Polyamide Microcapsules and Composites Thereof for Technical and Biotechnological Applications

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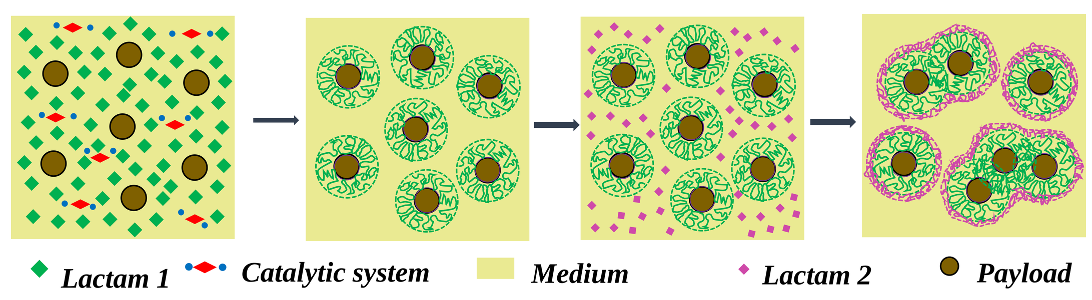
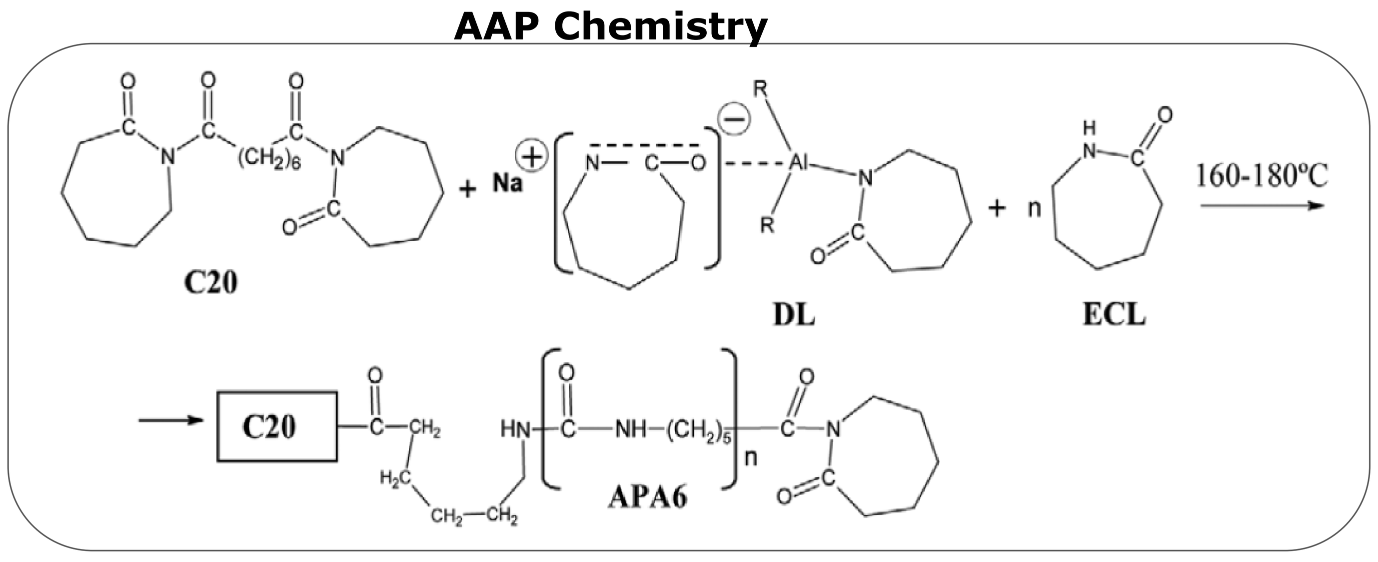
Polyamide microcapsules (PMC) were synthesized by an original one-pot method via activated anionic polymerization (AAP) of lactams [1]. The PMC contain in their cores a number of solid, finely divided materials: clays, metals or metal oxides, carbon allotropes, other polymer´s powders. The as-prepared PMC can be applied directly in biotechnology e.g., for protein and enzyme immobilization to produce stimuli-responsive microsystems, in solid-phase diagnostics, biosensors, biocatalysts, in extracorporeal therapy and bioseparation. Also, they have applications in fields of industrial materials for rotational molding, sintering, electro-conductive composites, etc. The PMC can also be transformed into micro- and nanocomposite materials through melt-processing techniques.

Activated Anionic Polymerization of Lactams (AAP)



AAP Chemistry



Objectives

The main objective was to develop and characterize PMC with controlled shape, size, porosity and molecular weights. The PMC useful in industrial applications (rotational molding, selective laser sintering, paint and textile industries) must be porous, conductive and be responsive to magnetic fields. The PMC designated for biological applications must be, in addition to this, responsive to pH triggers and bear immobilized enzymes on their shells. Detailed characterization of the chemical and physical properties of the PMC is foreseen on every stage of their synthesis, functionalization and enzyme immobilization using microscopy, thermal, spectral, magnetic susceptibility and X-ray scattering techniques. The final PMC with carbon, metal or clay payloads will be transformed via melt processing into micro or nanocomposites useful in automotive, aerospace, paint and textile industries. The final enzyme-bearing magnetic PMC will be tested in wine industry for control of the clarity, acidity and alcohol content. The magnetic responsiveness of these microcapsules should ensure their complete and simple removal from the treated wine product without affecting its organoleptic properties.

Methods and techniques

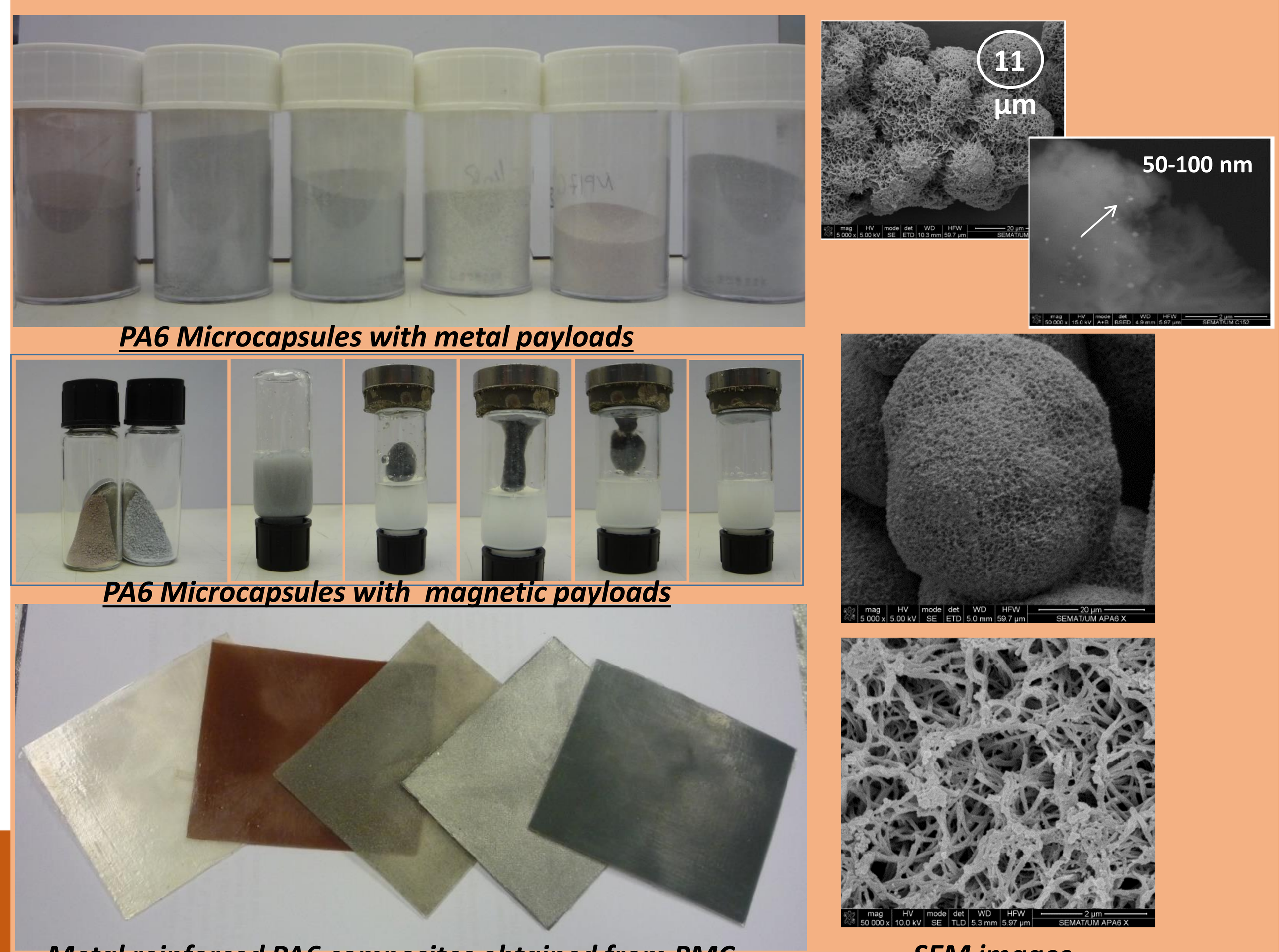
- Developing of PA6, PA12 and copolymeric PA6-PA12 PMC by incorporation of conductive and ferromagnetic payloads in the microcapsules´ cores through suspension/precipitation activated anionic polymerization of lactams in hydrocarbon solvents. [2]
- Functionalization of the shells of the PMC by grafting on their surfaces of polyacrylic acid or poly-N,N-dimethylaminoethyl methacrylate polyelectrolytes by means of a radical process creating responsive-ness to pH changes.
- Immobilization of enzymes from the groups of oxido-reductases e pectinases on the functionalized shell employing glutaraldehyde or carbodiimide precursors.
- Detailed characterization of the chemical and physical properties of the PMCs on every stage of their synthesis, functionalization and enzyme immobilization by microscopy, thermal, spectral, magnetic susceptibility and X-ray techniques. [3]

Results

The preparation process makes use of AAP of lactams carried out in hydrocarbon solvents in the presence of the respective payload. **FIG. 1** shows the visual aspect of various PA6@metal powder PMC with the metal load varying in the range of 1-20 wt%. According to SEM, the PMC are highly porous, with sizes in the range of 10-200 μm. The PMCs charged with various types and amounts of payloads can be directly used as-prepared or transformed into molded parts by means of conventional melt processing techniques. In such a way thermoplastic composites were obtained with polyamide matrix reinforced by finely dispersed with sizes are in the nano- or micrometer length scale.

FIG.2 shows the typical size distribution of the PMC. The magnetic susceptibility (Fe payloads) and conductivity (carbon allotropes payloads) were determined for thermoplastic composites produced from compression molded PMC. Significant improvements of conductivity is achieved using carbon black (CB) and carbon nanotubes (CNT), as well as mixed CNT/CB reinforcements. Magnetic properties are proportional to the Fe content.

FIG.3 shows the mechanical properties of thermoplastic composites produced from compression molded PA6@CNT PMCs. Tensile and impact properties are also shown of laminate composites obtained from PA6@MMT clay PMC and glass- or PA66 textile structures. Major improvement of the mechanical properties in tension and impact were achieved.



PA6 Microcapsules with metal payloads

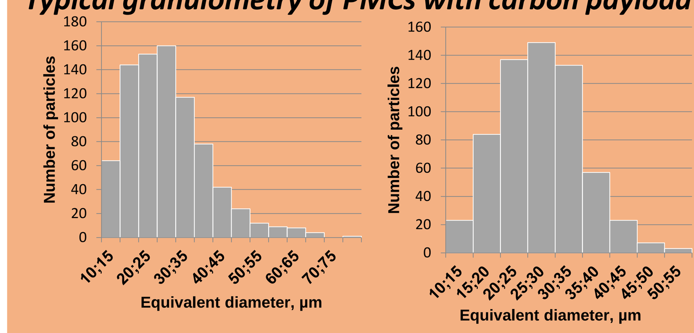
PA6 Microcapsules with magnetic payloads

Metal reinforced PA6 composites obtained from PMC

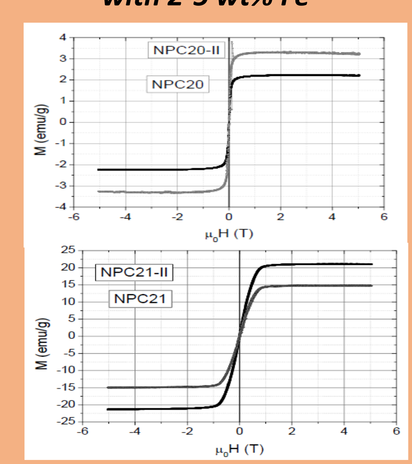
SEM images

FIG. 1

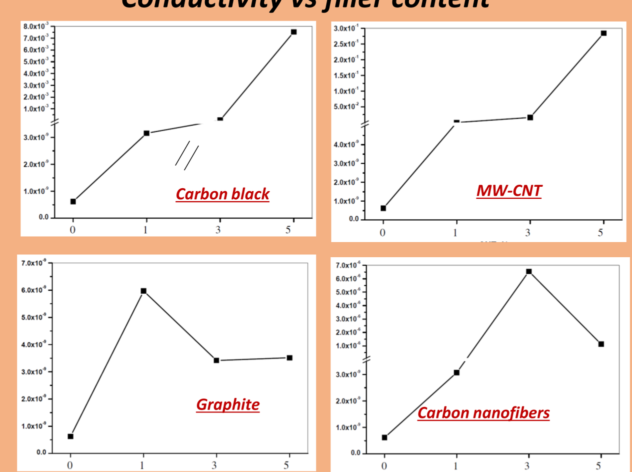
Typical granulometry of PMCs with carbon payload



Magnetic susceptibility of PMCs with 2-5 wt% Fe



Conductivity vs filler content



Conductivity vs filler content

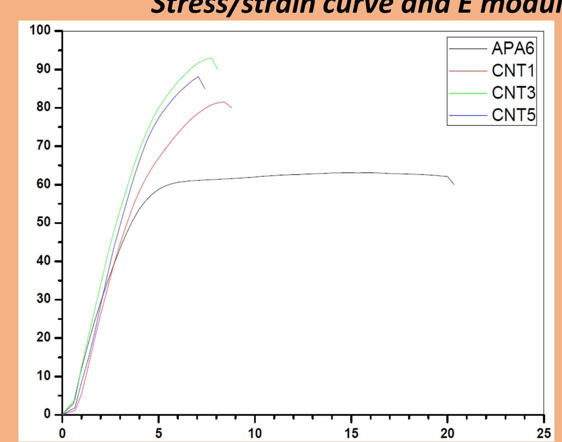
Filler, wt %	0	1	3	5
CB	5.10^{-10}	3.10^{-9}	1.10^{-3}	8.10^{-3}
CNT	5.10^{-10}	1.10^{-3}	5.10^{-2}	3.10^{-1}
GR	5.10^{-10}	6.10^{-9}	3.10^{-9}	4.10^{-9}
CNF	5.10^{-10}	3.10^{-9}	6.10^{-6}	2.10^{-6}

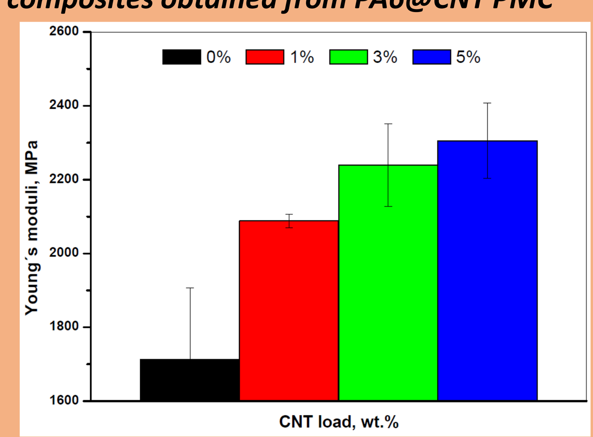
Conductivity of mixed composites, 2.5/2.5 wt%

APA6	GR/CB	CNT/GR	CNT/CB
5.10^{-10}	3.10^{-9}	5.10^{-3}	$3.0.10^{-2}$

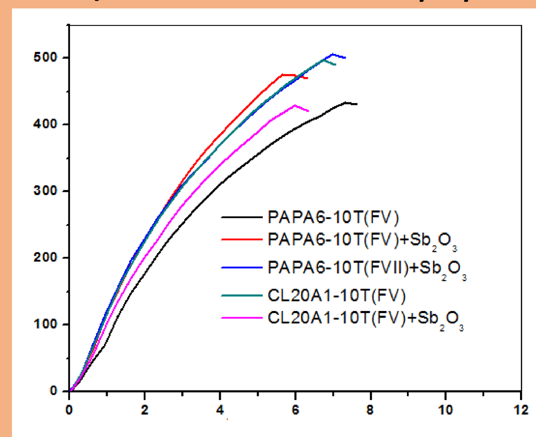
FIG. 2

Stress/strain curve and E moduli of composites obtained from PA6@CNT PMC





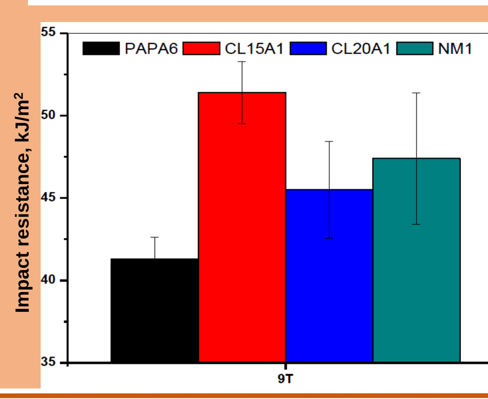
Stress/strain curve and tensile properties of glass fiber laminates from PA6@MMT PMC



Glass Fiber Textile Structures			
Sample Designation	Young Modulus [GPa]	Stress at Break [Mpa]	Strain at break [%]
PAPA6-10T(FV)	12.34 ± 0.35	411 ± 28	6.6 ± 0.6
PAPA6-10T(FV)*	13.97 ± 0.09	497 ± 30	6.4 ± 0.5
PAPA6-10T(FVII)*	14.14 ± 0.77	509 ± 24	7.0 ± 0.6
CL20A1-10T(FV)	13.36 ± 1.01	482 ± 21	6.5 ± 0.7
CL20A1-10T(FV)*	12.23 ± 0.73	417 ± 34	5.7 ± 0.4

* Matrix modified with transreaction catalyst

__Note:__ Laminates containing 10 plies of glass fiber textile, 2 mm thick



Impact properties of all polyamide composites (PA6 matrix/PA66 textile structures, 6 plies, 2 mm sample thickness)

FIG. 3

Publications

1. Denchev Z, Dencheva N – Polyamide Microcapsules and Method to Produce the Same, Patent Application No PT 107879, filed 03.06.2014;

2. Dencheva N et al – One-pot method for the preparation of polyamide shell-core microcapsules by solution/precipitaion anionic polymerization, Materials Letters (submitted)

3. Dencheva N et al – Microfocus synchrotron WAXS studies of PA6@payload microcapsules (in preparation)

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DESY

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