatography (LC)

8. ***Dynamic mechanical analysis (DMA)***

- Determination of the viscoelastic properties of polymers and polymeric materials, in dynamic regime
- Loading type: tension, shear, bending, compression
- Information: evaluation of polymer relaxations

and of activation energies, variation of storage modulus (E') as a function of temperature, glass transition temperature determination, estimation of polymer properties in time.

REPRESENTATIVE PROJECTS

- European Social Fund - Cristofor I. Simionescu Postdoctoral scholarship program POSDRU/89/1.5/S/55216
  Duration: 2010- 2013
  Project manager: Dr. Mihaela Olaru
  Postdoctoral training program in the field of biomaterials
  (http://postdoc.icmpp.ro/)
- Luminescent organometallic complexes with self-assembling properties (LUMINASSIL)
  PN-III-P2-2.1-PED-2016-1536, contract 130PED/2017
  Duration: 2017–2018
  Project director: Dr. Mihaela Avădanei
  Objective: validation of a demonstration technology for the obtaining of luminescent organometallic complexes with a well-defined architecture, created by supramolecular non-covalent interactions using silicon-containing Schiff bases ligands and 3d and 4f metal ions
- A next generation plant biostimulant based on strigolactones included into stimuli responsive nanoformulation
  ERANET-INCOMERA-2017-BENDIS, contract 7/2018
  Duration: 2018-2019
  Responsible PPIMC: Dr. Călin Deleanu
- Closing the value chain in bioeconomy through innovative bioproducts requested by the market (PROSPER)
  PN-III-P1-1.2-PCCDI-2017-0569, contract 10PCCDI/2018
  Duration: 2018-2020
  Responsible PPIMC: Dr. Călin Deleanu
- Partnership for knowledge transfer in the field of polymeric materials used in biomedical engineering (POINGBIO)
  P_40_443, contract no. 86/8.09.2016
  Duration: 2016-2021
  Project director: Dr. Magdalena Aflori
  The project is co-financed by the European Regional Development Fund through Competitiveness Operational Programme 2014-2020, Axix 1 Research, Technological Development and Innovation in support of economic competitiveness and business development, Action 1.2.3 Knowledge Transfer Partnership
  The project aims to increase the economic competitiveness of the SMEs partners due to the transfer of knowledge regarding the scientific and technological expertise in the design and implementation of multifunctional polymer systems.

REPRESENTATIVE PUBLICATIONS

- M. Aflori, M. Butnaru, B.-M. Tihauan, F. Doroftei, Eco-friendly method for tailoring biocompatible and antimicrobial surfaces of poly-L-lactic acid, *Nanomaterials* 9, art. 428 (16 pag), 2019
- I. Stoica, M. Aflori, E.-G. Ioanid, C. Hulubei, Effect of oxygen plasma treatment and gold sputtering on topographical and local mechanical properties of copolyimide/gold micropatterned structures, *Surf. Interf. Anal*. 50,154–162, 2018
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- I. Stoica, E.G. Hitruc, D. Timpu, V. Barboiu, D.S. Vasilescu, Establishing proper scanning conditions in atomic force microscopy on polyimide and polyurethane samples and their effect on 3d surface texture parameters, *SCANNING - The Journal of Scanning Microscopies* 37, 335–349, 2015
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- E. Georgescu, A. Nicolescu, F. Georgescu, F. Teodorescu, D. Marinescu, A.-M. Macsim, C. Deleanu, New highlights of the syntheses of pyrrolo[1,2-*a*] quinoxalin-4-ones, Beilstein *J. Org. Chem*.10, 2377-2387, 2014
- M. Aflori, M. Drobota,D. Gh. Dimitriu, I. Stoica, B. Simionescu, V Harabagiu, Collagen immobilization on polyethylene terephthalate surface after helium plasma treatment, *Mater. Sci. Eng. B*. 178, 1303–1310, 2013
- M. Silion, A. Dascalu, M. Pinteala, B.C. Simionescu, C. Ungurenasu; A study on electrospray mass spectrometry of fullerenol C60(OH)24, *Beilstein. J. Org. Chem*. 9, 1285-1295, 2013