6th WORKSHOP
Green Chemistry and Nanotechnologies in Polymer Chemistry

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Table of Contents

INVITED LECTURES .......................................................................................................................... 1

IL I. THE CHEMICAL MODIFICATION OF NATURAL POLYMERS BY THE DIELS-ALDER REACTION .......... 2
A. Gandini

IL II. NANOSTRUCTURED MULTILAYERS OBTAINED FROM NATURAL-BASED POLYMERS:
BIOMEDICAL APPLICATIONS ........................................................................................................ 2
J.F. Mano

IL III. GREEN SYNTHESIS OF POLYMERS USING SUPERCritical CO2 ........................................... 3
J.F. Rodriguez, C. Gutierrez

IL IV. APPLICATIONS OF NATURAL POLYMERS IN INDUSTRY AND MEDICINE ............................. 3
M.H. Gil, P. Alves, P. Coimbra, P. Ferreira

ORAL PRESENTATIONS ....................................................................................................................... 4

O01. INFLUENCE ON ISOCYANATE INDEX ON SELECTED PROPERTIES OF FLEXIBLE
POLYURETHANE FOAMS MODIFIED WITH VARIOUS BIO-COMPONENTS ........................................ 5
A. Prociaik, E. Malewska, S. Bąk

O02. OXYPROPYLATION OF GREY ALDER BARK AND ITS FRACTIONS TO OBTAIN POLYOLS USABLE
FOR PRODUCTION OF RIGID POLYURETHANE FOAMS ................................................................... 7
L. Vevere, A. Arshanitsa, G. Telysheva

O03. SYNTHESIS, STRUCTURE AND PROPERTIES OF NOVEL POLYHYDROXYURETHANES OBTAINED
BY NON-ISOCYANATE ROUTE ........................................................................................................ 9
M. Włoch, J. Datta

O04. RIGID POLYURETHANE FOAMS AS THERMAL INSULATION MATERIAL BASED ON RECYCLED
PET AND RAPESEED OIL .................................................................................................................... 10
A. Paberza, A. Fridrihsone-Girone, A. Abolins, U. Cabulis

O05. BALANCE BETWEEN RENEWABLE AND RECYCLABLE FEEDSTOCK FOR RIGID POLYURETHANE
FOAMS .................................................................................................................................................. 12
U. Cabulis, M. Kirpluks, A. Paberza, A. Fridrihsone-Girone, I. Vitkauskiene

O06. WATERBORNE POLYURETHANE-CELLULOSE NANOCRYSTALS NANOCOMPOSITES ................. 14
A. Santamaria-Echart, A. Saralegi, L. Martin, M.A. Corcuera, A. Eceiza

O07. BIO-BASED POLYURETHANE ELASTOMERS - SYNTHESIS AND CHARACTERIZATION ............... 16
J. Datta

O08. POLYURETHANE FOAMS OBTAINED FROM RECOVERED POLYOL THROUGH CHEMICAL
RECYCLING ........................................................................................................................................... 17
P. Kopczyńska, J. Datta

O09. INFLUENCE OF PROCESS VARIABLES IN ESTOLIDE SYNTHESIS AND THEIR ESTER
DERIVATIVES FROM OLEIC ACID ................................................................................................. 18
J.C. de Haro, M.P. Garrido, A. Pérez, M. Carmona, J.F. Rodríguez

O10. GREEN POLYMERS FROM BIOBASED-MONOMERS: KINETICS OF FREE-RADICAL
POLYMERIZATION OF ITACONIC ACID ............................................................................................. 20
A. Wesołowska, S. Bednarz, D. Bogdał

O11. THE INFLUENCE OF VARIOUS CATALYSTS OF EPOXIDATION OF SOYBEAN OIL ON THE COURSE
OF EPOXY FUSION PROCESS AND THE FUNCTIONALITY OF PRODUCTS OBTAINED ........................... 22
A. Sienkiewicz, P. Czub

O12. PREPARATION OF NANO-HYDROXYAPATITE/CHITOSAN SPONGE-LIKE SCAFFOLDS FOR TISSUE
ENGINEERING ...................................................................................................................................... 24
G. Ruphuy, M.M. Dias, J.C. Lopes, M. F. Barreiro

O13. MAGNETIC AND pH RESPONSIVE MICROCAPSULES WITH PROTEIN IMMOBILIZATION ............. 26
N. Dencheva, J. Braz, Z. Denchev
P37. MICROENCAPSULATION OF *Rosmarinus officinalis* L. (ROSEMARY) AQUEOUS EXTRACT FOR APPLICATION IN FUNCTIONAL FOODS ................................................................. 133

P38. MICROENCAPSULATION OF FENNEL AND CHAMOMILE AQUEOUS EXTRACTS FOR APPLICATION IN COTTAGE CHEESE ................................................................. 135
   C. Caleja, A. Ribeiro, I.C.F.R. Ferreira, M.F. Barreiro

P39. FUNCTIONAL SYNTHETIC TURF SYSTEM WITH IMPROVED COMFORT ................................................................. 137
   B. Moura, S. Silva, N. Durães, D. Coelho, L. Rodrigues, F. Monteiro, R. Silva, A. Moreira

P40. CERAMIC MATERIALS WITH IMPROVED THERMAL COMFORT ................................................................. 139
   A. Sampaio, J. Sousa, J. Branquinho, D. Coelho

P41. MELAMINE-FORMALDEHYDE RESINS MODIFIED WITH GLYCEROL ................................................................. 141
   A. Henriques, J. Ferra, J.M. Martins, F. Magalhães, L. Carvalho

P42. MODIFYING RIGID POLYURETHANE FOAM MECHANICAL PROPERTIES BY HIGH RENEWABLE CARBON CONTENT POLYOL MIXTURES ................................................................. 143
   L. Ugarte, T. Calvo-Correas, A. Santamaría-Echart, S. Gómez-Fernández, M.A. Corcuera, A. Eceiza

P43. THE USE OF BIO-BASED ADDITIVES (LIGNIN, STARCH AND CELLULOSE) IN THERMOPLASTIC POLYURETHANE FORMULATIONS TO ENHANCE THE BIODEGRADABILITY OF FOOTWEAR COMPONENTS ................................................................. 145
   I.P. Fernandes, M. Barbosa, J.S. Amaral, V. Pinto, M.J. Ferreira, M.F. Barreiro

P44. SYNTHESIS OF HYDROXYAPATITE WITH NANOARTICLES INCLUSIONS ................................................................. 147
   D. Malina, A. Sobczak-Kupiec, K. Pluta, K. Bialik-Wąs, B. Tyliszcak

P45. DRYING KINETICS AS TOOL FOR DYNAMIC POROSITY OF CATALYST-SUPPORT MATERIALS ................................................................. 149
   J.F. Mata-Segreda

P46. PREPARATION OF POLY(URETHANE-UREA) MICROCAPSULES BY INTERFACIAL POLYMERIZATION: EFFECT OF PEG MOLECULAR WEIGHT ................................................................. 151

P47. BIODEGRADATION PRETREATMENT OF WOOD OF *E. grandis*, *E. dunni*, AND *E. bentami* TO WORK IN BIORREFINERY PROCESSES ................................................................. 153
   M. Lopretti, S. Baldyga, M. Gonzalez, L. Olazabal, M. Torres

P48. MICROENCAPSULATION OF *Ceratonia siliqua* L. EXTRACT FOR FOOD PURPOSES: EFFECT OF EXTRACT/ALGINATE RATIO ................................................................. 155

P49. NATURAL ADDITIVES FOR REDUCING FORMALDEHYDE EMISSIONS IN UREA-FORMALDEHYDE RESINS ................................................................. 157
   F. Pereira, N. Paiva, J. Ferra, J.M. Martins, F. Magalhães, L. Carvalho

P50. PREPARATION AND CHARACTERIZATION OF POLYSACCHARIDES/PVA BLEND NANOFIBROUS MEMBRANES PREPARED BY ELECTROSPINNING ................................................................. 160
   A. Sampaio, C. Silva, D. Coelho, A. Zille

P51. VALORISATION OF ALMOND AGRO-INDUSTRIAL RESIDUES: PRODUCTION OF BIOPOLYOLS FROM ALMOND SHELL ................................................................. 162
   J.A. Pinto, I.P. Fernandes, M.F. Barreiro

P52. MICROENCAPSULATION OF PLANT EXTRACTS RICH IN APIGENIN TO BE USED AS CHEMOPREVENTIVE AGENTS IN FUNCTIONAL FOODS ................................................................. 164

P53. POLYUREAURETHANES WITH RAPSEED POLY FOR TECHNICAL APPLICATIONS ................................................................. 166
   M. Auguśćik, J. Ryszewska, M. Zieleniewska, M. Kurańska, A. Prociak, W. Karalus, K. Pietrzak

P54. INVESTIGATION OF TUNISIAN AGRICULTURAL RESIDUES TO PRODUCE CELLULOSE NANOCRYSTALS AND NANOFIBRILLAR CELLULOSE: APPLICATION TO NANOCOMPOSITE MATERIALS ................................................................. 168
   F. Bettaieb, R. Khiai, F. Mhenni, N. Belgamoune, A. Dufrêne, S. Boufi
P48. MICROENCAPSULATION OF Ceratonia siliqua L. EXTRACT FOR FOOD PURPOSES: EFFECT OF EXTRACT/ALGINATE RATIO

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Introduction
Human health, nutritional status and well being can be enhanced through consumption of foods containing specifically desired nutrients and bioactive agents [1]. Popularly known as St John’s Bread, Ceratonia siliqua L. (carob) has a long history of use in food (over 4000 years). It has a good nutritional value and its polyphenolic extract shows high antioxidant capacity and even higher antiradical activity than well-aged red wines. Its reducing power can also be four-fold higher than many well known potent antioxidant agents such as gallic acid, caffeic acid and catechin [2]. Nevertheless, preparing high quality nutritious food is critically dependent on availability of effective delivery systems. Such systems should preserve the specific nutritional, biological, chemical and functional properties of the sensitive constituent, and should effectively release the compounds, in a desired mode, after ingestion. Nowadays, the most promising technology that can allow overcoming the stated difficulties is microencapsulation [1]. In this context, a hydroethanolic (80:20, v/v) extract obtained from carob pulp by ultrasonic extraction was microencapsulated for further use in the development of functional yogurts.

Experimental
The bioactive extracts were obtained from powdered carob pulp through an ultrasound extraction process (testing different times - 5, 10 and 15 minutes and amplitudes - 50, 75 and 100%). The extracts were evaluated in terms of antioxidant activity (free radicals scavenging activity, reducing power, β-carotene bleaching inhibition and lipid peroxidation inhibition in brain homogenates - TBARS assay) and the most promising was encapsulated for food purposes. Three microencapsulation trials were conducted by an atomization/coagulation technique using different extract/sodium alginate ratios (50/400, 75/400 and 100/400, mg/mg, 10 mL) in order to choose the most suitable one. The solutions were then atomized through a nozzle (0.35 mm) and coagulated in a calcium chloride solution (250 mL, 4% (v/v)). The obtained microspheres were characterized by optical microscopy (OM) during the microencapsulation process to monitor morphology evolution and after being lyophilised. The encapsulation efficiency (EE) was evaluated by HPLC-DAD.

Results and discussion
The hydroethanolic extract obtained by ultrasonication using 75% amplitude during 10 minutes gave the highest antioxidant activity (data shown in Table 1).

Table 1. EC50 values (mg/mL) obtained according to different methodologies (effective concentrations providing 50% of antioxidant activity or 0.5 of absorbance in reducing power assay).

<table>
<thead>
<tr>
<th>Methodology</th>
<th>EC50 (mg/mL)</th>
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<tbody>
<tr>
<td>DPPH scavenging activity</td>
<td>2.96 ±0.05</td>
</tr>
<tr>
<td>Reducing power</td>
<td>0.78 ± 0.01</td>
</tr>
<tr>
<td>β-Carotene bleaching inhibition</td>
<td>1.59 ± 0.14</td>
</tr>
<tr>
<td>TBARS inhibition</td>
<td>0.33 ± 0.02</td>
</tr>
</tbody>
</table>

The evaluation of the obtained microspheres by OM, during different stages of the encapsulation process and after being lyophilised for storage purposes, revealed changes in their shape. In fact, at the end of the atomisation step (Fig. 1 A, D and G) and coagulation processes (Fig. 1 B, E and H),
microspheres with various dimensions and a clear spherical form were observed. After being dried (Fig. 1 C, F and I), the microspheres corresponding to the different ratios applied, showed a ruffled form being apparently glued to each other possibly due to the absence of water. Another perceptible point is the presence of a growing number of small microcapsules as the ratio extract/alginate increases. The HPLC-DAD analysis of the coagulation and the washing solutions, which revealed to present none or only traces of extract, let to estimate an EE around 100% for all the tested extract alginate/ratios.

Fig. 1. OM analyses with magnifications of 100X: microspheres after atomization (A, D and G, respectively for 50/400, 75/400 and 100/400 extract/alginate ratios); microspheres after four hours in contact with a solution of calcium chloride under stirring at 200 rpm (B, E and H, respectively for 50/400, 75/400 and 100/400 extract/alginate ratios); freeze-dried microspheres (C, F and I, respectively for 50/400, 75/400 and 100/400 extract/alginate ratios).

Conclusions
Viable microspheres were produced through the atomization/coagulation technique using different extract/alginate ratios, being obtained for all the produced samples, an EE of 100%. This final product will be incorporated into natural food matrices, specifically yogurts (work under progress). The main objective will be to infer the impact of using microcapsules with different extract concentrations, which will be reflected on the used microcapsules’ amount, on the extract delivery and bioactivity maintenance. With this strategy the delivery of bioactive phenolic compounds can be tailored enhancing the bioavailability of extracts and related health promoting properties of the developed food product.

References