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UTILIZATION OF INDUSTRIAL BY-PRODUCTS FOR OBTAINING NEW PRODUCTS LIKE DIETARY SUPPLEMENTS WITH NUTRITIONAL AND PHYTOTHERAPEUTICAL PROPERTIES

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The paper proposes exploiting natural products derived from food, to getting new products that can be use, in addition to nutritional properties and certain beneficial effects.

The new group of products is based on the exploitation of natural vegetable products resulting from edible oils getting virgin cold pressed (cake seeds), and which by their composition in natural compounds biocompatible naturals satisfy both properties, and nutrients and regeneration of body representing a staple in lock for cheap.

This type of products proposed for obtain are derived in the same time while enhancing long-term health to avoid lower immunity and installation of serious illness.

In the aftermath, the protein it is envisaged that the proposed recovery cake seeds have a good protein quality and a very high protein content (15-40%) which allows combinations and associations varied for consumption. Through such combinations can diversify the types of protein and amino acid sequence variation in inhibitors, stimulating and helping processes of biosynthesis in the liver and cell regeneration processes.

Also take into account that in the context of efforts and/or removal of pollutants of any kind, the material proposed for use is ecologically grown and processed according to European GMP, TUV approved for HOFIGAL.

Proposed plant material – Seed cakes from: Thistle, Sesame, Soybean, Pumpkin, Flax, Hemp, Safflower, Chick, Seabuchorn.

This plant material after oil extraction with oil in quantities exceeding 30%, is much richer in molecular species of interest both nutritional and phytoterapeutical. Thus, cakes studied were revealed protein, amnoacids, simple and complex sugars, mucilage, inulin, vegetable fibers, enzymes, minerals, lipids, lipoproteins, glycolipids, lecithins, flavones, polyphenols, phytosterols, and so on. The paper presents the main results as tables cakes seeds constituents analyzed.

DETERMINATION OF ANTIOXIDANT CAPACITY OF SOME FRUIT SEEDS EXTRACTS**DANET Andrei Florin¹, BADEA DONI Mihaela², POPA Valentina¹**¹*University of Bucharest, Faculty of Chemistry, Sos. Panduri 90-92, 050657, Bucharest*²*Icechim, Department of Biotechnology, Spl. Independentei 202, Bucharest*

The objective of the study has been to determine total antioxidant capacity (TAC) of some fruits seeds extracts by a chemiluminescence (CL) method, based on a luminol/Co(II)-EDTA/H₂O₂ system^{1,2,3}. In order to extract hydrophilic antioxidants, seeds of *Citrus x limon* (lemon), a variety of *Citrus reticulata* (clementine), *Vitis vinifera* (white grapes) and *Citrullus lanatus* (watermelon) were refluxed with 96 % ethylic alcohol. The CL measurements of TAC of hydrophilic extracts were done in an aqueous medium containing ethanol. The calibration curve was drawn by using the quercetin, over a concentration between 10⁻⁵ –10⁻³ moles L⁻¹. RSD was 2.65% (n = 10, c_{quercetin} = 3.5 x 10⁻⁵ M). TAC values determined for the hydrophilic seeds extracts were as follows: 603 for lemon, 594 for grapes, 437 for watermelon and 279 for Clementine, all in quercetin mg equivalent/100 g dw. The precision of the method was verified by applying a standard addition method.

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PRELIMINARY ANALYSES OF AN OINTMENT WITH INCREASED WOUND HEALING ACTIVITY AND SOME OF ITS NATURAL INGREDIENTS

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The object of this study is an ointment containing natural ingredients designed for wounds treatment. One of the main ingredients is a mixture of nine medicinal plants, namely: *Calendula officinalis* sp. (pot marigold, *Asteraceae*), *Matricaria chamomilla* L. (chamomile, *Asteraceae*), *Symphytum officinale* L. (comfrey, *Boraginaceae*), *Hypericum perforatum* L (St. John's wort, *Hypericaceae*), *Achillea millefolium* (common yarrow, *Asteraceae*), *Arctium lappa* L. (burdock, *Asteraceae*), *Plantago major/lanceolata* L (greater plantain, *Plantaginaceae*), *Althaea officinalis* L (marshmallow, *Malvaceae*) and *Quercus robur* (oak bark, *Fabaceae*), species with well known wound healing activity. In order to analyze the ointment and the ingredients, oil and alcoholic extracts from the mixture of plants and alcoholic extract from the ointment were obtained and evaluated for their polyphenols content and antioxidant activity. It is known that the antioxidants play an important role in the healing process¹. Polyphenols such as gallic acid, ferulic acid, caffeic acid, chlorogenic acid, quercetin and rutin were identified and quantified in extracts by LC-MS analysis². Also total phenols content and antioxidant activity were determined spectrophotometrically³. The effect of extracts on the growth of mouse fibroblasts cells NCTC clone 929 was assessed using neutral red (NR) assay⁴ to measure the cell viability in vitro.

The results showed that the extracts are rich in polyphenols and have good antioxidant activity suggesting that the mixture plant extracts has a good contribution to the wound healing activity of the ointment. No morphological alteration was observed at the fibroblast cells treated with extracts and the extracts do not affect cells viability in vitro, this showing that the ointment and extracts are not toxic to cells.

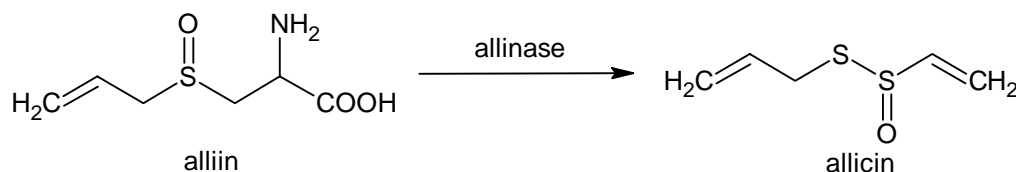
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THE VARIATION OF ALLICIN CONTENT, ANALISED BY HPLC, IN INDIGENOUS GARLIC LEAVES AND BULBS FOR ITS VALORIFICATION IN NEW PHYTOTHERAPIC PRODUCTS

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The garlic (*Allium sativum*) is known, from ancient time, both for its dietary uses and medicinal purposes (indigestion, wound healing, respiratory problems, intestinal parasites, etc.). The garlic's composition consists of sulphur compounds, carbohydrates, proteins, vitamins (B₁, B₂, B₃, B₅, B₆, C), Ca, P, Mg, K, Se, Mn, Fe, etc. In the last 30 years garlic and garlic extracts were intensely studied from a chemical, biochemical, pharmacological and even clinical trial perspective to determine the active compounds and their therapeutic action. This research studies showed that the active compound responsible for garlic's medicinal properties is allicin. Allicin is synthesized in garlic from alliin, under the influence of allinase enzyme, only when the garlic bulb is crushed or heated, according to the following reaction:



The clinical trials conducted on human patients revealed that allicin has the following pharmacological activities: antibiotic, antimycotic, antiviral, antiparasitic, antihypertensive, antitumour, antioxidant, antiaging, anticoagulation, lowers LDL cholesterol¹.

This paper presents the variation of allicin content in indigenous garlic, in leaves and bulbs, the final goal of this research being the valorification of the garlic's part with the highest content in allicin in new medicinal products. In this study we analysed fresh and dried garlic. The used HPLC chromatograph is Hitachi Elite LaChrom and the HPLC method is from the European Pharmacopoeia 7.0, Garlic powder monograph. To establish under what form the garlic will be used in the new medicinal products the content of allicin was analysed from: garlic bulb powder, bulb juice, bulb extract, garlic leaves powder and garlic leaves juice. Based on the results obtained from this study we can conclude that the highest amount of allicin is formed in the bulbs of garlic. Moreover the maximum content in allicin was obtained in dried powder from garlic bulbs, which is very convenient because it can be conserved under this form.

¹ Peter Josling – “Allicin – The hearth of garlic”, HCR Publishing, Chicago, Illinois, 2005.

Innovative products for honey bee treatments

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In last decade we developed several products for honey bees treatment, intended to stimulate the pollination activity, to protect honey bees against parasitic mite and to activate the defense systems. We made pollination attractants for bees by combining the brood pheromone, a mixture of ethyl and methyl esters of fatty acids, including (poly)unsaturated ones, with enhancers of the perception of volatile chemical signals (maltol, ethyl-maltol), which have also a role of protection of unsaturated links against the destructive action of reactive oxygen species. This combination, which is acting as an attractant for bees pollination, was conditioned as controlled release micro-beads and was used for the treatment of a sunflower crop, obtaining a production 23.27% higher than the control.

Varroa destructor mites is the parasite with the most pronounced economic impact on the beekeeping industry, due to the debilitation produced by the consumption of hemolymph and viruses transmission. In organic bee keeping systems are allowed to be used a number of volatile natural substances anti-*Varroa*, e.g. formic acid, menthol, thymol. The vapors of active ingredients are considered selective, acting mainly on mites. However, in case of high temperature, the concentration of active vapors may increase over the limit on which these start to become harmful also to bees, and especially to queens. We made a composition from which the release of active ingredients is reduced when the temperature rises over 32 ... 35 ° C, using thermo sensitive hydrogels based on starch cross-linked with citric acid and carboxymethylcellulose. These hydrogels swells at lower temperatures, increasing the volume and increasing the pore size, and collapses at higher temperatures, thus reducing the volume and size of the pores through which the active ingredients are released. We obtained a product which presents a controlled-release characteristic on a range of temperatures, and which could be formulated for an easy application (trays with a single dose, sealed with thermo-adhesive foil). By applying this product we obtained a 78.5% efficacy in treatment of *Varroa*, similar to that of other commercial products based on organic ingredients.

For the application of the compounds which activate the bee defense systems we developed a formulation as effervescent tablet; such formulation has the advantage of a precise dosing of active ingredients, which are self-dispersing due to effervescence. Following the application of these formulations as effervescent tablets we obtained a production increase of more than 15% on the treated bee families.

EFFECT OF GLYCEROL KETAL ON DIESEL ENGINE EMISSIONS

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In urban centers vehicular emission is being considered one of the most important sources of air toxics to the atmosphere^{1,2}.

The objective of this work is to study the possibility of using butan-2-one glycerol ketal as additive for diesel fuel in order to reduce emission from diesel engine. The glycerol derivative was obtained by catalytic condensation of glycerol with butane-2-one over solid superacid $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2$. The catalyst was prepared using coprecipitation and impregnation method and characterized by X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy. The surface acidity was measured by thermogravimetric analysis of adsorbed n-butylamine and titration with 0.01 N n-butylamine. In order to achieve the optimal reaction conditions, five impact factors were investigated in the experiments.

To study the effect of glycerol ketal on diesel engine exhaust characteristics, emissions of nitrogen oxides (NO_x), hydrocarbons (HC), carbon dioxide (CO₂) and smoke were measured on a diesel engine fueled with diesel blends containing 1 and 2 wt. % of butan-2-one glycerol ketal and working at constant speed of 3200 rpm and at four loads (25, 50, 75 and 100%).

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COMPARATIVE STUDY OF CERTAIN MINERAL CONTENT FROM VEGETABLE OILS AND SEEDS OF SOME INDIGENOUS PLANTS

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Defined as complex mixtures, containing, mainly fatty acid esters of glycerol (glycerides) with numerous other natural compounds and beneficial minerals, vegetable oils are used from ancient times in diet and in multiple industries.

This paper aims at achieving a comparable study, especially regarding the minerals from fatty oils and seeds of indigenous plants like: Hemp, Flax, Blackseeds, Thistle, Buckthorn, Sunflower, Safflower, using absorption spectrometry technique and atomic emission with flame.

Experimental study revealed the absence of heavy metals (lead, cadmium, copper) from fatty oils analyzed that is an important aspect knowing that it's have a harmful effect on the body by blocking the enzymatic reactions and accelerate the oxidation of fat-soluble vitamins and fats. At the same time we note that all oils shows similar compositions in terms of content in certain minerals. These are manganese, potassium, iron, zinc and molybdenum. Other minerals investigated from mentioned oils were not detected.

These vegetable oils assessed as high quality are based on complex analyzes performed (fatty acids, fat soluble vitamins, lecithin, carotene, etc.) derived from organic sources and that will be used as raw materials for making cosmetics and dietary supplements with good bioavailability, with a good effect in preventing widespread disease, such as the cardiovascular, rheumatic, geriatric and even some forms of cancer.

Keywords: fatty oils spectrometry AAS minerals.

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IMPROVED CURRICULA AND MODERN LEARNING SYSTEM TO PROMOTE THE NEW DIRECTIONS OF BUSINESS ENHANCEMENT IN LIFE SCIENCES APPLICATIONS

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Due to the increasingly ageing population and the demand for improved quality of life, the life sciences sector has strong growth potential (8.3% growth in 2007), the sustainable development applications being of utmost interest. But most of the countries recently entered the European Union, with real academic base in Life Sciences, and with an important request towards business of added value, lack of competences and skills to develop innovative companies in the domain. The situation in Romania was identified by the analyses did by the Romanian Society of Bioengineering and Biotechnology and compared with other EU countries, members of the European Federation of Biotechnology. The project will develop learning curricula and contents to be delivered to target-group by blended learning in order to provide training in business enhancement in life sciences for sustainable development applications. Two products from these foreign partners will be transferred, by integrating them, but also by adapting to an economic sector of interest and by introducing modern blended learning systems, and by increasing the value with a new specific content dedicated to sustainable life sciences applications. The enterprise business in life sciences module will complementary treat the Intellectual Property issues. The impact will be on 3 levels: (1) short term: acknowledge the key competences and skills needed to develop business in sustainable development applications of life sciences and develop blended learning by testing the training on a representative selection of persons from the target group; (2) medium term: formation in the involved countries and at EU level of a general vision about the training in the field of interest as products and methodologies; (3) long term: at EU level introduction into educational and vocational systems of advanced and coherent learning tools to enhance the needed competences.

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**THE BIOGAS – AN IMPORTANT CHALLENGE FOR
NEAR AND LONG FUTURE IN ROMANIA**
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Keywords: Miscellaneous wastes, manure, biogas systems, GHG reduction, economics

The challenge to approach this domain, in the frame of EU Directives and National Action Plan focused on renewable, where the biofuels play an important role, was given by the huge biomass and waste potential existing in Romania.

The biogas can essentially contribute to attend the prospective figures asked for renewable (20% from total energy demand till 2020). Renewable include wind, solar, hydro - electric, tidal power, geothermal and biomass resources as well.

The work takes in account the state of the art regarding the existing technologies and gives an image of current spreading around.

The available information on this topic was carefully collected and processed, in order to underline the importance of the subject and the methods to implement on local areas such useful technologies.

Although in the past Romania owned hundred of biogas plants, which were dismantled, today there are just a few based on outside technology (especially from Germany) having medium and small capacities.

On the other hand, the existing Romanian original technologies are waiting to be turning in account, being more than competitive with others, as regard the efficiency and exploitation.

Today, in Europe, the most applied concept for a biogas plant is to send the fuel directly to a cogeneration installation, producing electric and thermal energies. First is supplied to the existing grids, while the thermal one (hot water) is partially turned for internal needs (digester heating) and the rest to appropriate consumers [1]

Basically, the solution have to be carefully applied, based on local specific conditions, since sometime the thermal energy did not find a feasible utilization due to supplementary cost of distribution.

The Romanian technologies, which can compete the market, have big advantages, including reduced investment costs, simplicity of operation, easy maintenance and versatility of the materials to be processed into digester [2].

The work presents the current and future possible situation in Romania, where the existing raw materials and wastes can contribute on a real success for energy saving parallel with environmental protection.

[1] Utilizarea durabila a energiei termice a instalatiilor de biogas – Manual – BiogasHeat Project, 2010-2014

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**COMPLETE EXPLOITATION OF MICROALGAL BIOMASS,
TO OBTAIN SYNTHETIC AVIATION FUEL**

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Increasing demand for energy, diminishing fossil fuels, global warming along with the growing security and economic risks of supporting Middle East oil have set the stage for domestic green energy. Renewable, carbon neutral, transport fuels are necessary for environmental and economic sustainability.

The development of alternative fuel research for the aviation industry is crucial to securing the long-term future. Using microalgal biomass as the main raw material, would allow the aviation biofuel to be approximately carbon neutral over its life cycle; carbon dioxide absorbed by microalgae during the growth of the biomass is roughly equivalent to the amount of carbon dioxide produced when the biofuel is burned in a combustion engine - which is simply returned to the atmosphere.

Our research was focused on a new process for obtaining of aviation biofuel, by complete exploitation of microalgal biomass, using an integrated system consisting of following stages:

- selecting the microalgae able to grow in mixotrophic conditions for high yield algal oil production, algal biomass harvesting, algal oil extraction, FAME + glycerine obtaining;
- obtaining of furfural derivatives from de-oiled biomass, and of furan derivatives by condensation with ketone;
- hydrogenation of FAME and furan derivatives to obtain alcohol derivatives;
- catalytic dehydration, hydrocracking and isomerization of alcohols derivatives, for producing a mixture comprising iso/n alkanes, suitable for use as synthetic aviation fuel;

The reaction intermediates and final product will be characterized analytically by FT-IR and GC-MS methods.

Final product satisfied the requirements of the ASTM D7566 - 12a Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons.

EFFICIENT TRANSFORMATIONS OF δ -LACTONALCOHOLS INTO γ -LACTONALCOHOLS

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Synthesis of prostaglandins (racemic or optical pure enantiomers) by Corey methodology request a key step for obtaining γ -lactonolcohols, correspondingly functionalized for next sequence reaction(s); these further reactions are well established for introducing α -side chain or ω -side chain and as a consequence, the key γ -lactonolcohol intermediate must be correspondingly protected.

The procedure for obtaining γ -lactonolcohols consists of a basic opening of δ -lactonolcohol group in excess H_2O_2 , followed by γ -ring closure in a SN_2 reaction, or an acid opening of δ -lactonolcohol group followed by the same basic closure to γ -lactonolcohol skeleton.

Our procedure consists in an efficient alcohol esterification of the the δ -lactonolcohol group, followed by alkaline hydrolysis of ester group and next closing of the five ring of γ -lacton group. The sequence gave the possibility to manipulate the following reactions for protecting with different protecting groups the primary alcohol group and secondary hydroxyl group. These steps are crucial for next olefination reactions for introducing the side chains of prostaglandins and analogues.

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EVALUATION OF ELECTRO-FLOCCULATION FOR HARVESTING OF FRESHWATER MICROALGAE

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The harvesting and dewatering of algal biomass are the key processes before extraction of lipids and other high added products and need to be reliable, flexible and must be cost effective in the development of viable microalgae-based biofuels^{1,2,3}.

Various methods, including centrifugation, filtration, flocculation and flotation, have been developed for microalgae harvesting^{4,5}. However, some economic or technical problems still remain with current methods for algal recovery, such as high capital, energy and running costs, or low separation efficiency. Therefore, there is a great interest in developing new efficient approaches for harvesting microalgae, such as electro-flocculation^{6,7}.

In this study we develop an efficient electro-flocculation process, as a primary concentration step by using iron and aluminum plates as anode and graphite electrodes, as cathode, followed by subsequent further secondary dewatering step, namely filtration, for optimization of freshwater microalgae harvesting. There were evaluated current densities for a more rapid flocculation of the microalgal suspension, power consumption, expressed per kg of microalgae harvested, and release of iron both in the recovered microalgal biomass and in the liquid phase.

The efficacy of biomass recovery for *Desmodesmus communis* and *Nannochloris sp* was demonstrated by calculation of settling rate, concentration factor and power consumption and it reached about 98% after 40 min using an electro-flocculation process.

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Synthesis and Characterisation of Same Transitional Metal Complexes.

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Four new complexes of transitional metals Co (III), Ni (II) Cu (II) and Zn (II) with 4-bromo-2-[(E)-N-(2-sulfanyphenyl)carboximidoyl]phenol by template synthesis, at metal:ligand of 1:2 stoichiometry have been obtained. Complexes were investigated using elemental analysis, IR, UV-Vis, ¹H-NMR, ¹³C-NMR, EPR spectroscopy, magnetic susceptibility, electric conductivity and thermal behavior. This compounds were screened against same bacteria by Disc metod. The formulae of complexes were found of type: $[M(HL)_m]_n$ where $M^{III} = Co$, $m=3$, $n=1$; $M^{II} = Ni, Zn$, $m=2$, $n=1$ and type: $[M(L)_m]_n$ where $M^{II} = Cu$, $m=1$, $n=2$. The ligand acts as bidentate NO monoanionic ligand for Co (III), Ni (II) and Zn (II) ions and as ONS tridentate dianionic ligand for Cu (II) ions. Analisis results, suggested octahedral geometry for Co (III) ions, square-planare geometry for Ni (II) and Cu (II) ions and tetrahedral environment for Zn (II) ions. Complexes of Co (III), Ni (II) and Zn (II) are monomeric, Cu (II) complex is dimmer [1-5].

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USE OF FIXED BED PERCOLATION AT OIL SEPARATION FROM GRINDED CANOLA SEED

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An experimental bench-scale plant was built-up in order to investigate the oil separation from grinded canola seed by using heptane and hexane as extraction solvents, by employing different extraction times and solvent quantities.

The extraction is made in fixed bed extractive columns being based on the percolation method.

The experimental results, obtained for different working conditions, offer a detailed representation of the extraction yield dynamics and its correlation with the operating conditions.

The aim of this paper is to obtain experimental data for fixed bed extraction of canola seed oil using usual hydrocarbons in order to sustain that, at the bed level, the liquid flows with axial dispersion and, at the particle level, the process occurs according to shrinking core model^{1, 2}.

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INTERFERENCE – FREE DETERMINATION OF GLUCOSE IN VARIOUS BEVERAGES USING AN IMPROVED PRUSSIAN BLUE BASED BIOSENSOR

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An improved biosensor based on Prussian Blue (PB) and glucose oxidase (GOD) was developed for direct determination of glucose in beverages as natural juices and wines. The redox mediator PB was electrodeposited onto screen-printed carbon electrodes (SPCEs). The stability and life time of the PB film was improved using the anionic surfactant AOT during the potentiostatic deposition¹. GOD was immobilized during the electropolymerisation of a non-conducting film using glutaraldehyde (Glu). This film is a copolymer based on 2,6-DHN (2,6-dihydroxynaphtalene) and APEA (2-(4-aminophenyl)-ethylamine) which proved a very good permselectivity for hydrogen peroxide². This procedure allows not only the GOD entrapment in the film net, but also the covalent immobilization of the enzyme to the free amino-groups of the polymer via the reticulation reagent, Glu.

The SPCE/PB/copolymer/GOD biosensor demonstrates an improved stability in operational conditions and excellent interference rejection properties. This biosensor may be used on-field, using a portable potentiostat - galvanostat and the chronoamperometry technique, in the linear range of 0.05 mM - 2 mM glucose, with a detection limit of 0.025 mM. The biosensor has maintained for a long period its response for glucose (66 days and 120 days it showed 95.8%, respectively 52 % of the initial response for 1mM glucose).

Glucose was successfully measured in several commercially natural juices and wines with a minimum sample pre-treatment (filtration and dilution).

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PURIFICATION AND DISCOLORING OF 5-(METHOXYMETHYL)FURAN-2-CARBALDEHYDE USING HIGHLY ACTIVE BLEACHING EARTH

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The increasing demand on the fuel energy and the EU directives¹ on biofuels, has taken in light the advanced generation of biofuels. This new fuel candidates need to satisfying the requirement of EN 14214:2003, characteristics such as viscosity, combustion properties, sulphur content, freezing point, oxidation stability and so on. One of the very promising biofuel candidates is the 5-(alkoxymethyl)furfurals like 5-(methoxymethyl)furan-2-carbaldehyde(MMF)^{2,3}.

This paper provides a general description of the purification and discoloring of the MMF which we have obtained from fructose via 5-(chloromethyl)furfural⁴, in good yields. The obtained product is black viscous liquid and requires further purification process before it can be used as biofuel. This process need to be done in mild conditions because the methoxymethyl furfural boiling point higher than 200°C and undergo to a polymerization at higher temperatures. Purification by bleaching earth is a promising method for this task, used for absorbing the resins, in this way we have obtained the light orange-yellow less viscous product. We have studied the initial concentration of MMF in toluene, the used bleaching earth quantity reported to the MMF, the effect of the temperature in batch reactor and in multiple layer filled column. The analysis was made through comparing the color of the product with different concentration of potassium dichromate solution and measuring the viscosity.

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COSMETICS BASED ON PLANT POLYSACCHARIDES

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The modern cosmetology is facing to new formulations of products for skin and hair care based on protein hydrolysates, nucleic acids (DNA, RNA), polysaccharides, respectively to a switch from mainly lipid cosmetic to lipo-glycoprotein cosmetic. In this context, based on the composition and properties of bioactive polysaccharides and possible synergism with certain phytochemicals in tissue of medicinal plants and herbs Hofigal company aims to create new advanced cosmetic formulas for skin and hair care for: preventing the premature process of skin aging, deep moisturizing and stimulation of skin collagen metabolism against pollutants, maintenance and care of skin and hair nutrition, cellular regeneration and tissue detoxification.

As a consequence, the authors proposed capitalizing certain polysaccharides, the main mucilage of flax, psyllium, senna, fatty oils of hemp and thistle and essential oils of lavender, rosemary and sage and also extracts from marshmallow and licorice.

The result of the studies performed to date is the development of three formulas based on fatty oils and polysaccharides of flax, senna, psyllium acting like hyaluronic acid, involved in embryonic development and tissue regeneration addressing skin and body care.

Keywords: biocosmetics, polysaccharides, hyaluronic acid, herbs, cream, gel

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AUTOMATIC MAGNETIC PURIFICATION, QUANTIFICATION AND AMPLIFICATION OF HUMAN DNA IN FORENSIC CASEWORK SAMPLES

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A typical forensic casework sample usually contains low amounts of degraded DNA and PCR inhibitors. Therefore, it is very important that the samples are purified before subjected to polymerase chain reaction multiplication. This step can be performed either using different chelating ion exchange resins such as Chelex, using an organic extraction method or by using magnetic particles.

The automatic magnetic DNA purification method combines the speed and efficiency of DNA purification based on silica particles with easy handling of magnetic particles. Furthermore, it allows the user to elute the extract into very low volumes of buffer, and as a result to concentrate the small amount of DNA present in the sample. This method can be used for a wide variety of samples such as buccal swabs, body fluid stains, chewing gum, cigarette butts, nail clipping and hair, paper, blood, saliva, bones, teeth, sexual assault samples, etc.

After the purification step, the samples are automatically quantified and the results are used to determine the optimal DNA quantity necessary for sample PCR. After the amplification step, the amplicons are injected into a capillary electrophoresis instrument and the genetic profile is determined.

The main advantages of using this automated method are: the decrease of sample cross-contamination risk and the superior traceability of the data, as well as the lack of contact with toxic substances, a reduced time of analysis, a good sensitivity, efficient recovery of degraded DNA and complete removal of inhibitors.

This automated method was used to extract, purify, quantify and amplify low template DNA casework samples such as blood, epithelial cells, saliva and hair. The results were compared to manually extracted and purified samples in regards of DNA input and quality of the obtained genetic profile.

**THE INFLUENCE OF COORDINATION COMPOUND OF ZINC(II)
WITH DIOXIME ON PROTEOLYTIC ACTIVITY OF *F. GIBBOSUM* CNMN FD 12**
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Proteases are a complex group of enzymes, varied by substrate specificity, reaction mechanism, stability to pH and temperature. Due to the specificity of action and variety of properties, proteases have numerous applications in economy, mainly in the food, leather, pharmaceutical industries, diagnostics and zootechny.

The studies to increase biosynthesis of fungi exocellular hydrolases have revealed stimulatory effect of some metal complexes on growth and enzyme biosynthesis of fungi, reducing the technological cycle and directing differentially obtaining of enzyme products.

The aim of the research was to evaluate the effect of metal complex $[\text{Zn}_2(\text{NioxH}_2)_2(\text{CH}_3\text{COO})_4\text{dpy}(\text{H}_2\text{O})_2]$ on proteolytic activity of *Fusarium gibbosum* fungal strain - producer of acid and neutral proteases. In binuclear complex, the molecule of 1,2-cyclohexanediondioxime (NioxH_2), two acetate anions and one water molecules coordinate bidentate to the metal atom and molecule of 4,4-dipyridyl (dpy) functions as a bridge between the atoms of zinc¹. The compound was added to nutrient medium in concentration of 1, 5, 10, 15, 20 mg/L.

The optimal concentration for acid proteases was 5 mg/L, the maximal increase of proteolytic activity being 78.3% compared to epy control sample. The concentrations of 15 and 20 mg/L decreased the enzyme activity below the control.

Contrary was the effect of studied compound on activity of neutral proteases. The upper concentrations showed the highest stimulatory effect. The maximal increase of activity of 90% was obtained at concentration of 15 mg/L.

The differential influence of $[\text{Zn}_2(\text{NioxH}_2)_2(\text{CH}_3\text{COO})_4\text{dpy}(\text{H}_2\text{O})_2]$ on fungal proteolytic activity presents practical significance. Varying the concentration of compound, several enzyme preparations can be obtained, constitute from acid or neutral proteases, or active in a wide range of pH (3.6 to 7.4).

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COMPARATIVE STUDY OF CERTAIN VEGETABLE ENZYMES GERMS OF CEREAL SEEDS AND MEDICINAL PLANTS

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Enzymes from plants have great therapeutic potential for the human body they are indicated to increase vitality, the strengthening of the digestive system and the entire body. Endogenous enzymes are produced by living organisms, but in different diseases and with ageing process, their vitality decreases. Therefore, it is important to appeal to exogenous sources of enzymes by eating those products that meet our corresponding.

Knowing that all fresh seeds germ¹ contain enzymes in amounts significantly greater than the seeds as such, we have initiated the study of some germs that refers to cereal grains and medicinal herbs that have sprouted² (usually without the help of sunlight and soil), turning into young plants in for 3-6 days at 25 °C. So I used wheat (*Triticum aestivum L.*) germs, corn (*Zea mays L.*) germs, barley (*Hordeum vulgare L.*) germs and thistle (*Silybum marianum*) germs as sources of the following enzymes: cellulase, acid phosphatase, alkaline phosphatase, amylase, lipase, protease, peroxidase, catalase and superoxide dismutase. These germs were analyzed in fresh and dried form (in terms of household temperature) and found considerable quantities of hydrolytic enzymes and antioxidants, presented in the form of tables in the paper.

The purpose of survey is to compare the enzymatic activity of some germ of cereals and medicinal herbs for obtaining enzymatic plant products³.

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COORDINATION COMPOUNDS OF COPPER WITH AMINO ACIDS AS POTENTIAL STIMULATORS OF MICROMYCETES EXTRACELLULAR HYDROLASES BIOSYNTHESIS

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New copper (II) metal complexes with various stereoisomers of alanine: $\text{Cu}(\text{L-}\alpha\text{Ala})_2$ (1), $\text{Cu}(\text{DL-}\alpha\text{Ala})_2 \cdot \text{H}_2\text{O}$ (2), $\text{Cu}(\text{DL-}\alpha\text{Ala})_2$ (3), $\text{Cu}(\text{D-}\alpha\text{Ala})_2$ (4) were synthesised. The potential stimulator effect of the compounds on enzyme biosynthesis of *Aspergillus niger*-10 – producer of cellulases (cellobiohydrolase, endoglucanase and β -glucosidase) and xylanases, and *Trichoderma koningii* CNMN FD-15 – producer of acid and neutral proteases was tested.

Depending on type and concentration of metal complexes, the stimulatory effect was observed on day 7 for cellobiohydrolase and endoglucanase, being 6.67-66.67%, and 18.37-26.24%, respectively, and on day 6 for xylanase, representing 36.30-52.51%. The coordination compounds indicated a neutral or inhibitory action on β -glucosidase. Studied compounds stimulated the activity of acid proteases with 45.81-54.19% on day 8 and activity of neutral proteases with 34.96-46.85% on day 9 of *T. koningii* growth. Optimal concentration of metal complexes was within narrow limits and presented 5-10mg/L for *A. niger*-10, and 10-15mg/L for *T. koningii*-15.

Interest for biotechnology presents copper complexes 2 and 3 with racemic amino acid DL- α Ala. They differ among themselves just in the presence of crystallization water molecule in structure of one of them. Thus, complex $\text{Cu}(\text{DL-}\alpha\text{Ala})_2$ can be used as stimulator of enzyme biosynthesis for micromycete *A. niger*-10; the compound increased the activity of cellobiohydrolase with 66.67%, endoglucanase with 27.28%, xylanase with 31.53% and accelerated the endoglucanase and xylanase biosynthesis with 24 hours, while maintaining the activity of β -glucosidase at the control level.

The coordination compound $\text{Cu}(\text{DL-}\alpha\text{Ala})_2 \cdot 2\text{H}_2\text{O}$ presents perspective for *T. koningii*-15, demonstrating stimulatory effect of 31.93-26.67% on neutral protease and 46.85-44.75% on acid protease.

PHYSICO-CHEMICAL EVALUATION OF SOME COLLAGEN-BASED SPONGES WITH NIFLUMIC ACID

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The non-steroidal antiinflammatory drugs (NSAIDs) delivery directly at cutaneous wound level in a controlled manner, maintaining a sufficient and effective drug concentration, is essential to combat the inflammation and implicitly the pain that can occur during the wound healing process. In the recent years the strategy of using the NSAIDs topical administration route in cutaneous lesions with different ethiology is based on the use of natural origin biopolymers as potential vehicles for drug controlled release systems.¹ Particularly, a considerable attention was given to collagen which has characteristics recommending it as a very attractive material for the use as drug vehicle for different biomedical applications.² In this paper some collagen hydrogels with niflumic acid, selected as a non-steroidal antiinflammatory model drug, uncross-linked and cross-linked with glutaraldehyde and tannic acid were prepared. A stationary reological analysis was performed at two temperatures ($23^{\circ}\text{C}\pm 0.5^{\circ}\text{C}$ and $37^{\circ}\text{C}\pm 0.5^{\circ}\text{C}$) with a rotational viscometer Multi-Visc Rheometer Fungilab equipped with a standard spindle TR 9 and a ThermoHaake P5 Ultrathermostat. The hydrogels showed a non-newtonian behaviour with shear thickening. By freeze-drying of the above hydrogels the collagen sponges were obtained and the influence of different cross-linking agents on the drug kinetic release characteristics and water absorption capacity was investigated. *In vitro* niflumic acid release from the collagen sponges was performed using a sandwich device adapted to a paddle dissolution apparatus Essa Dissolver. The kinetic mechanism was established from drug release profiles. The sponges swelling capacity determination was performed through a gravimetric method and the results were in agreement with the kinetic data. Both the kinetic and water absorption results were strongly influenced by the cross-linking agent nature. By modulation of the cross-linking agent quantity as well as by combination of the two cross-linking agents in different ratios, the composition can be modeled obtaining sponges with kinetic and swelling profiles adequate for the cutaneous wound treatment.

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PEPTIDES WITH POTENTIAL BIOLOGICAL ACTIVITY

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The aim of the present study was to total synthesis of small peptides (linear and cyclic peptides) with biological activity obtained from natural aminoacids identified in medicinal herbs like *Viscum Album*, *Hellebore*, *Sideritis Scardica*. Reaction was performed at room temperature, in base catalysis (TEA). Maintaining the temperature at maximum 30°C, is important because otherwise the degradation would have occurred [1]. Obtained peptides can be utilized in a number of different ways in treating cancer. This includes using peptides directly as drugs (e.g., as angiogenesis inhibitors), tumor targeting agents that carry cytotoxic drugs and radionuclides (targeted chemotherapy and radiation therapy), hormones, and vaccines[2,3].

The precursors use was: natural amino acids (serine, valine, leucine, isoleucine), the solvents (dichloromethane, water, ethyl ether, petroleum ether), the coupled reagent (DCC, *N*-hydroxysuccinimide)[4].

It was investigated the morphology and chemical composition of the particles which were characterized by analytical methods: MS, FT-IR and NMR spectroscopy. The results of analysis showed that the peptides are obtained in good yield.

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THE CHANGE OF *CYCLOTRICHIMUM NIVEUM* (BOISS) MANDEN & SCHENG. ESSENTIAL OIL AND ITS COMPONENTS AT THE DIFFERENT GROWTH STAGES

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Cyclotrichium niveum (Boiss.) Manden.&Scheng. is an endemic species of *Lamiaceae* family spreading in different regions of Turkey. ^{1, 2} In order to determine the ontogenetic variability in this species, the plant was harvested in its natural growing area for three times including the period of pre-flowering, full flowering and post-flowering.³ In each harvest period, the changes at essential oil rate and essential oil components existing in plant leaves were determined. According to this, the highest rate of essential oil in plant was determined in post-flowering period (5.58 %), and this was followed by full-flowering (5.45 %) and pre-flowering periods (2.83 %). Whereas principal 28 components were determined in pre-flowering and full flowering periods, 21 components were determined in post-flowering period. In all harvest periods, the main component of the essential oil was pulegone, and depending upon the development of the plant, the rate of the essential oil increased, as well. The highest rate of pulegone was determined in full-flowering period as 74.37 %. The rate of isomenthone as another important component was determined as 18.48 % in pre-flowering period and the lowest value was determined in full-flowering period (6.61 %).

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CHEMICAL STUDIES ON AREAS AROUND OLD SALT MINES: ECOLOGICAL RECONSTRUCTION AND USES OF SALT WATER SOURCES FOR BALNEAL CURE TOURISM AND RELAXATION

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According to studies conducted in Europe, the environment plays a crucial role in physical, mental and social development of the population. In recent years, the continuous degradation of environmental quality due to factors such as air pollution, noise, chemical compounds and disappearance of natural areas, in combination with lifestyle changes led to the emergence of a growing number of diseases. The main goal of European policy is to ensure as far as possible, a natural setting without factors damaging human health and especially to find more and more ways to protect the health of vulnerable groups of the population.

This paper presents the results obtained in the frame of a National Research Programme which has in view the discovery, characterization and management of some still unknown or not yet fully characterised natural sources of mineral waters, in order to render them economically profitable and to contribute to the public health development. Following some empiric, local observations upon the qualities they have in the treatment of different maladies, a set of physical, hydrological and chemical analyses was established, in order to substantiate scientifically their therapeutic role. The mineral waters of Romania show a great hydrochemical variety. The three predominant types of mineral waters are: salty, sulfurous-sulfate and carbonated, in their composition appearing, depending on the nature of the rock leachates total, some secondary hydrochemical characters (iron, arsenic, potassium, calcium, magnesium, chlorine, etc.).

As models in Europe that can be followed for the resort Ocnele Mari are mentioned: in France (Thermes Sextius in Aix en Provence), Germany (Bad Sulza), Switzerland (Leukerbad) and Austria (Bad Loipersdorf).

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2. European Project Consulting, „Local Development Strategy for Ocnele Mari”, 2007-2013

IN VITRO ANTIMICROBIAL ACTIVITY OF *Thymbra spicata* L. ESSENTIAL OIL FOR APPLICATIONS IN MEDICAL IMPLANT COATINGS

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The implant-associated infection is significant and usually require revision surgery, with removal of the implant and prolonged antibiotic treatment.¹ Because of this reason different methods for reducing the infection have developed. One of the most used is coating onto implant surface consisting in antibiotics. Recently, the essential oils became of high interest because of their anti-infectious and antibacterial properties and could be successfully used instead of antibiotics.² The aim of this study was to investigate the antimicrobial activity of thymbra essential oil on different bacteria. The essential oil was obtained from *Thymbra spicata* L. Chemical composition of thymbra essential oil was performed using GS-MS analytical method and 69.28% carvacrol, 9.42% p-Cymene, 6.23% gamma terpinene and 2.35% linalool as main components were obtained. Their antimicrobial activity was tested against *S. aureus*, *P. aeruginosa* and *C. albicans*. Ampicillin and flucanazole were used as controls. The essential oil was able to inhibit *in vitro* the growth of three microorganisms with MIC values between 31.5 and 62.5 µg/mL. The most potent activity was obtained against *S.aureus*. MIC value of essential oil against both *P. aeruginosa* and *C. albicans* was 62.5 µg/mL. Based on its antimicrobial activity, the thymbra essential oil could be used in medical field for obtaining antimicrobial coating of implants.

Acknowledgements

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THE USE OF AMMONIUM PERSULFATE AS OXIDANT IN DELIGNIFICATION PROCESSES

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The growing necessities of human kind and also the limiting of fossil fuel resources ^[1] have led to the second generation of biofuels production which uses lignocellulose feedstock as raw material ^[2]. The use of this raw material for biofuels production has resulted in obtaining subproducts ^[3] with wide industrial applications ^[4]. These wastes, sources of lignocellulose, constitute important substrates in fermentative processes directed to biofuel production. The structural carbohydrates in the plant cell wall are wrapped up in lignin. The operation is aimed to increase the digestibility of constituent sugars through increment in gross material pore size ^[5, 6]. Many of the delignification methods employ mineral acid, alkaline or/and oxidative reaction conditions that lead to the reduction of the molecular weight of lignin and consequently to pass it into a solution ^[2, 5-8]; it can also be degraded by using fungi and bacteria ^[9]. Throughout this study we have performed a oxidative-alkaline delignification of grape stalk with ammonium persulfate, in different concentrations, by using an autoclave. Temperature and concentration of chemical agents are important factors in the delignification process.

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NEW OLEOYLAMIDE WITH POTENTIAL ANTI-OBESITY ACTIONS

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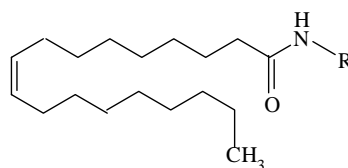
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N-Oleoylethanolamide is an endogenous regulator of food intake, and may have some potential as an anti-obesity drug. It is believed to act as a local satiety signal rather than as a blood-borne hormone. Oleoyl- and palmitoylethanolamides do not activate cannabinoid receptors directly, but can enhance the activity of anandamide by inhibiting its inactivation by fatty acid amide hydrolase. In addition, it has been demonstrated that oleoylethanolamide by acting as a PPAR- α agonist has a novel effect in enhancing memory consolidation through noradrenergic activation of specific regions of the brain. It may have an influence on sleep patterns and the effects of stress [1].

New N - substituted oleoylamides were synthesized by aminolysis reaction of methyl oleate with primary amines in search for obtaining the compounds with antiobesity actions.



Where: R is L-phenylalaninol, phenethyl, metoxyphenethyl, ciclohexyl, 1-adamantyl, α - naphthyl, β - naphthyl.

The new compounds were purified by pressure chromatography and their structure established by IR, ¹H-NMR and ¹³C-NMR. The compounds will be studied also by electrochemical methods.

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INFLUENCE OF THE EXTRACTION METHOD ON THE ANTIOXIDANT ACTIVITY OF VARIOUS AROMATIC HERBS EXTRACTS

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A large number of aromatic herbs and their purified constituents have shown beneficial therapeutic potentials. Various herbs and spices have been reported to exhibit antioxidant activity, including *Rosmarinus Officinalis*, *Salvia Officinalis* and *Rhus typhina*. The majority of the antioxidant activity is due to the flavonoids, anthocyanin, flavones, catechins, etc¹. Antioxidant-based drug formulation are used for the prevention of complex diseases like atherosclerosis, stroke, diabetes, Alzheimer's disease and cancer².

The ethanolic crude extracts of some commonly used herbs (*Rosmarinus Officinalis*, *Salvia Officinalis* and *Rhus typhina*) were screened for their antioxidant properties using an electrochemical method developed by our group. Free radical scavenging activity was also evaluated using 1,1-diphenyl-2-picrylhydrazil (DPPH) free radical method.

A comparative study was developed in order to choose the best extraction method between ultrasounds-assisted extraction and Soxhlet extraction.

All the ethanolic extracts exhibited a significant antioxidant activity even after 3 months.

The study confirms that the consumption of these herbs would exert several beneficial effects by virtue of their antioxidant activity.

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SENSORY ANALYSIS EVALUATION OF AGLUTENIC FIBRES BEVERAGES

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For the evaluation of the organoleptic properties of medicinal Valcele mineral water based drinks, which contain natural ingredients, carefully selected and evaluated at laboratory level (medicinal Valcele mineral water, aromas, sweeteners, dyes, gluten free dietary fibres, acidifiers), sensory analysis was conducted accordingly to the STAS 12656-88 standard: **Sensory analysis. Method with mark scales/sheets**, from 0 to 5 points, and obtaining of medium scores from the group of tasters. The panel was constructed of 5 evaluators that were instructed about the characteristics of the analysed product and who received one sheet for each mineral water based drink. The samples were encoded (LSP, PPI, PPP, MZI), so that the type of aroma in the sample remained unknown. The tasting sheet contained the following sensorial characteristics (quality indices): *appearance*: clearance (opaque, with or without sediment, separate phases); *colour*: corresponding to each aroma; *consistency*: liquid, syrupy, viscous; *smell*: characteristic for each aroma, without any foreign smell; *taste*: characteristic for each aroma, without any foreign taste.

Following the sensory analysis with mark scales/sheets, the marks given were: for the LSP sample (lemon) and MZI sample (apple), **“Very good”**; for the PPI sample (peach) and the PPP sample (orange), **“Good”**.

As far as the reference scale (hedonic) method is concerned, which makes it possible to establish the best sample, as well as the degree of preference for a particular characteristic, the following scoring was used: 1-I dislike it immensely; 2-I dislike very much; 3-I mildly dislike it; 4-I dislike it a little; 5- indifferent; 6-I like it a little; 7-I mildly like it; 8-I like it very much; 9-I like it immensely.

The highest marks were given to the LSP and MZI samples which respectively received “I mildly like it” and “I like it very much”. At the opposite end, the PPI and PPP samples were given an “I mildly like it”.

ESSENTIAL OILS WITH ANTIMYCOTOXIGENIC POTENTIAL**Popescu Mariana, Oancea Florin***R&D Institute for Chemistry & Petrochemistry – ICECHIM**202 Splaiul Independentei, Bucharest, Romania*

Diminution of residues and contaminants from the whole food chain is a great challenge for the world developed society. One of the most dangerous risk factors is represented by the agricultural insect pests and fungal diseases which destroy the crop plants in the field and post harvested yield in storage, generating huge economical losses every year. Mycotoxins are dangerous metabolites produced by pathogenic fungi developed in different sequences of the agro-food chain. They are transferred on cereal crops from field to storage, with feed in animal bodies and finally in food products of animal origin, such as eggs, milk and meat, decreasing the nutritional quality of food and producing health disorders to animal or human consumers. Five mycotoxins (aflatoxins, deoxynivalenol, zearalenone, fumonisins and ochratoxin A) are covered by EU legislation. Agrochemicals with fungicidal properties used in risk management programs implemented in agricultural practice to reduce mycotoxin transfer from storage to animal diet were not able to completely destroy mycotoxigenic fungi, nor in field or storage, moreover increasing toxic effects on human health and environmental impact. Essential oils of aromatic plants, fruit peels or seeds will play an important role in food chain protection due to their antimicrobial, antifungal, antioxidant and antimycotoxigenic properties, being cheaper, easy available for farmers, rapidly biodegradable, non-toxic for mammals, an excellent alternative to avoid the risks associated with the use of synthetic agrochemicals. Antifungal essential oils kill the causative organisms which produce toxic metabolites, thus reducing the mycotoxin accumulation. Thymus and oregano essential oils (containing carvacrol and thymol) are strong alternatives to chemicals for preserving stored grains, oregano being the best antifungic agent at 2-2,5 $\mu\text{L/l}$ against micelle and spores of *Aspergillus flavus*, *A. niger* and *A. ochraceus* on wheat grains. Liquid application of essential oils is practically unfeasible, due to large quantities requested to overcome the loss of activity through rapid evaporation in improperly conditions of time and temperature of storage and the possible unpleasant effect for consumers regarding the odor or taste remaining on the grains. Encapsulation in ecological slow release formulation will prevent all these problems by decreasing the evaporation rate of the volatile oils, promoting the ease of handling and extending shelf life of the bioactive constituents¹.

¹ Ahmed Y.E., Magdy A.M., Emad A.S. 2013 “*Encapsulated essential oils as antifungal fumigants: stored grains protection*”, LAP LAMBERT Academic Publishing, ISBN-13: 978-3659281815

PHYSICO-CHEMICAL CHARACTERIZATION OF FUNCTIONAL BEVERAGES BASED ON AUTOCHTHONOUS RAW MATERIALS

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Increasing interest is being focused on whey as a functional ingredient in pharmaceutical applications, and as nutrient in dietetic and health foods. Whey is a valuable by-product obtained during manufacture of cheese and usually dumped because it has no value. Whey constituents, notably proteins and peptides, are helpful to raise its status towards valuable dairy by-product. Additionally, it contains precious nutrients like minerals and vitamins which have an indispensable value in human dietary requirement. Consumption of the whey can supplement much of the lost organic and inorganic nutrients to the extra cellular fluid and utilization of these fluids can be targeted to the people working with strenuous occupation like sportsman.

The aim of this paper is to use the nutritional potential of whey, by preparing ready-to use beverages. In fact, the solubility of whey proteins, underlies its applicability to support getting beverages. The other raw material used in our laboratory to obtain a functional beverage was a Valcele mineral medicinal water. Whey and mineral water were enriched with natural ingredients: flavor, fructose, colorant, soluble gluten free dietary fibers and an acidity corrector.

The final beverages require sensory, physical and chemical characterization for quality control and product development. A wide range of analytical methods was used for characterization of these beverages, including:

- ✓ ICP-OES spectrometric method for determination of mineral profile;
- ✓ RP- HPLC method for separation and determination of vitamins;
- ✓ Munson-Walker method for quantification of carbohydrates;
- ✓ Kjeldahl method for protein content measurement.

Additionally, we have successfully in determining of free citric and lactic acids in co-presence, through a simple potentiometric method, based on differences of dissociation constants.

Energy calculation was done using the formula: ***Energy (Kcal) = T_P + T_L + T_G + T_F***

The energy values corresponding to the two drinks are correlated with those recommended for similar functional beverages.

Qualitative estimation of essential oils composition of some species of plants used as green pesticides

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Plants are, in effect, natural laboratories in which a great number of chemicals are biosynthesized. Many plants have developed natural, biochemical mechanisms to defend themselves from animal, insect and fungal attacks. By studying the chemistry of various species of plants, was discovered many active compounds used as biopesticides, which are natural compounds for pest control. On pesticides market, biopests have a continuously rising share due to their eco-friendly mechanism.. The Department of Bioresources from INCDCP-ICECHIM, was focused on rapid qualitative estimation of composition of essential oils from seven species of plants; basil (*Ocimum basilicum*), thyme (*Satureja hortensis*), dill (*Anethum graveolens*), mentha (*Mentha piperita*), rosemary (*Rosmarinus officinalis*), cinnamon (*Cinnamomum verum*), thuja (*Thuja standishii*), used as green pesticides. The analysis was based on Agilent Technology GC/MS Triple Quad using NIST Library for compounds identification. The results of present communication showed that presence of bioactive constituents as: menthol, eugenol, thujone, apiol, carvone, anethol, thymol, terpenes are responsible for biopests activity of the studied plants. The essential oils analyzed were used in formulation of some biopests, for seeds treatment in organic agriculture.

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ZINC AND CUPRU METAL-CHELATES OF HYDROLYZED-PROTEIN FROM YEAST

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Buffermins are mineral proteinates resulting from the chelation of minerals with amino acids and partially hydrolyzed proteins. By the chelation process, the minerals are more available to the animals and are safer to use than inorganic minerals or synthetic chelates. Zn and Cu proteinates resulting from the chelation of zinc and copper with amino-acids and/or partially hydrolyzed proteins are designed as nutritional supplements for animals and are formulated to prevent and /or correct zinc and copper deficiency in animals.

The aim of this study is to optimize the chelating process of Zn and Cu with amino acids in protein hydrolysates^{1,2} and to propose a technology for yeast valorification,

The yeast suspension, resulted from brewing industry, was purified by centrifugation and hydrolyzed using a cocktail of enzymes, followed by metal binding to protein-hydrolyzed, resulting as final products proteinates with high content in free amino acids chelates with Zn and Cu.

The products were analyzed through a modern analytical techniques: LC/ESI TOF MS for determination total amino acids after enzymatic hydrolysis and ICP-AES for determination the amount of metals.

¹ United States Patents 5698724,1997 Amino acid metal complexes using hydrolyzed protein as amino acid source and methods re same. Inventors: Anderson M.D.; Mahmoud M.A-M.

2. United States Patents 6166071, 2000 Zinc amino acid metal chelates having ligands comprised of glycine and a sulfur-containing amino acids. Inventors: Ashed S.D.; Wheelwright D.C.

AMPEROMETRIC BIOSENSOR FOR THE DETERMINATION OF ASPARTAME IN SOFT DRINKS

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Aspartame is an artificial high-intensity sweetener, intensely promoted by the food industry, and one of the most controversial food additives due to suspicions of adverse health effects¹⁻³. Aspartame is a methyl ester of the dipeptide of the natural amino acids L-aspartic acid and L-phenylalanine. Under strongly acidic or alkaline conditions, aspartame may generate methanol by hydrolysis. Based on this principle, a rapid, simple and stable amperometric biosensor for aspartame detection was developed. The aspartame biosensor was assembled by immobilization of alcohol oxidase (AOX) and carboxyl esterase (CaE) with glutaraldehyde and bovine serum albumin onto cobalt-phthalocyanine screen-printed electrodes. The biosensor response was very fast, 20 seconds are necessary to obtain the maximum response for aspartame concentration. The detection limit was 0.2 μM . Only minor effect on biosensors response was observed from different potentially interfering substances (citric acid, phosphoric acid, glucose, fructose, sucrose, caffeine, L-phenilalanine and sodium benzoate). The developed screen-printed electrodes were tested for the aspartame determination in two soft drink brands, Coca-Cola and Pepsi Cola. All the samples were analyzed after adequate dilution in PBS without preliminary preparation such as concentration or extraction. The obtained concentration levels of aspartame in the analyzed drink samples were found to vary between 58 mg/L and 152 mg/L and they did not exceed the maximum legally allowed UE concentration of 600 mg/L.

¹ Magnuson B.A., Burdock G.A., Doull J., Kroes R.M. (2007). Critical Reviews in Toxicology, 37(8), 629-726.

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EVALUATION OF ANTAGONISTIC ACTIVITY OF *BACILLUS* STRAINS AGAINST *RHIZOCTONIA SOLANI*

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Bacillus spp. is one of the biological control agents that has shown inhibitory effects against a considerable number of plant pathogens, and the antibiotics that it produces are generally assumed to be responsible for the control activity.^{1,2,3,4} In this study, five bacterial strains isolated from soil were screened for their antifungal activity against *Rhizoctonia solani*, a widespread soilborne pathogen responsible for serious damage in agriculture. The bacterial strains *Bacillus subtilis* 1016, *Bacillus subtilis* 1004, *Bacillus amyloliquefaciens* 1014, *Bacillus cereus* 1018, *Bacillus licheniformis* 1002 isolated from soil were inoculated on Luria-Bertani agar medium. The antagonistic activity of all bacterial isolates was determined by dual culture assay on PDA medium. A *Rhizoctonia solani* agar disk (6 mm) isolated from one day old culture was disposed at the center of Petri dishes and the bacterial strains were streaked in a square form around the agar disk at 2 cm distance. The antifungal activities of the bacterial isolates were calculated using the following equation:

$$I \% = (C - T) / C \times 100,$$

where: I = percent of inhibition; C= pathogen growth in control; T = pathogen growth in treatment. Three bacterial strains *Bacillus subtilis* 1016, *Bacillus amyloliquefaciens* 1014 and *Bacillus cereus* 1018 showed a clear antagonism against *Rhizoctonia solani* being efficient in the biocontrol of this major pathogen. Our future vision will be determined of antifungal activity from *Bacillus* strains against other phytopathogenic fungi.

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4. F. Constantinescu, A. Tomescu, T.E. Sesan, P.M. Stirbu. 2010. Biocontrol of soil borne fungi in tomato crop by using beneficial *Bacillus subtilis* strains, ISHS, Acta Horticulturae 914.

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SENSORY ANALYSIS EVALUATION OF WHEY-FRUIT BEVERAGES

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For the evaluation of the organoleptic properties of whey based drinks, which contain natural ingredients, carefully selected and evaluated at laboratory level (sweet whey, aromas, fruit concentrates, sweeteners, dyes, stabilizers, acidifiers), sensory analysis was conducted accordingly to the STAS 12656-88 standard: **Sensory analysis. Method with mark scales/sheets**, from 0 to 5 points, and obtaining of medium scores from the group of tasters. The panel was constructed of 6 evaluators that were instructed about the characteristics of the analysed product and who received one sheet for each whey based drink. The samples were encoded (ZPS, CPC, LMP, CBP, CMP), so that the type of aroma in the sample remained unknown. The tasting sheet contained the following sensorial characteristics (quality indices): *appearance*: clearance (opaque, with or without residue/sediment, separate phases); *colour*: corresponding to each aroma; *consistency*: liquid, syrupy, thick/viscous; *smell*: characteristic for each aroma, without any foreign smell; *taste*: characteristic for each aroma, without any foreign taste. Following the sensory analysis with mark scales/sheets, the marks given for the organoleptic quality of the drinks were: for the ZPS sample (raspberry) with fruit concentrate, “**Very good**”; for the CPC sample (chicory) and the LMP sample (lemon-mint), “**Satisfactory**”; for the CBP sample (cocoa-bananas) and the CMP sample (cocoa-mint), “**Good**”.

For the evaluation of the products acceptability by the tasters, a reference scale method (hedonic) was used, making it possible to establish the best sample, degree of preference for a particular characteristic, based on visual, olfactory, gustatory tests. Positive sensations are marked from 6 to 9, the negative ones from 1 to 4, and “indifferent” is marked with a 5. The taster tastes a sample from the whey based drink and marks on the sheet, according to preference, on a scale from 1 to 9 (9 being the highest, “I like it very much”; 1 being the lowest, “I dislike it immensely”), so that each sample receives only one mark on the hedonic scale. The highest marks were given to the ZPS samples with fruit concentrate and ZPS which respectively received “I like it very much” and “I like it mildly”. At the opposite end, the LMP sample was given an “I mildly dislike it”.

Cr (VI) IONS REMOVAL FROM WASTEWATER USING PURE AND PVP/PEG COATED MAGNETITE NANOPARTICLE

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Heavy metals such as hexavalent chromium are known for their negative health and environmental impact even at low concentration. Health effects related to chromium (VI) exposure are allergies, stomach and intestinal bleedings, liver problems, kidney damage, asthma and even cancer, being 1000 times more toxic than trivalent chromium ^[1]. Most countries apply a legal limit of 50 ppb chromium in drinking water. The discharge of chromium in surface water may be done by various industries since approximately 20,000 tons per year is applied worldwide ^[2]. In this study, pure magnetite (Fe_3O_4) and its nanohybrids obtained by coating with PEG/PVP polymers have been synthesized using cheap and environmentally friendly starting materials. The uncoated magnetite and its corresponding hybrid nanoparticles were characterized by XRD, AAS, TEM and FTIR analyses. The investigation of wastewater treatment properties of the prepared nanomaterials was done by measuring the removal efficiency of Cr (VI) ions (Fig.1). The removal efficiency of Cr (VI) ions during 100 minutes for all prepared samples is shown in Fig. 2.

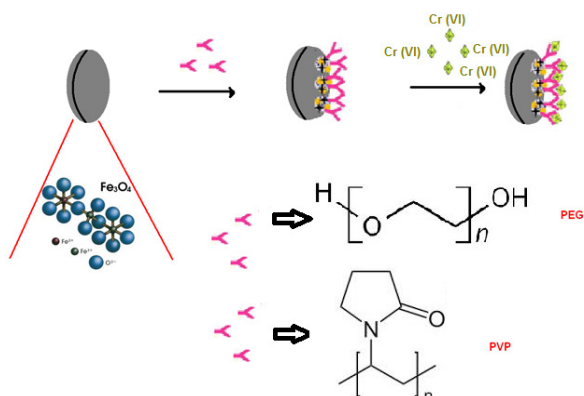


Fig.1 The wastewater treatment by removal of Cr (VI) ions using two nanostructured magnetite based hybrids

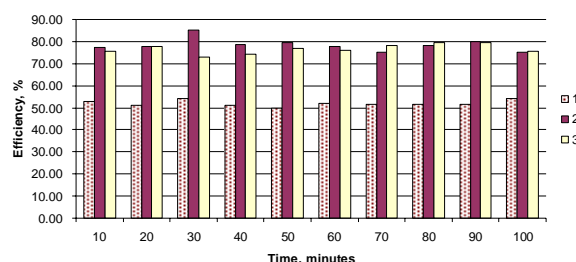


Fig. 2. Removal efficiency (%) of Cr(VI) for the three adsorbents: 1- Fe_3O_4 nanoparticles, 2- Fe_3O_4 -PVP nanohybrid and Fe_3O_4 -PEG nanohybrid

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MECHANICAL ASPECTS OF OLD BOOK CONSERVATION WITH NANOPARTICLES SUSPENSION

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The preservation and restoration of paper documents includes the totality operations applied in order to expand their life time, by minimizing the effects of chemical and physical deterioration, in order to prevent, as much as possible, their further damage. Approximately one third of the paper items from libraries are too brittle to handle, and new and efficient conservation methods are urgently imposed. Chemistry is the fundamental area for paper conservation. Paper in Europe was produced from cellulose resulted from linen and cotton rags. The cellulose is the principal component of paper, with hydrogen bonding capacity forming fibrils, which further associate to fibres, the basis of the structure of paper [1].

Gelatine and aluminium sulfate are known as traditional additives, strengthen the paper and prevent ink corrosion. Lignin, as the second component of the paper after cellulose, is a three-dimensional polymeric material that gives woody plants their physical strength. It reduces the paper strength by interfering with the way the cellulose fibres network.

The chemical degradation pathways of paper involve acid-catalysed hydrolysis and oxidation. A solution of 1 g of a piece of paper in 50 cm³ of water, offers the pH as a measure of its acidity [2]. More frequently, the paper become acidic either by absorbing pollutants such as sulfur dioxide and nitrogen oxides. Aluminium sulfate (or 'papermaker's alum') is recognized as a source of acidity, too, even it was added to gave initial strength.

The β -acetal oxygen bridge is responsible for acid hydrolysis, yielding to paper hardening and brittling, with a subsequent disintegration [3].

Oxidation, induced by light, discolours the paper. Both cellulose and lignin within the paper can be oxidised. In cellulose, the hydroxyl groups are transformed in aldehydes, ketones and carboxylic acids, that lead to paper discolouration. The photo-yellowing of paper is caused by lignin content, due to several chromophores with conjugated aromatic rings and carbonyl groups that absorb in the near UV spectrum (300-400 nm) and can decompose into yellow-coloured ketones and quinones, turning the paper yellow. Since these molecules themselves absorb visible light, they act as secondary chromophores and can react further, exacerbating the yellowing and degradation processes [4].

The aim of mass deacidification is to restore the pH of the paper to a neutral range (6.5-8) and keep an alkaline reserve against future acidification. One known method is that based on diethylzinc gas to neutralise the acid and leave an alkaline deposit of zinc oxide. But due to pyrophoric nature of diethylzinc and the production cost, this method is rarely used [5].

Another method is based on dispersions of metal hydroxide nanoparticles to neutralise acidity. The nanoparticles of calcium and magnesium hydroxide can penetrate the paper structure more easily, resulting in more complete deacidification. More recently, hydroxyapatite as hydroalcoholic suspension started to be used for book deacidification [6].

Also, inks and pigments themselves can degrade paper. Iron gall ink has an undesired effect on paper structure. This ink was formed by reacting gallic acid with iron(II) sulfate. The presence of excess Fe(II) ions can catalyse the oxidation of cellulose through the production of hydrogen peroxide (by Fenton mechanism). This can lead to significant destruction of the paper along the lines of the ink [7]. This decomposition process can be stopped by using chelating agents - as phytate (inositol hexakisphosphate) - to complex the Fe(II) in the ink.

In this study a new restoration method for historical paper, based on a special hydroalcoholic suspension of hydroxyapatite nanoparticles, was proposed. Hydroxyapatite, **HA**, treatment method in historical paper restoration wasn't used up to date. It is based on the nanoparticles properties to

penetrate the cellulose network, to adhere to it, covering and strengthening the damaged area. For this new method **HA** has been used for book conservation, with good results, because it's structure is identical to the phosphates found in paper as filling agents.

Some mechanical properties, of untreated and treated paper, such as: tensile strength, modulus of elasticity, breaking length and tensile index, have been studied. In this work only machine direction (MD) was performed, because the paper samples were too small in cross-machine direction (CD) for the existing clamps [8].

As general conclusions, regarding to all studied mechanical parameters, are that the treatment is definitely benefic [9].

The most efficient method for old papers treatment is to wash them firstly and then to spray them with HA nanoparticles hydroalcoholic suspension.

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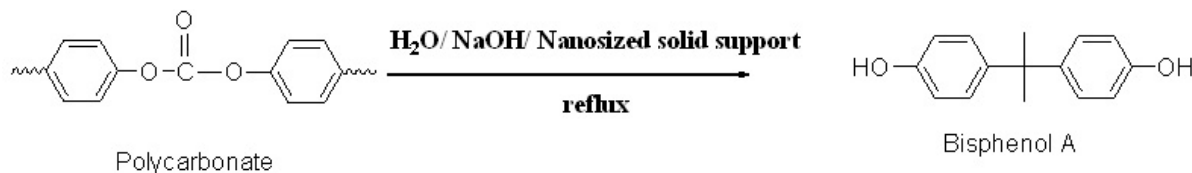
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GREEN and SUSTAINABLE METHOD in RECYCLING OF POLYCARBONATE WASTES USING NANOPARTICLES as the CATALYST SUPPORT

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Bisphenol-A (BPA) is one of the widely used industrial raw material in the world and mainly uses in production of polycarbonate block materials, fibers, optical materials, PC sheets and epoxy resins. In 2005, the world capacity of BPA production reported as 50000 tons, but in the end of 2007 year, only China BPA production capacity soared to 176000 tons/year which at the end of 2008, it reached to 296000 tons/year. It is estimated that by the end of 2012, China's BPA production capacity will reach to 760000 tons/year. PC is not a biodegradable polymer and the land filling is a bad option what may continue to leach of BPA. Increasing of PC productions and in order to recycling of used PCs, demands for PC wastes recycling are increased dramatically and scientists try to find an economical, green and convenient method for chemical recycling of polycarbonate wastes and recovering BPA. In continuation of our previous work on PC chemical recycling, we decided to examine the performance of Cloisite 30B (C-30B) as the solid support in bisphenol-A recovering from the CDs and DVDs wastes. The main aim of our report is based on usage of green solvent and performing the reaction under eco-friendly and convenient conditions. In order to studying the performance of solid supports in recovering of BPA four experiments set up in the absence and in the presence of Cloisite 30B, nano-TiO₂ and nano-Silica. Results showed that, the required recovery time for successful BPA recycling are different when various supports are used. In the meantime, an adequate reaction time consisting maximum BPA recovery yield is observed in using Cloisite 30B.



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**TECHNOLOGIES FOR SECONDARY PRODUCTS' VALORIFICATION OBTAINED
FROM NPK FERTILIZERS' PRODUCTION**

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The goal of these researches is to sustain the increase of Romania's durable economical competitiveness by improving the quality of the environment as to create the natural conditions for a harmonious socio – economical development of the country and to permanently improve living conditions. This was done by the elaboration of some technologies for the treatment of pit ponds present near nitrophosphates' synthesis installations, by recovering and valorification of the useful compounds that are present in these pit ponds in the form of commercial products, this being done simultaneously with the ecologization of the afferent areas^{1,2}.

During the experiments that were made in the Bioresources Department of ICECHIM, a technology based on suspensions' extraction from pit ponds and, afterwards, on the separation of the present solids, was investigated.

The results that were obtained led to several processing methods of the solid depositions, for all the proposed versions, based on the laboratory experiments. The research was based on the characterization and processing of the solid depositions extracted from the NPK suspensions present in the pit ponds and their valorification as mixed fertilizers, with or without the addition of other fertilizing substances.

Taking into account the laboratory experiments, several processing methods for these solid depositions resulted. It was established that the value of the macrofertilizers present in the final products – NP and NPK mixed fertilizers – mainly depends on the quantity of solid suspensions present in the pit pond that was used to formulate the mixed fertilizers, so that values of the microelements' content equal or higher to those of complex NP/NPK fertilizers can be obtained.

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Polymeric materials (plastics) are used in all sectors of life as very durable products with tailor-made properties. Due to their intense use, the accumulation of plastic wastes is a matter of great concern leading to long-term environment, economic and waste management problems. Biotechnology has the tools, methods and knowledge to solve this problem. The efforts are not only on to use biotechnology to protect the environment from pollution but also to use it to conserve the natural resources ¹⁻³. Microorganisms are natural agents that have a variety of capabilities to be exploited for waste management and disposal. Fungi are the most important microorganisms which colonize and degrade synthetic polymers and hence polymers degradability is a critical functionality in their application ⁴⁻⁵. Filamentous fungi such as *Aspergillus* ⁶ colonize substrates and the resulting mycelium secretes a wide variety and large amounts of proteins that degrade the substrate into molecules that can be taken up to serve as nutrients. The features of the selected *A. niger* are well suited for its use in biodegradable plastic recycling systems. The degrading potential of the fungal strain was evaluated *versus* polymer composites based on poly(vinyl alcohol) using microscopic observations and FTIR spectra. The polymeric materials subjected to microorganism contact undergo some type of transformation demonstrated by a significant increase of the peak around 1740 cm⁻¹ attributed to OH oxidation of the PVA to CO groups. Microscopic images revealed characteristics of fungal growth as dense networks of ribbon and tubular filaments, agglomeration of conidia on composites surface. The materials biodegradability is of interest for packaging applications and environment protection.

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ECOLOGICAL FORMULATION OF LUBRICANTS CONTAINING TITANIUM DIOXIDE NANOPARTICLES

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In recent years, the use of different kinds of nanoparticles in composition of oily lubricants has been investigated in many studies ^[1,2]. These research results show that deposition of nanoparticles on the rubbing surface improves the tribological properties of the base oil. Therefore, nanoparticles are added to lubricants with the goals of friction-wear reduction and lubrication effect improvement. When nanomaterials are used to improve lubrication effect, the selection of metal is very important ^[3]. In this paper we have chosen for tribological properties investigation two samples of TiO₂ with the mean diameter of 15 nm (n-TiO₂) and 250 nm (m-TiO₂) under different friction conditions. The tribological properties of TiO₂ samples mixed in one lubricant oil were investigated using a four-ball tribometer and a block-on-ring tribometer and show the lowering of friction coefficient in comparison with the lubricant oil (base oil) and TiO₂ having micronic particles size Fig.1.

The second purpose of the study, besides preparing two formulations of lubricants with enhanced tribological properties, was that they could be considered ecological. For this reason were used: an oil lubricant which is not classified as dangerous for the environment and the titanium dioxide nanoparticles added which are not considered pollutant agents for the environment.

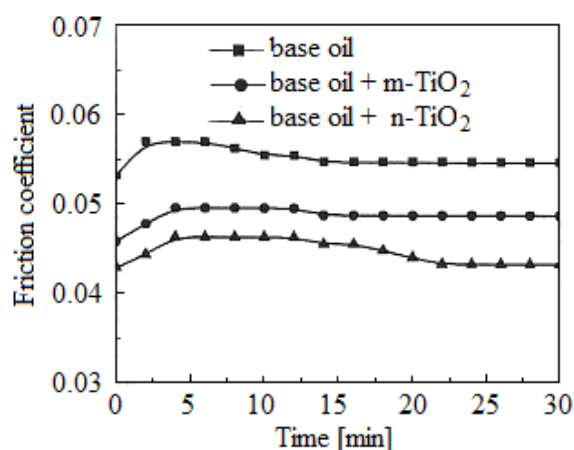


Fig.1. Variation of friction coefficient vs. time on four-ball tribometer

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2. Environment engineering and protection of cultural heritage - P
**RECYCLED POLYOLS FROM „SPLIT-PHASE” GLYCOLYSIS OF POLYURETHANE
INTEGRAL SKIN FOAMS**

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Environmental and economic considerations, as well as imperatives of European legislation, led to an intensive research effort to recycle polyurethane (PU) waste, originating, in significant quantities, from the automotive industry. Semi-flexible integral skin PU foams are extensively used in this field (protective padding, steering wheels), due to special physical characteristics resulting from the polymerization process itself¹. Glycolysis, a chemical recycling procedure resulting in products used in the manufacture of new PU, consists of cleavage of PU polymer with diols, to form polyols and other liquid products, mainly carbamates of diols used as cleavage agents². The PU foams chemical structure and the process parameters may favor a large number of side reactions^{3, 4, 5}. An additional problem in integral skin PU foams chemical recycling rises from their content of special additives and pigments.

This study intended to set up a process providing a recycled polyol similar to virgin polyol used in formulations for semi-flexible PU foams, by glycolysis of integral skin foams resulted from dismantling vehicles. A process of “split-phase” glycolysis⁶ was studied, using different cleaving agents, catalysts and reaction parameters, in order to avoid secondary reactions leading to formation of toxic and carcinogenic compounds, whose presence is required to be below the limit imposed by the regulations. The recovered polyols were characterized by physico-chemical methods, Fourier Transform Infrared Spectroscopy, ¹H- and ¹³C Nuclear Magnetic Resonance Spectroscopy, Gel Permeation Chromatography. The absence of undesirable by-products was proven and the chemical structure and average molar mass of the outcome products were emphasized. The recycled polyols obtained were similar to virgin polyols used for semi-flexible PU foams preparation. The products were tested in a conventional semi-flexible foam formulation.

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2. Environment engineering and protection of cultural heritage - P
Synthesis and characterization of hydroxyapatite and other calcium-substituted hydroxyapatite compounds

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The apatites are a family of compounds with similar structure but different compositions. They can be represented by the following general formula: $M_{10}(XO_4)_6Z_2$, where M is usually a divalent cation, XO_4 - most often a trivalent anion, and Z - is generally, but not necessarily, a monovalent anion. Hydroxyapatite ($M=Ca$, $XO_4=PO_4$ and $Z=OH$) is among the most studied ceramic materials; its studied properties varies from a with a wide range of medical applications as the reconstruction and regeneration of bone structures (for which researchers all over the world have shown interest), to applications in cultural heritage conservation or environment protection^{1,2,3}. The paper presents the synthesis and characterization of hydroxyapatite and other calcium-substituted hydroxyapatite compounds (where the calcium is half and totally substituted with Sr, Ba and Mg). The synthesized materials were characterized using modern analytical techniques (X-ray diffraction - XRD, energy-dispersive X-ray fluorescence - EDXRF, inductively coupled plasma – atomic emission spectrometry – ICP-AES, dynamic light scattering - DLS, Fourier transform infrared spectroscopy – FTIR and thermogravimetric analysis - TGA). The analytic results confirms the succesful synthesis. The synthesized materials have applications in the field of cultural heritage conservation (as antifungal agents for different types of support materials) and for environmental protection, as confirmed by our results^{4,5,6}.

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ADVANCED METHODS OF HEAVY METAL PURIFICATION AND RECOVERY FROM MINE WATERS

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ABSTRACT

Mining and metallurgy industry are the source of pollutants such as zinc, lead, copper, cadmium, arsenic, mercury and other¹. After Romania joined the European Union, retention of heavy metals from mine waters has become a mandatory operation, because ions are toxic and are currently discharged in the emissary, polluting and also the surface water is not drinking water. Retaining of these metals is also useful in economical terms², keeping typically heavy metals which are expensive⁴. Recovery of these metals decrease treatment costs of operations.

Depending on the physico-chemical characteristics of impure substances, treatment of mine water is achieved through various methods. The most used methods are: pH neutralization, cation contaminants precipitation, extraction with ions exchange³, flotation, reverse osmosis and chemical processes combined. This paper presents the results of treatment of mine water by use of three combined chemical processes (pH neutralization, the precipitation of cationic contaminants, extraction with ion exchange) for the copper recovery that is performed over 98% yield in the form of salable products and waste water discharge in the emissary after pH neutralization and separation of precipitates which can be used in the construction industry.

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2. Environment engineering and protection of cultural heritage - P
**INVESTIGATION OF TWO SYNTHETIC ROUTES FOR DEVELOPING
BIODEGRADABLE, WATER DISPERSIBLE COPOLYESTERS, STARTING FROM PET
WASTES AND RENEWABLE MATERIALS**

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Functionalized polymers provided lately the agricultural field with new tools for enhancing the ability of plants to absorb nutrients, increasing the efficiency of pesticides and herbicides and, at the same time, increasing the water retention^{1, 2}. Biodegradable and water absorbent polymers, such as natural polymers, are convenient candidates for those applications³, but their properties do not always fit the needs of specific applications. Blending with synthetic biodegradable polymers may be a way to gain the desired properties⁴. An attractive approach for biodegradable synthetic polymers manufacture might start from chemically recycled polyethylene terephthalate (PET) wastes and renewable resources. Given a wide range of depolymerisation agents and possible subsequent chemical reactions^{5, 6}, PET can be cleaved⁷, leading to other classes of polymers with tailored properties to meet specific needs.

This study presents the results concerning some biodegradable, water dispersible copolyesters for agricultural applications, developed using as raw materials PET wastes and isosorbide (IS), a diol derived from biomass. An aliphatic dicarboxylic acid and 1,3-dimethyl isophthalate 5-sodium sulfonate were also used as comonomers, to provide water dispersibility and biodegradability, while IS was expected to induce a higher glass transition temperature. Two synthesis paths were followed to ensure a higher content of IS into the polymer. The copolyesters were characterized by FTIR, ¹H-NMR and DSC, providing information on their chemical structures and glass transition temperatures. Water dispersions of the copolyesters were prepared and analysed by surface tension measurements, electrical conductivity tests, rotational viscometry, viscoelasticity and size distribution profile measurements (DLS). The results emphasized the hydrophilicity of the copolyesters, polyelectrolyte features, viscoelastic fluid behaviour and nanodispersion character of the samples.

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2. Environment engineering and protection of cultural heritage - P
**RESEARCH ON OBTAINING A LOW-COST AND ECO-FRIENDLY AGENT FOR THE
REMOVAL OF HYDROCARBONS (HC) FROM CONTAMINATED WASTEWATERS**

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The presence of hydrocarbons (HC) compounds in wastewaters from petrochemical industry and soils has become significant problems. Common commercial wastewater treatment methods utilize the combination of physico-chemical and biological treatment. Removal HC compounds from wastewater using an eco-friendly and low-cost agent (adsorbent / coagulant) has been the topic of scientific interest for a number of decades.

HC is not easily degradable, the performance of removal treatment systems is largely depend on the fundamental understanding the agent substrate utilization, which is essential for defining operational conditions for effective removal organic compounds during wastewater purification.

The work aims to obtain polymetal(Fe,Al)_n – zeolite tuff (CLN) composites with coagulation properties by valorising the red mud waste from the aluminium industry and the roumanian zeolite tuff (66-75% Clinoptilolite). The coagulation performance of the new obtained composites was evaluated in treating hydrocarbon-polluted waters

A variety of factors are known to influence the kinetics of HC removal including: initial HC concentration, pH, availability of the chemical agent used like adsorbent / coagulant.

The internal of environment for a good performance of all types agent tested in this work is believed to be approximately neutral or easy alkaline. At low (5.0) or high (9.0) pH values acids or bases can destabilization the flocculate forms more easily, because they tend to exist in dissociated form under these conditions and electrostatic force cannot prevent them from deflocculating phenomena. The optimum pH for HC removal was established for 6.0 to 9.0 pH values domain coagulant composition tested in our work.

The eco-friendly and low-cost agents tested in our work, with a composition comprise natural clinoptilolite and Fe and Al compounds based, have been demonstrated a highly efficiency in HC removal, more to 85%, a good performance versus conventional other agents.

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**RESEARCH ON THE ACTION OF METALIC CONTAMINANTS ABOUT MUREȘ RIVER
WATER AND ITS TRIBUTARIES, IN HUNEDOARA COUNTY AND THEIR INFLUENCE
OF FAUNA**

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Summary

The aims of this paper is to study the pollution of waters of the river Mureș with metallic pollutants, due to human activities and their effects on sediment and aquatic fauna by studying the degree of metal pollution in the sediments and bioaccumulation in aquatic organisms, especially fishes. One of the main problems associated persistence is the potential for bioaccumulation and bioamplification of heavy metals, which can lead to increased persistence of the pollutant in the ecosystem with long-term risks to the ecological systems. In terms of accumulated metallic elements studied biocenosis can be concluded that the trend of accumulation varies in the order of: zinc > lead > copper > nickel > cadmium.

Like the method of analysis used for determination of emission spectrometry was used inductively coupled plasma¹.

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FUEL CELL - NEW SOLUTION FOR CLEAN ENERGY PRODUCTION

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The use of fossil fuel is a major source of air pollution and contributes to global warming. The transportation sector is a major consumer of fossil fuel, thus eliminating or reducing pollution from transportation sources is a major policy objective. Therefore, it was found an alternative solution for producing clean energy. Polymer electrolyte membrane (PEM), which is our solution, convert the chemical energy of H_2 and O_2 directly into electrical energy with water and heat as the only reaction products.

In this paper, is presented a general formulation for a comprehensive fuel cell model, base on the conservation principle. This formulation includes the electro-chemical reactions, proton migration and mass transport of the gaseous reactants and liquid water. Also, in this paper we reffered to other components of the PEM fuel cell, such as: the bipolar plate, gas flow channels, electrode backing, catalyst and polymer electrolyte layers.

AMINOPHENOL'S TRANSPORT ASPECTS THROUGH BULK LIQUID MEMBRANES

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Wastewaters exhibit a relatively high content of aminophenolic compounds, resulted from the synthesis of pharmaceutical products and dyes which are further used in various industry branches (ranging from the textile to the plastic industries). Industrial activities that involve the use of these substances lead to aminophenol's presence in wastewater. The occurrence of these compounds has a high toxic potential impact on the ecosystem due to their high toxicity, even when are found in low concentrations. The transport and separation through liquid membranes is an efficient and economical process for removing organic compounds from wastewater. In this paper experimental results concerning the transport of o-, m-, p-aminophenol through a chloroform liquid membrane, in the presence of Aliquat 336 carrier are presented^{1,2}. The substance transport occurred from an alkaline feed source (pH=12) into an acid receiving phase using a transport cell tube in tube type. The transport conditions for aqueous phases (feed source and receiving phase) were based on the speciation diagrams of aminophenol function of pH. Recovery factor is greater than 90%. Experimental data have confirmed a 1st order kinetic characteristic consecutive reaction that takes place after the scheme:

(S_{FS} = feed source substrate, S_M = membrane substrate, S_{FR} = receiving phase substrate)

Pseudo-first-order apparent membrane entrance and exit rate constants (k₁ and k₂) were evaluated in order to develop a kinetic model.

MANAGEMENT OF TECHNOLOGICAL INNOVATIVE RESOURCES – A KEY FACTOR FOR INDUSTRIAL REVITALIZATION. MINI-CASE STUDY

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Converting knowledge, human skills, natural resources and capital (**inputs**) into new products and services (**outputs**), gradually generating national development and prosperity (**outcomes**), is a complex process influenced by economic, politic, cultural and geostrategic factors including the pressure of globalization.^{[1], [2]}

Industrial revitalization of a nation requires an effective management of the innovative technological resources based on (i) correlation between economic and innovation policies, (ii) public-privat consistent financial support, (iii) orientation of R&D activities to the real needs of the economy and society, (iv) fostering academic & industry partnerships and developing entrepreneurial skills, (v) great opening for international collaborations and (vi) maximize the specific opportunities.

From this perspective, the authors present the evolution of Romania after fifth years of EU membership (ie 2007-2011), compared to (i) Bulgaria (simultaneous accession), (ii) Estonia, Slovakia, Czech Republic, Poland and Hungary (2004 accession), (iii) Community assembly (UE 27) si (iv) Switzerland (ranked world's most innovative country 2011 and 2012). This analysis is based on relevant indicators for the R&D sector and innovative activities that generate technological changes^[3] : (i) Total R&D expenditure, (ii) Business enterprise sector expenditure, (iii) Risk capital, (iv) European Patent Applications, (v) High-tech exports and additionally (vi) Labour productivity per hour worked and (vii) Gross domestic Product. Anywhere, anytime, especially in times of crisis, should be studied the experience of developed countries and, carefully, adapting key elements^{[4], [5]}. We also present own recent proposal for industrial revitalisation (concerning textile field).

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Polymer nanonocomposite colloidal crystals obtained by surfactant free emulsion polymerization

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Abstract: Polymeric colloidal crystals are a particular class of structures able to support assembling phenomena up to large particle scale (particles of tens and hundreds of nanometers). The assembling phenomena occur by small area of contacts between particles obtained during the evaporation process from a colloidal dispersion. The entities able to promote the ordering planes are formed by spherical polymer particles. Surfactant free emulsion polymerization is a suitable technique aimed to obtain spherical monodispersed particles. In this work we try to respond to the following scientific paradox. Theoretically any foreign inclusion in a crystal structure induces a certain degree of disorder, which then affects the final properties. So apparently using a nanofiller for the polymer particles will decrease the order degree and properties as well. Our data sustain that a certain amount of nanofiller can be used ab initio for the polymerization process with benefits on both assembling ability of the final polymer particles and surface properties of the films obtained from the colloidal dispersions. Several polymerizations were conducted in presence of nanoclay particles at high monomer conversions. A mixture of monomers (styrene, butyl acrylate, acrylic acid) was used. Our experimental results showed that clay particles at low concentrations (below 0.2% wt. to monomer) are able to participate in the polymerization process by several directions: i) dispersion agents (similar to suspension polymerization or Pickering emulsion); ii) influence of the autoacceleration stage (Trommsdorff-Norrish effect in free radical polymerization); iii) stability of the final latex. Thin nanocomposite films were obtained by vertical deposition technique. The final materials were investigated by FTIR, DLS, AFM and Contact Angle measurements, in order to assess the particular assembling induced by clay particles.

Acknowledgement: The financial support offered by UEFISCDI through PCCA 137/2012 contract is gratefully acknowledged. The Ministry of National Education through Romanian National Program NUCLEU, 9-N/ 27.02.2009 contract, PN.09.09.04.15 Project, is also acknowledged for the support of this research.

**TECHNOLOGICAL SOLUTION FOR THE ELIMINATION OF WATER
CONTAMINATION IN THE SYNTHESIS OF GRAFTED VINYL-ACRYLIC CO-
POLYMERS IN WATER DISPERSION**

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For stiffening unwoven textiles, vinyl-acrylic co-polymers with self-cross-linking proprieties can be used. In water dispersion, these can have a dry mass of up to 44-45%, and their glass transition temperature (T_g) may be between 40-50°C, obtained by co-polymerization by grafting. The present work shows a technological solution for eliminating environmental contamination especially water, by the installations cleaning water. This would occur if the water with witch the installation is cleaned would be stored in a purification site or worse it would be dumped into the town's sewer system. This waste water can contain up to 3% polymer remnants and 1% unreacted monomers

Six batches were made by a predetermined recipe containing a styrene/ acrylonitrile core polymer (7%) and a grafting polymer composed of vinyl acetate - methyl metacrylate - N-methylolacrylamide (93%). The first batch was made with 100% deionized water. This served as a base for comparison. Five batches were made with the cleaning water from the previous reaction. The water was filtered to remove any unwanted agglomerates and introduced in the next reaction at a ratio of 2/3 next to fresh deionized water which was 1/3.

The results show that there is no change in the aspect of the polymer dispersion. In the cases in which cleaning water was used, the dry mass values show a slight increase. This influenced the density and viscosity of the product, which have also shown a slight increase. This shows that the partial replacement of deionized water with cleaning water does not influence the vinyl-acrylic copolymerization reaction. From this it can be concluded that it is possible to reuse the cleaning water, which would lead to waste water treatment and purification problems and contribute to the regions waste water build-up.

THE EFFECT OF THE NATURE OF ELASTOMER AND PLASTOMER BLOCKS FROM STYRENE-DIENE BLOCK-COPOLYMERS UPON THE MODIFICATION OF RECOVERED POLYPROPYLENE

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The waste polypropylene modification was made by melt blending using three block-copolymers with different blocks: styrene-isoprene, styrene-butadiene, and α -methylstyrene-butadiene. Their synthesis was carried out by sequential anionic polymerization of monomers, in cyclohexane solution, initiated with n-butyl lithium, followed by the coupling of active blocks with silicone tetrachloride.

The block copolymers molecular weight were determined by gel permeation chromatography (GPC) and were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), mechanical properties, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA).

The waste polypropylene was modified in melt state with 5 – 30 % amount of each block-copolymers were physical-mechanical characterized.

The study of the properties of recovered PP composites obtained by melt alloying with styrene and α -methylstyrene-diene block-copolymers emphasized that all block-copolymers have a good modification effect, manifesting his strength in the order: α MeSB α MeS, SBS, SIS. The maximal modification effect of the SIS block-copolymer can be explained by the superior adherence of the polyisoprene phase in contact with the polypropylene matrix, which leads to increased strength of the composite material, especially when subjected to mechanical stress.

Replacing polystyrene with poly- α -methylstyrene ones blocks do not greatly influence the modification effect of the polyolefin, as only the polybutadiene block, common of the two elastomers, is in direct contact with the polypropylene matrix, and having the same molecular mass, it is expected also that the modification degree to be very close.

In conclusion, we can say that the modification degree of recovered PP by melt alloying is significantly influenced only by the nature of the diene block from the block-copolymers.

ASSESSING THE BIODEGRADABILITY OF POLYMERIC MATERIALS USING THERMAL ANALYSIS METHODS

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Plastic packaging materials represent a large percentage of the materials which are used for food packaging. Because most of them are not biodegradable, a constant area of challenge for packaging material technology is to design environmentally friendly systems containing biodegradable materials. Biopolymers obtained from blends of synthetic and natural polymers are a new generation of materials capable to reduce significantly the environmental impact in terms of satisfying certain technical requirements and which are also much more susceptible to biodegradation.

The main concept of this work was to use the thermal methods of analysis (thermogravimetry (TGA), differential scanning calorimetry (DSC), microcalorimetry) complemented by structural and morphological analysis (X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscopy (SEM)) for characterization of new polymeric materials: poly(vinyl alcohol) (PVA) blended with cellulose obtained by microbial biosynthesis; low density polyethylene (LDPE) in which natural extracts of antioxidants have been incorporated; poly(vinyl alcohol) with polyhydroxybutyrate (PHB), etc¹⁻³. These materials were characterized before and after exposure to microbial attack.

The combination of the above mentioned methods may be used as a toolbox for the fast assessment and the forecasting of the potential of biopolymer materials to be biodegraded as an alternative to the standard methods used for biodegradability evaluation which are expensive and very long lasting.

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STABILITY TESTS FOR MAGNETIC OXIDES NANOSTRUCTURES USED FOR ENVIRONMENTAL APPLICATIONS

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The objective of this work was to establish a correlation between stability of some magnetic iron oxides as nanocrystalline materials and their dissolution capacity in different aqueous media. Preparation method was chemical coprecipitation (CC) as classical method, widely used in preparing ultrafine powders, including the ferrite powder¹. The synthesis of monodispersed particles was performed under kinetic control of the precipitation using very dilute solutions². Also, other metal atoms such as Zn, Ag and Cu were also used to prepare superparamagnetic nanostructured materials. The dimensions of the products were established by morphological and structural characterization with X-ray diffraction (XRD) and transmission electron microscopy (TEM)³. Concentration of dissolved iron was established with atomic absorption spectrometry (AAS). Results regarding the stability in different media of some magnetic nanostructures were evaluated using the following parameters: maximum quantity dissolved, time of dissolution, pH value of aqueous media. The stability was tested during 24 hours, in order to identify the best compatibility with aqueous media taking into account the real pH values of waters with variable values from acidic to basic pH values. Results indicate a high dissolution tendency under acidic conditions, especially for iron oxides in comparison with bimetallic oxides. The separation from the aqueous media was made by an external magnetic field, due to their super-paramagnetic behavior. The tendency of dissolution from these type of nanostructured materials represents the main step in choosing the right pH value of media where these particles can be used.

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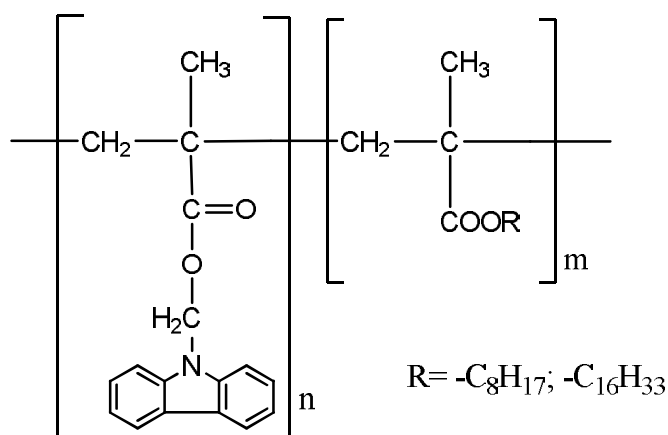
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PHOTOSENSITIVE MATERIALS FROM CARBAZOLECONTAINING PHOTOPOLYMERS FOR REGISTRATION OF THE HOLOGRAPHIC INFORMATION

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Carbazolecontaining polymers and copolymers allow creating photosensitive nanomaterials, which are successfully used in various areas of electronics, in particular, for the registration of the relief-graphic images via electrophotographic method [1, 2]. The aim of this work is the synthesis of new copolymers of carbazolimethyl methacrylates (9H-carbazole-9-methylmethacrylate, CMM) and the development of double-layer organic photothermoplastic carriers for registration of the optical information.



Copolymerization of the CMM monomer with alkyl (octyl, cetyl) methacrylates proceeds relatively easy according to the radical mechanism in presence of the azobisisobutyronitrile (AIBN) initiator. Were synthesized copolymers containing from 50 to 70 mol% of CMM. All copolymers were purified by reprecipitation from methanol followed by drying.

The obtained copolymers are soluble in organic solvents and can be fabricated in the form of thin films. They have a glass transition temperature (T_{st}) of 80-90 °C and an intrinsic viscosity of 0,20-0,30 dl/g, which meets the requirements of the photosensitive materials for creation of the electrophotosensitive carriers of optical information.

From synthesized copolymers of CMM:OMA (60:40 mol%), sensitized by 2,4,7-trinitrofluorenone and other sensitizers designed was double-layer carrier of information on which by the photothermoplastic method were recorded high-quality holographic gratings with resolution of up to 2000 mm⁻¹ and the diffraction efficiency till 10%.

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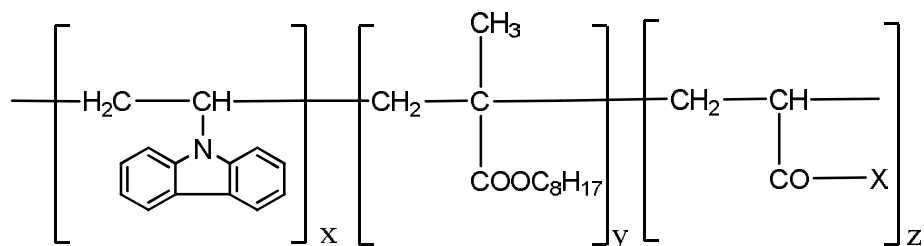
SYNTHESIS AND STUDY OF N-VINYL CARBAZOLE COPOLYMERS GRAFTED WITH AZONITRO-DYES TO DEVELOP NEW RECORDING MEDIA

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Polymer materials show their impact on optical storage technology for developing high information density with a high efficiency¹. It is known that the polymer layers based on 9-epoxypropyl grafted with azonitrodyes allow record high efficiency holographic gratings images in the green region of the spectrum by 520 nm laser². The diffraction efficiency of these gratings averages about 40% without chemical treatment in organic etchants. New azonitro-dye-doped copolymer materials based on vinylcarbazole, octyl methacrylate and chloride acryloyl have been developed and used for holographic recording of diffraction gratings. The chemical formula of synthesized copolymer is:



X = NH-; -O-colorant

A content of chloride acryloyl units in the copolymer was varied from 10 to 30 mol%. The structure of the colored copolymers was confirmed by IR spectroscopy by the appearance of new vibrational bands at the $\nu = 1540\text{-}1550\text{ cm}^{-1}$ for nitro and $\nu = 3420\text{-}3460\text{ cm}^{-1}$ for amide groups.

Thin polymer films with thickness about 10 μm were obtained from the solutions by casting. Green DPSS laser (532 nm) was used for recording of diffraction gratings by holographic recording.

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NEW DESIGN OF ANTIMICROBIAL MEMBRANES BASED ON POLYMERS COLLOIDS/MWCNT HYBRID MATERIALS AND SILVER NANOPARTICLES

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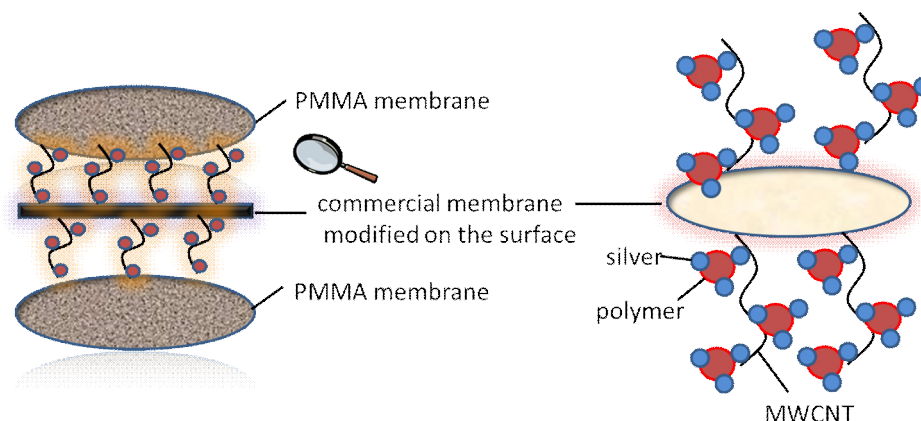
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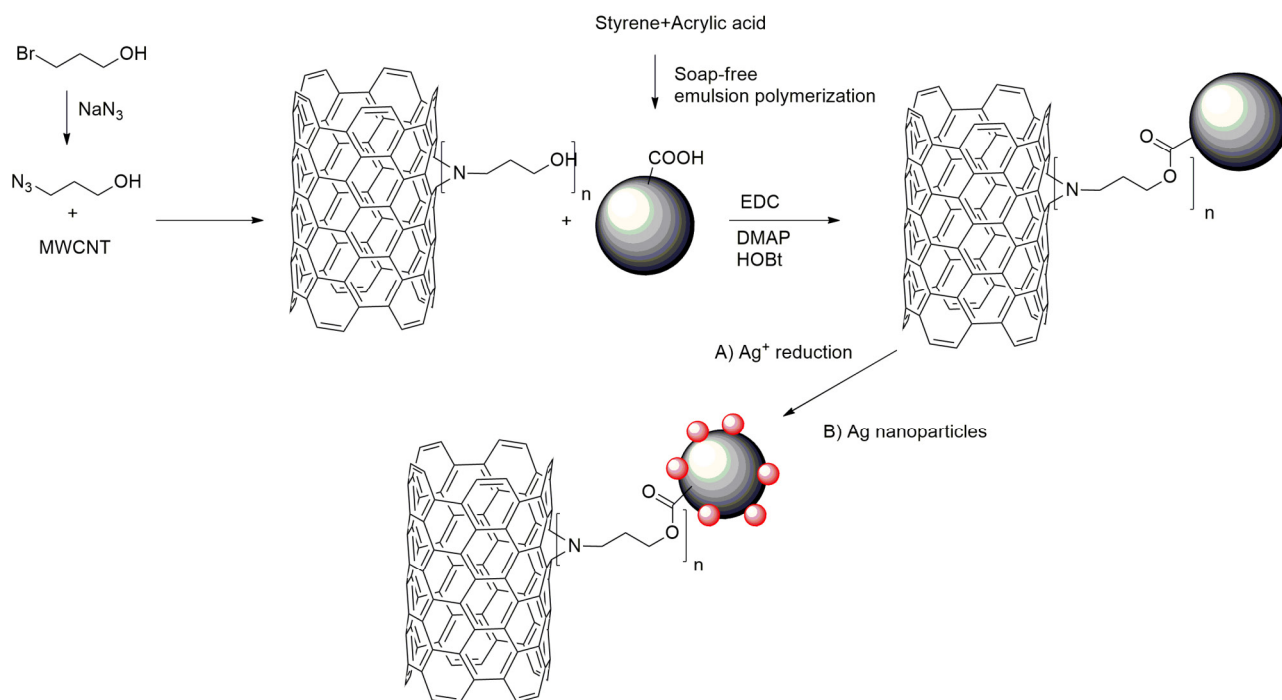
The aim of this study has been to obtain membranes with antimicrobial activity presenting a complex sandwich type structure (Scheme 1). The outer layers are comprised of a PMMA membrane, whereas the inner - active layer consists of a modified commercial membrane in order to achieve antimicrobial properties. This characteristic is a result of the presence of AgNps in the hybrid material composition deposited on the commercial membrane. This hybrid material consists of polymer colloids and MWCNTs which have been used for the stabilization of the active layer, respectively for the interconnection/joining of the polymer particles (Scheme 1).



Scheme 1: Antimicrobial membrane design

The methodology used for the synthesis of the active layer is presented in Scheme 2. The first step has been the obtaining of an azido alcohol and its reaction with the MWCNTs, resulting in a highly dispersible product. This aided during the next stage consisting in the esterification reaction with the carboxyl groups present at the surface of the polymer particles. This hybrid material has served as support for the fixation of nanoparticles with antimicrobial activity by employing two

synthesis strategies: **A)** the in situ generation of AgNPs in the presence of the hybrid material and **B)** realization of a physical mixture with preformed AgNPs (Scheme 2).



Scheme 2: Antimicrobial active layer preparation

SILVER NANOPARTICLES OBTAINED VIA MULBERRY (*MORUS NIGRA*) EXTRACT: SYNTHESIS AND ANTIOXIDANT ACTIVITY

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The fruits of mulberry (*Morus nigra*) are used in herbal therapies due to tonic and depurative properties. It is used to treat lung diseases, thrush, throat diseases, diabetes, gastric and duodenal ulcers. Research studies have revealed high content of phenolic acids, ascorbic acid (vitamin C), antioxidant and anti-inflammatory properties of mulberry fruit.^{1,2}

The synthesis of noble metal nanoparticles (Au, Ag, Pt) is an expanding research area due to the potential applications for the development of novel technologies. Also, silver nanoparticles have important properties which help in molecular diagnostics, in therapies that are used in several medical procedures.

In the present research, we have developed a simple green and economically method for preparation and synthesis of silver nanoparticles (AgNPs) using a type of fruits.

The analytical techniques (UV-VIS, DLS, XRF and FTIR) studies suggest that the mulberry fruits have played an important role in the reduction and stabilization of silver nanoparticles. Using UV-VIS method, it was observed an intense peak at 450 nm specific for silver nanoparticles. DLS was used to determine the size of particles. X-Ray Fluorescence analysis confirmed the silver presence in AgNP-mulberry sample. The FTIR spectra indicate the appearance of peaks in the amide I and amide II regions characteristic of proteins, which have been found to be possible responsible for capping and efficient stabilization of the metal nanoparticles synthesized by the mulberry fruit.³ The eco-friendly silver nanoparticles presented strong antioxidant properties: AgNP-mulberry sample (AA%=90,71) has a higher activity than mulberry extract sample (AA%=88,25).

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SYNTHESIS AND CHARACTERIZATION OF A NOVEL POLYMER NANOCOMPOSITE, BY POLYMERIZATION OF VINYL ACETATE IN SYNTHETIC ZEOLITE

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Considerable interest has focused on the encapsulation of polymers into host inorganic matrix. Poly(methyl methacrylate), polystyrene, polyaniline or polypyrrole¹ have been widely utilized as guest compounds in order to synthesize inorganic-organic composites with unique properties. The resulting hybrid materials may have potential innovative applications as ceramics filters, solar cells, materials for protective and decorative coatings, micro-optics articles.²

In this study we report the synthesis of new composites of microporous HZSM-5 host reinforced with polyvinyl acetate. The materials were obtained by the radical polymerization of the vinyl monomer within the synthetic zeolite pores. The chemical composition of the material bulk and surfaces was studied by elemental analysis (XRF) and X-ray Photoelectron spectroscopy (XPS) and also the morphology was pointed out by scanning electron microscopy (SEM). X-ray diffraction (XRD) shows that the obtained composites possess cellular structure with micronic cells. XPS indicated the preference of the acetate groups for the silicate surface. N₂ adsorption/desorption analysis (BET) confirm the filling of the micro- and mesopores with the polymer. Zeolite aggregates and agglomerations of the polymer covered HZSM-5/PVAc composites particles were observed by SEM.

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TOWARDS A NEW CLASS OF ORGANIC COMPOSITES

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Bacterial cellulose and chitosan are well known natural structures with involvement in a wide range of applications from food and biomaterials to industrial products or specialties materials. Bacterial cellulose (BC) nanofibers are known for their mechanical properties, but the thermal stability belongs to the same cellulose class. Solid reactions and BC solubility are major limitations for BC modification, processing and use in composite materials. BC cristalinity (superior to the average cellulose class) implies strong interactions and spatial orientation between the macromolecular chains, which makes an eventual functionalizing or modification even harder. In our study, assembling BC chains in different macromolecular stacking with other macromolecular structures like chitosan (Ch) was proven as an efficient technique towards a new class of fully organic composites. Ch macromolecule poses an isoelectric point and is showing an increased mobility by controlling the pH condition. Ch macromolecules are able to be swollen from water solutions in the bulk phase of the BC. Ch chains were able to re-assemble either the fibers packaging or even the BC nanofibers. The favourable interactions were easily followed by FTIR absorptions. The BC-Ch composite materials were washed with water several times in order to remove the "unpacked" Ch. After drying the final materials showed a drastically increase of thermal stability (as evidenced by TGA-DTG profiles). The method is a new and viable way for composites obtaining with increased thermal properties in comparison with neat BC and Ch.

Acknowledgement:

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ORGANOSILICA IMPRINTED MATERIALS FOR GALLIC ACID SEPARATION
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The versatility of sol-gel chemistry enables us to generate a wide range of silica and organosilica materials with controlled structure, composition, morphology, and porosity. These materials' hosting and recognition properties, as well as their wide-open structures containing many easily accessible active sites, make them particularly attractive for analytical purposes. Depending on the concentration of the surfactant added in the synthesis and temperature, hydrolyzed silicone alkoxides reorganise to form micelles in cubic ordered arrays (MCM-48) leading to various nanostructured materials¹ proper for separation applications. Generally, the stability of the monomer-template complex (and afterwards of generated imprinted cavities) is given by the nature of co-monomers, thus the strength of monomer-template initial interactions, which influences directly the sorption parameters of imprinted materials. Therefore, combining tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), aminopropyl triethoxysilane (NTES), vinyltriethoxysilane (VTES), phenyltriethoxysilane (PhTOES) as functional monomers, six formulations were obtained in order to optimise the nature of imprinted sieves. Styrene trimethyl ammonium chloride (STMACl) and tetramethyl ammonium hydroxide (TMOH) were used as stabilisers. The results obtained from thermal analyses, infrared spectroscopy, scanning electron microscopy, and dynamic light scattering were confirmed by specific equilibrium GA sorption tests of imprinted sieves.

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GEL PERMEATION CHROMATOGRAPHY STUDIES ON CHITOSAN-BASED HYDROGELS DESIGNED FOR TISSUE ENGINEERING

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Chitosan-based hydrogels attract the scientific community, as well as the biomaterial producers due to their proved biocompatibility¹, biodegradability², or drug delivery properties³, with direct applications in tissue engineering. The paper goal is to study the dependence between the polymer molecular weight (M_w) and solution acidity in view of explaining variation of the new hydrogel consistency with the solution pH.

For this purpose, eight chitosan solutions with different acetic acid concentrations (0.050 M, 0.075 M, 0.100 M and 0.150 M) were analyzed before and after centrifugation using an Agilent 1200 gel permeation chromatograph (GPC) and a solution of acetic acid – water as mobile phase (1 mL/min flow rate), at 25°C, 50-60 bar, and 20 μ L injection volume.

The obtained results show that the molecular weights (M_w) depends by the solution acidity. The centrifugation technique seems to dissociate or brake what initially appeared as one chitosan population, in two populations with M_w dependent by the solution acidity. At acidity greater than 0.075M after centrifugation the two main populations contains only oligomers with different M_w . The obtained result can explain the variation of the gel consistency with solution acidity.

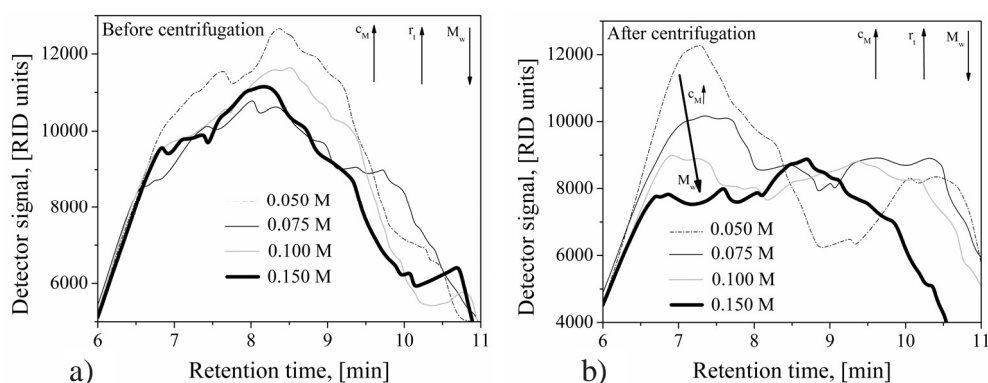


Fig.1. Influence of acidity (acetic acid concentration) and centrifugation on chitosan solutions.

Acknowledgement. This work was supported by the grant of the CNDI-UEFISCDI number 248/2010.

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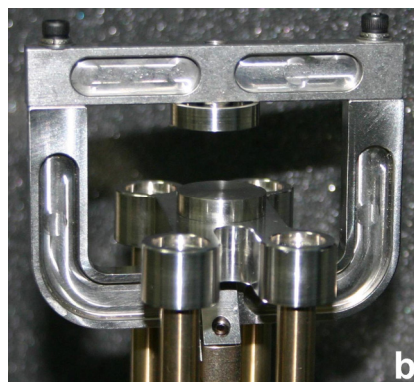
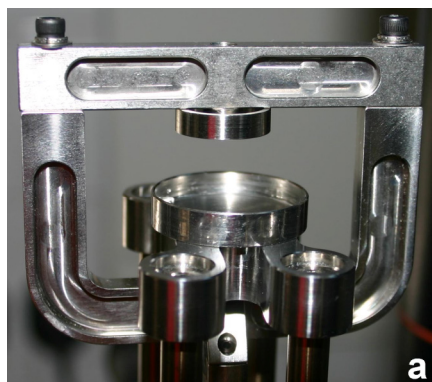
STUDY OF DYNAMO-MECHANICAL PROPERTIES OF SOME NEW HYDROGELS DESIGNED FOR TISSUE ENGINEERING

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Hydrogels are biomaterials that consist of a water-swollen network of crosslinked polymer chains. The hydrogel characterization as 3-D scaffolds involve the measurement of the engineering and biological properties. The dynamo-mechanical properties of the hydrogels are directly correlated with the nature of the tissue at which reconstruction can be used.

In this study the use of dynamic mechanical analysis (DMA) for the mechanical characterisation of some new biomedical hydrogels was evaluated. Two kinds of compression tests were made on hydrogels using a DMA Q800: first test for studying hydrogel formation in a dedicated device (a) and second test with compression clamp of DMA Q800 for studying the stability of mechanical properties of hydrogels. Hydrogels were analysed after swelling to equilibrium with DMA-compression clamp. The DMA was also used to define the hydrogel consistency and to chose the elastic properties at which the hydrogels can be manipulated and wich ensure optimal biological behaviour. Dynamic mechanical analyzer DMA-Q800 from TA-Instruments was used in isotherm “multifrequency-strain” mode at 34°C and 1 Hz frequency.



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INFLUENCE OF FORMULATION ON THERMOFORMING CAPACITY OF NEW BLENDS BASED ON STARCH

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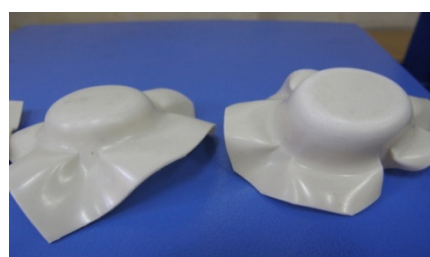
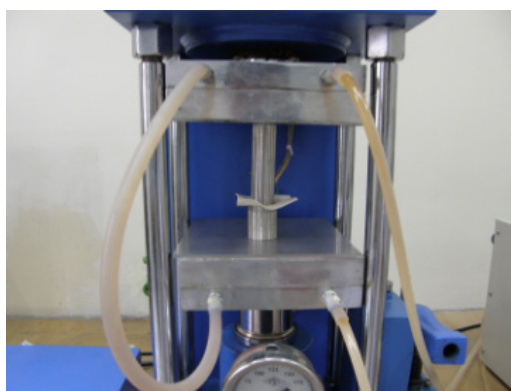
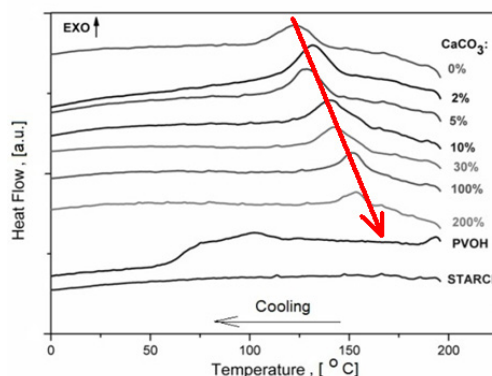
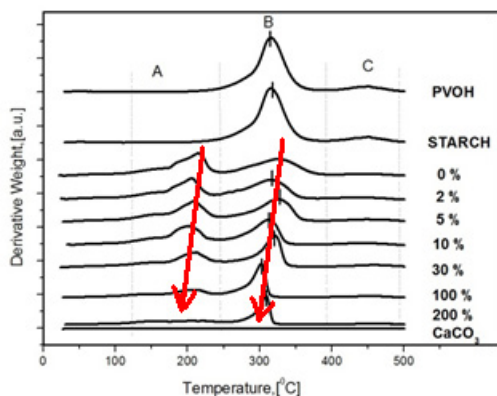
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In order to achieve new biodegradable materials based on starch moldable by thermoforming into short life products, was studied the influence of non reactive fillers on dynamo-mechanical, thermal and morphological properties.

Based on the obtained results were selected the material formulation which ensure the thermoformability properties. These materials simultaneous fulfillment the following conditions: T_g ranged as 80 – 120°C, low value of evaporation enthalpy, high melting temperature, do not degraded till 150 – 170°C, low elastic deformation capacity, high viscous (plastic) deformation capacity, medium or low damping factor (tan delta), high extension at tensile stress, low level of structural defects (voids, cracks, fractures), low shear rate values (1-100 1/s), melt processing conditions which do not degrade materials.



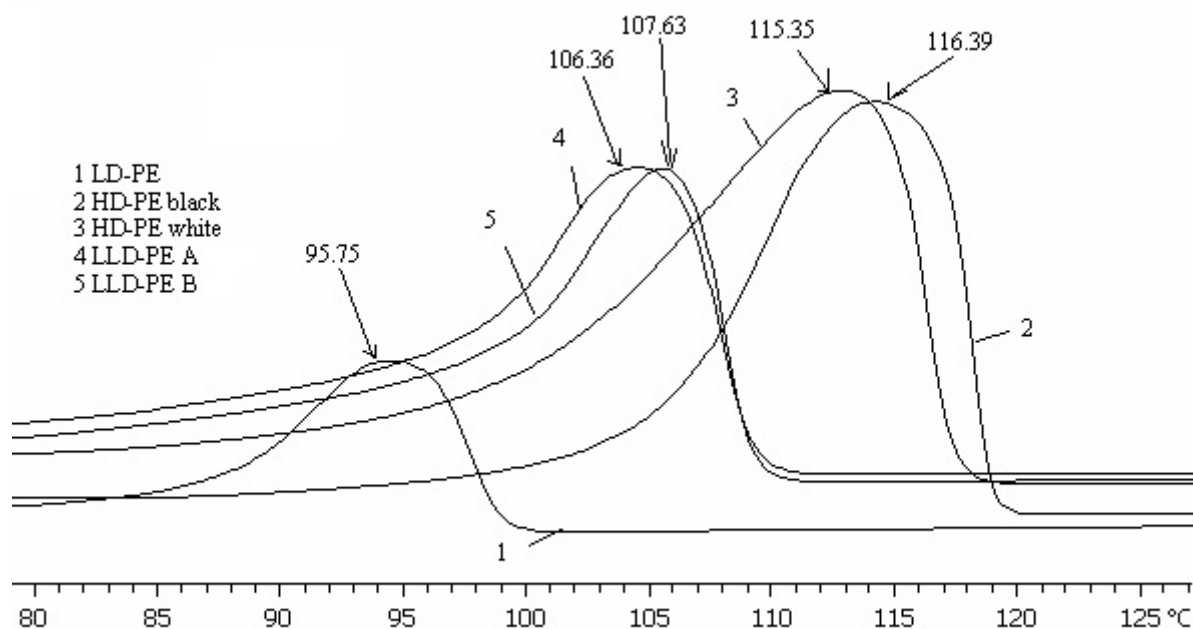
This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, project number 59/2012.

IDENTIFICATION OF INDIVIDUAL POLYMERS FROM POLYOLEFINIC BLENDS OBTAINED BY MELT PROCESSING TECHNIQUES

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For practical interests as mechanical recycling of secondary polymers it was found a method to identify the individual polymers from polyolefinic blends molded as films by melt processing techniques. It was found that by simultaneous measurement of thermal properties (melting and crystallization temperatures), density in solid state, melt rheological properties (melt flow index) and crystallinity content can be easily identify the individual polymers from a polyolefinic blends of low density polyethylene (LD-PE) as main component, different type of linear low density polyethylene (LL- DPE) and high density polyethylene (HD - PE). It was also found that by FTIR analysis can be highlighted the appearance of bands at 894 cm^{-1} for LDPE and 908 cm^{-1} for HDPE. With the twin peaks ratio from $1470\text{--}1460\text{ cm}^{-1}$ and $730\text{--}718\text{ cm}^{-1}$ it could be identify mixtures of these polymers in different samples¹.



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ANTIMYCOTIC MEDICAL COPOLYMERS OF FURACILINE DERIVATES

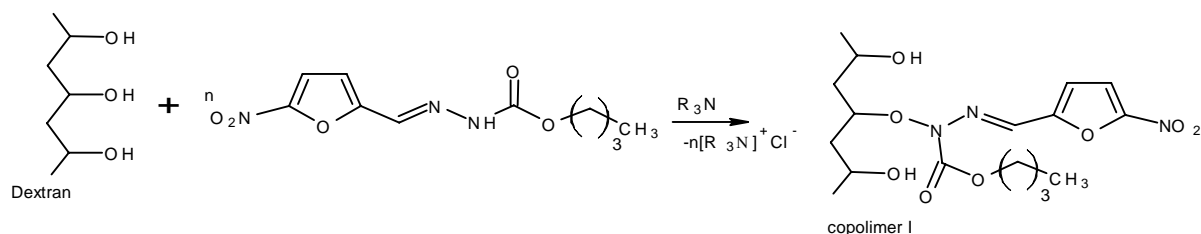
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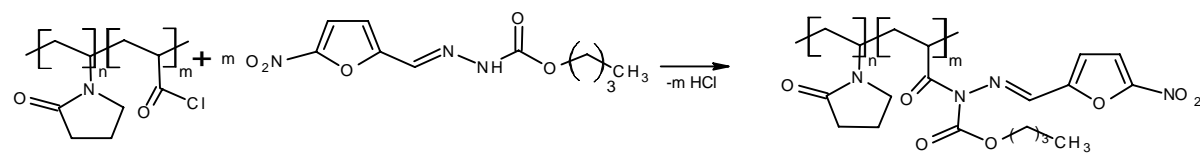
5-nitrofuranic micro molecular derivatives are a group of broad-spectrum bactericidal activity, bacteriostatic and notably antimycotic [1,2]. However, micro molecular 5-nitrofuranic preparations used in pharmacological practice have some disadvantages such as gastrointestinal disorders, blood aftermath (hemolysis, leucopenia, and in some cases allergic action). For the reduction of their toxicity it was achieved thier engraftment with some natural polymers like starch, dextran or copolymers of N-Vinylpyrrolidone.

As medicinal preparations furaciline and butyl ester of the acid there were selected 5-nitro-2-furfuliden-carbazic (ANF). The engraftment was carried out according to the scheme:



The reaction was carried out at low temperatures of 0 °C with the use of ethyl chlorformate. For the external use the furaciline as well as ANF was coupled with copolymers of N- Vinylpyrrolidone, by using acryloil chloride.

The structure of copolymerilor I and II was confirmed with the help of IR spectroscopy and by elemental analysis.



Medical testing of the engrafted copolymers showed the fungal activity at the furaciline level and a toxic activity less pronounced.

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CHARACTERIZATION OF POLYSTYRENE-CLAY-PPVK NANOCOMPOSITES BY THERMAL AND FT-IR ANALYSIS

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In the last years, PS was counted amongst the quantitatively most important thermoplastics, and continues to be ranked in fourth place after polyethylene, polypropylene and polyvinylchloride. The main applications include packaging, extruded sheets and consumer electronics. Improved mechanical properties with weight reduction, decreased vapor permeability and low oxygen diffusion are the main development areas for packaging (foamed and foils packaging). All these properties can be achieved using the "nanocomposite approach". The property improvements include improved mechanical properties, improved barrier properties, and lower water absorption and reduced flammability. To achieve these properties, layered silicates, a natural montmorillonite modified with a quaternary ammonium salts, are generally dispersed at the nanoscale level in the polymer to yield the so-called "nanocomposite". The nanocomposite can be prepared via several routes including melt-blending in high shear processing environments (extruder or other molding equipment). However, PS and its related plastic products are non-degradable in natural environment. In order to induce the photodegradation process in the thermoplastic polymers used in packaging a prodegradant, poly(phenyl-vinyl-ketone) (PPVK) was used in the PS-clay nanocomposites (PSN) synthesis. To have a good balance between processability, mechanical and thermal properties and ensure an appropriate photodegradability was necessary to study the effects of subsequent introduction PPVK and Cloisite 30B in PS to obtain photodegradable PSN.

In this work was investigated the effects of PPVK (2, 5 and 10%) and amount of layered silicates (Cloisite 30B) (1, 2.5 and 5%) on the thermal and mechanical properties of PSN obtained from two types of PS with different molecular weight performing different thermal analysis techniques: dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR).

The results have certified the processability, mechanical and thermal properties of PSN are equal or superior to those of PS.

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PHOTODEGRADABLE ELASTOMERIC TAPES FOR GRAFT PROTECTION

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Grafting or graftage is a horticultural technique whereby tissues from one plant are inserted into those of another so that the two sets of vascular tissues may join together. This vascular joining is called inosculation. The technique is most commonly used in asexual propagation of commercially grown plants for the horticultural and agricultural trades. In most cases, one plant is selected for its roots and this is called the stock or rootstock. The other plant is selected for its stems, leaves, flowers, or fruits and is called the scion or cion. The scion contains the desired genes to be duplicated in future production by the stock/scion plant. For successful grafting to take place, the vascular cambium tissues of the stock and scion plants must be placed in contact with each other protected to desiccation. Both tissues must be kept alive until the graft has 'taken', usually a period of a few weeks. Successful grafting only requires that a vascular connection take place between the grafted tissues.

Usually raffia yarn or fabric strips has been used to bind the rootstock and scion at the graft and wax or tar paint to protect the cut end of the scion from desiccation.

Tapes made of a new elastomeric compound with controlled photodegradability based on styrene-isoprene tri-block copolymer (SIS) and poly(vinyl-phenyl ketone) (PPVK) as prodegradant may be used to bind and protect the grafts. Variation of PPVK amount leads to different photolysis times allowing the control over the lifetime of the protective tape.

This work reports the photodegradation results of different compounds with different amount of PPVK (1 to 10%) in two SIS rubbers with 20 and 30% styrene content after exposure to UV radiation in atmospheric conditions between June and September 2012.

A particular attention is given to the influence of the poly(isoprene) content on the kinetic aspects and the distribution of the oxidation photoproducts within the polymeric sample. The studies are also focused on the analysis of the non-volatile products produced during the UV photodegradation. The presence of hydroperoxides, alcohols, ketones, aldehydes and carboxylic acids was detected by IR spectroscopy.

The as composites materials were characterized by thermal analysis ATG, DSC and mechanical analysis (DMA, hardness, strength) which confirm results obtained by FT-IR.

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WEATHERABILITY OF ENHANCED PHOTODEGRADABLE POLYSTYRENE

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Polystyrene (PS) is one of the most common materials in daily life. Examples of products made from PS include packaging foam and insulation, plastic cups, and housing such as computers and kitchen appliance. The disposal of PS, however, has been recognized as a worldwide environmental problem because PS and its related plastic products are non-biodegradable in natural environment. As a result, many research attempts have been made over the past years in order to enhance the degradation of this polymeric material.

Photodegradable packaging concept refers to their ability to decompose and disappear completely after depreciation and phase shift in waste in conditions of exposure to sunlight.

In the process of synthesis are used comonomers with the prodegrading effects, such as vinyl ketones to induce photodegradation followed by a photo-oxidative degradation without decrease processability and initial thermal and mechanical properties of PS.

Two aspects have been investigated. First, the initiation of the photodegradation followed very quickly by the photo-oxidative degradation of the copolymers which finally leads to the spontaneous coloration and fragmentation of the specimens. This aspect involves the identification and the quantitative determination of the functional C=O and –OH groups formed as a function of the exposure time. The second aspect involves measurements to appreciate the decrease of thermal and mechanical properties of the samples at different times of naturally UV radiation exposure: 0, 10, 20, 30 and 60 days.

The results obtained by FT-IR, TGA, DSC, DMA, molecular weight and tensile strength at break showed that an amount of 2% methylvinylketone (MVK) in styrene copolymers does not affect the initial thermal and mechanical properties compared with general purpose PS but it is enough to induce a satisfactory photodegradability. During natural photo-oxidative degradation of PS-MVK copolymers, after determination of the degree of photodegradation and the tensile strengths of the samples subjected to UV radiation were observed the mechanical properties decrease sharply in the first 10-30 days of exposure, when almost half of the macromolecular chains had an average of one scission. After that, by the end of the test time (60 days) decreasing of the properties is not so obvious.

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FORMATION OF PVP-INTERCALATED POLYPHENOL ANTIOXIDANTS

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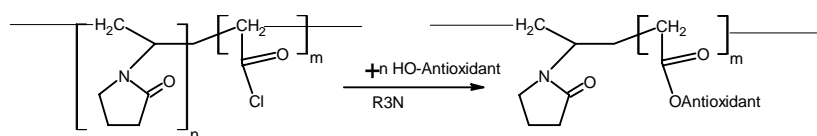
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Natural polyphenol antioxidants such as quercetin, resveratrol and others are designed to capture free radicals such as hydroxyl, peroxy and superoxide anions that are known to initiate oxidation at the cellular level in living cells. The exposure of the human skin to UV radiation induces profound biological changes and is considered to be the major cause of skin cancer and premature aging.¹

The use of antioxidants in various cosmetic and medicinal products can protect cells from inducing tumors.^{2,3} Due to the fact that quercetin is very poorly soluble in water, the development of new polymer intercalated quercetin have been studied.

In order to enhance solubility and bioavailability of the quercetin, grafting of antioxidant with vinylpyrrolidone copolymers of N-(N-VP) and methacryloyl chloride (Cl-Ac) by covalent chemical bonds, has been attempted. The copolymers N-VP: Cl-Ac were obtained by the method of free radical polymerization at $T \sim 70^\circ \text{C}$. The methacryloyl content in the copolymer have been varied from 5 to 20%. Furthermore, traces of Cl-Ac and copolymer's initiators have been removed by sedimentation. The viscosity characteristic is about 0.05-0.1 Mr / g and is dimethyl formamide, ethyl alcohol soluble. The grafting of the polymers was performed in dimethylformamide under the following reaction scheme:



Chemical structure of the graft copolymers with polyphenols were confirmed by IR and the UV-VIS spectroscopy. The antioxidant activities were determined by the ABTS radical method and DPPH test.³ The preventive research results have shown that the intercalation of quercetin in copolymer have not affected the antioxidant activity of pure quercetin.

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THE STUDY OF DNA-LINKED ANTHOCYANIN CHROMOPHORES
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The anthocyanin pigments present in the grape skin extract and aronian fruits, posses various pharmacological properties and have proven medical benefits as potential agents for the chemoprevention and therapy of cancer.

Anthocyanins are the most commonly dyes used for coloring of beverages, fruit preparations, confectionery and ice creams. Nevertheless these polyphenols has gathered attention on the possible health benefits of the anthocyanins in recent years.¹ In this research it has been studied the formation of some supramolecular structures like DNA-linked anthocyanin chromophores, which posses optical properties and could be used as composites in biophotonic research.² The ethanol extraction process of anthocyanins has been achieved by variation of the mass of organic matter(m,g) and the volume of the solvent(V,mL). It has been established that the optimal extraction yield depends on the ratios(m:V) that are 1:5 for grape skin extract and 1:10 for aronian fruits extract.

Furthermore, the optimal temperatures for the maximum extraction yield of the anthocyanins have been studied by temperature variation as it follows: 50,60, and 70°C. For a concentration of extracted anthocyanins of 350 mg/L from aronian fruits, optimal 70°C temperature was found and up to 50°C for the concentration's content of anthocyanins extracted from grape skin 240 mg/L, respectively.

The DNA-linked anthocyanin chromophores have been studied by means of UV-Vis and IR spectroscopy in aqueous solutions. It was found that a new maximum wavelength absorbs light in the range of 380-420nm, that may be due to the formation of the DNA-anthocyanin material. DNA concentration in aqueous solution was 1%(m/m) and the mass of anthocyanin have been varied between 0.5-5%(m/m).

Acknowledgment: Financial support for this study was provided by Romania (ANCS) and Moldova(ASM) bilateral project Nr.11/RoA

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THE EFFECT OF GRAPHITE-SEBS COMPOUNDS ON POLYPROPYLENE PROPERTIES

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Polypropylene (PP) is an easy processable, relatively cheap thermoplastic material with versatile properties suitable for a wide range of industrial applications. Its mechanical properties can be easily tailored using fillers and other polymers. Elastomers such as neat or maleinized polystyrene-*b*-(ethylene-*r*-butylene)-*b*-polystyrene (SEBS/SEBS-MA) are the most adequate toughening agents for PP. They can improve the compatibility between different fillers and the polymeric matrix so that balanced stiffness - toughness properties in ternary hybrid materials can be obtained.

The modification of PP was achieved by a melt compounding technique. First, graphite was dispersed into the elastomers and then the compounds containing 5 % filler were added to polypropylene in melt state. Morphological changes and mechanical properties were emphasized by X-ray diffraction, AFM and tensile tests. XRD parameters (inter-planar distances, median crystallite dimensions, integrated half widths, crystallinity and the relative amount of β -form of PP - K parameter) were determined for neat PP and composites and correlated with mechanical properties and AFM results. PP/SEBS-MA/G showed an almost two times lower area under the peak characteristic to graphite as compared to PP/SEBS/G which suggests a better intercalation and compatibility between phases in the first case ^{1, 2}.

The incorporation of elastomers, SEBS and SEBS-MA, was very effective in converting brittle PP into ductile materials. PP/SEBS and PP/SEBS-MA withstand large strains and yielding before specimens rupture. The fracture occurs at a strain of eight times higher in PP/elastomer blends than in neat PP. Graphite induced a slightly stiffening effect in both PP/SEBS/G and PP/SEBS-MA/G composites compared to the blends without filler. ^{1, 2}.

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² Panaitescu, D.M., et al., Morphological investigation of PP/nanosilica composites containing SEBS. Polymer Testing, 2012. **31**(2): p. 355-365.

TESTING OF ANTIBACTERIAL AND ANTIBIOFILM NANOSTRUCTURED MATERIALS FOR STRATIFIED PROSTHETIC TUBULAR DEVICES

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The medical device industry has been challenged to produce polymeric biomaterials with antimicrobial surface properties that are easily processable and have long term efficacy without leachables. Most of the plastic medical devices used are the tubing, such as wells, drains, catheters. Intravascular and urinary catheters are commonly used in hospitals. Bacterial infections are becoming one of the most serious complications related to the use of indwelling medical devices [1]. Some organisms such as coagulase-negative staphylococci may metabolize certain components of plastic catheters in the absence of nutrients and can use them to support growth on the surface of biomaterials [2]. The medical devices based on materials with antibacterial properties and antibiofilm, constitute a viable alternative to increase biocompatibility and duration of use in contact with human body [3]. Polyvinyl chloride is one of the most common choices because it is a material which can assure biocompatibility and mechanical properties necessary for use in medical devices. It is intended to obtain plasticized PVC tubing with antimicrobial properties, by a durable, non-leachable antimicrobial treatment that help inhibit the growth of bacteria in order to prolong product life [4]. This study was conducted to obtain two types of polymeric formulations stratified materials that will be used to make medical devices. Antibacterial plastified PVC was processed by planar coextrusion technology together with LDPE, to obtain a stratified material. The specimens were tested in terms of physical and mechanical properties (tensile strength, elongation at break, hardness Shore, flexural modulus, content of reducing substances) and microbiology. Results showed that the experimental materials present improved mechanical, biocompatibility and antibacterial properties.

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LUMINESCENT MATERIAL USED FOR OPTOELECTRONIC APPLICATIONS

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The aim of the present study was to synthesize luminescent material on the basis of $2 \text{ ZnO} * 1,1 \text{ SiO}_2 * 0,065 \text{ MnO}$, solid-state and sol-gel methods followed by calcination at 1000°C . Obtained nanomaterial can be utilized in optoelectronic applications. The used precursors are: $\text{Zn}(\text{CH}_3\text{COO})_2 * 2\text{H}_2\text{O}$, $\text{MnSO}_4 * 4\text{H}_2\text{O}$, SiO , TEOS, EtOH, $\text{Zn}(\text{NO}_3)_2 * 4\text{H}_2\text{O}$, $\text{MnCl}_2 * 4\text{H}_2\text{O}$, HCl, H_2O .

It was investigated the luminescent property of crystalline material phases, morphology and chemical composition of the particles were characterized by different analytical methods: UV radiation, luminescent spectroscopy, SEM/EDAX, RXD.

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SYNTHESIS OF 4-[2,4,6-TRIMETHYLPHENYL]-THIOSEMICARBAZIDE AND ITS DERIVATIVES

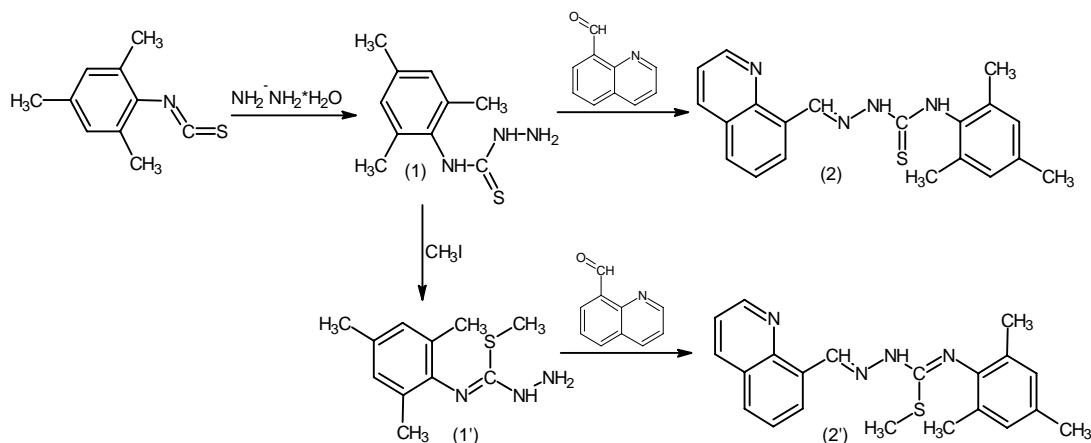
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The thiosemicarbazide derivatives posed valuable proprieties like: biological, analytical and electrochemical. This type of organic reagent can be used like a ligand in coordination chemistry with transition metals because they posed in structure nitrogen and sulfur donor atoms. Coordination compounds with this type of ligand have important biological properties: anticancer, antituberculosis and bacteriostatic etc.

In this abstract we show the synthesis of new thiosemicarbazide- 4-[2,4,6-trimethylphenyl]-thiosemicarbazide and its reaction with 8-formilquinoline.



As an initial reagents for synthesis of new thiosemicarbazide (1) was used 1,3,5-trimethylphenyl-2-isothiocyanate and hydrazine hydrate; after the product was condensed with 8-formilquinoline (2), or alkylation with CH₃I (1') and after condensed with 8-formilquinoline (2').

The structure was confirmed by ¹H RMN, ¹³C RMN and single X-ray crystallography methods.

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DETECTION OF PEROXYNITRITE WITH CHEMICALLY MODIFIED ELECTRODES BASED ON REDUCED GRAPHENE OXIDE

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Peroxynitrite (ONOO⁻) is a reactive nitrating and oxidative species that induces oxidative damage in proteins by several pathways¹. Nitration of tyrosine residues by peroxynitrite (ONOO⁻) with the formation of several species (e.g 3-nitrotyrosine) is considered an indicator of oxidative damage in proteins. On the other hand, peroxynitrite was shown to be efficiently scavenged by polyphenolic compounds in red wines². Our goal is to develop an electrochemical method for the detection of peroxynitrite, emphasize the effects of this radical on tyrosine and screen the antioxidant activity of several Romanian red wines based on their scavenging of peroxynitrite radical. To this end, we investigated as a first step the modification of glassy carbon electrodes with reduced graphene oxide, and hemin³. Adsorption of hemin on RGO/glassy carbon, electrochemical polymerisation of hemin and the direct detection on unmodified glassy carbon electrodes are compared as alternative strategies for the detection of tyrosine and peroxynitrite, using Cyclic Voltammetry, Differential Pulse Voltammetry and Square Wave Voltammetry.

Acknowledgements:

This work was supported by a grant of Romanian National Authority for Scientific Research, CNDI – UEFISCDI project numbers PN-II-PT-PCCA-2011-3.1-1809 (for AV) and PN-II 184/2011 (for ISH and SFP). I.S.H. thanks for funds via PN0909-2013 “Nucleu”

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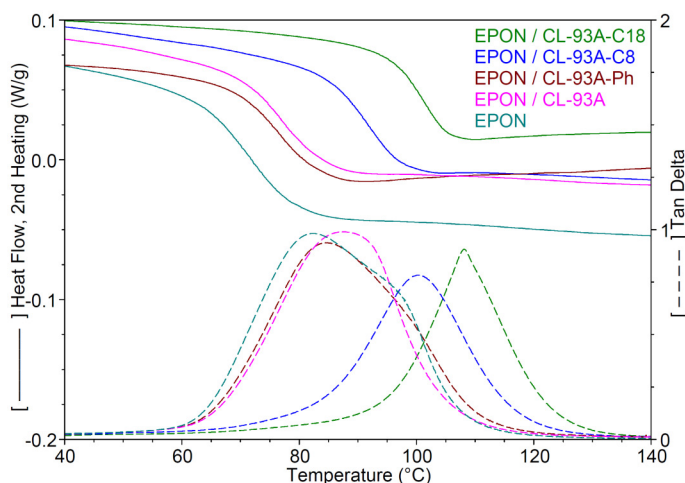
SYNTHESIS AND PROPERTIES OF EPOXY-ORGANOLAYERED SILICATES NANOCOMPOSITES

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Polymer layered-silicate nanocomposites have attracted worldwide attention because of the enhanced properties such as tensile and thermal properties, heat distortion temperature, resistance to flammability and reduced permeability to small molecules and solvent uptake. Property improvements are due the extremely large particle surface area available for interaction with the polymeric matrix coupled with a high aspect ratio. In this research, both commercially available and synthesized organolayered silicates were used to make epoxy nanocomposites. The epoxy resin used in this research includes Epon 862/curing agent tetra ethylene pentamine. The morphology of the composites was characterized using X-ray diffraction. FTIR spectra confirmed the silicates inclusion into the polymer matrix. Thermal behavior was evaluated by TGA and DSC. The cured samples have been characterized by DMA technique. Also, the determination of colour grades for the composites samples was followed. ESEM micrographs acquired from fracture surfaces of neat polymer samples and nanocomposites provided insight into the fracture mechanism.



DSC-DMA- Tg of EPON nanocomposites with different types of functionalized Cloisite

Mechanical Properties of polymers based on the 4- aminostirene

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The Study of Mechanical Properties of polymers allows establish the deformation regularities and gives the information which determines the of polymer reaction on external, heat and power impact in different physical states.

In this paper the results of polymer mechanical properties investigation were represented.

The microhardness (H) in this paper was used. Method in large interval of loads (P) and temperatures was applied

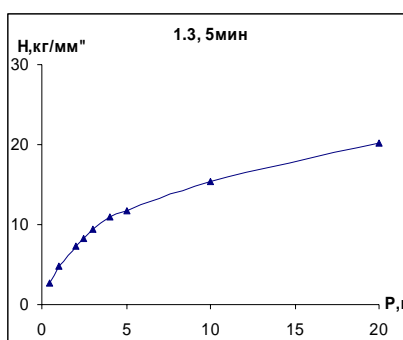


Fig. Dependence of microhardness on the load (deformation effort, P) on indenter.

As it is seen from figure the $H(P)$ represents the clear two-steps form. Microhardness is increased with increasing the load on indenter. However, velocity of microhardness change by deformation forces is determined. Analogous course of dependence is observed for layers of thickness in region near 10- 22 μm . The dependence $H(P)$ with time of indentation increase did practically not change: two-steps form of H change with P increase is saved. However, the step-like character of H change wherein occurs. Possible, such H behavior with creep modification of polymer materials is connected. Special investigations carried on such type polymers these assumptions are conformed.

Influence of temperature on H magnitude with a view of assess the glass transition temperature T_g (softening) for polymer was studied. Microhardness modifications in interval temperatures of 40 – 75°C were investigated. Temperature of vitrification (softening) T_g as temperature of interval middle was estimated and in our case for polymer №1 $T_g=57^\circ\text{C}$. Value of microhardness in interval temperature studied was varied from 7 to 12 kg/mm^2 .

The strength of polymers with structure loosening is connected. In structure of polymer the fluctuated microbubbles were formed which are open and close due to the thermal fluctuations. Hole state of polymer structure determines strength properties of polymer materials So, the microindentation process and material sealing are possible connected with the free volume concept.

Jitaru Raisa , report stand,

GLYCOLS DERIVATES EMULSIFIERS FOR EPOXY SYSTEMS

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One of the main areas of application of the epoxy consists of surface coatings. Due to the relatively high viscosity of epoxy systems their dilution with solvents is required. Environmental Protection Agency (EPA) limits the degree of VOC (volatile organic compounds) pollution by limiting the amount of the solvent which used in the production and application of paints ^[1]. The replacement of organic solvents with water may represent a way of reducing the environmental pollution. One of the key elements in getting water dispersible epoxy systems is the surfactant which allows to emulsify the resin ^[2]. In this work we intend to obtain a glycol-based epoxy surfactants. In laboratory it was successful to emulsify epoxy resins based on diglycidyl ether of bisphenol A (DGEBA) with the product resulting from the reaction of an epoxy resin with a low molecular weight modified polyglycols. For this reason, a tetraethylene glycol was used as a polyol component. The conversion's degree of the polyaddition reaction between epoxide resin and tetraethylene glycol was determined by FT -IR spectroscopic method ^[3] and by quantitative chemical analysis. By using the synthesized emulsifier there were obtained water stable epoxy resin emulsions. Crosslinking was performed using as hardener aliphatic polyamines (triethylenetetramine - TETA). To study the reaction of epoxy resin with hardener by Differential Scanning Calorimetry (DSC) method was used to determine the time evolution of exotherm process by curing water dispersible epoxy systems. Use of water- emulsifiable epoxy system can be considered as a solution of getting systems corrosion protection and waterproof concrete or metal surfaces exposed to harsh environments. This will eliminate the release of harmful organic solvents of the environment and health.

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CARBON MONOXIDE REMOVAL FROM HYDROGEN FUEL CELL USING HETEROGENEOUS CATALYST

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Proton exchange membrane fuel cells (PEMFC) are a type of fuel cell being developed for transport applications as well as for stationary fuel cell applications and portable fuel cell applications. Their distinguishing features include lower temperature/pressure ranges (50 to 100°C) and a special polymer electrolyte membrane.

Although the PEM cell is completely CO₂ tolerant, the anode is highly susceptible to CO poisoning with consequent voltage losses. Thus, the total concentration of CO in the gas stream should be reduced to below 10 ppm in order to obtain optimum performance.

There still exists a need to develop stable cost-effective catalysts for the PROX reaction with high activity, selectivity, and tolerance to CO and H₂O. Mixed copper manganese oxide catalysts have been extensively used to remove CO due to their low cost. In this work we are proposing to use the named catalysts for CO removal for the fuel cell application. The effect of the preparation conditions of hopcalite (copper manganese oxide) catalyst is investigated for the retention of carbon monoxide at ambient temperature.

In the present study the hopcalite is prepared by a novel redox and precipitation method. The catalysts were characterized by means of BET, SEM, EDX, and X-ray powder diffraction.

The catalytic activity was found to be compared favorably with a commercial Hopcalite catalyst. The results making them potentially useful in the removal of CO for low and medium temperature PEM fuel cells.

Mapping of the nitro-oxidative species (NOS) by microbiosensor-based scanning electrochemical microscopy (μ BS-SECM)

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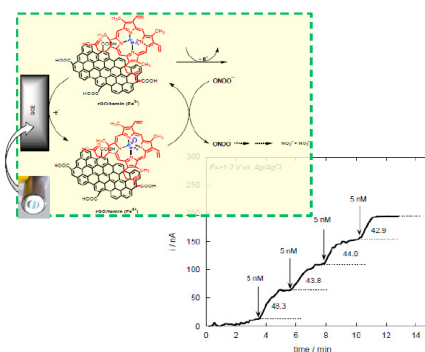
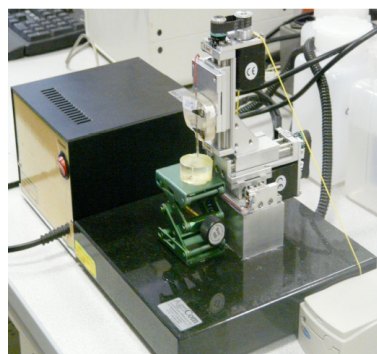
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ABSTRACT

The detection of chemicals released by living systems such as NOS is crucial to clarify signal transduction pathways and advance *in vivo* toxicology assays. However, these opportunities come with real challenges for chemists and engineers alike. Lately, the SECM methods have drawn intensive attraction, due to their simplicity and sensitivity¹. Herein we describe an advanced system for NOS mapping by μ BS-SECM, using optimized μ BS² multibarrel format to detect several nitro-oxidative species (NOS) integrated to a recently developed SECM with optimized methods for sensitive measuring performance. This will allow NOS investigation in model matrices by μ BS-SECM enhanced by optical-electrochemical imaging.



SECM system built with Domini Line 30 linear modules, 78 nm theoretic resolution, 2 cm travelling distance (*figure, left*). Synthetic graphene-metallo macrocycle film sensitive to ONOO^- and its detection calibration curve (*right*).

Authors acknowledge project funding, as follows: to I.S.H. *via* PN

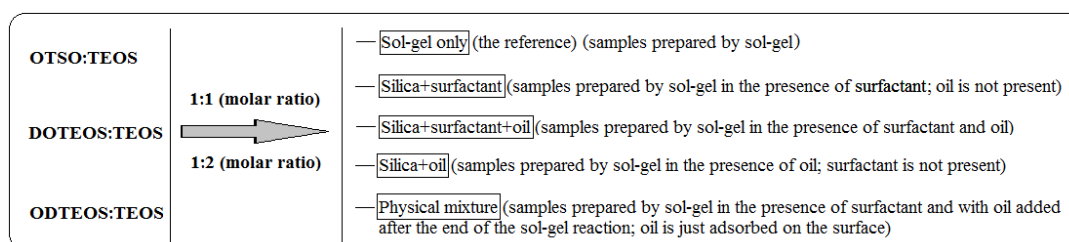
0909 2013 “Nucleu”; to G.N., L.N., A.K. from Romania-Hungary Bilateral Science Technology TÉT_12_RO-1-2013-0018 “Mapping of Nitro-Oxidative Species by Scanning Electrochemical Microscopy with Micro-(bio)sensors” and New Széchenyi Plan SROP-4.2.2.A-11/1/KONV-2012-0065 “Synthesis of supramolecular systems, examination of their physicochemical properties and their utilization for separation and sensor chemistry” and to S.F.P. from same Bilateral 2013-0018 and PNII 184/2011 by MEN-CDI (formerly ANCS) *via* UEFISCDI. Also, R. Oprea and A.M. Popescu are credited with initial help.

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CHARACTERIZATION OF THE MESOPOROUS LONG-CHAIN-MODIFIED SILICA PARTICLES DOPED WITH OLIVE OIL
NISTOR Cristina Lavinia, SOMOGHI Raluca, PURCAR Violeta, IANCHIS Raluca, PETCU Cristian, SPATARU Catalin-Ilie, GHIUREA Marius, DONESCU Dan
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Precursors of trialkoxysilanes and tetraalkoxysilanes are usually used for the preparation of hybrid materials, where one organofunctionalized trialkoxysilanes (as the organic functional groups providers) are mixed with tetraalkoxysilanes, (e.g. tetramethoxysilane, TMOS or tetraethoxysilane, TEOS). However, to our best knowledge, the literature about synthesis of mesoporous silica hybrids from co-hydrolysis of long-chains (C12-C18) alkyltrialkoxysilanes with TEOS is mainly focused on acid catalyzed sol-gel technique (preparation of hybrid films) or for surface chemical modification. Thus, so far there are just few reports regarding preparation of long-chain modified silica by based catalyzed sol-gel process (by a hydrolytic alkaline route). Here we report synthesis of novel mesoporous silica, stable in aqueous medium, starting from TEOS, as the main silica source and from 3 different co-precursors: octyltriethoxy silane (OTSO), dodecyltriethoxy silane (DOTEOS) or octadecyltriethoxy silane (ODTEOS), at two co-precursor/TEOS molar ratio: 1:1 and 1:2. Assessing the influence of co-precursor's nature (OTSO, DOTEOS or ODTEOS) and ratio (Co-precursor/TEOS = 1:1 or 1:2) on the physico-chemical properties of the resulted particles is the main go of this work.



The pristine or oil-doped ODTEOS/TEOS silica particles were characterized by N₂ adsorption-desorption (porosimetry), dynamic light scattering (DLS), and scanning electron microscopy (SEM). The results showed that the particles average diameter depends strongly of the molar ratios of silica precursors and of surfactant or oil presence in the reaction system. Variation of the silica co-precursor type and the presence of the surfactant in the sol-gel system also induced morphology transformation. The presence of oil in the sol-gel reaction mixture had a visible effect on the inner structure of the mesoporous silica: mean pore diameter is higher and pore size distribution is broader with the increase of the length of co-precursor's hydrophobic chains.

BIO-FUNCTIONAL FABRICS FOR COMPLEX APPLICATIONS

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The paper presents an advanced stage of researches conducted to establish a general procedure of achieving of woven fabric made by 100% cotton bio-functionalized, a bioactive barrier / physical type with antiallergy/sedative properties and antimicrobial due to intrinsic antimicrobial properties of selected polymeric materials having view this criterion.

Allergens and microorganisms are present in our daily lives without we notice this. They come in direct contact with human skin, the inside of the body by ingestion, with upper airways by breathing air with pathogens or through textiles that people uses 24 hours from 24 hours.

Clothing fabrics, linens, inner textile decorations and other items in the household, or institutions such as hospitals, kindergardens and schools or military field, bio-actively treated will have new properties antiallergy/antimicrobial and will lead to increased quality of life for allergic people/people with allergy potential by reduce itching and the amount of specific drugs among which cortisol is the most toxic.

Researches have continued in the direction of establishing an experimental model of obtaining a cellulosic fabric with active antiallergy/sedative effect followed closely by specialists in the field in the purpose which may result in a couple of variants of the procedure of bioactive functionalization of that fabric and can choose the right property /quality tracked by them, in the desired end use for fabric (body clothing, bedding, etc.), lower cost price, necessary equipment, testing options, etc.

This was possible by using of some products, methods / techniques for obtaining bio-finishing reagents, their application and testing / characterization of results obtained in an original way:

➤ Treatments were made with natural extracts containing bioactive compounds with synergistic anti-allergy/sedative/antimicrobial action by immobilization/binding on cellulosic substrate using polymer / polymer precursors, to obtain bioactive composite films after drying phases / crosslinking by gentle curing with protection protection of bio-layer.

➤ Were carried out physical, mechanical and chemical characterization of properties for the new fabrics treated with anti-allergic properties, coated with polymer biocomposites: skin characterization of humans, determining penetration, and cytotoxic action of bioactive compounds by in vivo studies on rats and mice; characterize the mechanism of initiation, development and release of mediators in allergic episode and physical characterization, chemical and colouring effects on textile surfaces.

➤ It was established a model for achieving functional bioactive surfaces functionalized textiles.

➤ It has started contacts with industry (SMEs) in the field of textile production and chemical processing of cellulose fibers and textile suprefete mixture.

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MORPHOLOGICAL INVESTIGATION OF POLYAMIDE – CELLULOSE NANOCOMPOSITES

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Polyamides show many superior properties such as high melting temperature and good toughness. Polyamide 11 is a semicrystalline polymer which exhibits several crystalline forms, the α and α' forms showing a triclinic structure and δ , δ' or γ a pseudohexagonal one. Different nanofillers such as multiwalled carbon nanotubes and montmorillonite were used in polyamide 11 with the aim to enlarge its application field.¹⁻³

Cellulose nanofibers were used as reinforcement in polyamide 11 and their influence on the morpho-structural characteristics of polyamide matrix was investigated in this paper. X-ray diffraction (XRD), atomic force microscopy (AFM) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) were used for this purpose.

XRD investigation revealed the peaks characteristic to the α' polymorphic form in both neat polyamide 11 and nanocomposites. ATR-FTIR results confirmed the presence of the α' form as majority phase in polyamide 11 and nanocomposites but also the presence of the γ phase in very small amount. AFM investigation emphasized the improvement in nanomechanical characteristics in polyamide nanocomposites as compared to neat polyamide and the dispersion of cellulose nanofibers in the matrix.

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THE USE OF BACTERIAL CELLULOSE-POLY (ETHYLENE GLYCOL) COMPOSITES IN DRUG DELIVERY APPLICATIONS

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Bacterial cellulose (BC) is a suitable material for drug delivery applications due to its remarkable properties, such as: biodegradability, biocompatibility and ready availability.

The aim of this study was to investigate the potential of Bacterial cellulose-Poly (ethylene glycol) composites (BC-PEG) for drug delivery. In this purpose, BC-PEG hydrogels with various polymer concentrations were prepared by impregnation method. Swelling behavior and drug release studies of these hydrogels were performed. Also, the absorption mechanism and the release mechanism were evaluated.

The composites obtained were stable with improved swelling and release rates. It was found that polymer composition influences swelling and drug release, best results were obtained at low poly (ethylene glycol) concentration.

The results obtained suggest that BC-PEG composites can be used in biomedical fields, especially for application in drug delivery.

DEPENDENCE OF THE MELT PROPERTIES OF SOME NEW MULTIFUNCTIONAL BIO-MATERIALS ON COMPOSITION AND MELT PROCESSING CONDITIONS

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In order to achieve new multifunctional bio-materials moldable by some melt processing techniques into products with short – life, the main parameters which control the bio-hybrids granulation were studied. The dependence of the melt rheological properties on the composition and melt processing conditions were also studied. Melts degradability was revealed by MFI, dynamic viscosity, flow ratio, material colour and extrudates appearance. It is obvious that the MFI increasing and the dynamic viscosity decreasing, can be associated either with melt fluidity decreasing or with the blend degradation through macromolecule crosslinking. The blend degradation in the melt state was also highlighted by the color of resulted granules, which varies mainly from natural to yellow, beige or brown shades. By controlling the material formulation and the melt processing conditions new starch blends as granules in natural color that were well processed into finished products were obtained (Fig.1, 2).

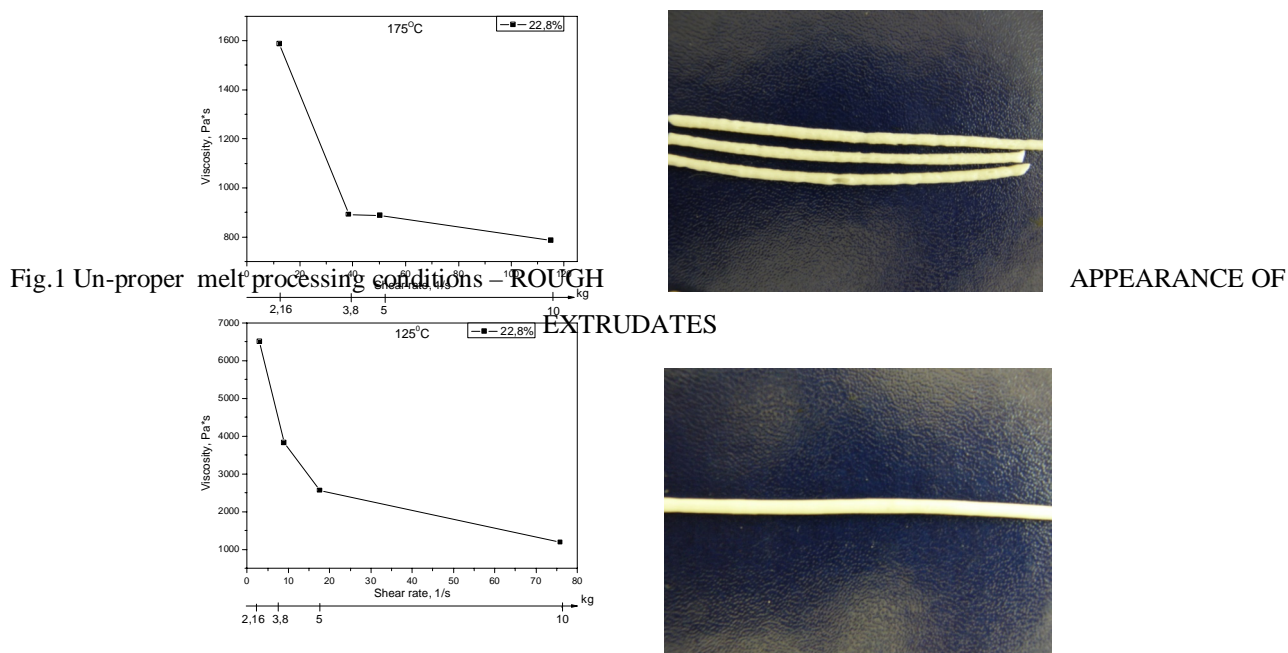


Fig.2 Proper melt processing conditions – SMOOTH APPEARANCE OF EXTRUDATES
This work was supported by the grant of the CNDI-UEFISCDI number 59/2012.

INFLUENCE OF THE MIGRATION DEGREE OF THE LIQUID COMPONENTS INTO POLYMERIC MATRIX ON THE PERFORMANCE OF NEW MULTIFUNCTIONAL BIO - MATERIALS

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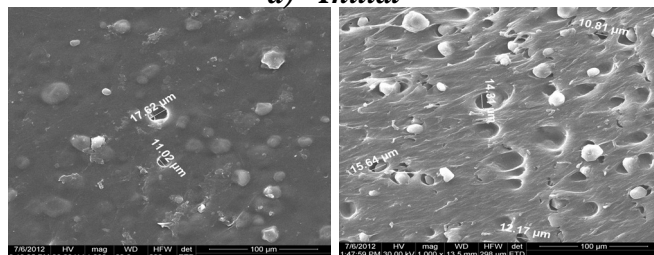
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The field of multicomponent polymer materials includes all cases where polymers are either mixed with other polymers or with nonpolymeric solid materials¹. The degree of miscibility at molecular level is a parameter which controls the properties of resulted materials and its behavior during the service life. The design of new materials means not only choosing the components considering their thermodynamic compatibility but also choosing those working procedure which ensure a uniform distribution of all components into the polymeric matrix. Into the researches to achieve new multifunctional bio-materials by multi-components type was observed that the material performances are controlled by the migration degree of the liquid components into the polymeric matrix. It was found a working procedure which enhances the performances of new materials based on starch melt processable by thermoforming.

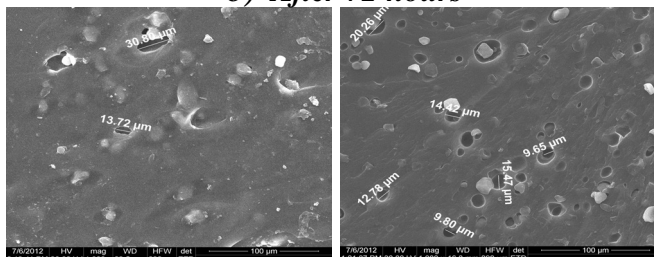
Surface

Fracture

a) Initial



b) After 72 hours



Acknowledgement. This work was supported by the grant of the CNDI-UEFISCDI number 59/2012.

¹ L.H.Sperling, *Polymeric Multicomponent Materials*, Wiley – Interscience publication, JOHN WILEY & SONS Inc. ISBN 0 – 471 – 04138 - 6

INFLUENCE OF FILLER PARTICLE SIZE ON MECHANICAL BEHAVIOR OF SOME NEW MULTIFUNCTIONAL BIO – MATERIALS

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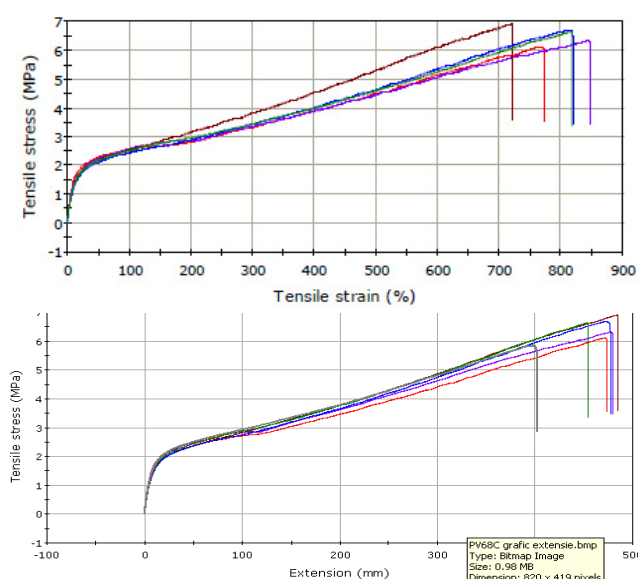
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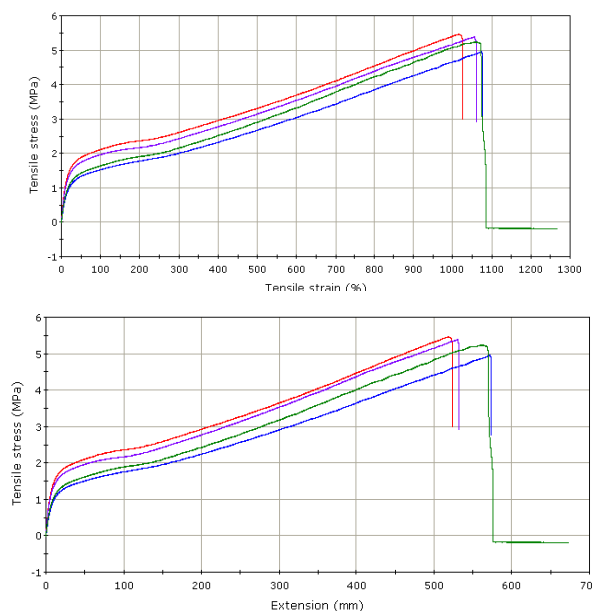
⁴*SC METAV Research and Development, C.A. Rosetti, Bucharest, Romania*

The fillers influences the application properties of multifunctional bio-materials by multicomponents type by many parameters such as: surfaces, chemical compositions, physical properties, morphology, acidity or alkalinity, ash content, distribution and orientation in polymeric materials, interaction with matrix, interphase organization, interfacial adhesion, interphase thickness. Among physical properties particle shape, size and distribution have an important impact on mechanical, rheological properties and on the characteristic of the degradative processes¹. Tensile strength testing is by far the most popular method of evaluation of filled materials. In researches to achieve new multifunctional bio-materials by multicomponent type it was observed that the tensile properties can be better controlled by using nanometric filler instead of micrometric those. The material ability to be thermoformed was improved in this way.

Micrometric filler



Nanometric filler



Acknowledgement. This work was supported by the grant of the CNDI-UEFISCDI number 59/2012

¹ George Wypych, Handbook of Fillers, Plastic Design Library, Chem Tec Publishing, ISBN 1-895198-19-4 Toronto – New York 2002,

MATHEMATICAL MODELING OF TRANSPORT PROPERTIES OF SOME IONOTROPIC ALGINATE HYDROGELS OBTAINED BY CONTROL DIFFUSION METHOD

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The hydrogel swelling was describe by the time variation of percentage swelling (or mass swelling) by using equation (1) in which: S is swelling ratio (percentage swelling), M swelled hydrogel weight (g), t -time (min), M_0 is dried hydrogel weight (g), at $t = 0$. Diffusion mechanism of solvent into polymeric networks was describe based on equation (2)^{1,2,3}, and the diffusion kinetics was described based on equation (3) and (4)⁴ in which: S = swelling ratio, at time t , M_{ec} = swelled

hydrogel weight, at equilibrium K_s = rate diffusion constant, $B = \frac{1}{S_{ec}}$

(reverse of swelling ratio at balance). The $A = \frac{1}{K_s \cdot S_{ec}^2} = \frac{1}{\left[\frac{dS}{dt}\right]_0}$ diffusion coefficients were determined by the short time approximation method^{5,6,7} depicted by equation (5) in which: M_t și M_{ec} represent, t = time, r = hydrogel average radius, D = diffusion coefficient

$$S, \% = \frac{M - M_0}{M_0} \quad (1) \quad S = \frac{M - M_0}{M_0} = Kt^n \quad (2)$$

$$\frac{dM}{dt} = K_s (M_{ec} - M)^2 \quad (3) \quad \text{or after integration} \quad \frac{t}{S} = A + Bt \quad (4)$$

$$Q = \frac{M_t}{M_{ec}} = 4 \left[\frac{Dt}{\pi r^2} \right]^{1/2} - \pi \left[\frac{Dt}{\pi r^2} \right] - \frac{\pi}{3} \left[\frac{Dt}{\pi r^2} \right]^{3/2} \quad (5)$$

The graph $Q = \frac{M_t}{M_{ec}} = 4 \left[\frac{Dt}{\pi r^2} \right]^{1/2}$ was linearized by plotting in coordinates Q , $t^{1/2}$. The slope of the resulted straight line has the expression: and $p = 4 \left[\frac{D}{\pi r^2} \right]^{1/2}$ the diffusion coefficient is $D = \pi \left[\frac{p \cdot r}{4} \right]^2$.

The used method have provided comparative quantitative dates for characterization and selection of the alginate hydrogels achieved in different reaction conditions. These dates were the basis for explaining the biological properties of new hydrogels designed for adipose tissue regeneration.

Acknowledgement. These researches were supported by UEFISCDI Romania by Complex Exploratory Research Project no.PCCE 248/2010

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³ N.A. Peppas and N.M. Franson, *J. Polym. Sci.: Polym. Phys. Ed.*, 21,983 (1983).

⁴ Yin Y et al, Swelling behavior of hydrogels for colon-site drug delivery, *JAppl Polym Sci*, 83, 2835-2842, 2002

⁵ E. Karada_g D. Sarayd_n and O. G'üven, *Turk. J Chem.*, 21,151 (1997).

⁶ D. Sarayd_n, H.N. et al, *Appl. Biochem. Biotechnol.*, 82, 115 (1999).

⁷ M.T. Ende and N.A. Peppas, *J. Contr. Rel.*, 48, 47 (1997).

A FTIR STUDY FOR POLYMERS IDENTIFICATION FROM INCOMPATIBLE BLENDS MELTED PROCESSED AS FILMS

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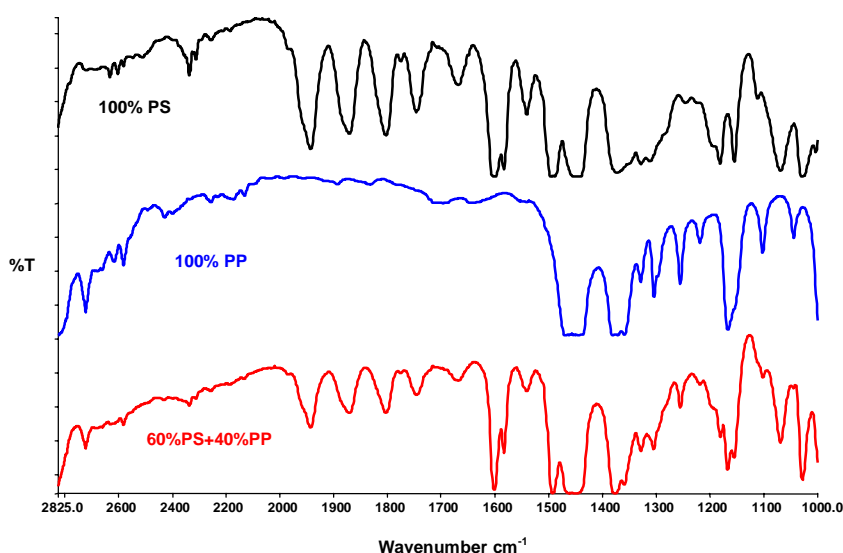
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The paper aim is to study the possibility to identify by FTIR method - transmission technique – polystyrene(PS) from incompatible blends with polypropylene(PP).

For this purpose, films of binary blends with have following composition have been achieved by melt processing techniques: (0 -100) % PS and (100 - 0) % PP. Each spectrum of every films were analysed considering the following criteria: the existence of false positive peaks, the accuracy and repeatability of wave numbers, the repeatability of transmittance absorption bands^{1,2,3}.

The obtained results have shown that there are no false positive bands and the criterium of the wave number accuracy criterion is fulfilled for all films with PS concentration higher than 5%. The criteria of repeatability of wave number repeatability and those of repeatability of transmittance are achieved for all compositions. Another observation from performed studies was that the detection limit is conditioned by the minimum concentration of 5% polystyrene for which all the vibration bands are presented in the spectrum.

Therefore, FTIR method can be used to identify PS form blends with PP for all composition with PS content higher than 5 %.



¹ A.Lee Smith – Applied infrared spectroscopy. Fundamentals, Techniques and Analytical Problem-Solving, John Wiley&Sons, SUA, 1979

² Japanese Industrial Standards JIS K0117: 2000

³ The Sixteenth Edition of Japanese Pharmacopoeia, from 2011, reviewed in 2013, pp. 53-54.

SULFONATED POLYPHENYLENE OXIDE - POLYMER ELECTROLYTE MEMBRANE FOR PROTON EXCHANGE MEMBRANE FUEL CELL

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Proton exchange membranes (PEM) represents one of the main components of the PEM Fuel Cells playing the role of electrolytic bridge for proton transport from the anode to the cathode. The proton transfer occurs through ionic channels developed by hydrating the sulfonic acid groups.

Commercial poly(2,6-dimethyl-1,4-phenylene oxide) was modified by attaching the sulfonic groups to the phenylene moiety and used to obtain the proton exchange membranes by recasting from solution of the 4-6wt-% sulfonated polymer in dimethylformamide (DMF). Physical and chemical characterization of sulfonate polymer was made by Fourier Transform Infrared Spectroscopy (FTIR), titration and thermogravimetric analysis (TGA).

The infrared spectra of sulfonate compound show specific absorption peaks at 675 and 1064 cm^{-1} . Ion exchange capacity (IEC) and sulfonation degree (SD) measured by titration have values between 1-1.5 meq/g for IEC and sulfonation degree below 23%. The thermal degradation behaviour was analyzed by thermogravimetry.

The membrane was studied by Scanning Electron Microscopy in the dry and hydrated state. The SEM images show a homogeneous structure of the dry film and a tendency to develop some channels on the film surface in the hydrated membrane.

The membrane based on sulfonate poly(2,6-dimethyl-1,4 phenylene oxide) provide an appropriate environment for proton transfer.

PREPARATION OF POLYMER-SILICA HYBRID LATEXES AND SOL-GEL-DERIVED FILMS

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Cristian Nicolae Andi, Dan Donescu, Cristian Petcu, Somoghi Raluca,
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Polymer/silica hybrid materials obtained through *in situ* emulsion polymerization and sol-gel process, using organic monomers and inorganic precursors, have been received attention in recent years because they are environmentally friendly, have good mechanical properties^{1,2}, and present promising applications in coatings, adhesives, electronics, catalysis³, etc. In the present work, we prepared polymer-silica hybrid latexes by emulsion polymerization of styrene (St), butyl acrylate (BuA) and 2-hydroxyethyl methacrylate (HEMA), followed by hydrolysis and polycondensation of different inorganic precursors (tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), isobutyltriethoxysilane (IBTES), diethoxydimethylsilane (DEDMS), vinyltriethoxysilane (VTES)). The obtained latexes, both as materials placed into plastic vials as well as films deposited onto clean glass slides (dried at room temperature), were characterized by various techniques including: Fourier Transform Infrared spectroscopy (FT-IR), UV-Vis spectroscopy, thermal gravimetric analysis (TGA) and contact angles (CA). CA analysis showed that the hybrid latex film with HIB4+TEOS/VTES has high hydrophobic properties. Analysing the FT-IR spectra of all hybrid latexes, a strong absorption band of Si-O-Si groups in the spectral region between 1250-1000 cm^{-1} (asymmetric stretching vibration) was observed, which confirms the silica network. The surface reflectivity of the latex films was changed as function of the organic group from the inorganic precursor used in the synthesis. The thermal stability of hybrid latexes is improved owing to the introduction of inorganic precursors.

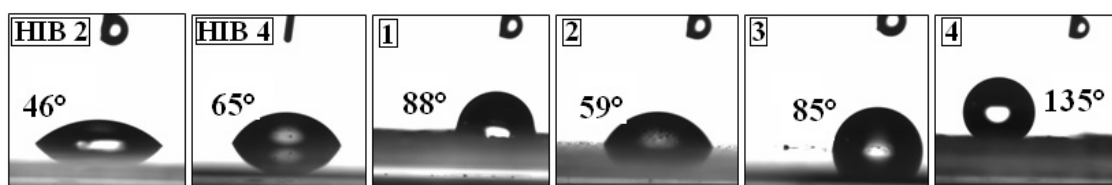


Fig. 1 – Profiles of water droplets on latex films synthesized with: St-BuA-HEMA (HIB2); St-BuA-HEMA-VTES (HIB4); HIB4+TEOS/MTES (1); HIB4+TEOS/IBTES (2); HIB4+TEOS/DEDMS (3); HIB4+TEOS/VTES (4)

¹ B. You, N. Wen, Y. Cao, S. Zhou, L. Wu, Polym. Int. 58, (2009), 519-529.

² W. Liao, H. Teng, J. Qu, T. Masuda, Prog. Org. Coat. 71, (2011), 376–383.

³ C. Sanchez, K.J. Shea, S. Kitagawa, Chem. Soc. Rev. 40, (2011), 471–472.

PROPERTIES OF SOME MULTIFUNCTIONAL BIOMATERIALS DERIVED FROM MICROBIAL BIOTECHNOLOGY

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Several species of fungi produce citrinin, a mycotoxin harmful to the hepatic and renal systems [1-5]. For this reason, the study for safety is necessary to evaluate the toxicological effect of fungal bioproducts obtained from solid state or submerged biosynthesis. So, in our study we evaluate the content of mycotoxin in some fungal products and the cytotoxicity effect of them. The study regarding citrinin content revealed a content of product obtained by solid state biosynthesis a maxim content of 145 mg/kg. In the case in which the biomaterials are obtained in submerged media, in the intracellular materials the citrinin concentration was 82.71mg/kg (or 0.827 mg citrinin/kg wet biomass). In the case of extracellular product obtained in submerged media, the mycotoxin content fluctuate in the range (7÷24.5) mg/kg. Study performed “in vitro” with product obtained in submerged media on fibroblast murine cell lines, reveals a cytotoxicity effect at the concentration more than 60 µg/mL.

Key words: fungal metabolites, fibroblast murine cell, cytotoxicity.

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STUDY ON THE POLYMER MEMBRANES FUNCTIONALIZATION PARAMETERS

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The aim of the present study was to investigate the ability of controlling the conversion (functionalization degree-FD) value of a polymer membrane in its reaction with glutardialdehyde (GA). A functionalized membrane was obtained, being intended to be further used for enzymatic composites useful in catalytic separations. The polymer membrane was prepared using a mixture of an acrylonitrile-vinyl acetate copolymer (AN-AV, with a ratio of AN/ AV in the monomer mixture of 2.35) with polyvinyl alcohol (PVA). According to literature, polyacrylonitrile-based membranes are often used as supports for enzyme immobilization ^[1]. The PVA was introduced in order to allow the membrane functionalization with glutardialdehyde. There are five parameters of the functionalization reaction: the amount of membrane, the GA volume, the catalyst volume, the time and the temperature of the reaction. To check the effect of each parameter, there were prepared various samples of functionalized membrane.

Pure membrane and samples of functionalized membranes were characterized in terms of their chemical composition (FD) by a chemical method and checked qualitatively by modern methods (FTIR). The determined FD values prove that it is possible to control the functionalization conversion, since FD can be increased by increasing the amount either of membrane or of GA. FTIR spectra of functionalized membrane are not significantly influenced by the FD values, confirming only that there occur changes in the chemical composition as a consequence of functionalization. The obtained functionalized membrane samples are able to covalently immobilize enzymes.

STUDIES ON APPROPRIATE ACRYLONITRILE-METHACRYLIC ACID MATRIX FOR MOLECULAR IMPRINTING OF HYPERICIN

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Introduction: Molecularly Imprinted Polymers (MIPs) are extremely selective materials due to their molecular recognition ability towards the template molecules, even in complex mixtures. MIPs are able to mimic natural recognition entities, such as antibodies and biological receptors, because the voids created in the polymer matrix are complementary to the target molecule in size, shape, and functional groups¹.

Methods: Four copolymer matrices were tested for the imprinting of hypericin, a natural compound with pharmacological activities. Acrylonitrile-methacrylic acid copolymers (AN-MAA) with different content of MAA: 10, 15, 20 and 25% (wt%) were synthesized. The obtained copolymers were dissolved in dimethylsulfoxide, followed by hypericin adding. The pearls were obtained by dripping the copolymer solution with a syringe in a coagulation bath.

Results: The molecular imprinting with hypericin for all AN:MAA matrices was demonstrated using Gel Permeation Chromatography (GPC). The pearls were dissolved in dimethylformamide in order to obtain a 0.1% solution. The experimental results show that the copolymer matrices retain different quantities of hypericin, although they are imprinted with the same concentration (5%). The best matrix seems to be AN:MAA 85:15, and further studies will be carried out, in order to understand and explain the imprinting mechanism.

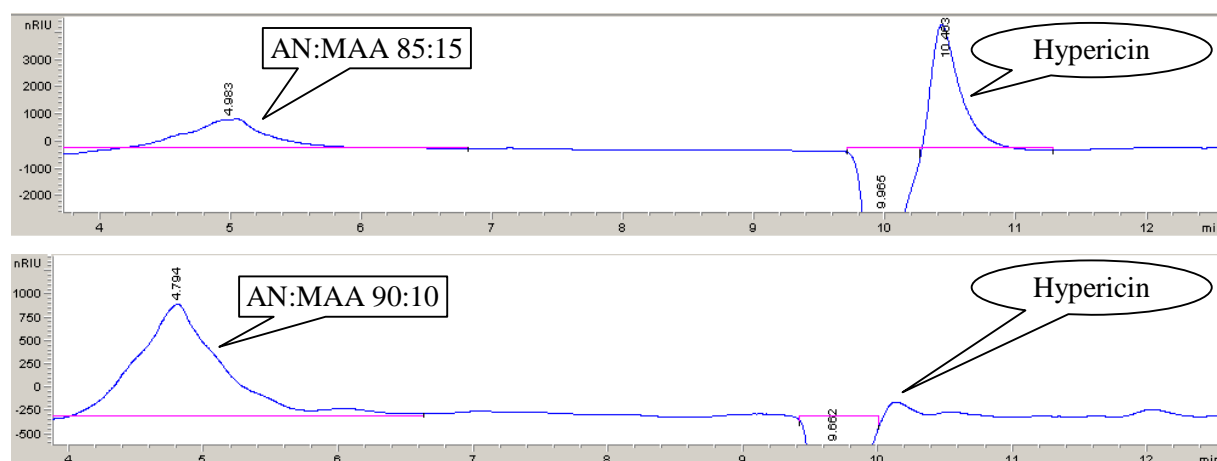


Fig. 1. Two of the AN:MAA matrices imprinted with 5% hypericin.

¹ Vasapollo, G., Del Sole, R., Mergola L., Lazzoi, M.R., Scardino, A., Scorrano, S. and Mele, G., 2011, *Molecularly Imprinted Polymers: Present and Future Prospective*, Int. J. Mol. Sci., 12, 5908-5945;

SYNTHESIS AND CHARACTERISATION OF COMPOSITE MATERIALS BASED ON POLYPROPYLENE AND GLASS FIBRES

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Composite materials based on polypropylene (PP) and glass fibres (GF) offer a very competitive property/price ratio. Polymers can be modified with different fillers, which enhance the mechanical, thermal, and wear resistance properties of matrix [1]. PP, one of the most widely used plastics, has been the subject of intensive studies with the objective to improve its mechanical properties. PP/GF composites are generally produced in two steps; namely the fibre/matrix impregnation and then composite forming. The most common impregnation processes are extrusion (using chopped fibres), strand impregnation (using fibre filaments) and compression molding (using glass-mats) [2]. The fibre/matrix adhesion plays also an important role. For adhesion to occur it is essential that intimate contact is established between the matrix and the fibre [3]. The present work presents the fulfilment of composite materials based on isotactic PP and short GF. Amino-functionalized GF were obtained by chemical modification of the type E GF by using 3-aminopropyltriethoxysilane. However, to ensure good interfacial adhesion and stress transfer across the interface, chemical or physical interactions between the matrix and the fibres need also to be formed due to their inert nature. The better interfacial adhesion is assured by the use of maleic anhydride grafted PP and amino-functionalized GF. The obtained composite materials were tested from the point of view of composition, morphology and mechanical properties.

Acknowledgement: This work was supported by the project 168/2012 “Hybrid composite materials with thermoplastic matrices doped with fibres and disperse nanofillings for materials with special purposes”, funded by the National University Research Council in Romania.

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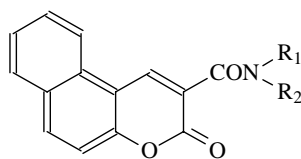
STUDY ON THE SYNTHESIS AND PHYSICAL – CHEMICAL CHARACTERIZATION OF SOME 5, 6 - BENZOCOUMARINES

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As an important class of organic heterocycles, coumarin derivatives have been widely reported to exhibit various biological activities^{1,2}, especially with regard to antioxidant and anti-inflammatory activities. Further, coumarin derivatives also show outstanding optical properties, which render them useful across a wide variety of applications, such as brightners, laser dyes, nonlinear optical chromophores, as well as fluorescent labels and probes in biology and medicine^{3,4}.

The aim of the work was to synthesize and characterize eight new 5,6-benzocoumarins, corresponding to the general formula (I).



(I)

$R_1 = \text{H}, \text{C}_6\text{H}_5, \text{C}_6\text{H}_{11}, \text{n-C}_4\text{H}_9, \text{iso-C}_4\text{H}_9, \text{3-OCH}_3\text{-C}_3\text{H}_6, \text{C}_2\text{H}_5$

$R_2 = \text{H}$ or R_1 and R_2 from a morpholinyl ring

The results of physical-chemical characterization (purity, melting point, IR, UV-VIS and fluorescence spectra) and structural resemblance with some natural compounds, such as odors and natural dyes, may recommend this type of compounds as an ecological alternative for UV protection both of textiles and cosmetics.

¹ Kontogiorgis CA, Handjipavlou-Litina DJ, *J Med Chem*, 2005, **48**, 6400-6408

² Hamdi N, Puerta MC, Valerga P, *Eur J Med Chem*, 2008, **43**, 2541-2548

³ Liu XG, Cole JM, Waddell PG, Lin TC, Radia J, Zeidler A, *J Phys Chem*, 2012, **116**, 727-737

⁴ Yu TZ, Zhang P, Zhao YL, Zhang H, *Spectrochim Acta A: Mol Biomol Spectrosc*, 2009, **73**, 168-173

GRAFTING OF CYCLOOCTENE ON STYRENE-BUTADIENE ELASTOMERS BY RING-OPENING METATHESIS POLYMERIZATION

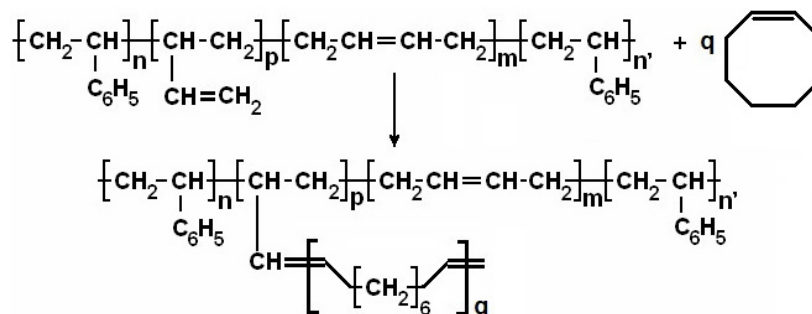
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Styrene-butadiene block-copolymers (SBS) with different vinyl content were synthesized via anionic three stages sequential polymerization, in cyclohexane solution, initiated with n-butyl lithium. By introducing different amounts of electron donors in the polybutadiene block synthesis the vinyl group's content of the elastomer was controlled.

The resulted styrene-butadiene block-copolymers with different vinyl content were grafted preferential at the vinyl groups, using cyclooctene, by ring-opening metathesis polymerization (ROMP), following the reaction:



The ROMP grafting reactions were performed in toluene, in the presence of Grubbs II catalyst (1,3-Bis-(2,4,6-trimethylphenyl)-2 (imidazolidinylidene) (dichlorophenylmethylene) (cyclododecene tricyclohexylphosphine) ruthenium).

The grafted SBS block-copolymers were characterized by Gel Permeation Chromatography (GPC), Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC), Nuclear Magnetic Resonance Spectroscopy (C^1 and C^{13} NMR), and Thermo-gravimetric Analysis (TGA).

INFLUENCE OF AMINO ACID-BASED SURFACTANTS ON THE SYNTHESIS OF TiO₂ NANOCRYSTALLINE POWDERS

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Victor FRUTH²

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The preparation of crystalline titania by the sol-gel method implies often surfactant templating. The most common are cationic surfactants, such as cetyltrimethylammonium bromide¹², but the literature also indicates anionic surfactants, such as sodium dodecyl sulfate¹ and sodium dodecylbenzene sulfonate³. The introduction of surfactants can control the shape, size and morphology of inorganic nanoparticles⁴.

In this study we report the synthesis of TiO₂ by surfactant-assisted sol-gel technique in alkaline catalysis, using amino acid-based surfactants: sodium lauroyl-glycinate and sodium lauroyl-glycylglycinate. TiO₂ powders were obtained through the hydrolysis of titanium precursor titanium tetraisopropoxide TTIP, at a molar ratio H₂O: surfactant: TTIP of 15:0.1:1. For comparison, TTIP was hydrolysed under identical conditions in the presence of water, without adding surfactants.

The recorded X-ray diffraction patterns revealed that in the absence of surfactants only anatase phase is formed upon calcination at 500°C, while the use of amino acid-based surfactants lead to a partial transformation of anatase phase into rutile phase. For sodium lauroyl-glycylglycine the crystalline phase composition is 88% anatase phase and 12% rutile phase and for sodium lauroyl-glycine the crystalline phase composition is 67% anatase phase and 33% rutile phase.

Beside the transformation of the anatase phase in rutile, which can be corroborate with the thermal decomposition of surfactants, a major influence of surfactants is the significant reduction in the size of powder particles of titanium dioxide, determined by DLS technique, from micrometric to nanometric dimensions.

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³ C. Zhang, R. Chen, J. Zhou, J. Cheng, Q. Xia, Synthesis of TiO₂ films on glass slides by the sol-gel method and their photocatalytic activity, Rare Metals, **28**(4), 2009, 378-384

⁴ I. Popovici, D. Perniu, L. Isac, R. Cioc, A. Duta, Surfactant assisted control over morphology and surface properties of sprayed TiO₂ thin films, Revue Roumaine de Chimie, **56**(10-11), 2011, 1075-1080

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Humidity and low temperatures in the cold season, favor a large number of freeze-thaw cycles, which accelerate the degradation of asphalt by microcracks. Such cracks appear also at high temperatures typical of the warm season. Surface treatments consist in applying a thin protective layer on the wear surface, using "hot" or "cold" technologies. The role of these coatings is the preventive maintenance from the negative effects of sunlight (UV radiation, temperature) and water (by freeze-thaw cycles). These treatments are applied in order to fill existing defects (pores, cracks) or as a wear course. The use of nanoparticles based nanocomposites dolomite and / or calcium carbonate in the asphalt road aims to obtain a nanocomposite asphalt that favor increasing the life of the road pavement, improving resistance to heavy traffic, sealing surface, increasing the stability of asphalt at excessive environmental conditions and increasing resistance to solvent attack. The nanoparticles were prepared by grinding in a 6 Fritsch Pulverisette laboratory mill shaft. For the preparation of nanocomposites have used commercial block copolymers of styrene / butadiene / styrene (SBS). Characterization of nanocomposites was achieved by dynamic mechanical analysis (DMA) and thermogravimetric analysis. Samples were conditioned in molds with a hydraulic press for 5 min. at 160 kgf/cm² and 120°C. DMA curves - the storage (E') and loss tangent ($\tan \delta$) with temperature were determined by applying an oscillating force and measuring the deformation of the sample material and implicit dynamic viscoelastic response of asphalt nanocomposites. Thermogravimetric analyzes have shown the thermal stability of nanocomposites asphalt until 200°C.

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Multi-electrode array to monitor reactive species in high throughput format

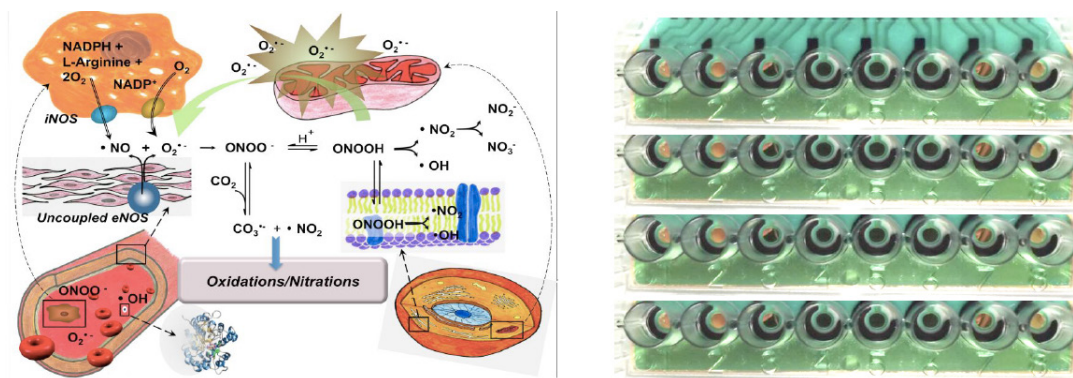
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The multi-electrode electrochemical formats (ME) are apt for array design (MEA) towards *high throughput cell monitoring*. Our goal is to develop an improved MEA to determine concurrently several reactive species (RS) involved in fast interactions in vivo (*figure, left*). First, the RS-sensitive films were synthesized, optimized and applied to electrodes and their response time, linear range, detection limit were examined¹⁻⁴. Next, MEA with nests of three electrodes (working, reference, auxiliary) were made with transparent cylinders in a multi-well MEA format (*figure, right*). The next step is to merge the RS-sensitive films into the multi-well MEA and to test the performance of the entire system. This improved design has a strong potential for miniaturization.



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PROVES CONCERNING THE INTERCALATION OF POLYACRYLAMIDE INTO KAOLINITE INTERLAYER SPACE BY CERIUM ION INITIATED POLYMERIZATION

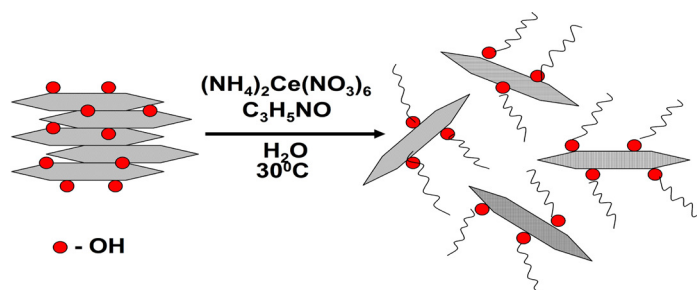
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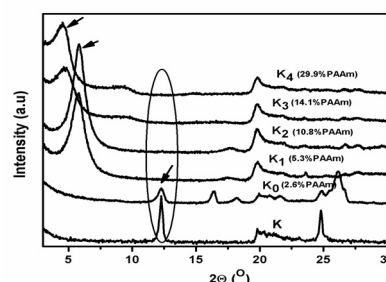
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The polyacrylamide (PAAm)-modified kaolinite was synthesized by cerium ion initiated polymerization of acrylamide on the surface of kaolinite platelets (Scheme 1). Five samples were synthesized using different PAAm/kaolinite ratios. The PAAm/kaolinite nanocomposites were characterized in terms of morphology (by SEM), thermal behaviour (by TGA), composition (FTIR) and of diffraction bands position (XRD).



Scheme 1. Cerium ion initiated polymerization of acrylamide on the surface of kaolinite layers.



XRD patterns of pure kaolinite and polyacrylamide modified kaolinite.

The TGA tests revealed the amount of organic matter loaded and also the thermal stability of new inorganic/organic materials. FTIR spectra of the new nanocomposites materials with different concentration of PAAm displayed not only the characteristic bands of the kaolinite but also of the PAAm, proving the presence of the inorganic and organic structures in the final material and showed important changes in the kaolinite inner surface OH region through intercalation with polyacrylamide chains. XRD analysis showed an extension of the kaolin interlayer space. All these characterization techniques confirmed the intercalation process of PAAm chains into kaolinite interlayer space occurred successfully.

A MODELING STUDY OF POLYLACTIDE SYNTHESIS BY REACTIVE EXTRUSION**Ionut BANU^a, Jean-Pierre PUAUX^b, Grigore BOZGA^a**^a*University Politehnica of Bucharest 313 Spl. Independentei, sector 6, 060042 Bucharest, Romania;*^b*Universite Claude Bernard-Lyon 1, 69622, Villeurbanne Cedex, France*

The reactive extrusion is a promising technique used for polymer synthesis, appropriate for systems where the necessary reaction duration is of the same magnitude order with the residence time achievable inside the extruder. The work presents the main results of a study regarding the reactive extrusion of L-lactide to polylactide. The experimental work was performed on a laboratory twin screw extruder with the possibility to control temperature profile on ten regions along the axis. Due to the lack of an appropriate tracer to measure the flow and mixing of the L-lactide/polylactide mixture in the twin-screw extruder, these characteristics were obtained by a simulation study of the residence times distribution (RTD) using a commercial software. The ability of this simulator to calculate the fluid mixing inside the extruder was confirmed by comparing the calculated RTD profiles with experimental RTD curves obtained on the twin-screw extruder. The simulated RTD was further used in the modeling of reactive extrusion process, by the means of the classical axial dispersion model. The polymerization kinetics was described by a model developed from own experimental data¹ obtained in batch reactors. The transport coefficients of the polymeric species were considered identical and calculated from the moments of the RTD data. The mathematical model included balance equation for initiator and monomer, as well as equations describing the axial evolutions of moments for live and dead polymer species distributions. The calculated conversion and number-average molecular weight values were in a good agreement with the measured ones.

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ADSORPTION ISOTHERMS IN MOLECULARLY IMPRINTED POLYMERS

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Introduction: Molecularly imprinted polymers (MIPs) are extremely selective materials that are characterized in literature using many and diverse methods¹. Using adsorption isotherms at equilibrium or in dynamic conditions is one of these methods.

Method: Eight adsorption isotherms (Linear, Langmuir, Freundlich, Jovanovic, Bradley, Stirling, Reciprocal, and Freundlich extended) and three kinetic adsorption models (Lagergren first order, pseudo second order, and Elovich) were applied to the experimental data obtained after the imprinted sorbents (MIPs) and the non-imprinted sorbents (NIPs) were submitted to batch adsorption experiments. The models were evaluated using three relevant statistic methods (adjusted R square, reduced chi-square test and sum of relative standard errors) combined together in a more powerful statistic tool: sum of normalized errors (SNE).

Results and discussions: For diosgenin MIPs, the order of all eight adsorption models, according to the “minimum SNE” criteria, is: Stirling > Freundlich > Linear > Freundlich extended > Bradley > Langmuir > Reciprocal > Jovanovic. The fact that Freundlich isotherm describes better than Langmuir the adsorption process suggest the heterogeneity of pores.

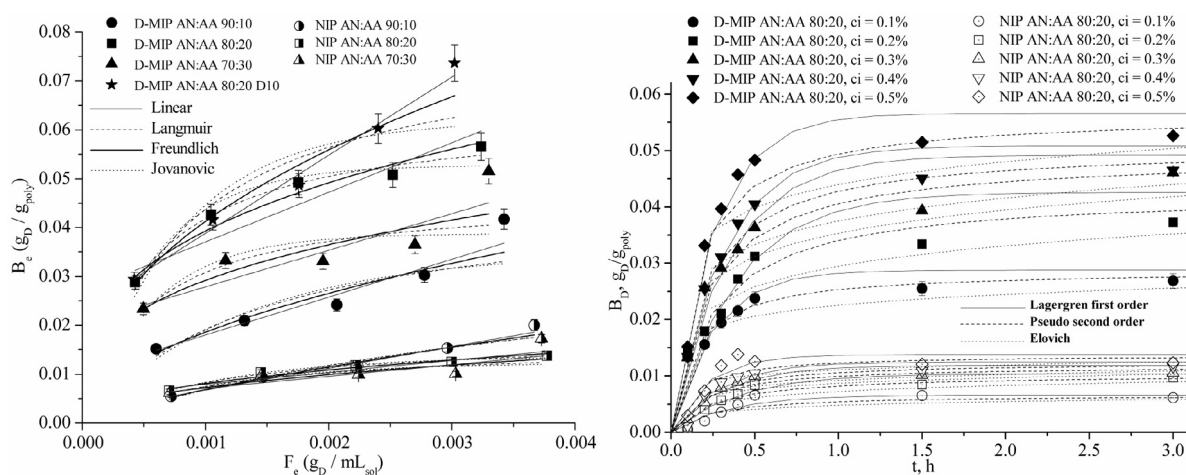


Fig. 1. Adsorption isotherms in diosgenin MIPs for: a) equilibrium data; b) kinetic data.

The pseudo second order kinetic model fits the best the kinetic data, suggesting that the rate-limiting step may look like a pseudo-chemical adsorption because of the non-covalent interactions that take place in the recognition process between template and imprinted matrix.

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Steam reforming of ethanol on Pt/Al₂O₃ catalyst**Danuta GHITA, Dorin Stanica EZEANU, Paul ROSCA***Petroleum-Gas University of Ploiesti, Blv. Bucuresti, nr. 39, Ploiesti*

Ethanol reforming process was performed using Pt catalyst supported on Al₂O₃ prepared by impregnation method. The catalyst was tested in a fixed bed reactor at atmospheric pressure over a temperature range of 300 to 500⁰C established by using an automatic panel control. Different flow rate of ethanol from renewable sources (with different alcohol %) was used as raw material for the experiment. The catalyst was prepared and characterized by N₂ adsorption/desorption, XRD, XPS and TGA techniques.

The results of different studies carried on ethanol steam reforming have shown that the main reaction is staged by a number of secondary reactions. The gaseous products resulting from the reaction were analysed on-line using a gas chromatograph Varian CP-3800 equipped with a thermal conductivity detector (TCD). Helium was used as carrier gas. Previous to reaction, catalyst was reduced under flowing hydrogen at 550⁰C for 6 h.

The ethanol conversion was almost 90% in the whole range of temperature studied. Thus on the alumina support, the conversion of ethanol is good, but the yield of hydrogen is low because the system reaction is promoted by the dehydration reaction which consumes hydrogen to ethane in ethylene saturation. Regarding the outlet gas composition, we conclude that the formation of ethylene by dehydration reaction is catalyzed by acids and support centers and is even more intense as the support acidity is higher, a fact mentioned by Iwasa and Takezawa¹. Al₂O₃ support which has higher acidity compared to other support used in literature will increase the ethanol dehydration to ethylene, but due to its saturation by hydrogenation of ethylene leads to the lower H₂ yields.

The catalytic results indicate that Pt/Al₂O₃ catalyst can be used as versatile and stable catalyst for steam reforming ethanol reaction involving new research directions in this area.

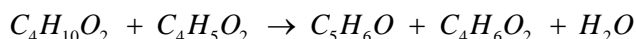
¹ Iwasa, N., Takezawa, N., *Reforming of ethanol-dehydrogenation to ethyl acetate and steam reforming to acetic acid over copper-based catalysts*, Bulletin of the Chemical Society of Japan, 64, 1991, p. 2619-2623.

[SIMULTANEOUS PRODUCTION OF γ -BUTYROLACTONE, FURFURAL ALCOHOL AND 2-METHYL FURAN IN A COUPLED ADIABATIC REACTOR]

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A coupling process of the hydrogenation of furfural (FFA) and the dehydrogenation of 1, 4-butanediol (BDO) has been studied for the simultaneous production of γ -butyrolactone (GBL), furfural alcohol (FOL) and 2-methyl furan (2MF) in a fixed bed adiabatic reactor, under different conditions of reaction temperatures and hydrogen to feed ratio. The coupled process has advantages like; easy temperature control, improved yield, good energy efficiency and optimal hydrogen utilization.



A plant model is built in ASPEN Plus. The feed Furfural and 1, 4-butanediol is fed at 10 kmol/hr and 20 kmol/hr respectively at 220 °C is introduced in the adiabatic reactor. The hydrogen to feed ratio is maintained at 15:1. The conversion of both reactants >99 % with uniform temperature profile along reactor length.

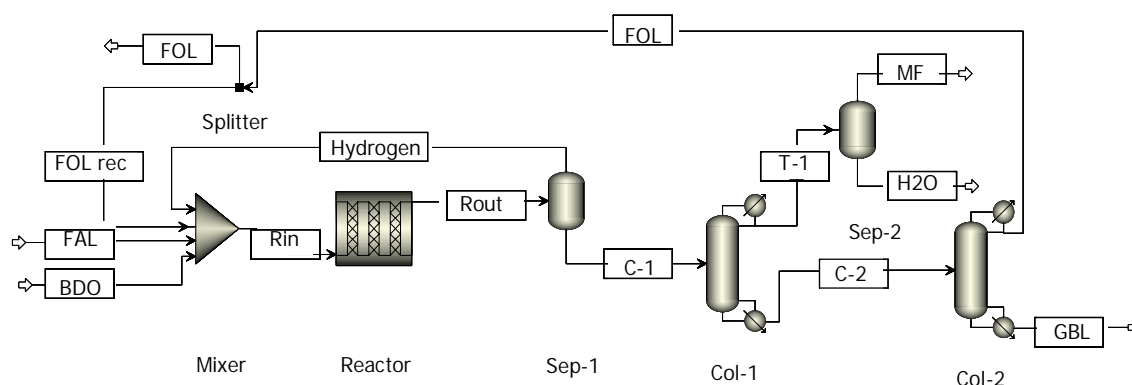


Figure 1 Integrated Plant

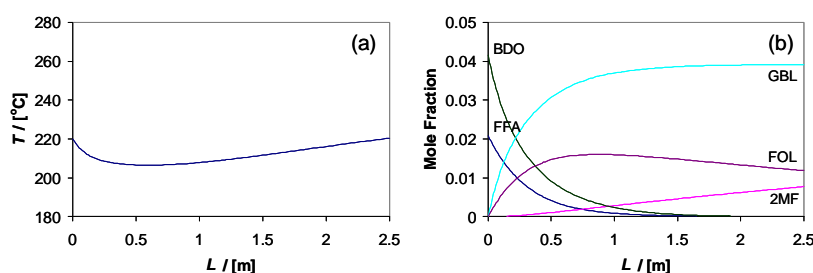


Figure 2 Reactor Profiles (a) Temperature (b) Molar

EXPLOSION PARAMETERS OF GASEOUS ETHYLENE-AIR MIXTURES IN ELONGATED CYLINDRICAL VESSELS

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Explosion propagation of gaseous ethylene–air mixtures with various concentrations between 3.0 and 14.0 vol.% and initial pressures between 0.20 and 1.10 bar was experimentally investigated at ambient initial temperature, using 5 closed cylindrical vessels with L/D (length to diameter) = 1.0 – 20.7 with central or bottom ignition. The maximum explosion pressures p_{max} , the explosion times θ_{max} and the maximum rates of pressure rise $(dp/dt)_{max}$ are strongly influenced by the length to diameter ratio of the vessels, by the position of ignition source, by the initial pressure and composition of the flammable mixtures. Even when important heat losses are present, linear correlations $p_{max} = f(p_0)$ and $(dp/dt)_{max} = f(p_0)$ were found for all examined fuel–air mixtures, in all closed vessels. For both central and bottom ignition, higher rates of pressure rise were observed in the early stage of explosion propagation^{1,2} (where a cvasi-spherical flame, characterized by a fast flame speed, propagates) as compared to later stages of the process, characterized by lower flame speeds.

Flame propagation in elongated vessels with asymmetrical ignition is characterized by lower explosion pressures and rates of pressure rise in comparison with the case of symmetrical ignition. This fact is assigned to the strong disturbance of the spherical propagation of the combustion wave³. The heat losses appearing in the last stage of explosions occurring in asymmetrical vessels have been estimated from the differences between the experimental and adiabatic maximum explosion pressures. These heat losses are higher when the asymmetry ratio L/D is higher and were found to depend linearly on the initial pressure.

In many experiments, strong pressure oscillations were observed in the later stage of explosions. Their amplitude depends on mixture strength and pressure, as well as on L/D. All data were examined in comparison with recently reported results¹ on deflagrations in cylindrical vessels with central ignition and with parameters describing the adiabatic isochoric combustion of flammable mixtures (maximum explosion pressure and maximum rates of pressure rise), computed by means of recent models.

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THERMAL STABILITIES OF SOME ALDEHYDE-2,4-DINITROPHENYLHYDRAZONES DERIVATIVES

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The derivatives of 2,4-dinitrophenylhydrazone [2,4-DNPHs] type have acquired special relevance for the analysis of carbonyl compounds such as aldehydes and ketones^{1, 2}. Identification of carbonyls by their 2,4-DNPHs are made by column and thin-layer chromatography. An important aspect with regards to the GLC separation of the 2,4-DNPH derivatives lies in their thermal stabilities.

The characteristic features of these compounds are primarily of interest for risk assessment and also for structure–property relationship analysis³⁻⁵.

The thermal stability of some aldehyde 2,4-dinitrophenylhydrazones has been studied using differential scanning calorimetry (DSC) technique. The crystalline solids are thermally stable and start to decompose after melting. Non-isothermal DSC curves, recorded at several heating rates, were used to evaluate the melting properties and the kinetics of thermal decomposition. Both isoconversional and model fitting methods were used for the evaluation of the kinetic parameters. Based on the results of the model free method, a kinetic model was derived and the kinetic parameters were obtained by means of a multivariate non-linear regression. A good agreement between the experimental and fitted data was found.

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**NEW ANTIMICROBIAL AGENTS WITH ACTIVITY AGAINST MULTI-DRUG
RESISTANT MICROORGANISMS GRAM-POSITIVE
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Quinolone compounds are characterized by a more rapid bactericidal activity and by a much wider antibacterial spectrum. They are active both Gram-negative and Gram-positive microorganisms, and the recently discovered intracellular development microorganisms (*Legionella*, *Mycoplasma*, etc.), or even acid-resistant bacilli (*M. tuberculosis* and *M. leprae*). Sphere of use of quinolones has expanded more from urinary tract infections in acute and chronic systemic infections (bronchopulmonary infections, osteoarticular, septicemia and endocarditis), chronic infections (chronic bronchitis, purulent osteoarthritis, chronic prostatitis, cystitis and chronic sinusitis). Resistant bacteria threaten virtually all classes of antibacterial agents and quinolones are no exception to this. But 4-oxo-1,4-dihydro-quinolones have proved less affected by bacterial resistance compared with other antibacterial agents.

Were obtained by chemical synthesis, a series of compounds that are registered in the following general structure (Fig. 1), and were characterized by physico-chemical and antimicrobial activity.

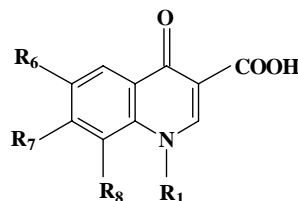


Fig.1 General structure of the new compounds synthesized

where: R₁ = ethyl, R₆ = F, Cl, R₇ = heterocycle, R₈ = Cl, H

Four compounds, which showed the best antibacterial activity against microorganisms collection: FPQ-27, FPQ-30, FPQ-28 and 6CIPQ-28, were tested against 30 strains of methicillin-resistant *Staphylococcus aureus* isolated in Laboratory Microbiology of the INBI „ Prof. Dr. Matei Bals” during 2012.

From the four compounds, the best antimicrobial activity was obtained for FPQ-30, all strains were inhibited at a concentration less than 8 µg/ml

Trends additives for motor fuels

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Using of additives in motor fuels aims to improve their performance without changing the fuel composition. The shortcomings of fuels are due either of low performance of some classes of hydrocarbons present therein, or by the absence for all kinds of hydrocarbons, of some characteristics necessary for optimal functioning of the internal combustion engine. On the other hand the requirements for pollution reduction and high toxicity of some hydrocarbons that are found in combustion fumes, have caused changing of the oil processing or of the catalysts used for it. Thereby some fuel characteristics were improved and the presence of additives is not necessary (e.g. octane additives for gasoline) and other fuel characteristics worsened requiring increased concentration of additives (e.g. lubricating additives in fuels with a low sulfur content). The main additives used for gasoline are anti-knock, antioxidants, anti-ice additives, detergent-dispersants, corrosion inhibitors, additives to prevent deposits in the combustion chamber, valve seat recession protection additives, dehazers additives, antistatic additives, corrosion inhibitors, and for diesel fuels are antioxidant additives, cold flow additives, lubricants additives, ignition improvers, detergent-dispersants, antifoaming, biocides, antistatic additives and reodorants¹⁻⁴. Reducing pollutant emissions from motor vehicles has been the subject of countless legislative initiatives over time. Last European document who makes references to the specifications of oil is Directive 2009/30/EC of the European Parliament whose decisions are binding on all Member States. The directive introduces a mechanism to monitor and reduce greenhouse gas emissions. This document states that the introduction of detergent - dispersant additives type is obligatory as it contributes to clean engines and thus to reduce emissions.

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KINETIC STUDY ON THE CONTROLLED RELEASE OF ANTIBIOTICS FROM POLYMERIC DOSAGE FORMS

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The aim of controlling the drug delivery is to achieve more effective therapies while eliminating potential for both under- and overdosing. Controlled delivery systems include the maintenance of drug levels within a desired range, the need for fewer administrations, optimal use of drug and increased patient compliance ¹.

In the design of drug delivery system, it is necessary to study and optimize the drug delivery profile specific for the release kinetics.

Over the past three decades, because the oral dosage forms are generally made of polymers in which the drug is dispersed, the controlled release from a polymeric matrix was a problem of special interest in the area of pharmacokinetics.

A large number of mathematical models were developed to describe the release of drugs from matrix systems ¹⁻⁴. They can be classified according to the controlling physical mechanism of release of drug (diffusion, erosion, osmosis). The choice of an appropriate model strongly depends on the type of drug, type of excipients and composition of the oral dosage form. Thus, it is crucial to identify an adequate model for a specific drug delivery system.

The aim of this paper is to simulate the kinetics of some antibiotics by using diffusional models (the classical unsteady state Fick's diffusion equation having appropriate boundary conditions and the Higuchi model). In order to illustrate the validity of the selected models, comparisons with experimental profiles obtained in simulated intestinal fluid (pH 7.4) and reported in the recent literature are presented. The predictions of the mathematical models are useful to improve the oral administration of the considered antibiotics.

A COMPARATIVE ANALYSIS FOR PERFORMANCES OF DOUBLE AND THREE CONCENTRIC TUBES HEAT EXCHANGERS

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The paper presents results obtained to cooling a petroleum oil in concentric tube heat exchangers. The heat exchangers analyzed are double and tri-concentric tubes. Compared to double tube heat exchanger, in which the hot fluid flows through the central tube and cold fluid flows through the annular space, in a triple concentric-tube heat exchanger the cold fluid flows through the central tube and the outer annulus and the hot fluid flows through the inner annulus, thus the energy of hot fluid is transferred in two opposite directions. Advantages of a triple concentric-tube heat exchanger compared to double tube heat exchangers are the larger heat transfer surface area per unit length and higher overall heat transfer coefficient due to higher fluid velocities fluid in the annular space. Therefore, the heat transfer from one fluid to the other is enhanced¹.

A triple concentric-tube heat exchanger designed and built for working conditions in the laboratory² has been tested experimentally to cooling of oil with water by network³. The geometrical data of heat exchanger and experimental data (flow, inlet and outlet temperatures) obtained for a set of experimental tests are used in determining the performance of a double tube heat exchanger. For both heat exchangers are calculated and compared the overall heat transfer coefficients and the heat exchange surfaces. The obtained results are consistent with literature data.

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HIGH VACUUM DISTILLATION FOR ω -3 FATTY ACIDS ESTERS SEPARATION

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The purpose of this work was to improve the quality of fish oil omega-3 supplements by increasing their concentration.

Fish oil is a rich source of ω -3 polyunsaturated fatty acids triglycerides. Particularly two ω -3 fatty acids, eicosapentaenoic acid (EPA, 20:5) and docosahexaenoic acid (DHA, 22: 6) are important functional constituents of the human body (Rossi P. *et al.*, 2013).

These fatty acids are compounds with low vapor pressure and this aspect requires advanced distillation techniques as high vacuum distillation (Shurong W. *et al.*, 2013).

Because fatty acids esters have significant lower boiling points than the triglycerides from fish oil, it was necessary a preliminary step of fish oil transesterification. Alkaline-based transesterification reaction with ethanol allowed the obtaining ethyl esters of ω -3 polyunsaturated fatty acids (Wang W. *et al.*, 2012). Then, high vacuum distillation was applied to increase the concentration of ω -3 polyunsaturated fatty acids. A separation scheme on three steps was proposed: two steps of high vacuum thin film distillation ($\sim 10^{-2}$ mbar) and finally short-path distillation ($\sim 10^{-3}$ mbar) (Stefan N. G. *et al.* 2013).

Thin film distillation is a special high vacuum technique which uses the differences in volatility to enrich fractions in certain compounds. The separation process was conducted in a laboratory-scale Thin Film Distillation Plant (DSL5 from UIC GmbH). Short-path distillation is based on differences in mean free path of the molecules according to their dimensions, due to very high vacuum. Short-Path Distillation Plant (KDL5 from UIC GmbH).

The fatty acids esters composition from different fractions was analyzed using a gas-chromatograph coupled with a mass spectrometer as a detector. According to the GC-MS chromatograms, ω -3 fish oil ethyl esters were concentrated from ~35% to ~87%.

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LIGNIN-BASED OIL-SORBENT PRODUCT**Reznikov Ivan V., Savitskaya T.A., Tsygankova N.G., Nevar T.N., Grinshpan D.D.***Belarussian State University, Minsk, Belarus**Scientific-Research Institute of Physical and Chemical Problems, Minsk, Belarus*

Lignins is a large group of aromatic polymers with p-coumaryl, coniferyl and sinapyl alcohol fragments randomly conglomerated together to compose cell walls of plants and maintain the integrity of the cellulose/hemicellulose/pectin matrix. Lignin is the second most abundant natural polymer.

Nevertheless for a long time lignin is known as a waste material. For a long time the simplest way of lignin's utilization is using it as a fuel. Unfortunately, due to the fact that it undergoes only incomplete combustion and releases a number of hazardous gaseous products under thermal treatment the application of lignin as a fuel nowadays is environmentally unfriendly. Employments of lignin as an additive or a binder to thermosetting resins and thermoplastic blends, as well as a source of wide range of chemicals that can be used for production of synthetic polymers following producing bio-ethanol from lignin makes lignin a perspective bio-resource, though it is still far from being economically profitable.

Hydrolyzed lignin has an absorptive capacity of up to 4 g/g, is cheap, features buoyancy in the oil-saturated state, and forms with oil solid products which are easy to remove from the water surface and are suitable for obtaining fuel granules and pellets¹. Such granules and pellets containing in their composition occluded oil have a calorie content from 25 to 40 MJ/kg, whereas the caloric content of the source lignin is 17–22 MJ/kg. This makes it possible to utilize the waste oil sorbent in the form of a solid fuel, which confers important advantages over other sorbents. At the present time, in spite of the various proposals for using lignin, which is a large-tonnage by-product of the hydrolysis industry, it has not found wide application and is accumulated at enterprises, occupying large territories and threatening the environment. In the Republic of Belarus such an ecologically unfavorable situation takes place in Rechitsa and Bobruisk. Therefore, the possible future application of lignin as oil sorbent will eliminate both ecological marine problems and the ecological problems of cities Rechitsa and Bobruisk.

¹ Rheological properties of disperse systems based on hydrolyzed lignin and oil/ T. A. Savitskaya, I. V. Reznikov, V. A. Shcheglov, N. G. Tsygankova, G. M. Telysheva, D. D. Grinshpan// Journal of Engineering Physics and Thermophysics, Vol. 85, No. 3, May, 2012

Hydrosulfurization of middle petroleum distillatesSorin ION*, Vasile MATEI*

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Abstract

Hydrotreating middle petroleum distillates, particularly gas oil, has experienced a surge during the last decades owing to several reasons. Gas oil use, especially Diesel fuel, has been subject to severe regulations concerning sulfur content for environmental reasons. Other distillates are subjected to hydrosulfurization prior to catalytic treatment thorough cracking or hydrocracking. Lowering sulfur content is presently achieved on Mo or W sulfide catalysts promoted with Co and Ni sulfide, on alumina bed support (classic industrial system), in trickle-bed reactors. The present paper aims to describe the characteristics of flow through trickle-bed reactors and the mathematical apparatus thereof. It is necessary to take into account that upon hydrotreating middle distillates at pressures above 50 bar and temperatures around 340-400°C, the raw stock will be in a liquid state, while the hydrogen required for hydrotreating will be in a gaseous state. Therefore, all data pertaining to kinetics as well as reactor sizing, need to take into account the concept of liquid holdup. Calculating liquid holdup for the reactor may be performed either using fluid velocity through the reactor, or through empirical formulas containing flow invariants above the catalytic layer.

METHOD TO PRODUCE GLYCEROL FORMAL BY GLYCEROL RECOVERY FROM BIODIESEL PRODUCTION PROCESS

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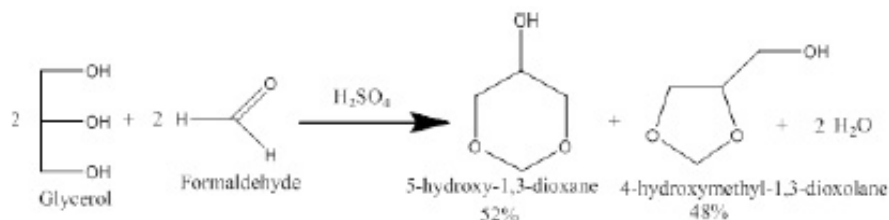
One of the major consequences of biodiesel industry development is getting a high amount of glycerin as a byproduct, which is obtained in a weight ratio of 1/10 glycerol/biodiesel [1]. Also because of inadequate purity, it is impossible to use residual glycerin in pharmaceuticals and cosmetics.

Glycerol recovery can occur by chemical and bio-chemical conversion [2], or by conventional catalytic conversion, within a process called acetalization [3]. Following that process dioxanes and dioxolanes that may have different uses are obtained.

This paper provides a general description of the residual glycerol recovery into a more valuable chemicals, namely glycerol formal, where the acetalization reaction between glycerol and paraformaldehyde is promoted by an acid catalyst. Glycerol formal is a low toxic solvent used for a wide variety of applications in pharmaceutical and cosmetics industry including anti-parasite veterinary injectable, intramuscular injections, sulphadiazine and trimethoprin preparation and as an improving agent of biodiesel proprieties at low temperatures.

The glycerol formal synthesis from glycerol and paraformaldehyde was conducted both with a solvent and a solvent-free when water removal was made through distillation. The solvent free process gave very good results, higher conversions and can be considered a green process.

General equation for glycerol formal synthesis in acid catalysis is :



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