NEW NANOSTRUCTURED MATERIALS PREPARED BY ELECTROSPINNING OF BIOBASED POLYMERS FOR BIOMEDICAL AND FOOD APPLICATIONS

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SEE Net PhytoChemNatProd
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### Biobased and (bio)degradable polymers

**Extracted from biomass**
- Proteins
- Polysaccharides

**Produced by bacterial fermentation**
- Poly(hydroxyalkanoates)
- Microbial cellulose

**By polymerization of monomers derived from renewable sources**
- Poly(lactic acid) and copolymers

**Novel materials for biomedical, agricultural and food applications**
120nm + POE

Electrospinning

Hydrogels

Capillary extrusion

POE + POE

Beads

Coprecipitation

Nanoparticles

Micro- and nanofibers
Preparation of stealth nanoparticles by polyelectrolyte complex formation

\[
\text{CH}_3\text{O}\left[\text{CH}_2\text{CH}_2\text{O}\right]_m\text{C}\left[\text{CH}_2\text{C}\right]_n\text{Br}
\]

Mean apparent particle size, nm

Intensity

10
20
30
40
50
60
70
80
90
100
120

10
45
51
57
64
72
82

X: 0.668 nm
Y: 0.668 nm
Z: 0.668 nm
Chitosan, N-carboxyethylchitosan (polyelectrolyte complexes at pH 1-14)
STEALTH NANOPARTICLES FROM N-CARBOXYETHYLCHITOSAN

Electrospinning of polymers

Schematic representation of electrospinning set up with appliance for enhancement of the electric field homogeneity
NANOFIBROUS MATERIALS FROM BIOPOLYMERS WITH TAILORED BIOLOGICAL PROPERTIES ON CONTACT WITH CELLS

wound healing devices

antibacterial non-woven textile

haemostatic non-woven textile

scaffolds for cell and tissue engineering

fullerene-containing nanofibers

> 200 cells/100 µm²

~ 5 cells/100 µm²

Destruction of tumor cells
Polylactide Stereocomplex-Based Electrospun Materials Possessing Surface with Antibacterial and Haemostatic Properties

Poly(L-lactic acid)

Contact with blood

Haemostatic effect

Poly(L-lactic acid) (PLLA)

Contact with S. aureus

Antibacterial effect

Drug-Loaded Electrospun Polylactide Bundles

SEM micrograph of drug-loaded PLA/PEG bundle

Multi-needle electrode

screen

jet

Al foil

Taylor cone

Multi-needle electrode

collector

syringe needle

syringe containing polymer solution

Lidocaine hydrochloride
local anesthetic

Diclofenac sodium
anti-inflammatory agent

Benzalkonium chloride
antibacterial

A. Toncheva, M. Spasova, D. Paneva, N. Manolova, I. Rashkov
Novel laboratory nanotechnology for one-pot preparation of nanofibrous materials with tailored surface chemistry.

An original approach combining the electrospinning and polyelectrolyte complex formation tools.

After immersion in aqueous solution of Fluorescein for 7 h

After 24h stay in aqueous solution (pH 4)
Tuning of the Surface Biological Behavior of Poly(L-Lactide)-Based Electrospun Materials by Polyelectrolyte Complex Formation

Electrospun nanofibrous materials containing ascorbyl palmitate

Antibacterial effect

Preserved antioxidant activity

$V_{50}$ AP extract ($\mu$L)

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<th>AP content</th>
<th>9%</th>
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Viability [log (CFU/ml)]

- S. aureus (control)
- PCL
- PCL/AP(9%)
- PCL/AP(30%)

Exposure time [min]

- 0
- 5
- 10
- 15
- 20
- 25
Electrospun non-woven nanofibrous hybrid mats based on chitosan or quaternized chitosan and poly(L-lactide-co-D,L-lactide) for wound-dressing applications

Development of *S. aureus* on contact with PLDLA, Ch/PLDLA и QCh/PLDLA mats

Antitumor activity of quaternized chitosan/poly(lactic acid) copolymer/DOX

Apoptosis in HeLa human cervical cancer cells

Antitumor activity of electrospun implants against Graffi myeloid tumor
Chitosan films - 3rd generation packaging materials

edible films and coatings; antimicrobial packaging

- completely or partially soluble in aqueous solutions
- easily processed, heat resistant
- environmentally friendly and biodegradable
- preserves the colour, flavour, acidity and sugar contents of fruits
- maintains the food quality during transportation and storage
- reduces the damage during storage
- hypocholesterolemic effect

- moderate water permeability
- good barrier properties to oxygen
- delayed ripening
- inhibited fungal growth
- controlled release of antimicrobials, antioxidants and flavours
Coating of strawberries, blueberries and grapes with chitosan reduced the growth of pathogenic microorganisms during 18 days of storage at 4°C.

N. Manolova, D. Paneva, O. Stoilova, I. Rashkov, Polymer materials for food packaging and preservation, in e-Reference tools for VET trainers in food industry, Leonardo da Vinci Pilot Project BG/05/B/F/PP-166054
New generation food products from polyelectrolyte complex - based materials

pectin/CECh complex
stable at pH = 1 - 6.5

Cucumber mash
Tomato mash
Olive mash
Orange pulp
Peach pulp
Apricot pulp

pectin/N-carboxyethylchitosan (CECh)
Lab-scale technology for embedding of biopesticides

- Stimulates the plant protection
- Impedes the development of plant pathogens
- Provides favorable conditions for plant growth

Environmentally friendly plant protection systems based on chitosan
“Tricho-kit” against Fusaruim

Production of biocides

Cucumbers

“Tricho-kit”

Control

Fusaruim
TAILORED NANOSTRUCTURED MATERIALS FROM BIOBASED POLYMERS (nanofibers, nanoparticles, beads, hydrogels, membranes)

medicine and pharmacy
  drug carriers (modified drug release, topical applications - buccal, rectal, vaginal, wound dressings, local antitumor drug delivery)

cosmetics
  skin care fibrous materials

food packaging and preservation

agriculture
  plant protection

biologically active substances (individual or blends) or extracts from medicinal aromatic plants – antioxidants, antimicrobials, antivirals, etc.
Acknowledgements to the National Fund for Scientific Research

Grants:

- **DO 02-164/08** Novel hybrid nanostructured materials for local cancer treatment
- **DO 02-237/08** Self-assembly of conducting nanofibers into yarns during electrospinning of polyelectrolyte solutions
- **DO 02-238/08** New antibacterial and hemostatic nanofibrous wound dressings
- **DO 02-333/08** Novel nanostructured materials with antioxidant activity for wound healing
- Participation in the Center of Excellence: NATIONAL CENTER FOR ADVANCED MATERIALS – UNION  **DO 02-82/08 and 02-2/09** Module 2: Advanced materials for medical and pharmaceutical applications
- **TC-Ch-1719** - Study of the interactions chitosan (solutions, microgels or nanostructured spheres) – beneficial/pathogenic microorganisms – agricultural crops (with Agricultural University, Plovdiv)
- **NT 4-01/04 (NANOBiomAT)** - Appliances development and technologies for electrospinning of biopolymers for preparation of nanofibre materials, characterization of the nanofiber morphology and interactions cell-nanoscale materials; in the frames of the National Program NEW MATERIALS AND NANO TECHNOLOGIES
- **Ch 1414/04** - Nanostructured materials – nanofibers and beads from biocompatible polymers for biomedical applications
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