

CELULOZĂ SI HÂRTIE

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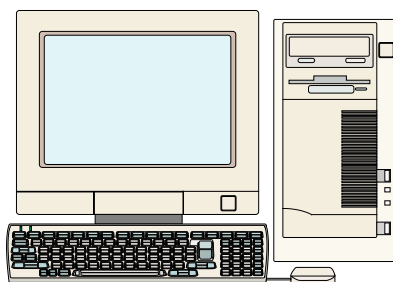
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SOME POSIBILITIES TO OBTAIN THE ANTIMICROBIAL PAPER

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Abstract

The antibacterial property is desired for many paper grades, such as tissue papers, hospital papers, but especially for food packaging. For this aim various bio-active molecules have been widely harnessed for analytical as well as other functional purposes. These bio-active molecules can be incorporated into cellulose fibres matrix, enabling the obtaining of functional papers with various applications: protection (water purification), diagnosis (food packaging) or security (anti-counterfeiting). In this context the main objective of this paper is based on research and validation of new technical solutions in the field of paper functionalising using the bioactive organic compounds based on quaternary pyridinium salts with antimicrobial and electrochromic properties. The experimental program consists of achieving the bioactive organic compounds based on bis-quaternary pyridinium salts, checking their functional characteristics and testing some techniques and methods for their embedding into paper structure or on its surface (as final functionalised product). Therefore, the bio-active-antimicrobial effect of papers treated with 4,4'-bispyridinium salts immobilised on pigment dispersions (ZnO) as coating surface, was analysed. Based on the obtained results, these functionalised paper products can be recommended to use for food packaging or hygiene applications.

Key words: cellulose fibres, antimicrobial properties, quaternary pyridinium salts

Rezumat

Proprietățile antibacteriene sunt importante pentru multe sortimente de hârtie, cum ar fi, hârtia tissue, hârtiile sterilizante utilizate în spitale, dar în special pentru hârtia de ambalaj alimentar. În acest scop, sunt utilizate diferite molecule cu proprietăți bioactive care pot fi înglobate în matricea fibrelor celulozice, permițând obținerea hârtiilor funcționale pentru diferite aplicații: protecție (purificarea apei) diagnoză (ambalaj alimentar) sau securitate (anti-contrafacere). În acest context principalul obiectiv al acestei lucrări are la bază câteva încercări preliminare pentru funcționalizarea hârtiei cu ajutorul unor compuși organici de tipul sărurilor cuaternare de piridiniu care au proprietăți antimicrobiene și electrocrome. Programul experimental constă în obținerea compușilor organici pe bază de săruri de piridiniu, verificarea proprietăților funcționale și testarea unor tehnici de înglobare a lor în structura sau la suprafața hârtiei. Prin urmare, a fost analizat efectul bioactiv-antibacterian al hârtiilor tratate la suprafață cu formule compozite pe bază de săruri de 4,4'-bipyridinium și ZnO. Pe baza rezultatelor obținute, aceste hârtii funcționalizate pot fi recomandate pentru ambalarea produselor alimentare (ca ambalaj secundar) sau în domeniul produselor igienico-sanitare.

Cuvinte cheie: fibre celulozice, proprietăți antimicrobiene, săruri cuaternare de piridiniu

1. INTRODUCTION

The antibacterial property is desired for many paper grades, such as tissue papers, hospital papers, but especially for food packaging. Protection against the action of microorganisms is a basic requirement for many current packaged foods. Traditional

preservation methods (e.g. thermal treatments, irradiation, salting) cannot be applied to certain types of food such as vegetables, fruits and fresh meats or ready-to-eat products. Consequently, antimicrobial paper for packaging is a viable and beneficial form of

limiting and controlling bacterial growth in food [1]. Conventional food packaging systems are designed to act as passive barriers, protecting food against the surrounding environment, while active food packaging systems are designed to interact with surrounding medium in order to prevent harmful effects, like microbial contamination. In the last years, the attention of researchers was focused on nitrogen heterocyclic compounds as antimicrobials or biomarkers (an important area in the chemical, pharmaceutical and medical research) that can be used for functionalizing of cellulose fibres or fibres based products. These functionalised papers can have large applications from *protection and safety* (purification of water and air, security against biological and chemical terrorism), *diagnostics of health, food safety and quality* (testing of microbial contamination and counterfeit prevention). [2, 3, 4, 8]

Quaternary ammonium salts are a versatile class of compounds having a wide range of interesting properties and continuing to receive an increasing attention [5,6] mainly because they can be easily functionalized at the nitrogen heterocyclic atom in order to obtain species useful for biological and industrial applications [7,10], as for example cosmetics, pharmaceuticals, gene delivery, polymerization. Selected salts named viologens (4,4'-bipyridinium salts) demonstrate electrochromic properties. Due to their broad specificity of antimicrobial activity, N-heterocyclic

Techniques for immobilisation of nitrogen heterocyclic compounds

The bio-active compounds based on 4,4'-bipyridinium salts were immobilised on

quaternary ammonium salts represent one of the most used antiseptics and disinfectant.

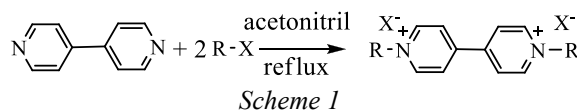
2. EXPERIMENTAL

The objective of experimental programme consists of achieving of the bioactive organic compounds based on bis-quaternary pyridinium salts and testing some techniques and methods for their embedding into paper structure or on its surface (as final functionalised product).

These experiments are the first applications of quaternary pyridinium salts on paper functionalising.

Obtaining of nitrogen heterocyclic compounds (4,4'-bipyridinium diquaternary salts)

The synthesis of the diquaternary pyridinium salts (Scheme 1) derived from 4,4'-bipyridine has been carried through the alkylation of 4,4'-bipyridine by reactive halogenated derivatives in anhydrous solvents, which seems to be the most convenient method between those reported in literature. [5]



pigment dispersions (ZnO) aiming to coat/treat the surface of paper. In table 1 are presented the compositions of dispersions.

Table 1 Composition of coating colors

Receipt	Composition
R1	100p ZnO (micro particulate powder) (0,05p; 0,06p; 0,07p; 0,08p; 0,09p; 0,1p) 4,4'-bipyridinium salts
R2	100p ZnO

Functionalizing of paper

The coating colours which had been prepared before were applied (about 15 – 20 g/m² weight) on the papers surface using the Mayer rod laboratory coating system. The base paper

was obtained in laboratory as hand sheets of 20 cm diameter using Rapid Koethen method and equipment. The composition of base papers consists of cellulose fibres (hardwood and softwood) without any filler or chemical

additives. The weight of base paper was about 50 g/m².

Testing methods of functionalised papers

Aiming to evaluate the effect of bioactive compounds based on nitrogen heterocycles, the functionalised papers has been testing regarding the specific properties of food packaging, such as: antimicrobial activity on different microorganism cultures and air permeability.

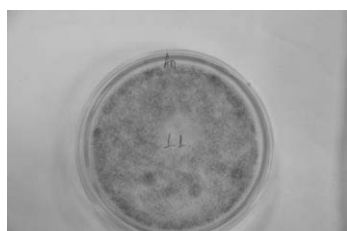
Antimicrobial activity

As microorganisms were used the following moulds: *Aspergillus niger* (*An*), *Penicillium*

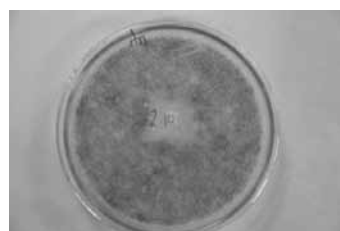
roqfortii (*P*) and *Geothricum candidum* (*Gc*) from Galați University Collection of Microorganisms. Antimicrobial activity was performed in Petri dishes on solid medium. The sterile discs with paper samples were immersed in culture medium and stored at 25°C. The inoculated plates were incubated for 120 hours and the inhibition zones around discs were controlled.

Air permeability as measure of time (s) for passing of air volume through paper sample with settled area. (Gurley method SR ISO 5636-5:1996).

3. RESULTS AND DISCUSSIONS



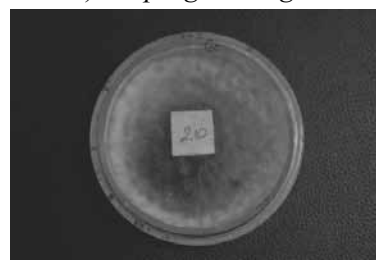
a) *Aspergillus niger* - *An*



b) *Aspergillus niger* - *An*



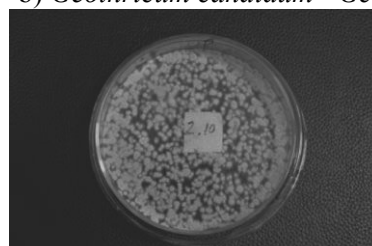
a) *Geothricum candidum* - *Gc*



b) *Geothricum candidum* - *Gc*



a) *Penicillium roqfortii* - *P*



b) *Penicillium roqfortii* - *P*

Fig.1 Antimicrobial activity: a) paper samples with 100p ZnO
b) paper samples with ZnO and 0,1p 4,4' bispiridinium salts

Antimicrobial activity

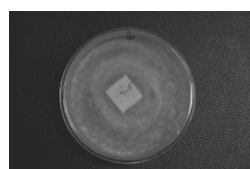
The antimicrobial activity of the functionalized papers is presented in figure 1. Aiming to emphasized the antibacterial activity of nitrogen heterocyclic compounds, during the

experimental programme, the paper samples functionalized with 4,4' bispiridinium salts were compared with paper samples treated with ZnO dispersions. This approach is based on the fact that inorganic materials (such as silver, copper, titanium oxide and zinc oxide

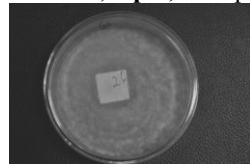
ZnO) have antimicrobial activity against some bacteria strains. Furthermore, ZnO in nanosize is a promising antimicrobial agent due to its activity against a wide range of microorganisms. [9]

Analysing the results from figure 1 (a) and (b), it can be observed that the paper samples treated with 4,4' bispiridinium salts and ZnO dispersions have a better antimicrobial activity (in case of *Aspergillus niger* – An and *Penicillium roqfortii* – P molds) comparing with the paper samples treated with ZnO dispersion only. In the center of disc, it can be observed a region without sporulation. Based on this, 4,4' bispiridinium salts can be used without ZnO to functionalize/protect the fibres based products (like as paper) against the

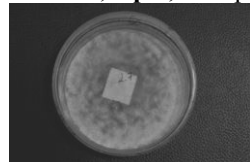
Aspergillus niger and *Penicillium roqfortii*. Regarding the *Geothricum candidum* – Gc, it can be observed that the both paper samples (functionalized with ZnO and ZnO + 0,1p 4,4' bispiridinium salt dispersions) have the similar antibacterial effect (although, the paper samples functionalized with ZnO + 0,1p 4,4' bispiridinium salt dispersions seem to have more pronounced antibacterial effect). This behavior is more clearly in images presented in figure 2, where it can be seen that all the samples of treated papers with ZnO + 4,4' bispiridinium salt dispersions have a more pronounced antibacterial activity against *Geothricum candidum* compared with the paper samples treated with ZnO dispersion only.



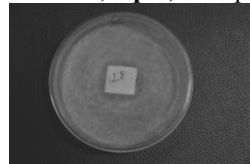
ZnO + 0,05p 4,4' bispiridinium salts – *Geothricum candidum*



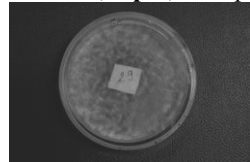
ZnO + 0,06p 4,4' bispiridinium salts – *Geothricum candidum*



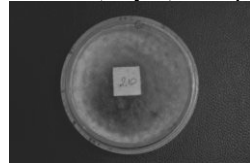
ZnO + 0,07p 4,4' bispiridinium salts – *Geothricum candidum*



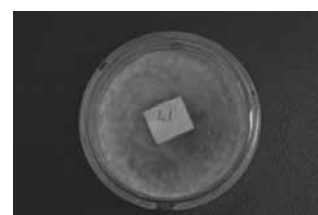
ZnO + 0,08p 4,4' bispiridinium salts – *Geothricum candidum*



ZnO + 0,09p 4,4' bispiridinium salts – *Geothricum candidum*



ZnO + 0,1p 4,4' bispiridinium salts – *Geothricum candidum*



100p ZnO - *Geothricum candidum*

Fig. 2 Antimicrobial activity on *Geothricum candidum*

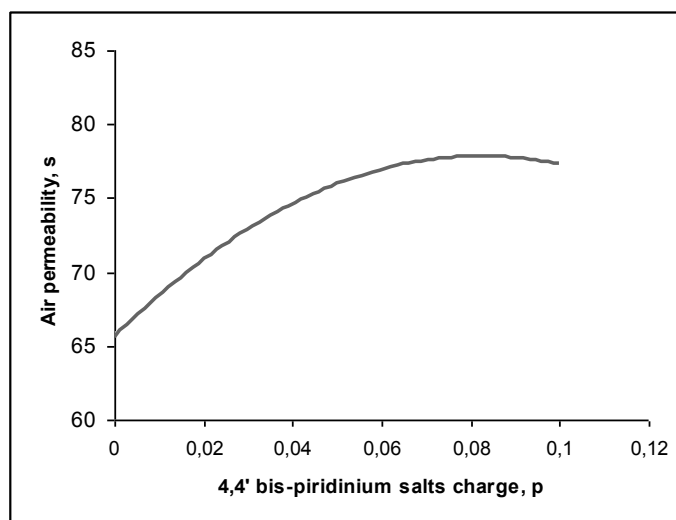


Fig. 3 Air permeability of functionalized paper samples

Increasing of air permeability of functionalized paper samples with 4,4' bispiridinium salts charge, indicates a closer structure of paper which show the slight barrier effect of these organic compounds (figure 3).

4. CONCLUSIONS

The nitrogen heterocyclic compounds, diquaternary salts of 4,4' bispiridinium obtained by N-alkylation of 4,4'-bipyridine with reactive halide derivatives, were used in inorganic pigment dispersions (ZnO) for functionalizing of paper samples by surface coating treatments.

The obtained results of testing (4,4' bispiridinium salts) as functionalizing compounds for papers or fibres based materials, show a good antimicrobial activity against *Aspergillus niger*, *Penicillium roqfortii* and *Geothricum candidum*, better than ZnO dispersions only.

This emphasizes that 4,4' bispiridinium salts can be recommended to functionalize the papers destined to antimicrobial/active packaging that interacts with the product to reduce, inhibit or retard the growth of microorganisms that may be present on food surfaces.

Furthermore, the results regarding the air permeability of functionalized paper samples reveals a slight barrier effect of these organic compounds.

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CELLULOSE CHEMISTRY AND TECHNOLOGY

Rezumatele lucrărilor publicate în Vol. 46 (2012)

NEW APPROACHES IN HYDROGEL SYNTHESIS – CLICK CHEMISTRY: A REVIEW

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“Claude Bernard” Lyon 1 University, Ingénierie des Matériaux Polymères, UMR CNRS 5223, Villeurbanne, France* *“Alexandru Ioan Cuza” University of Iasi, Faculty of Physics, Department of Plasma Physics, Optics and Spectroscopy and Structure of Matter, Iași, Romania*

Hydrogels have attracted great attention over the past decades, since they can be used for a variety of applications, including drug delivery systems and scaffolds for tissue engineering and repair. “Click chemistry”, in particular copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC), has been widely used in the preparation of complex architectures, such as hydrogel networks, due to its reaction specificity, quantitative yields and good functional group tolerance. The aim of this review is to present the synthesis and further use of “click” hydrogels composed of primarily natural components, using Cu as a catalyst or, following the latest trends, *via* a copper-free method.

Keywords: “click chemistry”, polysaccharide, crosslinking, hydrogel, catalyst-free

EFFECTS OF ACID HYDROLYSIS TIME ON CELLULOSE NANOCRYSTALS PROPERTIES: NANOINDENTATION AND THERMOGRAVIMETRIC STUDIES

P. KRISHNAMACHARI, R. HASHAIKEH, M. CHIESA and K. R. M. GAD EL RAB

*Materials Science and Engineering Program,
Masdar Institute of Science and Technology, Abu Dhabi, UAE*

Nanoindentation and thermogravimetric studies were performed on different samples obtained from acid hydrolysis of Microcrystalline Cellulose (MCC). Acid hydrolysis of MCC was carried out using 64% H₂SO₄ at 45 °C for 10, 20, 30 min, 1 and 5 h, respectively. Elastic modulus and hardness were assessed for each sample. The samples hydrolyzed for 30 min or more had a considerably lower elastic modulus than those hydrolyzed for 20 min or less. Thermogravimetric (TGA) studies revealed that the onset of thermal degradation of all samples occurred at a lower temperature than that of MCC.

Keywords: nanocellulose, nanoindentation, acid hydrolysis, thermal analysis

ENHANCED ANTIPYRETIC ACTIVITY OF NEW 2,5-SUBSTITUTED 1,3,4-OXADIAZOLES ENCAPSULATED IN ALGINATE/GELATIN PARTICULATED SYSTEMS

CORINA CHEPTEA,^{*}^{**} V. ȘUNEL,^{*} MIHAELA HOLBAN,^{*} J. DESBRIÈRES,^{***} M. POPA^{****} and CĂTĂLINA LIONTE^{*****}

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New 1,3,4-oxadiazoles with pharmacological potential, derived from 5-nitroindazole, have been synthesized. Their chemical structure has been established by elemental and spectral analyses (FT-IR and ¹H-NMR). The oxadiazoles presented low toxicity, one compound, either in a free form or loaded in polymeric microcapsules, also showing a remarkable antipyretic activity, similar to that of acetylsalicylic acid.

Keywords: *1,3,4-oxadiazoles, antipyretic activity, encapsulation, polymeric particles*

HYDRATE CELLULOSE FILMS AND PREPARATION OF SAMPLES MODIFIED WITH NICKEL NANO- AND MICROPARTICLES. II. INTERCALATION OF NICKEL INTO HYDRATE CELLULOSE FILMS

NINA E. KOTELNIKOVA and ALEXANDRA M. MIKHAILIDI*

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Nanocomposite materials containing stabilized nickel nano- and microparticles in the matrix of the hydrate cellulose film (HCF) have been prepared. Ni nanoparticles were synthesized directly in the film, by the diffusion-reduction method. The efficiency of reducers on the chemical reduction of nickel ions has been compared. The crystalline structure of the HCF-Ni samples was analyzed by X-ray diffraction, and their morphology was studied by SEM analysis. The structure of the cellulose remained unchanged was compared to the pristine one. Particle sizes, dependent on the reducer type, were measured in nanometers, according to the micrometer scale.

Keywords: *hydrate cellulose film, nickel nano- and microparticles, X-ray diffraction, SEM analysis*

CHITOSAN/MONTMORILLONITE COMPOSITES AS MATRICES FOR PROLONGED DELIVERY OF SOME NOVEL NITRIC OXIDE DONOR COMPOUNDS BASED ON THEOPHYLLINE AND PARACETAMOL

ANCA COJOCARIU, LENUTA PORFIRE,* CATALINA CHEABURU and CORNELIA VASILE

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Chitosan-montmorillonite nanocomposite hydrogels were prepared by crosslinking chitosan nanocomposites with glutaraldehyde. The following types of clays have been used: Cloisite 15A, Cloisite 93A, Dellite HPS and Dellite 67G. The swelling behaviour of the crosslinked hydrogels containing nanoparticles was followed in acidic media with pH = 2.2. These hydrogels have been loaded with paracetamol, theophylline, two xanthine derivatives 7-[2-hydroxy-3-(4-acetyl-amino-phenoxy)-propyl]-8-R-1,3-dimethyl-xanthine derivatives (with R=H and NO₂ for D1 and respectively D2) and two corresponding new nitric oxide donors (NO-donors) as 7-[2-nitroxyacetyl-oxy-3-(4-acetyl-aminophenoxy)-propyl]-8-R-1,3-dimethyl-xanthine compounds (R=H, NO₂ for 65 and respectively 77 compounds), their controlled release being also evaluated in an acidic solution (pH = 2.2) simulating gastric fluid. The swelling and release kinetics was studied. It has been established that almost all releases involve a non-Fickian or an anomalous transport mechanism.

Keywords: *chitosan, montmorillonite, NO-donor drugs, paracetamol, theophylline, drug release, kinetics*

FABRICATION OF AGAR/BIOPOLYMER BLEND AEROGELS IN IONIC LIQUID AND CO-SOLVENT MIXTURE

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In the present study, a biopolymer (cellulose, rice starch or zein protein) was dissolved in the ionic liquid (1-butyl-3-methylimidazolium chloride) and co-solvent (dimethyl sulfoxide) mixture (1:1 weight ratio), and then blended with the agar solution, followed by gelation at low temperature. The blends were soaked and shaken in 250 mL distilled water, washed and freeze-dried. The agar/biopolymer contents were varied as 1:1, 1:1.5 and 1:2 weight ratios. The bulk densities, melting point temperatures (T_m), FTIR spectra, surface morphologies, surface areas and pore size diameters of the blend aerogels were determined and characterized. The lowest bulk density (25.69 mg cm⁻³) was obtained for agar/rice starch, at a 1:2 weight ratio. DSC thermograms indicated depression in T_m with the addition of biopolymers. FTIR spectra showed the presence of functional groups of blend aerogels components. SEM micrographs of blend aerogels indicated the presence of pores in their internal surface. The BET surface areas and pore size diameters of the blend aerogels (1:2 weight ratio) ranged from 371 to 478 m² g⁻¹ and from 34 to

63 nm, respectively. This study led to the conclusion that the mixture of 1-butyl-3-methylimidazolium chloride and dimethyl sulfoxide could be used as a blend medium for the fabrication of agar/biopolymer blend aerogels.

Keywords: *agar, biopolymer, blend aerogel, ionic liquid, co-solvent*

GRAFTING OF BAMBOO RAYON WITH ACRYLIC ACID AND ITS EFFECT ON CATIONIC DYEING

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Bamboo is considered to be an important biopolymer source with useful applications in various fields, including the textile industry. In the present study, the bamboo rayon fabric has been grafted with acrylic acid using potassium persulfate (KPS) as an initiator. The graft copolymerization parameters were optimized in terms of temperature, time, initiator concentration and monomer concentration. The grafted product was characterized by FTIR, TGA and SEM analyses, and was further evaluated as to properties like moisture regain and yellowness index. The ungrafted and grafted fabrics were then dyed using cationic dyes. The colour strength increased with an increase in the carboxyl content of the grafted product. The dyed samples showed a distinct improvement in fastness properties.

Keywords: *bamboo rayon, grafting, dyeing, cationic dyes*

COMPARATIVE KINETIC ANALYSIS OF ENZYME HYDROLYSIS OF STEAM-EXPLODED WHEAT STRAW

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The present work represents a comparative kinetic analysis of enzyme hydrolysis, using two kinetic variables to describe both reducing sugars and glucose. The preliminary treatment of wheat straw by steam explosion was followed by enzyme hydrolysis using the NS 50013 and β -glucosidase NS 50010 enzyme cellulase complex. The hydrolysis has been described by an exponential kinetic equation valid for processes developed on uniformly inhomogeneous surfaces. The wheat straw–enzyme system has been observed to behave as an energetically homogeneous one. The preexponential factor decreased with the increase of the hydrolysis degree, some kind of compensation effect between the change of activation energy and the preexponential factor being derived. The isokinetic temperature at which a complete compensation was observed was calculated, the rates of reducing sugars and glucose formation being equal.

Keywords: *wheat straw, cellulose, cellulase, exponential equation, correlations, compensation effect*

LDPE/GLUCURONOXYLAN BLENDS: PREPARATION AND STUDY OF THERMAL AND MECHANICAL PROPERTIES

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The continually growing utilization of non-degradable and environment-unfriendly polymeric materials stimulates further research on their possible applications. Estimates show that 2% of all plastics eventually reach the environment, extensively contributing to the currently acute ecological problem. The present study, concentrated on the preparation of natural and synthetic degradable polymers and of their blends, deals with the preparation of low density polyethylene (LDPE) and glucuronoxytan (LX) blends and of their laurate (LaCOLX) with DS = 1.9, in four different amounts (1, 3, 5, 10 wt%), with and without poly(ethylene-coacrylic) acid (EAA) as a compatibilizer, in three different amounts (10, 25 and 50 wt%) with respect to polysaccharide. The compatibility of the LDPE/LaCOLX prepared blends has been studied by ATR (Attenuated Total Reflectance) spectroscopy and REM (Reflection Electron Microscopy). The presence of the LaCOLX filler and the effect of the compatibilizer have been studied *versus* the mechanical properties (tensile strength, elongation at break and Young's Modulus) of the blends. The prepared LDPE/LaCOLX blends, containing 25 and 50 wt% EAA, evidenced good mechanical properties. The increasing amount of LaCOLX and the presence of the compatibilizer had positive effects on the thermal stability of LDPE/LaCOLX blends.

Keywords: *4-O-methyl-D-glucurono-D-xylan, low-density polyethylene, blends, thermo-mechanical properties*

PREPARATION OF ACTIVATED CARBON FROM LIGNIN OBTAINED BY STRAW PULPING BY KOH AND K₂CO₃ CHEMICAL ACTIVATION

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Activated carbon was prepared through chemical activation of lignin from a straw pulping precursor, using K₂CO₃ and KOH as chemical agents. To optimize the preparation method, the effect of the main process parameters (such as impregnation ratio, activation temperature and activation time) on the performance of the obtained activated carbon (expressed in terms of iodine number and yield of activated carbon) was investigated, and the actions of the activating agents were compared. The activated carbon prepared by K₂CO₃, under optimum conditions, permitted to obtain a BET surface area of 1104 m²/g, including an external or non-microporous surface of 417 m²/g, an average adsorption pore width of 2.0 nm, the amount of methylene blue, iodine number and the yield of activated carbon being of 10.6 mL/0.1 g, 1310 mg/g and 19.8%, respectively. As to the carbon activated by KOH under optimum conditions, its BET surface area was of 917 m²/g, including the external or non-microporous surface of 231 m²/g, the average adsorption pore width of 2.5 nm, while the amounts of methylene blue, iodine number and yield of activated carbon were of 9.6 mL/0.1 g, 1180 mg/g and 18.7%, respectively.

Keywords: *lignin, K₂CO₃, KOH, activated carbon*

LIGNIN AS A CARBON SOURCE FOR THE CULTIVATION OF SOME *Rhodotorula* SPECIES

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The paper presents the results obtained in the cultivation of two strains of *Rhodotorula spp.* yeast producing carotenoid pigments, in a medium with different lignin concentrations. Lignins separated from wheat straw (L1) and from Sarkanda grass (L2), provided by Granit Recherche Développement SA, Lausanne, Switzerland, were used for the study. The evolution of yeasts in the culture media in which lignins represented the carbon source was observed as to wet biomass yield, pH and content of carotenoid pigments. At the end of the cultivation process, the residual lignin was recovered by precipitation and subjected to FTIR spectroscopic investigations, to highlight the structural changes caused by these microorganisms. It was found out that biomass yield and carotenoid pigment biosynthesis were influenced by the presence of lignins, which were deeply modified from a structural point of view.

Keywords: *Rhodotorula spp.*, lignin, biomass, carotenoid pigments, FTIR spectroscopy

TCF BLEACHING OF *EUCALYPTUS UROPHYLLA* × *EUCALYPTUS GRANDIS* LH107 OXYGEN-DELIGNIFIED KRAFT PULP – PARTIAL Mg^{2+}/Ca^{2+} SUBSTITUTION FOR CHELANTS IN THE CHELATION STAGE

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The optimization of bleaching, following the sequence of chelation, peroxyacetic acid and hydrogen peroxide treatments of *E. urophylla* × *E. grandis* LH107 oxygen-delignified kraft pulp, was carried out and the optimal parameters were obtained. In the chelation stage, the effect of partial magnesium acetate and calcium acetate substitution for ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid was studied in terms of brightness and polymerization degree of the bleached pulp. It was evidenced that (magnesium acetate + calcium acetate)/ethylenediaminetetraacetic acid was optimal, compared to other treatments in the chelation stage, especially as no washing between (magnesium acetate + calcium acetate) and ethylenediaminetetraacetic acid treatments was necessary. This partial Mg^{2+}/Ca^{2+} substitution for chelants in the chelation stage had a positive impact on totally chlorine-free bleaching, providing pulps with higher brightness and small loss of physical strength.

Keywords: *E. urophylla* × *E. grandis* LH107 kraft pulp, chelation, calcium acetate, magnesium acetate, totally chlorine-free bleaching

A NEURAL FUZZY MODEL APPLIED TO HYDROGEN PEROXIDE BLEACHING OF NON-WOOD SODA PULPS

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A neural fuzzy model was used to examine the influence of pulp bleaching variables of empty fruit bunches from oil palm (EFB) and *Hesperaloe funifera*, such as soda concentration (0.5-3%), hydrogen peroxide concentration (1-10%) and processing time (1-3 h), on Kappa number, brightness and viscosity. The experimental results are reproduced with errors below 10% and 15% for EFB and *H. funifera*, respectively. Bleaching pulp simulation permits to obtain optimal values of the operating variables, so that the properties of bleached pulps will only slightly differ from their best values, while the lower values of the operating variables will save chemical reagents, energy and plant size. Thus, if applying 0.5% soda and 3% peroxide for 3 h, it is possible to get a pulp with a brightness of 74.9% and a viscosity of 716 mL/g, for EFB pulp, and of 63.3% and 584 mL/g, respectively, for *H. funifera* pulp.

Keywords: *non-wood material, pulp, bleaching, hydrogen peroxide, neural fuzzy model*

A HIGHER BRIGHTENING OF MECHANICAL PULPS

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Enhanced utilization of mechanical pulp is an ideal strategy for countries such as China, whose supply of wood and of other high quality biomass is limited. The objective of this study was to minimize the brightness difference between hydrogen peroxide (H₂O₂) bleached mechanical pulps and bleached chemical pulps. The relationships between alkalinity and brightness, alkalinity and H₂O₂ consumption, H₂O₂ application and brightness, H₂O₂ application and its consumption, maximum brightness *versus* H₂O₂ consumption, and extinction coefficient *versus* bleaching time were investigated. The investigation was conducted on Norway spruce (*Picea abies*) thermomechanical pulp (TMP). A bleached brightness of 81.1% was obtained with H₂O₂ application of 4.0% on pulp for 3.0 h at 30.6% consistency and 60 °C. The optimization of the sodium hydroxide application dose was the key to such a high final brightness. Preliminary results suggest that a higher brightness could be obtained if two-stage bleaching with liquor recycle was used. However, the concentrations of TOC and calcium in the recycled liquor have to be carefully controlled.

Keywords: *mechanical pulp, alkalinity, hydrogen peroxide, pulp consistency, brightness*

REMOVAL OF LEAD (II) FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO CHITOSAN BEADS

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The adsorption of Pb (II) ions onto chitosan beads and cross-linked chitosan beads has been investigated. The epichlorohydrin (ECH) was used as a cross-linking agent. Experiments were carried out as a function of pH, stirring time, adsorbent dosage and concentration of Pb (II) ions. The experimental data of the adsorption equilibrium from Pb (II) solution correlated well with the Langmuir isotherm equation. The uptake of Pb (II) ions on chitosan beads was of 72.89 mg Pb (II)/g chitosan, while on ECH cross-linked chitosan beads, it was of 39.42 mg Pb (II)/g chitosan.

Keywords: *chitosan beads, cross-linked chitosan beads, adsorption, metals*

RING WIDTH, PHYSICAL AND MECHANICAL PROPERTIES OF ELДАР PINE (CASE STUDY ON MARZANABAD SITE)

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The present study aims at investigating the variation in average ring width, physical properties (oven-dry density, basic density, volumetric shrinkage, maximum moisture content, percentage of cell wall, percentage of porosity) and mechanical strength (modulus of rupture, modulus of elasticity and compression parallel to the grain) of eldar pine tree wood (*Pinus eldarica* Medw.), cultivated in the north of Iran (Marzanabad site). To carry out the measurements, the test specimens were prepared from three stands and 3 logs at breast height, based on ASTM-D143 standard. The testing samples were cut along radial axis, from pith to bark, to determine annual ring width and physical properties, mature wood being used to measure mechanical strength characteristics. The results showed that oven-dry density, basic density, volumetric shrinkage and percentage of cell wall increased along radial direction from pith to bark, while ring width, maximum moisture content and porosity decreased. The average density at 12% moisture content was of 578.35 kg m⁻³, the modulus of rupture (MOR) – of 73.77 MPa, modulus of elasticity (MOE) – of 6.73 GPa, and compression parallel to the grain – 43.82 MPa. The relationships between ring width and wood density, and between density at 12% moisture content and mechanical strength properties were determined by regression analyses. Positive relationships were found between density at 12% moisture content and mechanical strength properties, while the annual ring width showed a negative correlation with wood density. Overall, eldar pine trees growing in this site have low wood quality, according to the static quality and reference p value (ratio of static bending strength and compression strength parallel to the grain).

Keywords: *Pinus eldarica, ring width, physical properties, mechanical characteristics*

ORGANOSOLV PULPING OF COTTON LINTER. II. EFFECT OF DIOXANE AND ANTHRAQUINONE ON COTTON LINTER PROPERTIES

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Compared to soda pulping, soda-dioxane pulping of cotton linter stabilizes the long-chain cellulose macromolecules against alkaline degradation. The presence of dioxane also results in a more open and accessible fine structure, higher chemical reactivity (upon xanthation), and better viscose filterability. Soda dioxane anthraquinone (AQ) pulping increases the stabilization of cellulose in cotton and gives pulp with higher accessibility, higher chemical reactivity and better viscose filterability, especially at a higher anthraquinone charge – of 0.1%. Acid prehydrolysis of cotton linter prior to soda dioxane AQ pulping favors the penetration of AQ and dioxane molecules among cellulose chains and breaks the hydrogen bonds, thus providing better accessibility of the hydroxyl groups to the reactant molecules, which leads to a pulp with higher chemical reactivity and better viscose filterability. It is evident that both the soda and the prehydrolyzed soda dioxane AQ pulping methods give cotton linter with better reactivity than that of commercial softwood viscose pulp.

Keywords: *anthraquinone (AQ), cotton linters, chemical reactivity (xanthation), prehydrolysis soda pulping, prehydrolysis soda dioxane anthraquinone pulping*

IMMUNOHISTOLOGICAL STUDY OF MANNAN POLYSACCHARIDES IN POPLAR STEM

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Mannan polysaccharides serve as storage reserves in seeds and as structure elements in cell walls, but they may also perform other important functions during plant growth. As one of the major hemicelluloses in angiosperm wood, little is known about the presence and localization of mannan polysaccharides during xylem development in the model tree, *Populus trichocarpa*. In this study, we used mannan-specific recognized antibody to label mannan polysaccharides in stem tissues at different developmental stages. Immunofluorescence microscopy showed that the epitopes were localized in xylem elements, especially in thickened secondary cell walls and interfascicular fibers, while other cell types revealed a low level of mannan epitopes. The signals were possibly masked by acetylation, glucuronoxylans or pectic polymers depended on cell types, but were less affected by lignification. These results demonstrate that mannans are of particular significance in the secondary cell walls of the xylem tissue, which provides us a further opportunity to study the biosynthesis of mannans during xylem development in wood.

Keywords: *carbohydrate-binding module (CBM), immunofluorescence, mannan polysaccharides, monoclonal antibody, plant cell walls*

ANATOMY, CELL WALL ULTRASTRUCTURE AND INHOMOGENEITY IN LIGNIN DISTRIBUTION OF *BROUSSONETIA PAPYRIFERA*

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Broussonetia papyrifera (Linn.) Vent has been attracting interest recently as a valuable wood source for pulping and papermaking manufacturing. The present study aims to determine the anatomical structure, ultrastructure and distribution of lignin in the fiber cell walls of this shrub, using electron microscopy, fluorescence microscopy (FM) and confocal Raman microscopy, which, to our knowledge, has not been reported before. Anatomical observation by electron microscopy indicates that *Broussonetia papyrifera* (Linn.) Vent is a diffuse-porous wood, consisting of fibers, vessel members and ray parenchyma. As shown by TEM images, the fiber cell wall is typically divided into three layers: middle lamellar (ML), primary wall (P) and secondary wall (S1, S2 and S3). TEM and fluorescence analyses showed that lignin concentrations in compound middle lamella (CML) and cell corner (CC) were higher than in the secondary wall. More detailed information on lignin composition and distribution in different cell wall layers was obtained *in situ* by confocal Raman microscopy. Raman images of lignin distribution were generated by integrating over the intensity of the 1605 cm⁻¹ band (1712-1519 cm⁻¹). Raman images and spectra of lignin in various morphological regions revealed that the lignin content followed a decreasing order: CC > CML > S2.

Keywords: *Broussonetia papyrifera* (Linn.) Vent, anatomy, ultrastructure, lignin distribution, fluorescence microscopy (FM), confocal Raman microscopy

STRUCTURAL CHARACTERIZATION OF HEMICELLULOSES FROM BAMBOO CULMS (*NEOSINOCALAMUS AFFINIS*)

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Dewaxed bamboo culms (*Neosinocalamus affinis*) were sequentially extracted with distilled water and 70% ethanol at 80 °C for 3 h, 0.2 and 0.5 M NaOH, 70% ethanol containing 0.6 M NaOH, and 1.0 and 2.0 M NaOH at 50 °C for 3 h using a solid to liquid ratio of 1:25 (g/mL). The hemicellulosic fractions obtained were characterized by high performance anion exchange chromatography (HPAEC), gel permeation chromatography (GPC), Fourier transform infrared (FT-IR) spectroscopy, ¹H and ¹³C nuclear magnetic resonance (NMR), and 2D heteronuclear single quantum coherence (HSQC) NMR spectroscopies. Compared to the water-soluble fraction, the alkali-soluble hemicelluloses primarily consisted of xylose (73.5-92.7%), and had a more linear structure and larger macromolecules, evidenced by Xyl/Ara ratios (11.0-22.9) and higher average molecular weights (*M_w* = 41200-68770 g/mol). Increasing the alkaline concentrations from 0.2 to 2.0 M NaOH decreased the molecular weights from 68770 to 42790 g/mol, but increased the Xyl/Ara ratios from 11.0 to 22.9 in the hemicellulosic fractions. The

fractions isolated with 0.5 and 1.0 M NaOH were found to be composed of a linear (1→4)- β -D-xylopyranosyl main chain substituted by a small amount of L-arabinofuranosyl at C-2 and/or C-3 together with a minor quantity of 4-O-methylglucuronic acid at C-2, representing typical polysaccharide structure in bamboo.

Keywords: *bamboo culms, hemicelluloses, structural characterization, xylan, NMR*

ISOLATION AND FRACTIONATION OF HEMICELLULOSES FROM *SALIX PSAMMOPHILA*

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Water- and alkali-soluble hemicelluloses were isolated with hot water and 10% KOH at 25 °C from dewaxed and delignified *Salix psammophila*, respectively. The alkali-soluble hemicelluloses were then successively subfractionated by neutralization and subjected to gradual precipitation in the end, using ethanol concentrations of 15, 30, 45, 60, 75 and 90%, respectively. Chemical composition, physico-chemical properties and structures of the 8 precipitated hemicellulosic fractions obtained were established by sugar analysis, molecular weight determination, FT-IR, ¹H, ¹³C and 2D HSQC NMR. It was found out that the water-soluble hemicelluloses were more branched, having a low molecular weight (6060 g mol⁻¹), whereas the alkali-soluble hemicelluloses were less branched, having higher molecular weights (17110-85540 g mol⁻¹), with xylose and uronic acid as the main sugar components. In addition, the less branched hemicelluloses with large molecules were precipitated in lower ethanol percentages while, with increasing ethanol concentration, more branched hemicelluloses with low molecular weights were obtained. That is why, linear hemicelluloses could be recovered at lower ethanol concentrations, and more branched hemicelluloses could be obtained at higher ethanol concentrations. According to FT-IR, ¹H, ¹³C and 2D HSQC NMR studies, the alkali-soluble hemicelluloses had a main structure composed of a (1→4)-linked β -D-xylopyranosyl backbone with 4-O-methyl- α -D-glucuronic acid attached to the O-2 of the xylose residues.

Keywords: *Salix psammophila, hemicelluloses, alkali, fractionation, xylans*

STRUCTURAL CHARACTERIZATION OF ISOLATED LIGNINS FROM *CARAGANA KORSHINSKII* KOM.

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Lignin fractions, isolated from *Caragana korshinskii* Kom., were subjected to extensive structural characterization, including chemical component analysis, gel

permeation chromatography (GPC), Fourier transform infrared (FT-IR), ultraviolet (UV), thermo gravimetric/differential thermal analysis (TGA/DTA), and nuclear magnetic resonance (NMR). The structural differences caused by different solvent treatments (water, ethanol and NaOH alkaline solution in concentrations of 1%, 3%, 5%, 8% and 10%) were studied comparatively. The results indicated that 84.1% lignin was fractionated with the successive treatments. The weight-average molecular weights of all lignin fractions ranged from 926 to 2686 g/mol. Noticeable amounts of esterified hydroxycinnamic acids were identified in the lignin fractions obtained from water and ethanol treatments. The cleavage of ester and other types of lignin-carbohydrate interaction was obviously induced under basic conditions, and the purity of the isolated lignin was consequently improved. However, the thermal stability of the lignin fraction was slightly enhanced. Some substructures, such as β -O-4, β - β' , were also detected in *C. korshinskii* Kom. lignin by NMR technology.

Keywords: Caragana korshinskii Kom., lignin, fractionation, structural characterization

FRACTIONAL AND STRUCTURAL CHARACTERIZATION OF ALKALINE LIGNINS FROM CAREX MEYERIANA KUNTH

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Successive extractions with distilled water, 0.25% NaOH-95% ethanol solution, 0.5%, 1%, 1.5% and 2% NaOH aqueous solutions at a solid-liquid ratio of 1:25 (g mL⁻¹) at 80 °C for 3 h from *Carex meyeriana* Kunth released 4.4%, 6.9%, 10.9%, 13.2%, 7.9% and 4.9% of the original lignin, respectively. The physico-chemical properties and structural features of these lignin fractions were comprehensively characterized by HPLC, GPC, NMR spectroscopy, and TGA. The alkali concentration increment had a positive influence on the purity of the lignin fractions, but a negative influence on the average molecular weight and thermal stability. The FT-IR spectra showed that the lignin fractions had similar structural features with those of HGS lignin. The ¹H, ¹³C and 2D NMR spectra illustrated that typical lignin fractions had predominantly β -O-4 aryl ether linkages followed by β - β and β -5' ones.

Keywords: *Carex meyeriana* Kunth, alkaline lignin, fractionation, β -O-4 aryl ether linkages

PHYSICO-CHEMICAL CHARACTERIZATION OF DIFFERENT ALCOHOLSOLUBLE LIGNINS FROM RICE STRAW

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The treatment of dewaxed rice straw with 60% methanol, 60% ethanol, 60% *n*-propanol, 60% *n*-butanol, 60% ethanol containing 0.01 M HCl and 60% ethanol

containing 0.25 M NaOH at 75 °C for 3 h resulted in the solubilization of 14.6, 13.0, 16.3, 12.2, 13.0 and 75.6% of the original lignin, respectively. All alcohol-soluble lignin fractions showed spectral features of GSH-type lignin. The yield and purity of the acid-insoluble lignin extracted with 60% ethanol containing 0.25 M NaOH was much higher than of those prepared with other alcohols. The purity of lignin prepared with different alcohols followed the order: methanol > *n*-propanol > *n*-butanol > ethanol. Furthermore, the treatment of 60% ethanol under alkali catalyst produced purer lignin than the 60% ethanol treatments with or without acid catalyst. The six alcohol-soluble lignin fractions were comparatively characterized by both destructive methods, such as alkaline nitrobenzene oxidation, and non-destructive techniques, such as ultraviolet (UV), Fourier Transform Infrared (FTIR), ¹³C and two-dimensional Heteronuclear Single Quantum Correlation Nuclear Magnetic Resonance (¹³C and 2D-HSQC NMR) Spectroscopy, and Gel Permeation Chromatography (GPC). The 2D-HSQC NMR spectrum showed that the prominent linkage of the lignin fraction obtained with 60% ethanol containing 0.25 M NaOH was between the β -O-4 ether substructure and the β -5' and β - β' ones.

Keywords: *rice straw, lignin, alcohol, 2D-HSQC, FT-IR, ¹³C NMR*

LIGNIN PURIFICATION WITH GREEN SOLVENTS

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Nowadays, lignin is gaining importance as a potential source for aromatic chemicals. Commercial lignins are usually contaminated with cellulose, hemicelluloses and other inorganic impurities, which constitute an obstacle in their direct processing for obtaining aromatic precursors. In this work, lignins obtained from *Malus domestica* by alkaline extraction (7.5% NaOH, 90 min, 90 °C) and organosolv (60% ethanol, 90 min, 180 °C) processes were treated with green solvents, to reduce their impurities. The green solvents used were water and [BMI][MeSO₄], and the obtained lignin was characterized by different techniques (ATR-IR, TGA, and HPLC). The results showed that soda lignin has more impurities than organosolv lignin, and that ionic liquid (IL) is the best purification method.

Keywords: *lignin, ionic liquid, purification*

ISOLATION AND IDENTIFICATION OF MICROORGANISMS FROM SOIL ABLE TO LIVE ON LIGNIN AS A CARBON SOURCE AND TO PRODUCE ENZYMES WHICH CLEAVE THE β -O-4 BOND IN A LIGNIN MODEL COMPOUND

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Several strains of fungi were isolated and identified from Scandinavian soil using agar plates with lignin as a carbon source. The strains grew significantly faster on this medium than on control plates without lignin. Different types of technical

lignins were used, some of which contained trace amounts of sugars, even if the increased growth rate seemed not related to the sugar content. Some strains were cultivated in shaking flask cultures with lignin as a carbon source, with lignin apparently consumed by microbes – while accumulation of the microorganism biomass occurred. The cellfree filtrates of these cultures could reduce the apparent molecular weights of lignosulphonates, while the culture filtrate of one strain could cleave the β -O-4 bond in a lignin model compound.

Keywords: *lignin biodegradation, carbon source, soil microorganisms, extracellular enzymes, β -O-4 bond*

SYNTHESIS AND PROPERTIES OF GLYCIDYL-METHACRYLATE-GRAFTED EUCALYPTUS FIBERS

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To promote the value-added utilization of natural, renewable and sustainable eucalyptus fibers, a glycidyl-methacrylategrafted fiber (GMAGF) was synthesized by grafting glycidyl methacrylate (GMA) onto bleached eucalyptus fiber induced by a Fe^{2+} - H_2O_2 -thiourea dioxide (TD) redox system, *via* cross-linking reaction of diallyl phthalate (DAP), followed by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) characterization. The effects of the dosage and concentration of DAP, H_2O_2 and TD and of the temperature of the reaction system on the grafting percentage (G%) and oil absorptivity (OAP) of GMAGF were studied. The main results obtained are as follows: (1) G% increased as the monomer dosage increased to a given content; (2) GMAGF crystallinity considerably decreased, compared to that of the original fiber; (3) GMAGF, carrying glycidyl groups and improving its non-polarity, is able to adsorb hydrophobic substance molecules like diesel; OAP rose with the increase of grafting percentage; a maximum OAP (17.6 g/g) improvement, by 320%, compared to the original fiber, was obtained when G% ranged from 85 to 90%, at a DAP dosage of 5.0%; (4) OAP was closely related to both G% and the cross-linked network formed between copolymers.

Keywords: *glycidyl methacrylate, oil absorptivity, contact angle, grafted eucalyptus fiber*

PRETREATMENT OF FURFURAL RESIDUES WITH ALKALINE PEROXIDE TO IMPROVE CELLULOSE HYDROLYSIS. CHARACTERIZATION OF ISOLATED LIGNIN

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Furfural residues were pretreated with alkaline peroxide (AP) to remove lignin and then hydrolyzed to produce glucose. The maximum glucose yield – of 92.38% – was achieved when the pretreated sample with a lignin removal of 56.7% was hydrolyzed for 120 h at an enzyme loading of 25 FPU/(g cellulose), which was 48.3% higher than that attained from the raw materials. However, the glucose yield decreased when the removal of lignin exceeded 56.7%. The effect of enzyme loading on enzymatic hydrolysis was also investigated. In addition, three AP lignin fractions were successively isolated and comparatively characterized by gel

permeation chromatography, Fourier transform infrared spectroscopy, ^{13}C -nuclear magnetic resonance spectroscopy and thermal analysis. Depolymerization, including destruction of the aromatic skeleton in lignin, and repolymerization of AP lignin occurred during peroxide delignification; however, depolymerisation dominated the reaction, especially at high pretreatment severity. It was also found out that the AP treatment increased the thermal stability of the lignin fractions.

Keywords: *alkaline peroxide pretreatment, furfural residues, enzymatic hydrolysis, lignin removal, lignin structure*

ISOLATION AND CHARACTERIZATION OF LIGNIN FROM PREHYDROLYSIS LIQUOR OF KRAFT-BASED DISSOLVING PULP PRODUCTION

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Lignin separation from the prehydrolysis liquor (PHL) resulting from dissolving pulp production will create new revenue for the dissolving pulp sector, fitting well into the integrated forest biorefinery concept. Lignin will likely become a valuable source of renewable energy (e.g. biofuel) and biomaterials (e.g. plastics, adhesives). In this study, lignin was isolated from PHL by acidification with a dilute H_2SO_4 solution, followed by purification through dissolution in a dioxane solution (9:1) and re-precipitation with diethyl ether. The characteristics of PHL lignin were compared with those of the dioxane lignin isolated from hardwood (maple, poplar and birch wood chips, in a ratio of 7:2:1), which is the raw material used for dissolved pulp production. Thus, the obtained lignin samples were characterized by UV, FTIR, ^1H -NMR spectroscopy, molecular weight determination, elemental and methoxyl analyses. The absorptivity of hardwood lignin at 276 nm was of $10.0 \text{ l g}^{-1}\text{cm}^{-1}$, while that of PHL lignin was of $17.2 \text{ l g}^{-1}\text{cm}^{-1}$. The presence of condensed structures in PHL lignin (intense bands at 870 and 890 cm^{-1} in the FTIR spectrum) was observed. The lignin isolated from PHL has low molecular weight, and a low methoxyl group per C9 unit, in comparison with other lignin samples. ^1H -NMR data indicate a significant increase of the phenolic hydroxyl content in PHL lignin, caused by the cleavage of the aryl-ether bonds during prehydrolysis. Based on these results, it can be concluded that the lignin isolated from PHL may have a potential for polymer industry.

Keywords: *PHL lignin, dissolving pulp process, phenolic hydroxyl group, molecular weight, methoxyl group*

INVESTIGATING THE LIGNOCELLULOSIC COMPOSITION DURING DELIGNIFICATION USING CONFOCAL RAMAN SPECTROSCOPY, CROSSPOLARIZATION MAGIC ANGLE SPINNING CARBON 13 – NUCLEAR MAGNETIC RESONANCE (CP/MAS 13C-NMR) SPECTROSCOPY AND ATOMIC FORCE MICROSCOPY

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Changes in the lignocellulosic composition of four hardwoods, *i.e.* *Eucalyptus grandis camaldulensis* (*E. gc*), *E. grandis urophylla* (*E. gu*), *E. dunnii* and *E. nitens*, were investigated during different delignification processes using confocal Raman spectroscopy, Cross-Polarization Magic Angle Spinning Carbon 13 - Nuclear Magnetic Resonance (CP/MAS 13C-NMR) spectroscopy and Atomic Force Microscopy (AFM) in conjunction with image analysis. The confocal Raman results evidenced differences in the distribution of lignin between the middle lamella and the secondary cell wall layer for all clones and species investigated. The *E. gc* clone showed high levels of lignin in the secondary cell wall layer, compared to the *E. gu* clone, *E. dunnii* and *E. nitens* species. CP/MAS 13C-NMR spectroscopic results revealed an increase in cellulose crystallinity during chlorite delignification, acid bisulphite pulping and subsequent oxygen delignification, accompanied by an increase in the cellulose 'aggregate' area with a corresponding decrease in the 'matrix' area for each clone and species.

Keywords: *atomic force microscopy, cellulose 'aggregate' area, cellulose crystallinity, confocal Raman spectroscopy, 'matrix' area, CP/MAS 13C-NMR spectroscopy*

EFFECTS OF BEATING ON TOBACCO STALK MECHANICAL PULP

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Tobacco stalks represent a type of abundant renewable resources. In the present study, tobacco stalks were treated by water at 60 °C for 100 min, to remove water-soluble matters, and then refined at concentrations of 20% (m/m), by refiner mechanical pulping (RMP). To obtain good fiber fibrillation, the pulp was beaten in a PFI mill. The fiber parameters were detected by Kajaani FS-300 and SEM. The analysis revealed that the length of the fibers was similar to that of non-wood material pulp, and also that beating affected fiber morphology. At a PFI mill revolution number of 3500 r (beating degree 33oSR), the physical properties of paper reached the optimum values. The water permeability of the paper recommended it as a hydrophilic material suitable for subsequent papermaking processing. In conclusion, the properties of tobacco stalk pulp recommend it as a papermaking material.

Keywords: *tobacco stalk, beating, fiber morphology, SEM analysis, physical properties of paper, water permeability*

INFLUENCE OF XYLANASE PRETREATMENT ON REFINING ENERGY AND BRIGHTNESS OF P-RC APMP PULP OF ITALIAN BLACK POPLAR BRANCHES

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The study evaluates the influence of commercial xylanase (AU-PE89 and 51024) pretreatment applied in different refining stages of pulping on refining energy and properties of P-RC APMP pulp of Italian black poplar branches. Compared to the non-pretreated P-RC APMP pulp, the refining energy consumption of the pulps pretreated by xylanase before the second and third refining stages, performed during P-RC APMP pulping, decreased by 8-17% and 9-21%, respectively, while the brightness value of the pretreated pulp improved by 1.0-2.3 and 0.9-1.2% ISO, respectively, with minor changes in pulp strength properties. The pretreated pulp had longer fiber length, a higher fiber torsion index, smaller fiber width and a higher degree of cellulose crystallinity. The effect of xylanase pretreatment before the third refining stage was better, compared to the one applied before the second stage, as to refining energy saving, while the effect of xylanase AU-PE89 pretreatment was better than that of xylanase 51024.

Keywords: *Italian black poplar branches, xylanase, pretreatment, P-RC APMP pulp, refining energy*

INCLUSION COMPLEXES OF PROMETHAZINE WITH MONOCHLOROTRIAZINYL- β -CYCLODEXTRIN

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Formation of inclusion complexes of monochlorotriazinyl- β -cyclodextrin with promethazine was studied, for establishing the optimal conditions of their formation, in view of subsequent grafting on cellulose textiles with potential medicinal use. The infrared spectral study of inclusion in solid state indicated that the complex can be even formed by physically mixing the two substances. By the co-precipitation method, one can obtain a complex with obvious spectral changes, compared to the spectra of the two substances viewed separately. The stability constants of the complex in aqueous medium, in both acid and alkaline environment, were established by means of UV spectra and Benesi-Hildebrand equation. The value of the stability constant obtained is ten times higher in acid than in alkaline medium, which indicates that the alkaline medium is more favourable for producing the complex.

Keywords: *promethazine, monochlorotriazinyl- β -cyclodextrin, UV spectra, Benesi-Hildebrand equation*

SYNTHESIS AND CHARACTERIZATION OF NEW HETEROCYCLIC COMPOUNDS WITH POTENTIAL ANTITUBERCULOSIS ACTIVITY AND THEIR IMMOBILIZATION ON POLYMER SUPPORTS

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New biologically active compounds, obtained by synthesizing new hydrazides derived from benzoxazolyl-2- mercaptoformic acid, respectively benzoxazolyl-2-mercaptoacetic acid, have been chemically immobilized onto poly (maleic anhydride-*alt*-vinyl acetate) supports, forming drug-polymer conjugates with controlled delivery. The reaction products were characterized by elemental and spectral analyses (FT-IR, ¹H-NMR). Toxicological and tuberculostatic activity tests recommend certain reaction products as therapeutic candidates with pharmacological application.

Keywords: *2-mercapto-benzoxazole derivatives, hydrazides, drug-polymer conjugates, tuberculosis inhibitors*

LIGNIN SEPARATED FROM THE HYDROLYZATE OF THE HYDROTHERMAL TREATMENT OF BIRCH WOOD AND ITS SURFACE PROPERTIES

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The chemical composition, structural features and surface active properties of alkali lignin, separated from the hydrolyzate of the birch wood sawdust treatment in a moderately alkaline water solution at a temperature below 100°C, were studied. The separated lignin was rich in p-oxyphenylpropane fragments and carbonyl groups, but contained a relatively low amount of aliphatic hydroxyl and methoxyl groups. The carboxyl groups were weaker than those in kraft lignins. The lignin aqueous solutions were structured, containing both nano- and micro-sized colloidal particles. The pronounced amphiphilic character of the lignin molecules governed their low critical micelle concentration (CMC) values and enhanced the surface activity at the water-air and liquid-liquid interfaces. When decreasing the pH and increasing ionic strength, the surface activity of lignin at the air-water interface grew, while that at the oil-water interface dropped. Scanning electron microscopy (SEM) images revealed that the microstructure of the lignin surface consisted of globules, forming extended clusters of the “grape-bunches” type.

Keywords: *alkali lignin, globular structure, hydrolyzate, nanoparticles, oil-in-water emulsion, polyelectrolyte effect, stabilization, surface tension, wood hydrothermal treatment*

SEPARATION OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS BY CELLULOSE MODIFIED WITH D-GLUCOSE AND QUATERNARY AMMONIUM GROUPS

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A novel method for D-glucose (D-Glu) and trimethylammonium chloride immobilization onto the surface of cellulose powder was studied. Cellulose powder was grafted with vinyl monomer glycidyl methacrylate (GMA), using ceric ammonium nitrate as an initiator, and further derived with quaternary ammonium groups to build the D-GluN⁺-type cellulose absorbent (Cell-g-GMA-D-GluN⁺). Epoxy cellulose was found to contain 5.48 mmol/g epoxy groups. The adsorption process of modified cellulose was described by the Langmuir model of adsorption well, the maximum adsorption capacity of chromium (VI) reaching a value of 71.79 mg/g. Adsorption–desorption tests of the D-GluN⁺-type cellulose derivatives showed a good reproducibility of the adsorbent, so that the adsorbent could be reused for at least six times.

Keywords: *chromium (VI), modified cellulose, D-glucose, trimethylammonium chloride*

FORMATION OF ACETIC AND FORMIC ACID IN UNMODIFIED AND MODIFIED PAPERS DURING ACCELERATED AGEING

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Organic acids are spontaneously generated in significant concentrations during natural ageing of all cellulose-based papers, the alkaline ones included. The present study reviews the paper degradation research devoted to the identification and determination of the role of light products formed during paper ageing. Accelerated ageing was performed at 98 °C and 50% RH, for 60 days. The main objective of the present study was to investigate the influence of the Mg cations included in the alkaline reserve on the progress of degradation during accelerated ageing of paper. The changes in the ratio of acetic/formic acids and the role of Mg²⁺ ions during accelerated ageing – in the investigated unmodified and modified papers – with dispersion of MgO or MgO and MMMC (methyl methoxy magnesium carbonate) mixture are discussed. The obtained results show that, during accelerated ageing, acetic and formic acids are produced in both unmodified and modified papers. The higher content of Mg²⁺ ions in modified paper increases the formation of acetic and formic acids more than in unmodified paper. The reason for this behaviour might be the strong promoting role played by the Mg²⁺ ions in the formation of the mentioned organic acids.

Keywords: *acetic acid, formic acid, degradation, Mg²⁺ ions*

EFFECT OF ACETATE ON FERMENTATION PRODUCTION OF BUTYRATE

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A carbon source for the fermentation production of butyrate is xylose extracted from ligno-cellulosic material by hot water extraction. Although this auto-hydrolysis of hemicellulose can provide a low-cost source of xylose, the process generates a high level of acetic acid that might inhibit subsequent fermentations. This study focuses on the effects of acetate on the production of butyrate from xylose by batch fermentations with a selected strain *Clostridium tyrobutyricum*. At initial acetate concentrations of 17.6 g L⁻¹ and 26.3 g L⁻¹ in the media, *C. tyrobutyricum* cultures exhibited a lag phase (45 and 118 hours, respectively) in terms of sugar consumption, butyrate production and cell biomass growth, lowering the overall production rate. Butyrate fermentations performed with high concentrations of acetate in the media demonstrated a re-uptake of acetate into the butyrate production pathway and after the lag phase, all cultures adapted to the inhibitory acetate, which increased the final butyrate yields by 12.6% (32.6 g L⁻¹ compared to 28.5 g L⁻¹).

Keywords: *Clostridium tyrobutyricum*, butyrate, xylose fermentation, hemicellulose utilization, acetate inhibition

CELLULOSE PRETREATMENT WITH 1-METHYL-3-METHYLIMIDAZOLIUM DIMETHYLPHOSPHATE FOR ENZYMATIC HYDROLYSIS

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This work has been focused on a cellulose pretreatment process using 1-methyl-3-methylimidazolium dimethylphosphate ([DMIM] DMP) for subsequent hydrolysis over cellulase. Different operational variables (the amount of [DMIM] DMP, the pretreatment temperature, the pretreatment period) affecting the pretreatment were investigated. Additionally, the crystallinity index (CI) was characterized by FT-IR spectroscopy. The CI values including CI (IR), CI (IR-CI) and CI (IR-CII) were calculated. When correlated with these values, the concentrations of total reducing sugar (TRS) released after the pretreatment of microcrystalline cellulose (MC) were found to show a distinct relationship with the [CI (MC-CI) – CI (IR-CI)] values, and the result was verified by X-ray diffraction (XRD). Consequently, the optimum pretreatment conditions of crystalline transformation (from cellulose I to cellulose II) characterized by XRD are different from those of hydrolysis. This result suggests that other factors, in addition to cellulose crystallinity, affect the yields of glucose and total reducing sugar obtained by hydrolysis.

Keywords: enzymatic hydrolysis, crystallinity index, ionic liquid, pretreatment

REACTIVE RED 3 AND DIRECT BROWN 95 DYES ADSORPTION ONTO CHITOSAN

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The chitosan availability in adsorption of C.I. Reactive Red 3-18159 (RR-3) and C.I. Direct Brown 95-30145 (DB-95) dyes from aqueous solutions was investigated by using the batch method. Experiments were carried out as a function of contact time, dye concentrations and temperature. The influence of pH and sodium chloride concentration were also investigated. The adsorption parameters were determined based on Langmuir and Freundlich isotherms obtained from the equilibrium adsorption data for the reactive dye and for the direct dye, while the kinetic and thermodynamic parameters were used to establish the adsorption mechanism. As an adsorbent, chitosan was found to prefer the RR-3 dye, retaining up to 151.52 mg textile dye per gram at 20 °C, whereas a retention of only 41.84 mg textile dye per gram at 50 °C has been achieved for DB-95 dye.

Keywords: *adsorption isotherm, adsorption kinetics, chitosan, direct dye, reactive dye*

EXPERIMENTAL CHARACTERIZATION OF SHRINKAGE AND DENSITY OF *TAMARIX APHYLLA* WOOD

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Athel (*Tamarix aphylla*) is one of the important species planted for fixing the dune sands in the Iranian hot desert region. The variations in physical properties of Athel wood were studied on ten 48-52 year-old trees from the southeastern part of Iran (Zabol region). The samples were taken at breast height and from the entire disc surface. The physical properties, including oven-dry density (686 Kg m⁻³), basic density (521 Kg m⁻³), tangential shrinkage (7.13%), radial shrinkage (4.14%), longitudinal shrinkage (1.96%), volumetric shrinkage (13.23%), fiber saturation point (25.4%), maximum humidity content (125.60%), tangential to radial shrinkage ratio (1.72), percentage of cell wall (46.06%) and porosity (53.93%), were determined. The relationship between wood density and shrinkage (tangential, radial and longitudinal) and maximum moisture content was determined by Pearson matrix correlation analyses. It was found that the relationships density–shrinkage and density–maximum humidity content were positive and negative, respectively. The correlation coefficient between wood density and longitudinal shrinkage was found to be higher than those of the relationships wood density–tangential shrinkage and wood density–radial shrinkage.

Keywords: *Tamarix aphylla, density, shrinkage, fiber saturation point, maximum moisture content, cell wall, porosity*

A BIOREFINERY INITIATIVE IN PRODUCING DISSOLVING PULP FROM DHAINCHA (*SESBANIA ACULEATA*) – A SHORT-ROTATION CROP

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Dhaincha (*Sesbania aculeata*) is a short-rotation crop cultivated for its nutritional value to soil. Dhaincha chips were pre-extracted with acidic and alkaline solutions at 165 °C for 60 min to produce dissolving pulp. The pH of the preextracted liquor reached a near-neutral value (pH 6.8), when 3% NaOH was added. Pre-extraction dissolved 17-20% biomass from dhaincha. From the pre-extraction liquor, 1.6-2.6% lignin, 1.5-1.7% acetic acid and about 7% sugars (on o.d. dhaincha) were extracted. Pre-extracted dhaincha was cooked by the kraft process. Pre-extraction with alkaline solution produced higher pulp yield and lower kappa number than simple water and H₂SO₄-water pre-extraction. After D0EpD1 bleaching, the pre-extracted pulp showed almost similar pulp brightness. The pulp obtained after alkaline preextraction exhibited higher pulp viscosity and higher α -cellulose content. It can be concluded that pre-extraction at near-neutral pH produces pulp with higher yield, purity and viscosity with good brightness.

Keywords: Dhaincha, pre-extraction, pulp yield, viscosity, pulp brightness

INVESTIGATION OF STRUCTURAL AND THERMAL PROPERTIES OF DIFFERENT WOOD SPECIES TREATED WITH TOLUENE-2,4-DIISOCYANATE

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A chemical reaction between some reactive compound of different wood species and a chemical reagent, without catalyst, to form a covalent bond between them was performed in the present study. Wood samples of a softwood species, namely spruce (*Picea abies*), and a hardwood one, eucalyptus (*Eucalyptus globulus*), were treated with toluene-2,4-diisocyanate (TDI) at 60 °C, for 1.5 h. Structural changes in wood structure were evidenced by means of Fourier Transform infrared spectroscopy (FTIR). Spectra data gave good evidence for the formation of carbamate ester (urethane bonds) in the treated wood, with some differences related to the wood species. The thermal behavior of untreated and treated wood was also evaluated.

Keywords: softwood, hardwood, toluene-2,4-diisocyanate (TDI), FTIR analysis, TG-DTG-DSC analysis

USE OF NANOTECHNOLOGY FOR HIGH PERFORMANCE CELLULOSIC AND PAPERMAKING PRODUCTS

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Nanotechnology is of great importance in almost all modern day industries targeting high quality, efficiency and market potential. The large interest in the nano-scale range is due to the fact that nanomaterials can have enhanced properties, as compared to the same material with larger particle size. The modification of cellulose into different types of micro- and nano-structures has been reported in literature. In papermaking, nanotechnological advances were reported about a decade ago, though it could not be commercialized at a large scale. Nanofiber, nanofiller, nanocomposites and nanoscale chemicals to be used in pulp and paper applications are in main focus. Because of the wide abundance, renewable and environmentally benign nature, and outstanding mechanical properties of nano-based cellulosic materials, great attention has been paid to their use in pulp and paper, and other industries. There are a few challenges associated with their efficient use at a commercial scale, such as cost, lack of compatibility among materials and knowledge gap. This review of recent work discusses the manufacturing, application and properties of different nanoparticles and nano-based technological developments reported by researchers worldwide, related to cellulose and paper manufacturing.

Keywords: *Cellulose, microcrystalline cellulose, microfibrillated cellulose, nanocomposites, nanofiller, nanofiber*

THE EFFECT OF RELATIVE HUMIDITY ON THE PHYSICAL AND MECHANICAL PROPERTIES OF OIL PALM TRUNK AND RUBBERWOOD

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Some physical and mechanical properties of oil palm trunk (OPT, *Elaeis guineensis*) and rubberwood (*Hevea brasiliensis*) were investigated by exposing to relative humidity, and sorption, dimensional changes and compression strength were determined. Both OPT and rubberwood showed a sigmoidal relationship of relative humidity and equilibrium moisture content. The fiber saturation points of OPT and rubberwood were found in the ranges 22-25% and 25-27%, respectively. The percent swelling of OPT in both the tangential and radial directions was almost identical – of about 2.2%. On the other hand, the swelling of rubberwood was of about 5.7% in the tangential direction and of about 3.2% in the radial direction. The ratio of tangential to radial swelling for oil palm trunk ranged from 1.03 to 1.12, while that for rubberwood ranged from 1.56 to 2.09. The longitudinal specific compression strength of OPT and rubberwood was affected by the moisture content.

Keywords: *oil palm trunk, rubberwood, compression strength, relative humidity, swelling*

ISOLATION AND PHYSICO-CHEMICAL CHARACTERIZATION OF LIGNIN FROM HYBRID POPLAR IN DMSO/LiCl SYSTEM INDUCED BY MICROWAVE-ASSISTED IRRADIATION

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In this paper, the effect of microwave-assisted heating (60, 80, 100 and 120 °C) on lignin separation from ball-milled hybrid poplar wood in dimethyl sulfoxide and lithium chloride (DMSO/LiCl) system was examined. The isolated lignin fractions were characterized by HPAEC (high-performance anion exchange chromatography), FT-IR, ¹³C NMR and 2D-HSQC NMR techniques. The results showed that extraction of lignin assisted by microwave irradiation at 60, 80, 100 and 120 °C resulted in an increase of lignin yield by 2.4, 8.8, 13.5 and 24.6% (% Klason lignin), respectively. The content of neutral sugars in these lignin fractions was relatively lower as compared with the milled wood lignin (MWL) obtained by the classical method. Structural characterization by 1D and 2D NMR demonstrated that these lignin fractions were classified as syringyl-guaiacyl lignin as they were mainly composed of syringyl units with noticeable amounts of guaiacyl units. In addition, the results of semi-quantitative NMR spectroscopy showed that these lignin fractions mainly consisted of β -aryl ether linkage (β -O-4', 53.3-74.1%) and resinol substructure (β - β ', 15.1-28.5%) combined with small quantities of phenylcoumaran substructure (β -5', 3.1-8.2%) and spirodienone substructure (β -1', 3.2-8.4%).

Keywords: *Hybrid poplar, lignin, microwave-assisted heating, DMSO/LiCl, 2D-HSQC NMR*

NEUTRON TECHNIQUES FOR WOOD CHEMISTRY

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When a new biopolymer is incorporated into an industrial process (e.g. to improve the specificity of an emulsion or a foam or to replace a similar polymer derived from petrochemicals), its interactions with the other components of the solutions have to be well understood to ensure a controlled process. Such knowledge can be obtained through neutron scattering experiments. For instance, neutron scattering experiments allow investigation of the interaction of polysaccharides in solution with surfactants or evolution of films at the surface of a solution. Furthermore, neutron scattering allows us to study how water or a polymer modifies the structure of cellulose fibres, while inelastic and quasi-elastic neutron scattering allows us to follow the dynamics of water adsorption.

Keywords: *neutron, characterisation, structure, polymer, wood*

RECOVERY OF ANTHOCYANINS FROM GRAPE POMACE EXTRACT (PINOT NOIR) USING MAGNETIC PARTICLES BASED ON POLY (VINYL ALCOHOL)

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The paper is devoted to the possibility of separating a concentrate of anthocyanin pigments from an aqueous extract (0.1% HCl) of grape pomace (Pinot noir) with the use of magnetic particles based on poly(vinyl alcohol) (M-PVA) having an average size of 1-3 microns. Due to their magnetic properties, these biologically inert, hydrophilic particles provide the possibility of fast and efficient separation from crude suspensions using an easily scalable magnet technology. The application of magnetic separation technology allows carrying out the process of isolating anthocyanins within 25 minutes. The sorption capacity of M-PVA is 4-5 times higher compared to other non-ionic sorbents (Amberlite XAD 16, Stirosorb MCDS×100), widely used for the extraction of polyphenolic compounds. In the developed process, the M-PVA particles adsorb up to 40-60% of the anthocyanins present in the initial solution. Afterwards, ethanol containing 0.1% HCl extracts 85% of the absorbed anthocyanins resulting in a purified and threefold concentrated solution if compared to the original extract. HPLC indicated that the pigment composition of the concentrate is the same as in the original extract. The efficiency of the magnetic particles does not decrease by the adsorption in turbid media and reuse is possible without special treatment.

Keywords: *anthocyanins, magnetic particles, M-PVA, magnetic separation, concentration*

VALORIZATION OF MARITIME PINE WOOD (*PINUS PINASTER*) WASTE BY VACUUM EXTRACTION OF VOLATILE COMPOUNDS. COMPARISON WITH CONVENTIONAL METHODS

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This study is a part of a work on the double valorization of industrial waste from the wood sector. The proposed process is composed of two-step extraction of volatile compounds and production of activated carbon from the residue. The innovative aspect of this project is that the first step of the process acts as a pretreatment for the second step. The presented study concerns only the first step. Essential oil of *Pinus pinaster* was extracted by conventional steam distillation and hydrodistillation techniques at normal temperature and pressure. For the two techniques, vacuum extraction was also performed. Yields of 0.25 and 0.15% on dry basis were obtained, respectively, by steam distillation and hydrodistillation for processing time of 10 hours. For the extraction by vacuum steam distillation, the essential oil yield remained sensibly the same by increasing processing pressure from 60 mbars (0.24% dry basis) to 200 mbars (0.23% dry basis) and these

maximum values were reached after 8 hours. The chromatographic analysis confirmed that the contents of the main components, such as caryophyllene and L-fenchone, were more important for the vacuum extraction, indicating a better quality of the obtained oil. Due to these improvements, the extraction of *Pinus pinaster* essential oil under vacuum can attract considerable interest for its application in high-class perfumes, flavours and other formulations.

Keywords: *Pinus pinaster, volatile compounds, vacuum extraction, steam distillation, hydrodistillation*

CHEMICAL MODIFICATION OF WOOD TO PRODUCE STABLE AND DURABLE COMPOSITES

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Dimensionally stable solid wood and wood composites can be achieved by several methods, including cell wall bulking, cell wall polymer crosslinking and removal of hygroscopic components in the cell wall. Bulking the cell wall with bonded chemicals produces dimensionally stable products that can withstand wet and dry cycles. Crosslinking with a short difunctional chemical, such as formaldehyde, can produce dimensionally stable products that can also be used in wet-dry cycles and the amount of chemical add-on is very small (4 to 6%), but the wood is brittle. Wood heated to temperatures where the hygroscopic hemicellulose polymers are degraded produces a dimensionally stable product, but with reduced strength. Controlling the moisture content in the cell wall is one of the keys to biological resistance. If the equilibrium moisture content in the cell wall is below that required for a microorganism to attack wood, the chemically modified wood is then resistant to attack. The modification of the configuration and conformation of the substrate polymers, so that enzyme recognition cannot take place, may also be part of the protection mechanism.

Keywords: *chemical modification, composites, heat treatments, crosslinking, acetylation, formaldehyde, bulking, dimensional stability, decay resistance, equilibrium moisture content*

DEVELOPMENT OF GREEN ADHESIVES FOR FIBREBOARD MANUFACTURING, USING TANNINS AND LIGNIN FROM PULP MILL RESIDUES

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In order to reduce formaldehyde emissions from wood panels and to develop green adhesives, natural phenolic polymers of tannins and lignin have been investigated as substitutes of petrol-based chemicals used in wood panels. The potential of several wood barks, obtained from pulp mills as industrial wastes, has been evaluated for tannin extraction and further for their adhesive properties. Aqueous extractions were carried on wood barks of five different tree species on a laboratory

scale – Aleppo pine barks led to the highest yield (15%) compared to spruce, Douglas fir, maritime pine and eucalyptus. Urea and sulfite used as water-additives favoured the extraction of condensed tannins, especially for spruce and Douglas fir barks. Eucalyptus barks presented the lowest tannins contents. Pyr-GC/MS of the bark extracts showed that Douglas fir and Aleppo pine tannins were mainly constituted of phenol and catechol tannins. The adhesive potential of these tannins was also established. Cooking liquors from pulp mills are very rich in lignin. Lignin was isolated by acidification/precipitation of black liquors. The abilities of softwood and hardwood kraft liquors under several extraction conditions were compared. After glyoxylation, these lignins presented interesting adhesive properties. Furthermore, novel formulations of [tannin/hexamine + glyoxylated lignin] were tested for wood particleboard manufacturing. The internal bond strength of a panel manufactured with 60% tannin/40% lignin satisfied the value required by the European standard.

Keywords: *lignin, tannin, pulping liquor, bark, adhesives, phenol, particleboard, panel, green chemical, wood, residues, sustainability, formaldehyde*

WOOD ADHESIVES FROM AGRICULTURAL BY-PRODUCTS: LIGNINS AND TANNINS FOR THE ELABORATION OF PARTICLEBOARDS

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Organosolv lignins were extracted from lignocellulosic raw materials (*Miscanthus x Giganteus* and Empty Fruit Palm Bunch) and condensed tannins were extracted from grape by-product in an aqueous medium using different catalysts. Resin formulations with total polyphenolic contents (tannin and/or lignin) ranging from 70% to 95% of the total resin solids content were employed for the elaboration of particleboards. Mixtures of glyoxylated lignin/tannin and pure tannin were produced and tested. The importance of the nature of the basic reagent used for the extraction of tannins from grape pomace was demonstrated. Most of the adhesives produced yielded good internal bond strength results of the panels, enough to meet relevant international standard specifications for interior-grade panels (European Norm EN 312).

Keywords: *Lignin, tannin, grape pomace, adhesives*

EFFECT OF MOLAR RATIO AND FILLERS ON CREEP BEHAVIOR OF PHENOL-FORMALDEHYDE AND MELAMINE-UREA-FORMALDEHYDE THERMOSETTING ADHESIVES

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This paper investigates the effect of molar ratio and three kinds of fillers (poplar wood flour, wheat flour and glass particles) on the creep behavior of two

thermosetting adhesives used for wood-based panels – phenol-formaldehyde (PF) and melamine-urea-formaldehyde (MUF) – by dynamic mechanical analysis (DMA). The results obtained indicate that the ability of high molar ratio PF or MUF adhesives to resist deformation is largely superior to that of low molar ratio adhesives. In high molar ratio PF and MUF adhesives (P/F=1:2.20 and (M+U)/F=1:2.26), all fillers had a negative effect on the creep behavior. However, the fillers could markedly improve the creep behavior of PF and MUF adhesives with low molar ratio (P/F=1:1.98 and (M+U)/F=1:1.50). Moreover, glass particles and poplar wood flour proved to have a stronger effect, compared to wheat flour. The results obtained provide insights into easy ways to improve the creep behavior of wood adhesives for structural purposes.

Keywords: *creep behavior, phenol-formaldehyde, melamine-urea-formaldehyde, molar ratio, filler*

IMPROVEMENT OF BONDING PERFORMANCE OF LIGHTWEIGHT PANEL COMPOSED OF POLYSTYRENE FOAM CORE AND POPLAR VENEER WITH PINE TANNIN AND LIGNIN

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The study describes the improvement of the bonding performance of lightweight panels, faced with poplar veneer and with a polystyrene foam core, treated with a solution of pine tannin and lignin. Contact angle values, measured with water droplet as liquid, indicate that the wettability of the polystyrene foam soaked in pine tannin and lignin has been remarkably reduced, from 87.5° to 28.5°. The bonding performance demonstrates that a higher concentration of pine tannin and a lower concentration of lignin present a high failure ratio of the polystyrene foam. The concentration of 10% pine tannin and 5% lignin presented a failure ratio higher than 90%. The results provide a simple and effective method to improve the adhesion between polystyrene foam and poplar veneer in the manufacture of lightweight panels.

Keywords: *polystyrene foam, poplar, tannin, lignin, contact angle, bonding performance*

WOOD COATING BY UV POWDERS

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Many wood-based panels are nowadays used in the furniture industry. Their coating is of high interest to ensure high protection properties and decoration features. UV powders recently emerge among the current existing technologies as an alternative to coat wood panels due to the following advantages: they are environmentally friendly, based on 100% solid formulations, their curing process is

fast and operated at relatively low temperature, which fully preserves wood structure. Polymerization of UV powders is monitored by Real Time-FTIR under temperature control. The influence of temperature on reactivity is highlighted. Characteristics of UV powder resins, particularly molecular weight and viscosity in melted state, are related to reactivity parameters. The influence of additional multifunctional monomers within the formulations is afterwards investigated. Finally, Dynamic Mechanical Analysis is performed to determine glass transition temperature, crosslinking density and Young's modulus of the final coatings. Resistance to scratch and methyl ethyl ketone (MEK) is evaluated as well.

Keywords: *wood-based panels, UV powders, crosslinking density, Young's modulus, flexibility, scratch and solvent Resistance*

AN OVERVIEW OF BIOMASS AND BIOGAS FOR ENERGY GENERATION: RECENT DEVELOPMENT AND PERSPECTIVES

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Biogas from biomass appears to have potential as an alternative energy source, biomass resources being available worldwide. This is an overview of some salient points and perspectives of biogas technology. The current literature is reviewed regarding the ecological, social, cultural and economic impacts of biogas technology. This article gives an overview of present and future use of biomass as an industrial feedstock for the production of fuels, chemicals and other materials. To be truly competitive in an open market situation, higher value products are required. Results suggest that biogas technology must be encouraged, promoted, invested in, implemented and demonstrated, especially in remote rural areas.

Keywords: *biomass resources, biogas application, sustainable development, environment*

ASSESSMENT OF SUSTAINABILITY BASED ON LCA – CASE OF WOODY BIOMASS

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Biomass represents both the dominant source of feedstock for biotechnological processes and the renewable foreseeable sustainable source of organic fuels, chemicals, and other materials. In particular, woody biomass is one of the most efficient sources for renewable energy on a large scale. Converting biomass to fuels, pulp and paper, chemicals, power, and/or feed is essential to be analyzed in terms of economic viability, as well as environmental friendliness. The benefits of using biomass as feedstock for bioenergy may include: the reduction of the use of nonrenewable fuels, less dependence on foreign fuels, stabilization of income in rural areas, and reduced carbon dioxide emissions into the atmosphere. Taking into account the current data in the literature and some Romanian practices, an analysis was developed considering woody biomass use. The paper discusses some stages of the biomass life cycle: extraction of forestry biomass–transport–biomass valorization. The way the Life Cycle Assessment (LCA) approach was further applied to assess the environmental impacts associated with the production of electricity and biofuels, starting from resource extraction until the end-of-life, is

addressed. LCA has been discussed in relation to the estimation of biomass distribution on the land together with an evaluation of different chains, including harvesting, biomass transport, and final utilization through combustion and biorefining. System boundaries address cradle-to-gate, gate-to-gate and cradle-to-grave approaches. The results of the analysis based on LCA allowed for the identification of some environmental indicators that makesustainability criteria measurable, and also the assessment of the potential for sustainable valorization of biomass, together with benefits and drawbacks from the economic, environmental and managerial points of view. The most relevant indicator analyzed was the climate change potential, in terms of greenhouse gas (GHG) emissions. It was found that woody biomass can often be associated with positive environmental impacts, since CO₂ emissions have biogenic character.

Keywords: *biomass, bioelectricity, biofuel, life cycle assessment, sustainability indicators*

CONTRIBUTION TO THE DEVELOPMENT AND VALIDATION OF A HIGH PERFORMANCE LIQUID CHROMATOGRAPHY BY THE UV DETECTION METHOD FOR ISONIAZID AND OMEPRAZOLE DETERMINATION

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The objective of this study was to develop and validate a method for isoniazid and omeprazole determination in human serum. Solid phase extraction techniques have been used for sample preparation. The analytical method was applied on a Thermo Fisher Scientific Surveyor Plus chromatographic system, equipped with an autosampler and UV-VIS with diode array detector. Separation was performed on a C8 chromatographic column Octasilil (Purospher RP8) of the 250 mm x 4.6 mm i.d. type (5 μm). A mixture of 10 mM triethylamine (with a pH value of 10.5): acetonitrile (67:33, v/v) has been used as mobile phase. The obtained retention times were the following: 2.323 min for isoniazid; 3.497 min for 2-pyridylamine (used as an internal standard); 4.013 min for omeprazole and 6.837 min, respectively, for lansoprazole (used as internal standard). Detection was in UV at 260 nm for isoniazid and 2-pyridylamine, and at 300 nm, respectively, for omeprazole and lansoprazole. The method is linear, selective, accurate and precise in the 50-5000 ng/mL concentration range.

Keywords: *HPLC-UV, validation, isoniazid, omeprazole*

COMPARATIVE STUDY OF *OLEA EUROPEA* AND *EUCALYPTUS UROGRANDIS* KRAFT PULPS

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The aim of the present work was to find an optimum Kraft pulping of olive tree prunings to obtain pulp with a Kappa number of about 17, in order to compare its properties with those of *Eucalyptus urograndis*. The sulfidity used was of 30%, the liquid/solid ratio was 4:1 and the effective alkali applied was 20%. The maximum cooking temperature was of 165 °C with a heating rate of 70 minutes and a working time of 60 minutes (after reaching the temperature). The produced pulps were subjected to chemical and morphological analysis and to PFI mill refining. Then, handsheets were formed in order to carry out physical-mechanical and optical tests. The hemicelluloses content of these agricultural residues is higher than that presented by *E. urograndis*, which makes olive tree prunings interesting for a secondary industry. The values of the analyzed properties of olive tree prunings are not higher than those found for *E. urograndis*, and in some cases they are very close. Also, some values found for olive tree prunings are higher than those of *E. urograndis*, such as the values of opacity, which makes Kraft olive pulp appropriate for printing and reading paper.

Keywords: *Kraft pulping, Olea europea, Eucalyptus urograndis, agricultural wastes*

USE OF ELECTROSPINNING TECHNIQUE IN PRODUCTION OF CHITOSAN/CARBON NANOTUBES

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Chitosan/carbon nanotube nanocomposite fabrics have been successfully prepared through electrospinning. The electrospun nonwoven fabric was characterized by scanning electronic microscopic (SEM) imaging. Under optimization conditions, homogenous chitosan/carbon nanotube nanofibers with a mean diameter of 455 nm and known physical characteristics were prepared.

Keywords: *carbon nanotubes, chitosan, electrospinning, biocomposites, nanocomposites, industrial tools*

ANALYSIS OF LIPOPHILIC EXTRACTIVES IN POPULUS×EURAMERICANA ‘NEVA’

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Lipophilic extractives in the stemwood and bark of *Populus×euramericana* ‘Neva’ were analyzed by GC, GC-MS, and high-performance size exclusion chromatography (HPSEC). The top stemwood and bark contained much larger amounts of lipophilic extractives than the corresponding bottom ones. The lipophilic extractives identified were composed of five component groups, i.e. glycerides, steryl esters, free fatty acids, sterols and free fatty alcohols, both in the stemwood and bark. 4-Hydroxycinnamic acid esters of fatty alcohols were identified in a small amount in this wood species. Glycerides, mainly triglycerides, were the largest component group of the lipophilic extractives, and linoleic (18:2) acid was the major fatty acid in triglycerides. The low ratio of acids to unsaponifiables of this aspen wood, especially in the bottom stemwood, could probably have a negative effect on pitch problems. Small amounts of oligomeric or polymeric material with higher molar mass than the triglycerides were present only in bark.

Keywords: *lipophilic extractives, Populus×euramericana ‘Neva’, stemwood, bark, wood resin, pitch control*

SPRUCE BARK HYDROLYSIS TO OPTIMIZE PHENOLIC CONTENT

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In this study, the optimization of polysaccharides hydrolysis in order to increase the phenolic content of *Picea Abies* bark was investigated by screening experimental design. The high phenolic content of bark was interesting in the thermosetting resins synthesis, but the carbohydrate fraction had a negative effect on the mechanical properties and durability of phenolic resins. The purpose of this paper was to determine the main factors influencing the phenolic content of bark during acid hydrolysis. The hydrolysis was performed under atmospheric pressure in an aqueous solution of sulfuric acid. The effects of the reaction time (5 to 24 hours), acid concentration (3 to 10%), solid/liquid ratio (1/10 to 1/5), and particle sizes on the weight loss, lignin content, holocellulose content, and sugar, as well as degradation products of the hydrolysis, were studied.

Keywords: *Norway spruce bark, acid hydrolysis, high phenolic content, experimental design*

CHARACTERIZATION AND MONOMER REACTIVITY RATIOS OF GRAFTED CELLULOSE WITH N-(4-NITROPHENYL)ACRYLAMIDE AND METHYL METHACRYLATE BY ATOM TRANSFER RADICAL POLYMERIZATION

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N-(4-nitrophenyl)acrylamide (4NPA) original monomer was synthesized and characterized by FT-IR, ¹H and ¹³C NMR techniques. The atom transfer radical polymerization (ATRP) of 4NPA with methyl methacrylate (MMA) were performed in dimethylformamide (DMF) at 130 °C in the presence of cellulose chloroacetate (Cell.ClAc) macro initiator, Cu(I)Cl/2,2'-bipyridine catalytic system. The graft copolymers were characterized by elemental analysis, FTIR spectra and thermal analysis. Thermal stabilities of the graft copolymers were determined by the TGA method and it was established that thermal stability of the copolymers increased with the increase of MMA units, while it decreased with the increase of 4NPA units. In order to investigate the effect of 4NPA with MMA monomer interactions on grafting, the graft copolymerization was also studied using different feed compositions, ranging from 0.15 to 0.85. The reactivity ratios of 4NPA and MMA by ATRP on cellulose were determined using the Finemann–Ross (F–R), inverted Finemann–Ross (inverted F–R), Yezrielev–Brokhina–Roskin (Y–B–R), Kelen–Tüdös (K–T) and extended Kelen–Tüdös (extended K–T) linearization methods. The reactive ratios of r_1 and r_2 were found to be 0.017–0.116 and 1.209–1.472, respectively. The graft copolymers on cellulose $r_1.r_2$ are close to zero.

Keywords: *ATRP, cellulose, graft copolymer, monomer reactivity ratios*

CHEMICAL CHANGES OF CELLULOSE PULPS IN THE PROCESSING TO VISCOSE DOPE

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A selection of cellulose pulps was investigated for their chemical changes during the required process steps to viscose dope. The selection of the pulps was based on pulping process, original wood type and intrinsic viscosity. In total, five sulfite pulps and four sulfate pulps were chosen, of which all but one sulfate pulp were of dissolving grades. The physical and chemical properties of the pulps were analyzed as well as important qualitative parameters of the cellulose intermediates during mercerization, pre-aging and in the final viscose dope. Pre-aging curves were reported as a measure of each pulp's reactivity with respect to oxidative degradation, where high hemicellulose content and small pore area and pore diameter were found to hamper cellulose degradation. The correlations in pre-aged pulps of intrinsic viscosity to M_z , M_v and M_w were found to be ambiguous and show the need for a description of total molecular weight distribution of the alkali celluloses to better understand the degradation behavior of each pulp, instead of only intrinsic viscosity. It was also shown that R18 and R10 are insufficient analyses to determine pulp, and to predict viscose quality. Further, many pulps, independently of initial hemicellulose content, reached the same level of

hemicellulose content after mercerization. The presence of crystalline hemicelluloses could be a possible cause for this level-off behavior, combined with hemicelluloses resistant to caustic lye treatment. The change of both low-molecularweight celluloses and PD in the process to viscose dope was investigated due to the importance of these variables on dope spinnability and viscose fiber strength. Caustic resistance of cellulose and hemicelluloses and a more rigid fiber structure in some pulps are suggested to contribute to the different degradation behavior.

Keywords: *aging, cellulose pulp, hemicelluloses, long fiber, short fiber, sulfate, sulfite, mercerization, molecular weight, reactivity, viscose*

MORPHOLOGICAL, THERMAL AND RHEOLOGICAL CHARACTERIZATION OF POLYVINYL ALCOHOL/CHITOSAN BLENDS

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The present study deals with the preparation of polyvinyl alcohol (PVA)/chitosan (CS) blends with different compositions. The physico-chemical characterization and compatibility have been studied by means of polarized light optical microscopy, FT-IR spectroscopy, DSC, DMTA, TG/DTG and rheological measurements. The film-forming ability of the blends was confirmed by rheological tests, as they showed higher viscosity and improved viscoelastic properties in comparison with pure PVA. The obtained films were transparent and homogenous with enhanced mechanical properties and thermal stability.

Keywords: *poly(vinyl alcohol), chitosan, blends, film-forming*

MOLAR MASS CHARACTERISTICS OF CHERRY TREE EXUDATE GUMS OF DIFFERENT SEASONS

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The polysaccharide components of cherry tree exudate gum (*Prunus cerasus*, *Prunus avium*) belong to the arabinogalactan group. There are structural variations in the proportion of monosaccharides, molar ratio and glycosidic linkages, which determine the properties and use of exudate gums. In this paper, Size Exclusion Chromatography (SEC/GPC) is applied for determining polydispersity and molecular mass (Mw) of the cherry tree exudate gum of *P. avium*, *P. cerasus* and egg plum (*P. domestica*). The intrinsic viscosity values of cherry tree EAL gum solutions were also obtained, confirming the existence of a compact internally crosslinked structure of the exudate gum polysaccharide. The results of Brookfield viscosity characterization outline the essential characteristics of the cherry gum exudates.

Keywords: *exudate Prunus gums, SEC/GPC chromatography, molecular weight, polydispersity*

CHEMICAL AND SPECTRAL CHARACTERISTICS OF ANNUAL PLANT LIGNINS MODIFIED BY HYDROXYMETHYLATION REACTION

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This paper aims at the synthesis and chemical and spectral characterization of lignins from annual plants (L1 – lignin from wheat straw, and L2 – lignin from grass), modified by hydroxymethylation with formaldehyde in alkaline environment. The derivatives synthesized by this reaction were characterized by the introduced functional groups, which has been related to the consumption of formaldehyde under different conditions. Subsequently, additional information on the changes has been obtained by spectral studies (FTIR, ¹H NMR) and high performance steric exclusion chromatography (HPSEC). Studies have revealed some functional changes, related to both different reactivity of lignins and reaction conditions.

Keywords: *lignin, hydroxymethylation, FT-IR, ¹H NMR, HPSEC*

ECOLOGICAL BIOCIDES SYSTEMS BASED ON UNMODIFIED AND EPOXYDATION LIGNINS, FURAN RESIN AND COPPER

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The paper presents the results obtained in the characterization of some products based on lignin, its epoxy derivative and furan resins as potential biocides. These compounds were studied comparatively with inorganic copper ions, using samples of fir and beech wood as a substrate. With this end in view, the samples of fir and beech wood were impregnated with the solutions of the above-mentioned compounds with a 5% concentration. The efficiency of the treatment has been established *versus* the inhibition of the development of some fungi (*Alternaria geophola*, *Chaetonium funicola*, *Chaetonium olivaceum*, *Fusidium viride*, *Humicola grisea*, *Stachybotrys alternans*, *Penicillium brevi-compactum*, *Penicillium funiculosum*). The results of these tests evidenced that lignin, its derivative and the furan resins, although having a lower inhibition capacity for fungi development – compared with copper compounds – could be used to develop environmentally friendly biocides to be applied in wood preservation.

Keywords: *lignin, epoxy lignin, furan resin, copper ions, biocide systems, fir and beech wood, fungi*

AFM SURFACE ANALYSIS OF FUNGAL MODIFIED CTMP FIBERS

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Fungal treatment can significantly improve the strength properties of chemithermomechanical pulp fiber, and it can help to expand the utilizations of the pulp. In this study, surface morphology of the eucalyptus chemithermomechanical pulp fiber before and after fungal treatment was studied with AFM. AFM phase images revealed that fungal treatment could remove part of lignin and extractives from fiber surface resulting in high carbohydrate content in the S1 layer of the fiber. This observation was further supported by 3-D topograph AFM images.

Keywords: *white-rot fungus, eucalyptus chemithermomechanical pulp, surface analysis, AFM*

EFFECT OF ENZYME CONCOCTIONS ON FIBER SURFACE ROUGHNESS AND DEINKING EFFICIENCY OF SORTED OFFICE PAPER

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Bio-deinking of sorted office paper (SOP) by various enzyme concoctions having cellulase, xylanase, amylase and lipase was investigated. The effect of various enzyme concoctions on pulp brightness, effective residual ink concentration (ERIC), deinkability factor based on brightness (DB), deinkability factor based on ERIC (DE), dirt counts, strength properties and effluent characteristics was studied and compared with their respective control. Also, the effect of different enzyme concoctions on fiber surface and fiber morphological changes during the deinking process were studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Results showed that, compared to control, a maximum improvement in brightness by 13.30% (ISO), DB 37.79%, and DE 83.0% and a reduction in ERIC and dirt counts by 68.18 and 88.04%, respectively, were achieved with a concoction of cellulase+xylanase+amylase+lipase at a dosage of 6, 3, 1.5 and 6 IU/mL, respectively. This indicated that there was a synergistic deinking effect among the concoctions of these enzymes as fiber surface roughness increased by 159% compared to control.

Keywords: *sorted office paper, biodeinking efficiency, enzyme concoctions, fiber surface roughness*

KINETIC DEPENDENCES FOR THE DECREASE OF POLYMERIZATION OF PAPER UNDERGOING ACCELERATED AGEING

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Degradation of cellulose is an important factor influencing its physical, mechanical, optical and chemical properties and the lifetime of paper in libraries and archival holdings. Groundwood paper made around the middle of the 19th century is endangered. Documents in poor condition need treatment to prolong their lifespan for the use of future generations. To investigate the ageing stability, model groundwood newsprint paper was used. A study of the accelerated ageing of newsprint paper was performed at 98 °C during 0, 1, 2, 3, 5, 7, 10, 15, 20 and 30 days. The efficacy of treatment using MgO in perfluoralkanes or a mixture dispersion of MgO in perfluoralkanes and methyl methoxy magnesium carbonate in methanol (ratio 3:1) was investigated. This paper aims at finding kinetic dependences for the degree of polymerization (further DP) decrease and time stability of pH value of paper undergoing accelerated ageing. The highest rate of degradation ($k_{DP} = 0.0105 \pm 0.0023 \text{ h}^{-1}$) was determined for the unmodified control sample. In the case of the treated samples, the rate constants of DP degradation were lower ($k_{DP} = 0.0073 \pm 0.0010 \text{ h}^{-1}$ and $k_{DP} = 0.0053 \pm 0.0009 \text{ h}^{-1}$) for samples treated by MgO and MgO+MMMC, respectively.

Keywords: *deacidification, efficacy, degradation, ageing*

CHANGE IN THE CAPABILITY OF CELLULOSE FIBRES TO RETAIN WATER DURING THERMALLY ACCELERATED AGEING OF PAPER

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The water retention value (WRV) as a measure of the capability of cellulose fibres to retain water (swelling of fibres) was evaluated during accelerated ageing of acidic wood pulp newspaper containing 20% chemical fibres. It has been found that the WRV considerably decreases with accelerated ageing. Relations between the WRV properties and the mechanical properties of paper have also been evaluated. The characterization of samples by mercury microporosimetry has shown that the cumulative column of the pores increases with the period of ageing. On the other hand, the average radius of the pores, as well as their specific surface, decreases. This supports the process of hornification, which occurs during accelerated ageing of paper, as the small pores get smaller and the larger ones get even larger as a result of shrinkage of fibres. When considering accelerated ageing, hornification of fibres as one of the outcomes of fibre brittleness has to be taken into account.

Keywords: *hardwood bleached kraft pulp, recycling, swelling kinetics, hornification, thermal treatment*

WASTE PAPERBOARD IN COMPOSITION PANELS

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Waste paperboard could potentially be used as raw material for fiber or particle based composites without the resorting, deinking, and decontamination required for paper manufacturing. The objective of this study was to evaluate singlelayer particleboards made with various ratios of waste paperboard fibers to wood particles. Urea formaldehyde resin in different amounts of 9 and 10% were applied. Static bending strength, internal bonding, and thickness swelling were measured. The results indicated that applying waste paperboard fibers satisfied the minimum MOR (modulus of rupture) and MOE (modulus of elasticity) requirements for load-bearing boards for use in humid and dry conditions, respectively. The IB (internal bonding) values of all panel types decreased with the addition of waste paperboard fiber. However, all of the produced panels met the IB requirement for general purpose end-use. By increasing the resin content, all properties of the boards and particularly internal bond and thickness swelling were improved. Nevertheless, thickness swelling values were higher than those required. For this reason, additional work needs to be done to improve the physical properties of the particleboard produced from waste paperboard fibers.

Keywords: *waste paperboard fibers, wood chips, urea-formaldehyde resin, particleboard*

USE OF BUCKWHEAT STALK IN PARTICLEBOARD BONDED WITH UREA-FORMALDEHYDE RESIN ADHESIVE

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Buckwheat stalks were used as a raw material for particleboard. A urea-formaldehyde resin was synthesized in the laboratory with a 50% content of resin solids as particleboard binder. The laboratory particleboards were made using buckwheat stalks and hybrid poplar bonded with urea-formaldehyde resin, at a buckwheat stalk content of 0, 23, 48, 73 and 100% oven-dry weight. The physical and mechanical properties of the particleboards were tested according to the ASTM D 1037-99 procedure. The internal bond and flexural strength properties of the particleboards decreased gradually with an increasing buckwheat stalk content. However, the properties of all the particleboards exceeded the minimum requirements for the Korean Standard KS F 3104 for particleboard type 8.0. These results demonstrated the potential of buckwheat stalk as an alternative raw material for particleboard manufacture.

Keywords: *buckwheat (Fagopyrum esculentum L.), agricultural residues, hybrid poplar, urea-formaldehyde resin, particleboard*

BOOK REVIEW

MĂRIMI ȘI UNITĂȚI DE MĂSURĂ. INDUSTRIA CELULOZEI ȘI HÂRTIEI

Autor: Dan Gavrilescu

Editura ECOZONE, Iași, 2013, ISBN 978-973-7645-94-4

Cartea „Mărimi și unități de măsură. Industria celulozei și hârtiei”, autor prof.dr.ing. Dan Gavrilescu de la Universitatea Tehnică „Gh. Asachi” din Iași, abordează într-o manieră originală mărimile și unitățile de măsură folosite în industria de celuloză și hârtie care vizează fabricarea celulozei și hârtiei, procesarea maculaturii, obținerea cartonului ondulat și ambalajelor. Nu se neglijează nici domeniul protecției mediului.

Lucrarea își propune să fie un ghid al mărimilor și unităților de măsură folosite în industria de celuloză și hârtie, cu referire îndeosebi la cele care vizează tehnologiile implicate și produsele care se obțin. Mărimile și unitățile de măsură sunt prezentate pe linii tehnologice (materii prime, producerea celulozei, fabricarea hârtiei, prelucrarea hârtiei reciclate, fabricarea cartonului ondulat și ambalajelor) și sunt discutate în ordine alfabetică, pentru a se putea identifica mai ușor. Se prezintă, de fiecare dată, definiția mărimii, semnificația ei, numărul standardului pentru metodele de analiză și testare, sau, dacă nu există standarde, trimiterile relevante de literatură. Sunt incluse și listele numerice ale

familiilor reprezentative de standarde folosite în industria de celuloză și hârtie (SR, ISO, TAPPI). Lucrarea se încheie cu anexe în care sunt trecute unitățile de măsură recomandate în standarde și factorii de conversie ai unităților de măsură.

Deși autorul nu a intenționat să epuizeze domeniul abordat, lucru imposibil într-un număr limitat de pagini, el a încercat să accentueze latura practică a lucrării, care se dorește să constituie într-un material unitar de studiu pentru cei care se pregătesc sau care activează în domeniul fabricării hârtiei, cartonului ondulat și ambalajelor. Deși cartea se adresează în mod deosebit studenților, masteranzilor și doctoranzilor specializării *Ingineria Fabricației Hârtiei* de la Iași, o recomandăm călduros tuturor celor care se pregătesc în domeniu sau care activează în sectorul de profil, cu convingerea că ne aflăm în fața unei lucrări utile și valoroase.

București, iulie 2013,

Ing. Constantin Chiriac

Director General Executiv
*Patronatul Industriei de Celuloza si Hartie –
ROMPAP*

STRATEGIA CERCETĂRII EXPERIMENTALE

Autori: Valentin I. Popa și Irina Volf, , Editura Politehniun, Iași, 2013, 180 pagini,

ISBN 978-973-621-403-5

Activitatea de cercetare științifică trebuie să reprezinte o componentă majoră a educației pentru a contribui la dezvoltarea gândirii creative și participării conștiente a indivizilor la rezolvarea unor probleme globale cu care se confruntă societatea. În același timp, această activitate trebuie promovată cu convingerea că știința deține un rol important în dezvoltarea culturală și tehnică a unei țări, iar într-o strategie națională contribuie la siguranța, independența și dezvoltarea sa durabilă. La nivelul învățământului superior, activitatea de cercetare științifică trebuie promovată în toate cele trei cicluri de studiu (licență, masterat și doctorat) pentru a asigura competențe la fiecare nivel, care să permită participarea conștientă a absolvenților în activități creative, indiferent de domeniul în care vor lucra. Din acest motiv considerăm binevenită inițiativa de a oferi studenților un curs privind **Strategia cercetării experimentale** și acoperirea sa cu un suport corespunzător.

Supportul de curs la care facem referire este destinat doctoranzilor și este structurat în cinci capitole urmate de concluzii și de o bibliografie selectivă, recomandată pentru întregirea volumului de informații prezentate. Capitolul I – *Aspecte privind configurarea studiilor de masterat și doctorat la nivel european* este consacrat prezentării organizării celor două cicluri de pregătire, așa după cum rezultă din recomandările Declarației de la Bologna. Introducerea informațiilor privind masteratul a fost determinată de faptul că în acest ciclu trebuie asigurate condițiile pentru crearea unor competențe privind abordarea cercetării științifice care vor contribui la continuarea acestei activități la nivelul doctoratului. Din sursele bibliografice analizate s-au extras aspectele importante care trebuie să caracterizeze cele două cicluri educaționale și care vin unul în continuarea celuilalt. În capitolul II este analizată *Cercetarea științifică ca o componentă a strategiei de dezvoltare*. Element al dezvoltării durabile, cercetarea științifică trebuie să constituie, alături de educație un element de strategie națională, și prin urmare, o preocupare de bază pentru guvernul

unei țări care dorește să asigure bunăstarea cetățenilor săi. De asemenea, în concordanță cu principiul humboldtian trebuie să existe sinergism între educație și cercetare. Clasificată, doar didactic în diferite forme, cercetarea științifică trebuie coordonată de guvern într-o structură coerentă pentru a include activitățile desfășurate în universități, laboratoare industriale, laboratoare finanțate de stat și în laboratoare de cercetări și institute de cercetări tutelate. Organizarea activităților de cercetare prin dimensiunea și masa critică a unui laborator, asigură eficiența și succesul, indiferent unde acestea se practică. Având în vedere că, pentru cei care finalizează doctoratul apare ca potențială o carieră în cercetare sau conducerea unor activități de acest gen, se prezintă spre exemplificare sistemul de organizare matriceală care poate fi implementat într-o întreprindere, și nu numai. *Fundamentele gândirii științifice și creativității* sunt prezentate în capitolul III. În prezent există un volum important de informații în care se dezbate diferite aspecte ale factorilor care influențează creativitatea, de la cei de natură neurobiologică, psihologică și caracterologică, până la cei organizaționali. Dezbaterile în jurul acestui subiect au permis identificarea elementelor de stimulare a creativității și de elaborare a unor tehnici diferite pentru rezolvarea practică a unor probleme ale cercetării științifice și de valorificare a rezultatelor sale. O altă problemă mult discutată în prezent, menită să ajute în activitatea de cercetare nu numai pe cei începători, ci și pe cei inițiați este *Planificarea cercetării științifice* – capitolul IV. Creativitatea științifică, mai ales atunci când privește cercetarea fundamentală, nu poate fi planificată din punct de vedere al rezultatelor sale. În schimb, referitor la acest subiect se pot identifica etapele ce trebuie parcurse în abordarea unui proiect de cercetare. Astfel, într-un sistem organizat se poate vorbi de o metodă științifică de abordare a cercetării care va trebui să includă o fază de documentare în urma căreia să poată fi definite obiectivele, etapele ce trebuiesc parcurse pentru obținerea rezultatelor și posibilitățile de prelucrare și

valorificare ale acestora. În capitolul menționat se acordă un spațiu suficient și se oferă detalii utile începătorilor în activitatea de cercetare. Se discută aspecte privind nu numai modul de abordare a cercetării ci și elemente importante privind elaborarea lucrărilor, evaluarea prin sistemul peer-review, semnificația elementelor de recunoaștere științifică și a vizibilității individuale și colective. În același context sunt abordate posibilitățile de comunicare orală a rezultatelor. În prezent, în condițiile exploziei informațiilor științifice, comunitatea cercetătorilor se confruntă cu probleme de etică și de proprietate intelectuală. Pentru cei care se străduiesc să pătrundă tainele cercetării este important să cunoască *Aspectele etice ale cercetării științifice*, așa cum sunt ele prezentate în capitolul V. Folosirea unor instrumente prevăzute de o legislație corespunzătoare, poate preveni cazurile de încălcare a principiilor de etică între care, alături de abordarea unei tematici cu rezultate periculoase, plagiatul și prezentarea unor rezultate false, ocupă un loc important. Protejarea rezultatelor obținute este recomandată folosind brevetarea și înregistrarea drepturilor de autor pentru care în România există organisme specializate. Odată apelate astfel de instrumente, activitatea de protecție constituie și o etapă pregătitoare pentru transferul tehnologic.

O astfel de acțiune, din păcate, mai puțin organizată și promovată la nivel național trebuie să reprezinte pentru tinerii cercetători elemente de educație antreprenorială inclusă în planurile de învățământ ale universităților și însoțite de o legislație corespunzătoare care să asigure o legătură funcțională -universitate-industrie-guvern.

Informațiile prezentate în acest suport de curs pot fi considerate extrem de utile pentru doctoranzi, ca și pentru cei din celelalte cicluri de studii, care se inițiază în activitatea de cercetare pentru că “Știința mai întâi se învață și apoi se practică.”

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