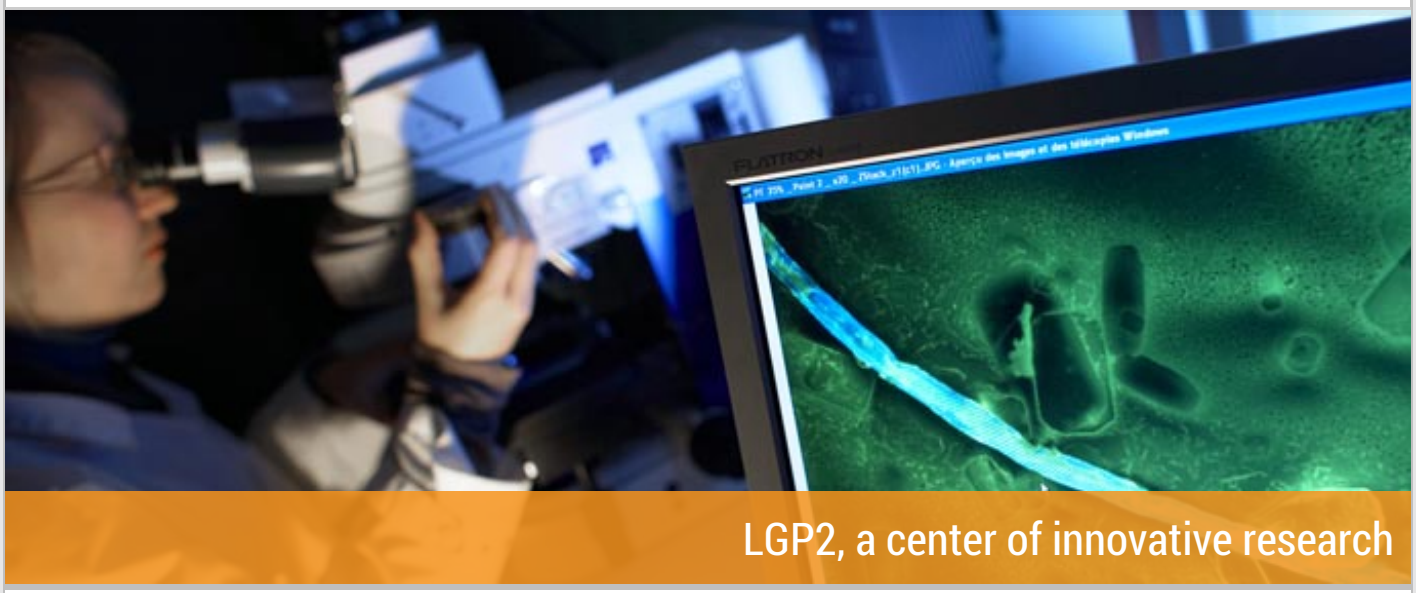


LGP2 - Ph.D. thesis defended in 2010

Alireza SAIDI

December 14, 2010 - Fluid Mechanics, Energetics, Processes

Ph.D. title

Drop impact of yield stress fluids.

Supervision

Albert MAGNIN, Research Director, Laboratoire Rhéologie & Procédés (Grenoble) ♦♦ Céline MARTIN, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

The drop impact process occurs both in various industrial applications and our daily life. A drop of rain on a window, a drop of paint spray, ink droplet ejected from an inkjet printer... involve various surprising physical phenomena dependent on the impact velocity, the impacted media and the nature of the fluid. Control the final shape of the droplet then is of major importance. Upon impact, the drop may be broken thereby creating small droplets and splashes, it may also bounce on the support or, after spreading, retract... To minimize these instabilities, it is possible to act on intrinsic fluid properties including the introduction flow threshold.

In this study, millimeter drops were generated under their own weight through a capillary. Their dynamic behavior was visualized and caracterized from the formation to the balance after the impact and this, over a wide range of impact velocity. Just prior to impact, the drops lose their spherical shape when the yield point increases. They become more and more elongated. Thus, diets low in inertia, they collapse upon impact, under the effect of hydrostatic pressure. This subsidence phase is mainly governed by the interface properties of the substrate. In systems with high inertia, increasing of the yield point and of viscous properties of the fluid inhibits inertial spreading and withdrawal phases. Moreover, experimental data were correlated with theoretical data derived from models of drop impact of elastoplastic viscoplastic fluids, demonstrating the involvement of the two mechanisms both viscous and elastic in the impact process.

Other members of the jury

Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Dominique DUPUIS, Professor, ENSISA-Laboratoire de Physique et Mécanique Textile (Mulhouse) ♦♦ Salaheddin SKALI-LAMI, Associate Professor, Université de Nancy ♦♦ Lazhar BENYAHIA, Professor, Université du Maine, Le Mans ♦♦ Brice LOPEZ, CEO, Siliflow (Valence)

Claudia SASSO

December 9, 2010 - Materials, Mechanical, Civil Engineering, Electrochemistry

Ph.D. title

Polymerization of pyrrole with wood composites and development of conductive films from lignocellulosic materials.

Supervision

Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Davide BENEVENTI, Researcher CNRS, LGP2

Abstract

This thesis deals with the development of compounds of polypyrrole (PPy) and derivatives of wood for applications in the field of organic electronics. Ligno-cellulose derivatives have been used as additives in a system where there was the polymerization of pyrrole (Py). These agents have been added due to their film-forming properties for the production of self-supporting films. Thus, the effect of the addition of carboxymethylcellulose (CMC), xylans, cellulose fibrils nano (NFC) and lignosulphonates on morphological and electrical properties of PPy was evaluated. The concentration of additives, the temperature and the polymerization time are the main parameters considered. It was shown that the xylan is more efficient to increase the conductivity of the PPy. These PPy particles were mixed in aqueous medium at different film formers (CMC and NFC) to produce self-supporting conductive films. The contribution of these binders in the electrical, mechanical and morphological properties of the films prepared was also studied.

Other members of the jury

Roberta BONGIOVANNI, Associate Professor, Politecnico di Torino (Italy) ♦♦ Alessandro GANDINI, Professor, Universidade de Aveiro (Portugal) ♦♦ Lionel HIRSCH, Professor, Université de Bordeaux 1 ♦♦ Elisa ZENO, Research Engineer, Centre Technique du Papier ♦♦ Jérôme FAURE-VINCENT, Commissariat à l'Énergie Atomique et aux Énergies Alternatives

Jacq-André NGUEGAN BOTOO

December 2, 2010 - Fluid Mechanics, Energetics, Processes

Ph.D. title

Study of the introduction of hydrogen peroxide in the process of water treatment by activated sludge: quality and quantity of sludge produced.

Supervision

Marc AUROUSSEAU, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Agnès GUILLET, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

Management of sewage sludge is global, one of the major concerns of operators of wastewater treatment plants (WWTP) a qualitative and quantitative point of view. Increasing volumes of sludge from WWTP and significant treatment costs lead to seek new strategies to reduce sludge production.

Therefore, in this context, this thesis focuses on the potential of H2O2 used without catalyst or activator, the quantity and quality of sludge from an activated sludge process treating municipal or stationers wastewater effluents. Different cropping patterns (discontinuous, SBR, continuous) and scale (2L, 5L and 70L) with H2O2 doses between 0.08 and 2 g / g DCOentrante have been studied and do not demonstrate a significant reduction in the sludge production. However, if no significant change in the reduction of carbon compounds are observed, a process/speed change of nitrogen transformation cycle is highlighted.

Moreover, various analytical techniques, including spectroscopy X and environmental scanning electron microscopy, show that the action of the H2O2 is located on the surface of the flocs and leads to a change in the nature and amount of present functional groups. This results in improving the settleability and filterability of the sludge treated with H2O2. Finally, a disintegration of flocs partly attributed to the solubilization of exopolysaccharides was highlighted and helped explain the measured improvement in the ability to sludge dewatering.

Other members of the jury

Etienne PAUL, Professor, INSA Toulouse ♦♦ Evelyne GONZE, Professor, Université de Savoie ♦♦ Bruno BARILLON, Project Engineer, Suez Environnement ♦♦ Eric FOUREST, Project Manager, Centre Technique du Papier

Aurore DENNEULIN

October 26, 2010 - Materials, Mechanical, Civil Engineering, Electrochemistry

Ph.D. title

Inkjet printing of conductive inks for RFID technology : Influence of substrate, ink and process.

Supervision

Anne BLAYO, Lecturer-Researcher, Grenoble INP-Pagora / LGP2 ♦♦ Julien BRAS, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

This work investigates the inkjet printing process to print conductive patterns for producing low cost electronic components. Three fields were explored: (i) substrates, (ii) conductive inks, and (iii) process. Substrate surface properties su ch as roughness or surface energy have a significant impact on conductivity of printed tracks. An innovative solution to make any paper suitable for printed electronics has then been proposed. Infrared and electrical treatments were tested as potential sintering alternatives of nanometallic inks, and new conductive inks based on carbon nanotubes (CNT) and conductive polymers were formulated. This new CNT-based ink has been studied more in details by analyzing influence of inkjet printing parameters and their impact on the CNT network organization and on the conductivity. This study represents an important step in the field of printing electronics, and also opens windows to new low cost applications such as smart packaging or flexible electronics.

Other members of the jury

Arthur SOUCEMARIANADIN, Professor, Université Joseph Fourier (Grenoble) ♦♦ Philippe COLLOT, Professor, École Nationale Supérieure des Mines de Saint-Étienne ♦♦ Tim CLAYPOLE, Professor, Swansea University (UK) ♦♦ Stéphane CROS, Research Engineer, CEA-INES, Chambéry ♦♦ Charles NEUMAN, CEO, Polypore

Jérémie VIGUIE

May 10, 2010 - Fluid Mechanics, Energetics, Processes

Ph.D. title

Mechanical and hygroexpansif behavior of lignocellulosic materials for rigid packaging.

Supervision

Evelyne MAURET, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Isabelle DESLOGES, Lecturer Researcher, Grenoble INP-Pagora / LGP2 ♦♦ Pierre DUMONT, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

This thesis is a particularly important topic in the field of manufacturing and processing of paper and cardboard. Indeed, the behavior of cartons conventional conditions is not always well known and understood, which greatly limits the possibilities of optimization of these structures.

In this context, the study focused specifically on the hygroexpansif behavior of boxboard and mechanical behavior of corrugated packaging structures. The hygroexpansifs wide fiber network mechanisms of such laminates have been studied from a 2D correlation method of images from X-ray microtomography. This method revealed, for example, the relationship between density of layers boxboard and their hygroexpansion in thickness. The compression behavior of simple geometries packaging corrugated boxes G flute profile has been studied from a broad base of experimental data. A method stereocorrelation images allowed us to describe the kinematic fields associated buckling panels of these boxes. These data can be used to improve behavior patterns in order to optimize the packaging structures.

Other members of the jury

Christine DELISEE, Associate Professor, Université de Bordeaux 1 ♦♦ Alain VAUTRIN, Professor, École des Mines de Saint-Étienne ♦♦ Frédéric JACQUEMIN, Professor, Université de Nantes ♦♦ Per ISAKSSON, Professor, Mid Sweden University (Sweden) ♦♦ Pierre VACHER, Professor, Université de Savoie

Franck MEDLEGE

April 13, 2010 - Fluid Mechanics, Energetics, Processes

Ph.D. title

Manufacture of electrodes for lithium-ion flexographic.

Supervision

Grenoble INP-Pagora / LGP2 ♦♦ Commissariat à l'Énergie Atomique et aux Énergies Alternatives

Abstract

Demand of special rechargeable batteries in various fields require electrodes shapes. The best way to produce them is to use a printing process such as flexography. The difference between an electrode coating paste and a printing ink is the low surface tension of fluorinated binder used, PVDF, which limits the transfer of ink. The PVDF was mixed with a second polymer to increase the polar contribution of the surface energy of the binder. The behavior of polymer blends was studied using the Flory-Huggins theory and a permanent binder, based on a PVDF / PVA (polyvinyl alcohol) mixture, allowed to give the ink a good transfer on a flexographic printing unit, with dry ink thicknesses around 80 microns on four passages. Functional prototypes of batteries with printed electrodes were performed. Furthermore, high-performance electrodes fabricated by coating were carried out with the new binder, which is the subject of a patent.

Other members of the jury

Hervé CHERADAME, Professor, Université d'Evry-Val-d'Essonne ♦♦ Antonio L. TORRES, Professor, Universitat Politècnica de Catalunya (Spain) ♦♦ Renaud BOUCHET, Associate Professor, Université de Provence ♦♦ Jacques FOULETIER, Professor, Grenoble INP-LEPMI ♦♦ Hélène ROUAULT, Researcher, Commissariat à l'Énergie Atomique et aux Énergies Alternatives, Grenoble ♦♦ Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2

Gilberto DE FREITAS SIQUEIRA

March 3, 2010 - Materials, Mechanical, Civil Engineering, Electrochemistry

Ph.D. title

Processing and thermo-mechanical characterization of polymer bionanocomposites reinforced with microfibrillated cellulose and cellulose whiskers .

Supervision

Alain DUFRESNE, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Julien BRAS, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

This work describes the use of some Brazilian natural fibers (Sisal, Luffa Cylindrica and Capim Dourado) as sources of cellulose nanowhiskers and microfibrillated cellulose (MFC) for the preparation of polymeric nanocomposites. It proposes a new way of obtaining cellulose nanoparticles and exploits their intrinsic properties. For this purpose two main routes were investigated, namely (i) use of chemically grafted cellulosic nanoparticles reacted with isocyanates and incorporated in a []-polycaprolactone (PCL) matrix, and (ii) direct use of cellulose nanoparticles as reinforcement in a natural rubber (NR) matrix. The thermo-mechanical properties were investigated by DSC and DMA. In both cases it was demonstrated that low amounts of fillers provides high mechanical properties when compared to the neat matrix, PCL or NR. The study of crystallization kinetics of PCL and PCL-nanocomposites provided additional information for cellulosic nanofillers acting as nucleating agents accelerating the crystallization process of nanocomposites. Enzymes were also used to prepare such nanoparticles thus yielding nanofillers with different morphologies. As a result, the final NR-nanocomposites showed different mechanical performances and gain in both Young's and storage modulus with respect to the neat polymeric matrix.

Other members of the jury

Redouane BORSALI, Research Director, CERMAV ♦♦ Tanja ZIMMERMANN, Senior Scientist, Group Leader Cellulose Nanocomposites, EMPA (Suisse) ♦♦ Jannick DUCHET-RUMEAU, Associate Professor, INSA (Lyon) ♦♦ Anne BERGERET, Professor, Ecole des Mines d'Alès

Shree Prakash MISHRA

February 24, 2010 - Fluid Mechanics, Energetics, Processes

Ph.D. title

Bleaching of cellulosic paper fibres with ozone : effect on the fibre properties.

Supervision

Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

The effect of ozone on viscosity, fibre morphology, beating behaviour and strength properties of kraft pulp has always been a matter of discussion among the mill experts, ozone suppliers and research groups. The present thesis research work is aimed at further advancing and enriching the knowledge base in the area and to help proliferation of the ozone bleaching technology for a more sustainable pulp industry. It has been established that incorporating an ozone stage in an ECF bleaching sequence of eucalyptus and Pinus radiata kraft pulps is a straightforward way to reduce the chemical cost with a possibility of having higher brightness ceiling. Bleaching with ozone results in a substantial decrease of the pulp viscosity which is shown to have no consequence on the main strength properties and fibre morphology of the pulp. Other advantages of the ozone containing ECF sequence are the smaller content in residual extractives, the savings in the beating energy and the lower water retention value.

Other members of the jury

Bernard de JESO, Professor, Université Bordeaux 1 ♦♦ Monica EK, Professor, KTH (Sweden) ♦♦ Jean-Christophe HOSTACHY, Pulp & Paper Director, ITT Water & Wastewater ♦♦ Serge KOCIMSKI, Ozone Paper Pulp Manager, Degremont Technologies

Research

Research

Director & Managers

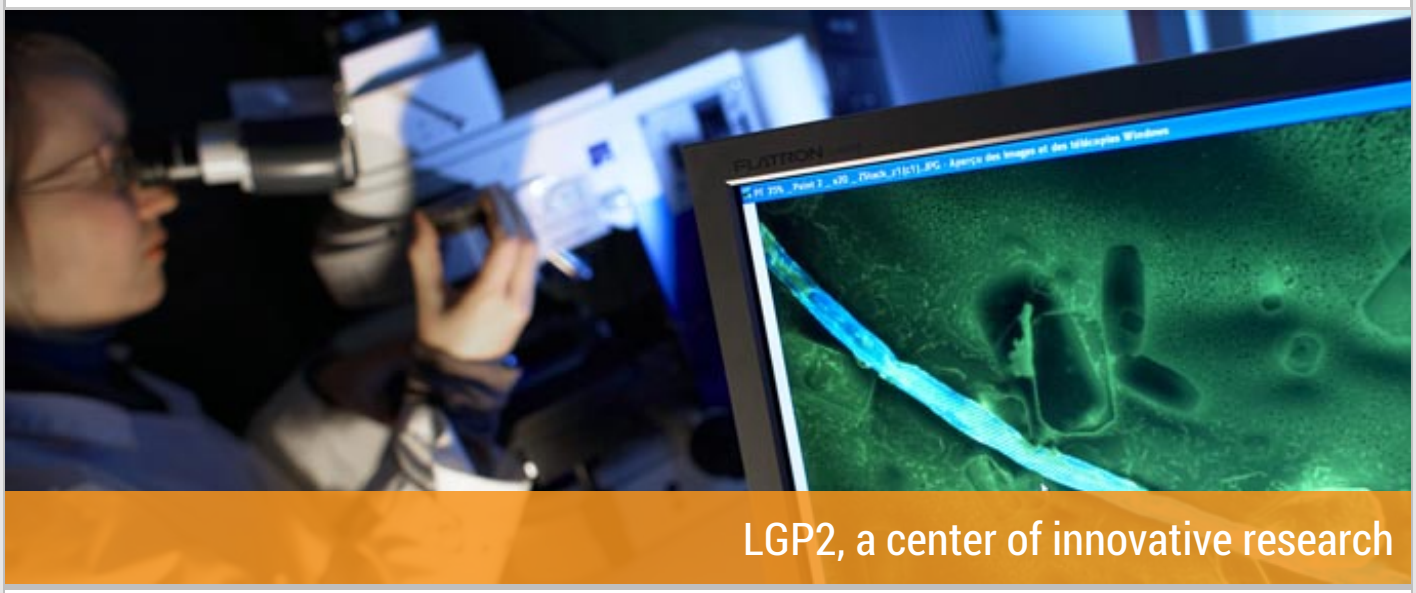
Research groups

Scientific production

Doctorate, post-doctorate

Partnerships-Projects

Equipments & pilots



LGP2 - Ph.D. thesis defended in 2011

Olivier PRAS

December 12, 2011 - Fluid Mechanics, Energetics, Processes **[Thesis online]**

Ph.D. title

Use of cellulose for the elaboration of photoluminescent or conductive materials.

Supervision

Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Davide BENEVENTI, CNRS Researcher, LGP2

Abstract

The context of this project is the cellulosic material functionalization in the printed electronic domain.

The first part of the thesis work highlighted the printability of aqueous dispersion of semiconducting photoluminescent polymer nanoparticles. The influence of the size and the composition of the particles on the emission colour was studied. Security paper is one of the main potential application of these particles.

The second part dealed with the use of cellulose microfibrills and copper microparticles for the elaboration of conductive composite films. The films were self-supporting thanks to the high mechanical properties of the microfibrills. A study on the effect of calendaring pressure and temperature on electric conductivity was carried out, demonstrating that the composite film conductivity can be increased from the 10 S/m of the pristine film up to 70000 S/m.

Other members of the jury

Stéphanie BRIANCON, Professor, Université Claude Bernard Lyon 1 ♦♦ Roberta BONGIOVANNI, Associate Professor, Politecnico di Torino (Italy) ♦♦ Nathalie DESTOUCHES, Professor, Université Jean Monnet (Saint-Étienne) ♦♦ Paul PIETTE, Manager UST9, Centre Technique du Papier

Déborah LE CORRE

October 27, 2011 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Starch nanocrystals: preparation and application for bio-based flexible packaging.

Supervision

Alain DUFRESNE, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Julien BRAS, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

The present work investigates the potential of starch nanocrystals (SNCs) for industrial scaled-up preparation and use. An extensive characterization (morphology, viscosity, thermal stability and properties in nanocomposite) of 5 different SNCs shows, contrary to nanocrystalline cellulose, the limited influence of the botanic source. The analysis of the current preparation process led to three optimization strategies, and to the definition of a new generation of SNCs with smaller dimensions and more homogeneity. A new application of SNCs is presented (multilayer packaging); and showed that SNCs can effectively reduce water vapor permeability of some biopolymers coatings. The life cycle assessment (LCA) of SNCs in this application is also proposed. This study contributes greatly to the advancements of the field and offers perspectives for the industrialization of SNCs.

Other members of the jury

Eliane ESPUCHE, Professor, Université Claude Bernard Lyon 1 ♦♦ Denis LOURDIN, Research Director, INRA - Patrice DOLE, Regional Director, CTCPA ♦♦ Hélène ANGELLIER-COUSSY, Associate Professor, Université de Montpellier 2 ♦♦ David GUERIN, Research Unit Manager, Centre Technique du Papier ♦♦ Timo MAKARAINEN, Manager of R&D Projects, Cargill

Olivier GUIRAUD

September 23, 2011 - Materials, Mechanical, Civil Engineering, Electrochemistry

Ph.D. title

Rheology of concentrated fibre suspensions : Application to polymer composite forming.

Supervision

Denis FAVIER, Professor, Université Joseph Fourier (Grenoble) ♦♦ Laurent ORGEAS, Researcher CNRS, Laboratoire 3S-R ♦♦ Pierre DUMONT, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

This study focuses on the processing of composite materials reinforced with short fibres or fibres bundles such as SMC or BMC. Firstly, an experimental work was carried-out at the macroscopic scale. This work led to the development of a lubricated compression rheometer and associated analysis methods to better characterize the rheology of SMC and BMC compounds, by accounting for the compressibility of compounds and the possible friction between the rheometer wall and the flowing composite. Numerical simulation was then achieved in order to simulate the forming of a BMC. For that purpose, the constitutive parameters of a simple tensorial rheological model were determined from experimental data obtained with the rheometer. Finally, an experimental work at the microscopic level allowed (i) the microstuctures of SMC models from X-ray microtomography micrographs and (ii) fibre pull-out experiment to be characterized, and the interaction mechanisms between the fiber bundles forming the fiber reinforcement of these materials to be modelled.

Other members of the jury

Véronique MICHAUD, Professor, École Polytechnique Fédérale de Lausanne (Swiss) ♦♦ Gilles AUSIAS, Associate Professor, Université de Bretagne-Sud ♦♦ Steven LE CORRE, Professor, Université de Nantes

Aymen BEN MABROUK

July 25, 2011 - Fluid Mechanics, Energetics, Processes **[Thesis online]**

Ph.D. title

Chemical modification of cellulose nanofibers by grafting polymer chains in order to prepare high performance nanomaterials.

Supervision

Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Sami BOUFI, Professor, University of Sfax, Tunisia

Abstract

A stable aqueous nanocomposite dispersion containing cellulose whiskers and a polymer matrix was prepared via miniemulsion polymerization. We were able to prepare a stable dispersion with a 250 wt % solid content and a cellulose whiskers content ranging from 1 up to 5 wt % based on polymer content. Cellulose nanocrytals suspension was mixed with monomers phase in presence of anionic or cationic surfactant and a stabilizing additive acting as a hydrophobe. After sonication for a short time to obtain a stable emulsion of small droplet polymerisation reaction was trigged by the addition of the initiator. The nanocomposite dispersion was characterized using dynamic light scattering, ζ-potential measurement, transmission electron microscopy (TEM), atomic force microscopy (AFM) and FE-SEM. It was found that the particle size of the prepared suspensions is in the range of 90-600 nm, and the final nanocrystals composite is stable for months.Films obtained by casting followed by water evaporation and particle coalescence were analyzed by differential scanning calorimetry, dynamic mechanical analysis, and tensile testing. The nanocomposite maintained high transparency, and their storage elastic modulus increased tediously with the increasing nanowhiskers content.

Other members of the jury

Ali KALLEL, Professor, University of Sfax, Tunisia ♦♦ Mustapha MAJDOUB, Professor, University of Monastir, Tunisia ♦♦ Alessandro GANDINI, Professor, University of Aveiro, Portugal ♦♦ Albert MAGNIN, CNRS Research Director, Grenoble

Philippe MARTINEZ

June 23, 2011 - Fluid Mechanics, Energetics, Processes **[Thesis online]**

Ph.D. title

Experimental study and CFD simulation of the flow of model fluids and coating colours in a slide die curtain coater.

Supervision

Véronique MORIN, Research Director, & David GUERIN, Research Unit Manager, Centre Technique du Papier ♦♦ Martine RUEFF, Ingénieur de Recherche, Grenoble INP-Pagora / LGP2

Abstract

Curtain coating is a contactless coating process which permits a contour coating of the paper and the key parameter of this process is a perfect stable curtain. This technology is expected to spread widely for graphic paper grades and boards in the next few years. Nevertheless, the observations sometimes show defects of regularity of coating which could be connected to instabilities of flow.

In this work, we performed CFD simulations both for Newtonian and Non-Newtonian fluids on the internal flow in a pilot curtain coater and on the flow down the inclined plane. The CFD study of the internal flow revealed the cause of vortex creation into the coater. To maintain vortex-free operation, the Reynolds number at the inlet must remain below a critical value whatever the fluid, which is equal to 20 with the studied geometry whatever the studied fluid. Moreover, a second cavity is useful since instabilities coming from the first cavity could be filtered for low shear-thinning fluids, which is the case of the WFC coating colours. These simulation results were validated thanks to flow visualization experiments with tracers and PIV using a transparent replica of the coater.

Finally CFD simulations on the inclined plane were carried out and permitted to conclude that for the range of operating conditions used on the pilot curtain coater, some issues presented in literature should not exist industrially.

Other members of the jury

Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Raj CHHABRA, Professor, Indian Institute of Technology Kanpur (India) ♦♦ Samuel SCHABEL, Professor, Technische Universität Darmstadt (Germany) ♦♦ Yann COUILLAUD, Account Manager, Allimand

Jérémy ALLIX

January 20, 2011 - Fluid Mechanics, Energetics, Processes

Ph.D. title

Understanding and modelling of the mechanisms of flotation applied to the de-inking of recovered papers.

Supervision

Patrice NORTIER, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Davide BENEVENTI, CNRS Researcher, LGP2

Abstract

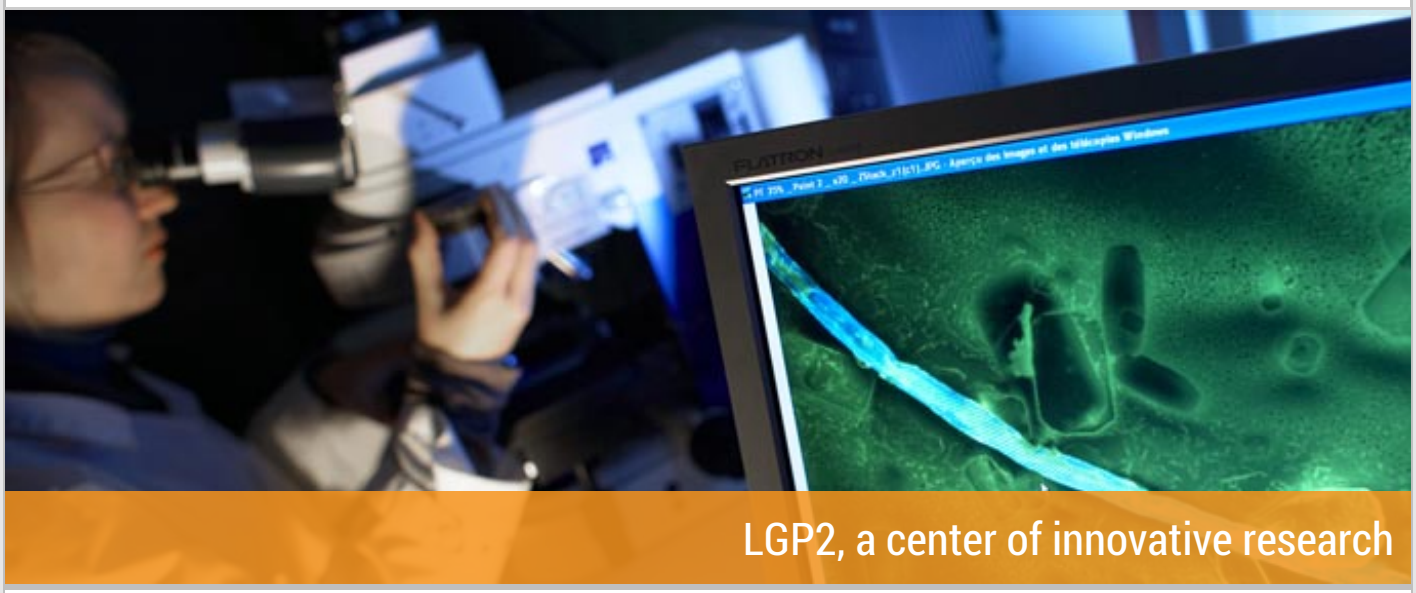
Flotation is the main step of de-inking to remove the ink from the pulp. Whereas the target is toremove 2% of ink from the pulp, there is a loss of 20% of total matters (fibers, fillers and ashes). Theflotation process is the only process allowing to more or less selectively separate the particles frominks during recycling of recovered papers. This process is applied by all the European deinking millsand, although being recognized as being the most selective, it generates solid losses which remainstill too important (15 to 20% of losses) compared to the 2% of ink in weight applied to printed papers.Thus, the selectivity of flotation requires to be improved. Such improvement would at the same timeallow to increase the deinking process yield but also to reduce in parallel the volumes of sludgegenerated during de-inking and thus to simplify all the problems connected with the valorisation ofthese sludges. On the one hand, the objectives of this study are to improve fundamental knowledge ofthe phenomena occurring during flotation, in particular to obtain a better knowledge i) on mechanismsof transport of the various particles (ink, fibres and fines cellulose, mineral loads) during flotation in thepresence of various surface-active components from de-inking, ii) of the role of surface-activesubstances and their elimination during flotation. On the other hand, modelling of the mechanisms oftransport in the pulp and in the froth, taking into account mechanical parameters (air ratio, turbulence,design of the cells) and physico - chemical parameters has been highlighted to finally develop asimulation of the flotation process allowing to evaluate the incidence of the design of the cells,simulation which should then make it possible to improve the effectiveness of the existing cells.

Other members of the jury

Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Maria ANGELS PELACH, Professor, Universitat de Girona (Spain) ♦♦ Edouard PLASARI, Professor, ENSIC (Nancy) ♦♦ Marc SANQUER ♦♦ Bart VAN TIGGELEN - Régis DE GAUDEMARIS ♦♦ Pierre EYMARD BIRON ♦♦ Françoise MASSINES.

Research

Research



LGP2 - Ph.D. thesis defended in 2012

Jean-Baptiste PICOT

December 21, 2012 - Fluid Mechanics, Energy, Processes

Ph.D. title

Modeling and simulation of the recovery workshop in a kraft mill.

Supervision

Gérard MORTHA, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Martine RUEFF, Research Engineer, Grenoble INP-Pagora / LGP2

Abstract

Chemical recovery at the kraft mill is the process whereby the valuable inorganic elements are extracted from spent kraft liquors and regenerated under their form effective to the cooking of the wood and energy is produced from the dissolved organic fraction. Many unit operations are involved and sometimes insufficiently described in terms of chemical engineering and thermodynamics.

In the general framework of the conversion of kraft pulp mills into wood biorefineries, this thesis aims at developing mathematical models of the overall kraft recovery process for implementation in a decision tool.

A comprehensive literature review was made regarding the models of the unit operations and the properties of the constituents. A database of the thermodynamic, physical and chemical properties of the constituents was created. The existing models were analysed and a new modelling approach for the evaporators was developed. The models were implemented in a C/C++ library which was called in an object oriented simulation platform using the Modelica language (OpenModelica/Dymola) and were validated against literature results.

Several simulation scenarii have put forward the main issues for global energy gains and the directions for possible improvements of some operations. More particularly the high refinement of the evaporator model in terms of thermodynamics and chemical engineering, above the published literature on the topic, opens novel perspectives in terms of strategy for process control of the evaporator train.

Other members of the jury

Patrice NORTIER, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Xavier JOULIA, Professor, ENSIACET (Toulouse) ♦♦ Éric SCHAER, Professor, ENSIC (Nancy) ♦♦ Thierry MAYADE, Director R&D, Munksjö (Sweden)

Céline GUEZENNEC

December 20, 2012 - Materials, Mechanical, Civil Engineering, Électrochimique **[Thesis online]**

Ph.D. title

Development of new packaging materials based on micro- and nano-fibrillated cellulose.

Supervision

Alain DUFRESNE, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Florence GIRARD, Research Engineer, Centre Technique du Papier

Abstract

The micro- and nanofibrillated cellulose (MFC/NFC) are nanomaterials from renewable resource with a high interest and partly for the packaging development. MFC combined both interesting properties (high tensile strength, good barrier to oxygen and grease, good transparency) and the advantages of natural cellulose source.

The objective of this thesis was to develop a barrier packaging board based on MFC/NFC by coating processes. Firstly, the study focussed on the characterisation of the MFC suspensions, on the manufacturing of MFC self-standing films and on the determination of their properties. Secondly, the development of MFC based composites was studied as model films. The last part was devoted to the introduction of MFC in coating colours in order to develop a barrier layer at the board surface. Trials at pilot scale demonstrated the industrial feasibility of this product. The potential of the use of MFC/NFC was demonstrated to be used as a drying additive and as a main component of barrier layer.

Other members of the jury

Hamid KADDAMI, Professor, Université Cadi Ayyad (Marrakech, Maroc) ♦♦ Nathalie GONTARD, Research Director, INRA Montpellier ♦♦ Marie-Pierre LABORIE, Professor, University of Freiburg (Germany) ♦♦ Noël CARTIER, Head of R&D Projects, Ahlstrom

Satyajit DAS

December 17, 2012 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Pure cellulose production from kraft pulp by an environmentally friendly process using catalysed hydrogen peroxide.

Supervision

Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Nathalie MARLIN, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

The aim of the thesis was to develop a process for "green" pure cellulose production obtained from hardwood kraft pulp.

The proposed treatment includes a first step of hot-acidolysis for reducing the content of hexenuronic acids and transition metallic cations (Cu, Fe, Mn) in the pulp. The second step is the pulp delignification using alkaline hydrogen peroxide catalyzed by the Cu-phenanthroline complex. The presence of the catalyst improves the delignification efficiency since alcohol functions carried by the lignin macromolecule in position of the aliphatic chain are selectively oxidized.

To eliminate residual hemicelluloses, it is proposed to carry out a cold caustic extraction. Finally, the last unsaturated impurities are degraded by pulp ozonation. After the full sequence of treatments, the chemical composition of the produced cellulose is similar to that of market pure celluloses (for textile or plastic uses), in line with the objectives. The addition of the catalyst reduces the polymerization degree of cellulose. It thus makes it possible to adjust the value of the cellulose DP according to the targeted applications.

Other members of the jury

Monika EK, Professor, KTH Royal Institute of Technology (Sweden) ♦♦ Rogério SIMOES, Professor, Universidade da Beira Interior (Portugal) ♦♦ Vanessa DURRIEU, Associate Professor, ENSIACET (Toulouse) ♦♦ Alain DERONZIER, Research Director, Université Joseph Fourier (Grenoble)

Robin ABDERRAHMEN

December 12, 2012 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Design of self-adhesive labels by microencapsulation adhesive.

Supervision

Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2

Abstract

The main objective of this study is to prepare innovative silicone liner-free labels. It can be achieved by the adhesive self protection', thanks to its incorporation into microcapsules. This allows the preparation of dry labels' gluing under the application of a pressure, which induces the rupture of the microcapsules, thus releasing the core material, a pressure sensitive adhesive.

The first step was to analyse 3 water-based PSA in view of their encapsulation. Then, the most suitable adhesive was microencapsulated by coacervation (using biopolymer as shell) and by in situ polymerisation. Two other encapsulation processes (spray-cooling and spray-drying), were also carried out and were compared with the 2 former processes. Coating colour formulations were prepared with spray-cooling microcapsules (the most adhesive ones). Coating trials were carried out by blade coating, and by screen printing.

Compatibility between microcapsules and the label making process, using a flexographic printing press, was determined. Finally, the mains characteristics of the prepared innovative products (adhesion, application pressure) were compared to industrial self-adhesive homologues, and found that they could be suitable for the preparation of silicon liner-free envelops and stamps.

Other members of the jury

Stéphanie BRIANÇON, Professor, LAGEP (Villeurbanne) ♦♦ Roberta BONGIOVANNI, Associate Professor, Politecnico di Torino (Italy) ♦♦ Salaheddine SKALI-LAMI, Associate Professor, LEMTA (Nancy) ♦♦ Gilles BRUAS, Director, Papeterie Gerex (Voreppe) ♦♦ Bernard PINEAUX, Research Engineer, Grenoble INP-Pagora / LGP2

Karim MISSOUM

November 22, 2012 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Functionalization and surface modification of nanofibrillated cellulose.

Supervision

Naceur BELGACEM, Professor, Julien BRAS ♦♦ Julien BRAS, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

Since last decades, nanocelluloses know a strong interest and they are the subject of many studies led by industrials and/or academic consortia. This study is a part of the European project SUNPAP for the industrialization of nanofibrillated cellulose (NFC). This thesis is the state of new methods for the chemical surface modification of NFC with a view of green chemistry.

Several strategies have been developed such as the use of ionic liquids as reaction solvents (described as green solvents) or the use of an aqueous nanoemulsion in order to graft the surface of NFCs. Thus, the treated substrates were then used in various applications. Also, bionanocomposites were produced, the impact of the introduction of NFC (modified or not) in paper sheets has also been studied. A study on the antibacterial properties and biodegradability of modified NFC is also proposed. Several characterizations of neat and modified NFC were performed. Powerful and innovative techniques have been used to characterize these substrates such as XPS (X-ray Photoelectron Spectroscopy) or SIMS (Secondary Ion Mass Spectrometry).

All these chemical modifications, applications and characterizations are offered promising prospects in the world of nanocelluloses.

Other members of the jury

Etienne FLEURY, Professor, INSA de Lyon ♦♦ Monika ÖSTERBERG, Associate Professor, Aalto University (Finland) ♦♦ Stéphane GRELIER, Professor, Université Bordeaux 1 ♦♦ Noël CARTIER, Senior Scientist, Ahlstrom.

Souheila ADJIMI

October 30, 2012 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Contribution to the development of a photocatalytic paper. Application to the reduction of Volatile Organic Compounds

Supervision

Pierre-Xavier THIVEL, Associate Professor, Université Joseph Fourier (Grenoble)

Résumé

The objective is to elaborate a based-paper titanium/silica photocatalysis for on stream flue gas depollution (volatile organic compounds) stemming from processes of printing. The volatile organic compound used in this study is the ethanol. Particles of hollow silica were synthesized and used as a support for nanoparticles of titanium dioxide, which were elaborated by sol-gel method. A continuous reactor was designed and used to treat the polluted gaseous flow. The ethanol passes through the photocatalytic paper irradiated by a UV lamp. Several photocatalytics papers were elaborated and characterized by several techniques (MEB, Spectroscopy Raman, DRX). A modeling of the reactor and the support (photocatalytic paper) was developed and proposed. This modeling integrates the Langmuir - Hinshelwood kinetic and the variation of the intensity with position in layer's paper using the Kublka-Munk model.

Other members of the jury

Jean-Claude ROUX, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Laurence LE COQ, Professor, École des Mines de Nantes ♦♦ Jean-Michel GUILLOT, Professor, École des Mines d'Alès ♦♦ Abdelkrim BOUZAZA, Associate Professor, ENS Chimie de Rennes ♦♦ Nicolas SERGENT, Associate Professor, Grenoble INP-Phelma

Lara JABBOUR

October 26, 2012 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Elaboration of Li-ion batteries using cellulose fibers and papermaking techniques.

Supervision

Davide BENEVENTI, CNRS Researcher, LGP2 ♦♦ Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 - Claudio GERBALDI, Associate Professor, Politecnico di Torino (Italy).

Abstract

This work investigates the production of low cost, low environmental impact, easily up-scalable and recyclable cellulose-based Li-ion batteries.

Two main research approaches were explored. At first, microfibrillated cellulose was used for the production of paper-like anodes by means of a water-based casting process. Then, a papermaking approach was adopted and the majority of the experimental work was focused on the use of cellulose fibers for the production of paper-electrodes (i.e. anodes and cathodes) and paper-separators by means of a water-based filtration process.

The prepared electrodes are easy to handle and self-standing with good electrochemical characteristics, comparable with that of standard synthetic polymer-bonded electrodes.

Other members of the jury

Nadia EL KISSI, Research Director CNRS, Université Joseph Fourier (Grenoble) ♦♦ Lars WAGBERG, Professor, KTH Royal Institute of Technology (Sweden) ♦♦ Bernard LESTRIEZ, Associate Professor, Université de Nantes ♦♦ Hatem FESSI, Professor, Université Claude Bernard Lyon 1.

Chloé BOIS

October 26, 2012 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Manufacture of membrane-electrode assembly of fuel cells by printing processes.

Supervision

Anne BLAYO, Lecturer Researcher, Grenoble INP-Pagora / LGP2 ♦♦ Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2

Abstract

In a context of fossil fuel shortage and hydrocarbon emission reduction, fuel cells are a promising solution for energy production. However, the cost of the energy they produce remains too expensive to be competitive and the conventional manufacturing processes used limit the scaling up of the production.

The core of Proton Exchange Membrane Fuel Cells (PEMFCs) is a stack composed of five constituents, in which the proton exchange membrane and the two gas diffusion layers can be considered as printing substrates, and the two catalyst layers can be printed by continuous printing processes.

This work demonstrated the relevance of flexography for manufacturing fuel cell components. It allows large production with low waste of expensive elements. Despite of the poor printability of the substrates, the catalyst layers printed by flexography reached similar electrochemical properties than those made by conventional processes.

Other members of the jury

Yann BULTEL, Professor, Grenoble INP ♦♦ Reinhard BAUMANN, Professor, Chemnitz University of Technology (Germany) ♦♦ François LAPICQUE, Research Director CNRS, Université de Lorraine

Imtiaz ALI

September 28, 2012 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Study of the mechanical behavior of recycled fibers. Applications to papers and paperboards.

Supervision

Jean-Francis BLOCH, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Raphaël PASSAS, Research Engineer, Grenoble INP-Pagora / LGP2

Abstract

By nowadays, the environmental politic is important: the deforestation or the stress on the wood market contribute to the increased interest to improve the recovered rate in papers. Particularly, high value papers constitute a specific target due to their high amount of virgin fibres.

The aim of this work was to characterise the modifications of morphological and physical properties occurring during drying and rewetting cycles. To reach this aim, experimental technics have been revisited or developed like the inverse size exclusion chromatography, the atomic force microscopy, the environmental scanning electron microscopy and the micro-tomography.

This experimental study showed that the main morphological changes occur during the first cycle. Furthermore, delamination and densification of cell wall fibres were highlighted. Evolutions of the mechanical behavior of handsheets and their 3D structures were analysed in function of the proportion and the quality (number of cycles) of fibres.

This work demonstrates the potential of valorisation of the recycled fibres in the paper area, especially for high value papers.

Other members of the jury

Christian GEINDREAU, Professor, Université Joseph Fourier (Grenoble) ♦♦ Ana Paula COSTA, Professor, Universidade da Beira Interior (Portugal) ♦♦ William SAMPSON, Professor, University of Manchester (UK)

Ragab ABOUZEID

September 27, 2012 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Advanced cellulose composites, preparation and properties.

Supervision

Alain DUFRESNE, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Mohamed Adel YOUSEF, Professor, Helwan University, Egypt

Abstract

The present study deals with utilization of Egyptian bagasse in both conventional and non-conventional fields. The conventional application is devoted to papermaking, where bagasse pulp is the most appropriate pulp for this purpose due

to the suitability of fiber length and high cellulose and hemicellulose contents. The non-conventional application is dedicated to the preparation of cellulosic derivatives having liquid crystalline properties.The first approach deals with using modified soy protein isolate (SPI) as binder for cellulosic fibers in paper composites. Modification of SPI was carried out through i) denaturation with urea and NaOH. ii) addition of acrylamide to the denatured SPI. iii) changing pH of SPI. These types of modification were used to improve the adhesion properties of SPI. Pronounced mechanical and physical properties of paper sheets filled with 0.5, 2.5 or 5% denatured SPI was obtained upon using 2.5%. The optimum condition of SPI addition was used in ii and iii modifications. The additional effect of acrylamide on SPI was pronounced where the mechanical and physical properties were enhanced. Correlation between the mechanical and physical properties of paper sheets with the pH of SPI was studied. The used pHs were 3, 5, 7 and 10.The results showed that the maximum breaking length was obtainedAbstract - xix -at the isoelectric point of SPI at pH 5 (at the isoelectric point (IEP) the number of positive and negative charges on the polyion is the same, giving a net charge of zero) and it began to decrease when the pH is increased to pH 10. Both the burst index and the tear index showed parallel trends.In the second approach, a series of 4- alkyoxybenzoyloxypropyl cellulose (ABPC-n) samples were synthesized via the esterification of hydroxypropyl cellulose (HPC) with 4-alkoxybenzoic acid bearing alkoxy chain with different lengths. On the other hand, cellulose was isolated in pure form from Egyptian bagasse pulp. Hydroxypropylation was then conducted on the isolated cellulose. 4-alkyoxybenzoyloxypropyl cellulose (ABPC-m) samples were synthesized via the esterification of the latter product with the same acid, bearing 2, 10 and 12 carbon atoms in the side chain and characterized.The molecular structure of both esters (ABPC-n and ABPC-m) was confirmed by Fourier transform infrared (FT-IR) and 1H NMR spectroscopy. The liquid crystalline (LC) phases and transition behaviors were investigated using polarized light microscopy (PLM), and differential scanning calorimetry (DSC), respectively. The lyotropic behavior of the derivatives was investigated in DMA solutions using PLM andAbstract - xx -the critical concentration was firstly determined via refractive index measurements.

Other members of the jury

Aid KHALIL, Professor, Helwan University, Egypt ♦♦ Magdi NAOUM, Professor, Cairo University, Egypt ♦♦ Étienne FLEURY, Professor, INSA Lyon, France ♦♦ Nahla EL-WAKIL, Professor, National Research Center, Egypt ♦♦ Ali SARHAN, Professor, Mansoura University, Egypt

Lucie BOIRON

September 7, 2012 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Study of the impact of hemicellulose extraction from wood on cellulose fibres and ethanol production as part of a lignocellulosic biorefinery .

Supervision

Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2

Abstract

Biofuel revival could be a great opportunity for the chemical pulp industry to widen the range of its products made from wood. This thesis deals with the integration of a softwood hemicellulose extraction step prior to the Kraft pulping process in order to produce both cellulose fibres and bioethanol.

In this study the experimental work covers the entirety of the process: from the extraction of more than half of the hemicelluloses from wood either by autohydrolysis or dilute acid hydrolysis to the production of bleached cellulosic fibres as well as ethanol from fermentated wood hydrolyzates.

Prehydrolyzed wood and their subsequent pulps stood out by their excellent delignification ability during Kraft cooking and oxygen bleaching. Quantitative analysis of the main constituants of the pulps showed why prehydrolysis leads to decreased Kraft pulp yields (extra lignin loss and hemicelluloses loss including xylans). A range of hypotheses to explain the good delignification ability of prehydrolyzed wood Kraft pulps during oxygen bleaching was narrowed to one by Kraft lignin analysis.

The overall results of the hemicellulose extraction prior to Kraft pulping as it has been defined in this study showed that from 100 kg of softwood, 27 to 36 kg of bleached cellulosic fibres and 6 litres of ethanol could be produced. The bleached cellulosic fibres are of great interest for dissolving pulp or cellulose nanocrystals production.

Other members of the jury

Nicolas BROSSE, Professor, Université de Lorraine ♦♦ Ana Paula DUARTE, Professor, Universidade da Beira Interior (Portugal) ♦♦ Marie-José VILLETTE, Head of R&D, Fibre Excellence R&D Kraft.

Nicoleta-Ioana VLADUT

July 20, 2012 - Fluid Mechanics, Energy, Processes

Ph.D. title

Delignifying chemical system based on hydrogen peroxide.

Supervision

Gérard MORTHA, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Vanessa DURRIEU, Associate Professor, INP Toulouse / LCA

Other members of the jury

Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Stéphane GRELIER, Professor, Université de Bordeaux 1 ♦♦ Carlos PASCOAL-NETO, Professor, Universidade de Aveiro (Portugal) ♦♦ Pierre LARNICOL, Business Manager, Arkema

Saurabh KUMAR

June 14, 2012 - Fluid Mechanics, Energy, Processes

Ph.D. title

Deinking pulp fractionation: characterization and separation of fines by screening.

Supervision

François JULIEN SAINT AMAND, Deputy Director R&D, & Benjamin FABRY, Manager Deinking Process, Centre Technique du Papier ♦♦ Raphaël PASSAS, Research Engineer, Grenoble INP-Pagora / LGP2

Abstract

Deinking is a key process in a sustainable strategy for papermaking, where the ink contained in the fine fraction (defined as passing a 76µm screen) is eliminated from the fibrous suspension. Fines sub-fractions analysed by a new manual classification method showed that the major contamination of ink occurs in the fraction which passes 11µm openings. Visual analysis of the microscopic images revealed that fibrils are in majority almost ink free whereas flakes from mineral fillers or cellulosic origin have ink deposition with varying coverage. Pulp fractionation is a viable option which opens avenues for separation of fines from pulp and offers opportunity of dedicated treatment to each fraction.

Separation of fines by a pressure screening system equipped with a micro-hole screen plate showed a higher selectivity towards the separation of fines into the accepts than conventional slot-screen cylinders. Comprehensive understanding of rotor hydrodynamics helped to understand the capacity constraints and inlet concentration limits. Studies showed that such a micro-hole screen plate is well adapted to rationalize deinking operations, where dedicated treatment on different fractions could be envisaged.

The study highlighted that new optimised deinking lines could be envisaged by introducing a specific fractionation technology and that pulp fines can be valorised, with an important impact in future manufacturing concepts as specifically engineered multilayer papers.

Other members of the jury

Evelyne MAURET, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Harald GROSSMANN, Professor, Technische Universität Dresden (Germany) ♦♦ Paulo FERREIRA, Assistant Professor, Universidade da Coimbra (Portugal) ♦♦ Frédéric VAULOT, Director R&D, Kadant-Lamort (France)

Basile GUENEAU

June 13, 2012 - Organic chemistry

Ph.D. title

Study and use of copper(II) polypyridinic complexes in catalysis of dioxygen delignification of cellulosic pulps.

Supervision

Alain DERONZIER, Research Director, Université Joseph Fourier (Grenoble) ♦♦ Nathalie MARLIN, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

Dioxygen delignification considerably reduces the operating cost of the bleaching process and decreases the environmental impact of the bleaching effluent. Unfortunately the performance of dioxygen delignification is limited since part of the residual lignin is not reactive toward dioxygen while cellulose depolymerisation occurs.

Studies suggested that dioxygen delignification could be improved thanks to the use of catalysts such as copper(II)-phenanthroline type complexes which have shown promising results on delignification efficiency. However cellulose was also more degraded. Different polypyridinyl ligands have been studied in this work, in an attempt to find copper(II) complexes that have more affinity toward lignin and less toward cellulose. Complexes have been characterised by UV/Vis spectroscopy, cyclic volammetry, and they were studied for the catalysed oxidation of various substrates: a non phenolic lignin model compound and lignocellulosic substrates (a model of cellulose, a model of native lignin and an industrial kraft pulp).

It has been shown that the nature of the ligand had a significant effect on the catalytic activity of Cu(II) complexes in the oxygen oxidation of the lignin model compound. However, the active complexes only show a limited activity during the delignification of a kraft pulp and oxidize carbohydrates. This lack of selectivity prevents from an industrial application for paper pulp production but may be useful for the design of products with fewer constraints on cellulose polymerization degree.

Other members of the jury

Alain CASTELLAN, Professor, ENSCBP/IPB (Bordeaux) ♦♦ Joël ALBET, Associate Professor, INP Toulouse ♦♦ Jean-Marie HERRMANN, Research Director, IRCELYON (Lyon 1) ♦♦ Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2

Olivier PAQUET

June 6, 2012 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Surface modification of cellulose by the organosilanes.

Supervision

Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Evelyne MAURET, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Elisa ZENO, Research Engineer, Centre Technique du Papier

Abstract

This thesis describes the chemical modification of cellulosic fibers by organosilanes. The reactions of silanes bearing various functional groups were carried out in pure aqueous solution and followed in-situ by nuclear magnetic resonance spectrometry. The effect of pH, concentration, and temperature on the reaction kinetics was studied. Aminosilanes could be processed in conditions similar to those commonly used in the papermaking.

Furthermore, the adsorption of the most promising grafting agents on model cellulose surfaces was investigated by mean of a quartz crystal microbalance, and the effect of the same parameters was evaluated. This study showed that a good surface coverage is attained rapidly, i.e., within only a few minutes. Then, a slower but continuous adsorption was observed over time. The nature of the interactions between various silanes and cellulose was tested. It was shown that the grafting was successfully performed, thus giving rise to the formation of strong interactions between the adsorbate and the adsorbent.

Finally, two types of fibers (softwood and hardwood) were used in order to evaluate the effect of organosilanes on mechanical properties and the softness of paper. The results obtained showed quite modest effects, even though the success of the grafting was assessed on both type of fibers.

Other members of the jury

Didier LEONARD, Professor, CPE Lyon ♦♦ Antonio PIZZI, Professor, ENSTIB (Nancy) ♦♦ Maria Emília CABRAL AMARAL, Professor, Universidade da Beira Interior (Portugal)

Eder José SIQUEIRA

June 5, 2012 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Polyamideamine epichlorohydrin-based papers: mechanisms of wet strength development and paper repulping.

Supervision

Evelyne MAURET, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2

Abstract

Polyamideamine epichlorohydrin (PAE) resin is a water soluble wet strength additive used for preparing wet strengthened papers (WSP). Even if PAE is largely used in the papermaking industry, there is still a lack of knowledge concerning the cross-linking reactions, the effect of the operating conditions on the properties of the produced papers as well as the recycling of WSP.

The first part of this work showed that the main PAE cross-linking reaction occurs by a nucleophilic attack of N atoms in the PAE structure forming 2-propanol bridges between PAE macromolecules. A secondary contribution of ester linkages to the PAE cross-linking resulting from the reaction between carboxylic groups and azetidinium rings was also observed. This reaction is important in the presence of carboxylmethyl cellulose (CMC). However, it can be postulated that ester bond formation has a negligible impact on the wet strength of PAE-based papers because the amount of carboxylic groups present in lignocellulosic fibres is considerably less high than in CMC and the resulting formed ester bonds are hydrolysable.

In the second part of this work, the obtained results showed that, when PAE is added to a fibrous suspension (bleached chemical pulp - Eucalyptus), the adsorption, reconformation and/or penetration phenomena reach an apparent equilibrium after 10 min of contact time. An increase of the conductivity of the pulp suspension (from 100 to 3000 S/cm) negatively impacts the strength of the WSP, but for high dosages only (1%). Finally, the degradation of PAE films and PAE-based papers was studied in order to improve the recycling of WSP. For the tested conditions, sodium persulfate is the most effective reagent but the efficiency of the treatment is decreased when coated papers are used.

Other members of the jury

Ana Paula COSTA, Professor, Universidade da Beira Interior (Portugal) - Marie-Pierre LABORIE, Professor, University of Freiburg (Germany) ♦♦ Jean-Pierre JOLY, Researcher CNRS, Université Henri Poincaré (Nancy) ♦♦ Séverine SCHOTT, Engineer, Ahlstrom LabelPack (Pont-Evêque)

Rita FADDOUL

May 3, 2012 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Printing processes dedicated to the mass production of ceramic based electronic microdevices.

Supervision

Anne BLAYO, Lecturer Researcher, Grenoble INP-Pagora / LGP2 & Nadège REVERDY-BRUAS, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

This work demonstrates the printing processes potential for manufacturing ceramic based electronic devices. Several printing techniques were studied: screen printing, flexography, rotogravure and inkjet. Ceramic tapes surface properties were characterised: surface pore size, roughness and surface energy.

These analyses allowed the selection of the inks raw materials adapted to the substrates and the printing processes. Water-based silver inks were formulated. Inks properties, rheology and surface tension, were analysed and their effect on line properties was investigated. Printed substrates were afterwards sintered. Resistivity values close to that of bulk silver were reached (2 to 12x10-8 Ohm.m).

These work novelties are mainly the formulation of water-based environmentally friendly screen printing pastes and the flexography printing of silver inks onto ceramic substrates. This study offers new perspectives for the industrialisation and the mass production of electronic components on flexible ceramic substrates.

Other members of the jury

Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 - Martine LEJEUNE, Professor, Université de Limoges - Arnaud MAGREZ, Doctor, École Polytechnique Fédérale de Lausanne (Swiss) - Leszek GOLONKA, Professor, Wroclaw University of Technology (Poland) - Stéphane BREDEAU, Doctor, Commissariat à l'Énergie Atomique et aux Énergies Renouvelables

Magalie PERALBA

February 14, 2012 - Fluid Mechanics, Energy, Processes

Ph.D. title

The X-ray microtomography as a tool for solving industrial problems in pulp and paper.

Supervision

Jean-Francis BLOCH, Associate Professor, Grenoble INP-Pagora / LGP2 - Patrice MANGIN, Professor, Université du Québec à Trois-Rivières (Canada)

Abstract

The X-ray microtomography can provide useful innovative information for solving current industrial problems. Indeed, to better understand the behavior of a material during its use, we must study its structure on a microscopic scale, that allows the X-ray microtomography.

In this thesis, the use of this technique was used to analyze the phenomena of flow and filtration in the pulp and paper.

In the first part, flows through forming fabrics were studied by connecting the structure measured by microtomography to the flow simulations and experimental measurements.

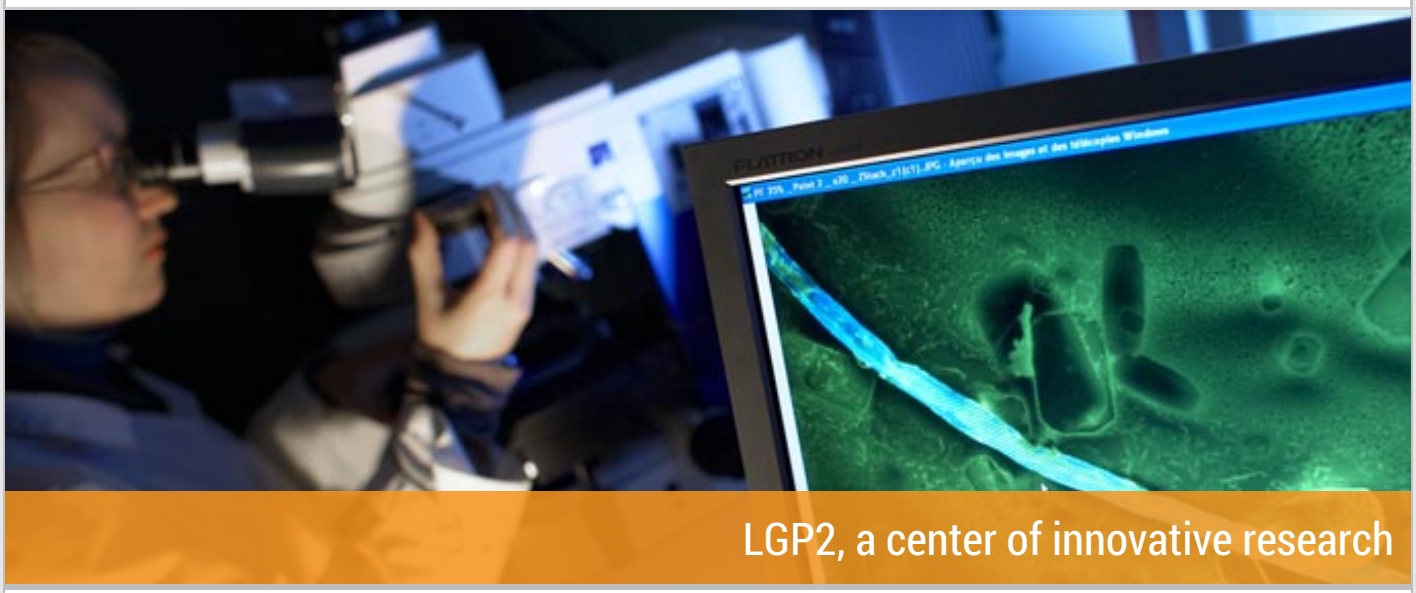
In the second part, the filtration of mineral fillers through a fibrous mat was tested in order to understand the phenomena occurring during filtration of the formation of the paper.

The last part was devoted to the print quality of paper attached to its structure.

Other members of the jury

Christian GEINDREAU, Professor, Université Joseph Fourier (Grenoble) - Laurence SCHACHER, Professor, ENSISA (Strasbourg) - Dominique THOMAS, Professor, INPL (Nancy) - Martin DUBE, Associate Professor, Université du Québec à Trois-Rivières (Canada) - Pierre DUMONT, Associate Professor, Grenoble INP-Pagora / LGP2 - Sabine ROLLAND DU ROSCOAT, Associate Professor, Université Joseph Fourier (Grenoble)

Research



LGP2 - Ph.D. thesis defended in 2013

Zied MARRAKCHI

December 1, 2013 - Materials, Mechanical, Civil Engineering, Electrochemistry

Ph.D. title

Valorization of Alfa fibers.

Supervision

Evelyne MAURET, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Farouk MHENNI, Professor, University of Monastir (Tunisia) ♦♦ Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2

Abstract

This thesis aims at valorizing herbaceous plant called Alfa (Stipa tenacissima) in added value application. This raw material is very abundant in Tunisia. Thus, the main idea of this work is to use Alfa fibers as reinforcing elements in bio-composites.

The literature review revealed that this plant has not been extensively studied, which motivated undertaking a comprehensive study of these fibers. A systematic and deep study of the chemical composition, the morphological properties, the electrical charges, the refining kinetics of pulp as well as the physical properties of the paper produced from these fibers was performed and gave several rational insights on Alfa fibers in the context of papermaking.

The second part of this work was devoted to the use of Alfa fibers, as reinforcing fiber mat in composite materials based on biodegradable polymer matrices. In this context, an impregnation technique of the paper films in solutions of two biodegradable polymers – polycaprolactone (PCL) and poly-L-lactide (PLLA) – was chosen. The structural, morphological, thermal and mechanical properties of these new composites were analyzed and discussed.

In addition, an original microwave-assisted grafting of surface chemical modification of Alfa fibers was proposed. In this context, stearic acid was used as a coupling agent. Finally, the effect of the surface modification of the reinforcement on composites properties was assessed and analyzed.

Other members of the jury

Limam ALOUI, Professor, University of Gafsa (Tunisia) ♦♦ Jean-Yves DREAN, Professor, Université de Haute Alsace ♦♦ Sami BOUFI, Professor, University of Sfax (Tunisia)

Bertrand QUESNE

December 5, 2013 - Fluid Mechanics, Energy, Processes

Ph.D. title

Study of the marbling phenomenon on flexible PVC printed in rotogravure

Supervision

Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Nadège REVERDY-BRUAS, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Davide BENEVENTI, CNRS Researcher, LGP2

Abstract

The objective of this thesis is to study a recurrent printing defect when industrial printing of PVC flooring, the marbling. This defect appears randomly in the printing production line with variable levels. It appears like a textured print instead of normally uniform solid print which generates many nonconformities of the products. The purpose of this work is to understand the origin of the phenomenon of marbling in order to identify the cause(s).

To achieve this objective, it was necessary to develop a reliable and non-subjective tool to quantify the defect based on an image analysis technic. This was used to study the main parameters that may be the cause of the marbling: the substrate wettability, the printing process parameters as well as the inks properties (surface tension, rheology). All of this work has highlighted the role of the formulated inks flow threshold, the phenomenon being linked to instabilities like Saffman-Taylor type raising in the cleavage of the ink film during the printing step of the flooring.

Other members of the jury

Roberta BONGIOVANNI, Associate Professor, Politecnico di Torino (Italy) ♦♦ Salaheddine SKALI-LAMI, Associate Professor, LEMTA, Université de Lorraine ♦♦ Thierry FOURNEL, Professor, Laboratoire Hubert Curien, Université Jean Monnet (Saint-Étienne) ♦♦ Philippe DOUCY, Engineer, Gerflor (Saint-Paul-Trois-Châteaux)

Nathalie LAVOINE

November 15, 2013 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Design, processing and characterization of innovative functional bio-nano-materials for packaging.

Supervision

Julien BRAS, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Isabelle DESLOGES, Research Engineer, Grenoble INP-Pagora / LGP2

Abstract

The present work investigates the potential of microfibrillated cellulose (MFC) coated onto cellulosic substrates as controlled delivery system (CDS) of antibacterial molecules for food-packaging.

Two coating processes and three substrates were compared. MFC was coated onto paper and cardboard substrates, enhancing their air resistance and bending stiffness with a minimum coat weight of 8 g/m². Microscopic analyses at nanoscale underlined the nanoporous MFC network preserved onto the substrate surface even after coating. For the first time, this network was used as CDS of various molecules and proved its efficiency by releasing molecules more progressively and over a longer period. The antibacterial activity was effective against non-pathogenic bacteria, leading to the improvement of the food shelf-life. The application of this new material was broadened up by using simultaneously cyclodextrins and MFC, which also led to very promising results.

This PhD proposing 8 articles in scientific journals, paves the way for new high-added value applications in the field of controlled delivery systems by using MFC-based materials, within active packaging or medical fields.

Other members of the jury

Nathalie GONTARD, Professor, Université Montpellier 2 ♦♦ Kristin SYVERUD, Professor, NTNU (Trondheim, Norvège) ♦♦ Véronique COMA, Associate Professor, Université Bordeaux 1 ♦♦ Eliane ESPUCHE, Professor, Université Lyon 1 ♦♦ Nicolas TABARY, Associate Professor, Université Lille 1

Antoine DUVAL

November 15, 2013 - Materials, Mechanical, Civil Engineering, Electrochemistry

Ph.D. title

Contribution to the study of gluten as material: contribution of different types of lignins

Supervision

Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Sonia BOISSEAU, Associate Professor, CERMAV

Abstract

Wheat gluten, a set of proteins from the wheat kernel, is commonly used to process polymeric materials, usually in the presence of glycerol as a plasticizer. Its use is however limited, because of its high sensitivity to water and relatively poor mechanical properties when compared to synthetic polymers. The influence of the glycerol content on the water absorbance, the phase separation and their glass transition were first studied.

Then, another biopolymer, wood lignin, has been incorporated into the materials in order to enhance their properties. The influence of different types of lignin from the paper pulp industry, Kraft lignin and lignosulfonates, have been investigated. Kraft lignin addition enhances materials rigidity and thermal properties, and reduces the water sensitivity, whereas lignosulfonates allow to decrease the glycerol content, resulting in better mechanical properties and reduced water sensitivity.

To gain insights into the interactions between gluten and lignins, several fractionation procedures have then been carried out. The influence of the protein type and lignin molecular mass could be pointed out, and were correlated to the materials macroscopic properties.

Other members of the jury

Denis LOURDIN, Research Director, INRA Nantes ♦♦ Stéphanie BAUMBERGER, Professor, AgroParisTech ♦♦ Dominique LACHENAL, Professor, Grenoble-INP Pagora / LGP2 ♦♦ Marie-Hélène MOREL, Research Director, INRA Montpellier

Cyril MARULIER

October 17, 2013 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Multiscale study of the coupling between hygroelastic properties of papers and their microstructure.

Supervision

Pierre DUMONT, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Denis CAILLERIE, Professor, Grenoble INP / 3SR ♦♦ Laurent ORGEAS, Senior Researcher, CNRS / 3SR

Abstract

The objective of this work is to study the coupling between the hygroelastic properties of papers and their microstructure. The use of images of model paper acquired by X-ray microtomography allowed the characterization in an unprecedented manner of the evolution of microstructural properties of these materials according to their production conditions and during tests where they were placed in atmosphere at controlled relative humidity.

These results provide a new contribution to the knowledge of the statistical nature of the descriptors of fibre properties (size and orientation) and their contacts (surface, bonding degree ratio), of the architecture of fibrous networks that papers constitute (number of fibre-to-fibre bonds) as well as of the size of the representative elementary volumes of microstructural and elastic properties. Based on this information, various models, more or less sophisticated, were developed in the framework of the theory of homogenisation of discrete periodic structures to describe the mechanical properties of paper. This approach sheds new light on the role of fibre-to-fibre bonds on the mechanical behaviour of these materials.

Other members of the jury

Olivier ARNOULD, Associate Professor, Université de Montpellier ♦♦ Frédéric JACQUEMIN, Professor, Université de Nantes ♦♦ Steven LE CORRE, Professor, Université de Nantes ♦♦ Dominique POQUILLON, Associate Professor, INP Toulouse

Elsa CORROYER

September 16, 2013 - Fluid Mechanics, Energy, Processes

Ph.D. title

Using the flexographic process for the printing on flexible materials for decorations of laminated glazing.

Supervision

Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2

Abstract

The objective of this project is to offer laminated glass incorporating decorations. To do this, the printing of a polymeric insert by flexographic process is studied. Initially, commercial inserts are thoroughly analyzed (composition, mass and surface properties), as well as consumables inherent in flexographic process (inks and print form). Then, the printing of different types of patterns shows that flexography provides prints with most optical specifications. In addition, adhesion and mechanical strength properties of different types of laminated glass, and durability of these, are studied. Finally, the results of industrial tests are used to define a concept of printing press allowing the integration of flexographic process in production lines of laminated glass.

Other members of the jury

Etienne FLEURY, Professor, INSA Lyon ♦♦ Yves GROHENS, Professor, Université de Bretagne Sud ♦♦ Antonio L. TORRES, Professor, Universitat Politècnica de Catalunya (Spain) ♦♦ Sébastien WERY, Head of R&D, Saint Gobain Glass

Marion SANGLARD

January 11, 2013 - Fluid Mechanics, Energy, Processes

Ph.D. title

Simultaneous production of bleached cellulose fibers and polyxylosides alkyl through a biorefinery paper.

Supervision

Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2

Abstract

This project aims at converting a Kraft pulp mill into a biorefinery by removing hemicelluloses from Hardwood in order to convert them into surface-active agents, namely alkylpolyxylosides, while high quality bleached pulps must still be obtained.

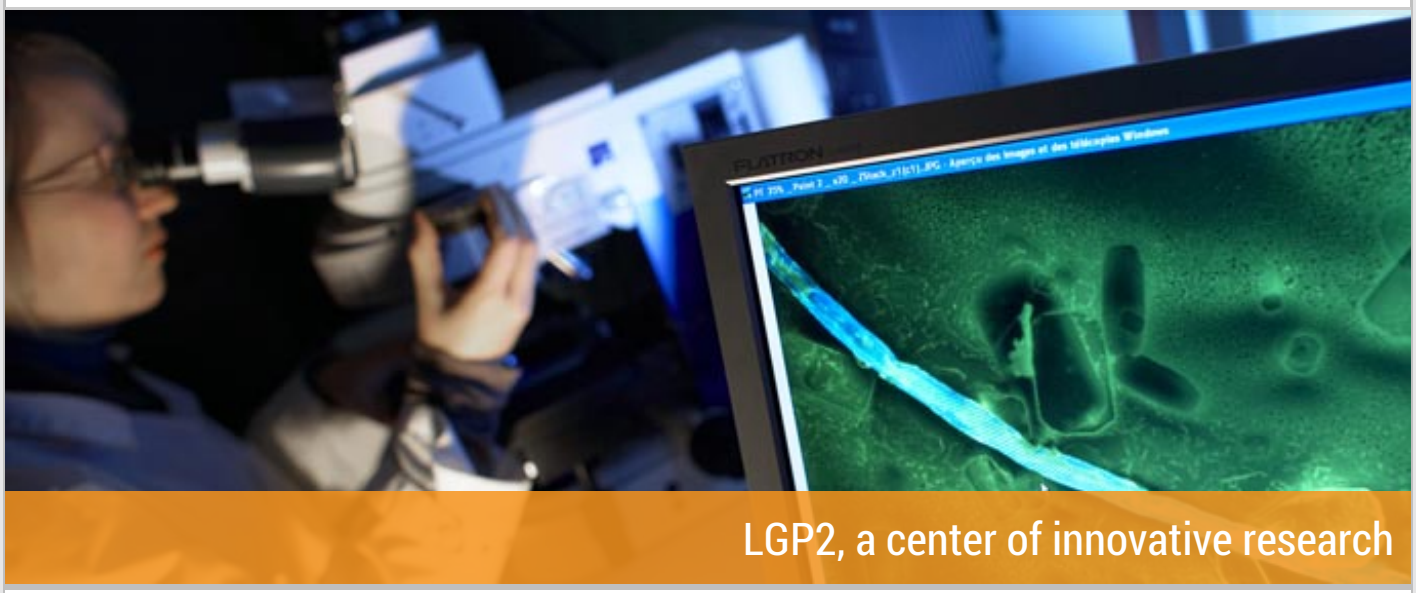
Industrial Eucalyptus globulus woodchips were submitted to different autohydrolysis conditions so as to extract a substantial amount of hemicelluloses, composed mainly of xylose. The prehydrolysis liquors were purified with activated charcoal and concentrated. Then the extracted saccharides were successfully used to synthesise alkylpolyglycosides. These surfactants have a saccharide as their hydrophilic part, while their lipophilic part is a fatty alcohol. Moreover, the impact on the glycosylation reaction of the saccharides' concentration and of the other species found in the prehydrolysates was studied.

In parallel, the pretreated woodchips were much easier to delignify using Kraft cooking than the control ones. This allowed the use of soda-anthraquinone cooking at reduced alcali and temperature. The resulting pulps had lower lignin and hexenuronic acid content than the pulps from untreated wood, with higher DPv and brightness. The pulps from prehydrolysed wood reacted as well as the control pulps to oxygen delignification. All pulps were fully bleached to a 90% ISO brightness through an ODEPD sequence.

Other members of the jury

Yves QUENEAU, Research Director, CNRS ♦♦ Dmitry EVTUGUIN, Associate Professor, Universidade de Aveiro (Portugal) ♦♦ Jérôme GUILBOT, Scientific Coordinator Sugars, Protein and Green Chemistry, SEPPIC

Research



LGP2 - Ph.D. thesis defended in 2014

Ahlem ROMDHANE

December 12, 2014 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Membrane separation processes for continuous production of nanocrystals of polysaccharides: experimental approach and modeling.

Supervision

Marc AUROUSSEAU, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Agnès GUILLET, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

The current work investigates the use of cross flow microfiltration using ceramic membrane to fractionate the heterogeneous suspension obtained after starch hydrolysis in order to isolate starch nanocrystals. The final aim is to evaluate the possibility of coupling the filtration step to the hydrolysis step in a single production loop in order to enhance the starch nanocrystal production yield. The characterizations of the suspension (particle size and charge) obtained with the classic production process indicates that it was a mixture of starch nanocrystal aggregates and starch residues, individualized starch nanocrystals represent only 5 % of the initial starch. The fractionation study was done using two pilot plans, in a dead end configuration at laboratory scale (plate membrane) and in a cross flow configuration at semi-industrial scale (tubular membrane). Design of experiments methodology was used to optimize the fractionation efficiency when filtering a neutral suspension considering the effect of filtration parameter on the transmission yield and membrane fouling. In the optimized condition, it was possible to recover 25 % of starch nanocrystals while keeping the permeate flux at its highest value. Mean diameter of the recovered particle was less than 300 nm. At this condition, it was also possible to recover the starch nanocrystals directly from the acidic mixture obtained at the end of the hydrolysis step. The analysis of fouling mechanism using dead end filtration experiments highlights that membrane fouling occurs because a cake bult up at the membrane surface. This study investigates also the use of ceramic ultrafiltration membrane in a diafiltration process in order to purify the acidic suspension from soluble molecules without modifying particle size distribution which is a promising technique for a large scale production.

Other members of the jury

Murielle RABILLER BAUDRY, Professeur, Université de Rennes 1 ♦♦ Marc HERAN, Maître de Conférences HDR, Polytech Montpellier ♦♦ Sami BOUFI, Professeur, Université de Sfax (Tunisie) ♦♦ Évelyne Mauret, Professeur, Grenoble INP-Pagora

Nicolas FULLERINGER

December 11, 2014 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Contribution to the study of friction phenomena. Application to paper materials.

Supervision

Jean-Francis BLOCH, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

The optimization of numerous technological processes requires a deep understanding of the paper friction phenomena. This thesis aims to better understand these phenomena in order to improve the envelopes separation in franking machines.

First, standardized methods for measuring the paper-on-paper friction force having proved limited in terms of repeatability and experimental conditions, two measurement methods – low and high speed – were developed. Similarly, the friction measurement has been adapted to the different contacts encountered in franking machines.

Secondly, these methods have been used to study the mechanisms of friction with the paper material including the dependency of the paper-on-paper friction to length of the displacement, the influence of both temperature and humidity on the paper-on-paper friction, and the main frictional properties of the envelope-on-envelope, rollers-on-paper, and pads-on-paper contacts, respectively.

Thirdly, a comprehensive model of the envelopes separation in a franking machine was created. This process aims at displacing, with no damage, only the bottommost envelope of a stack of envelopes. This model allows to identify, characterize and propose an optimization of the main process parameters.

Other members of the jury

Marie-Ange BUENO, Professor, Université de Haute Alsace ♦♦ Maxence BIGERELLE, Professor, Université de Valenciennes et du Hainaut-Cambrésis ♦♦ Carlos CANUDAS DE WIT, Research Director, INRIA ♦♦ Thomas MATHIA, Research Director, École Centrale de Lyon ♦♦ Laurent FARLOTTI, Innovation & IP Director, Neopost

Daniele SETTE

December 11, 2014 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Functional printing: from the study of printed layers to the prototyping of flexible devices

Supervision

Anne BLAYO, Lecturer-Researcher, Grenoble INP-Pagora / LGP2 ♦♦ Christophe POULAIN, CEA Grenoble

Abstract

In the last decade, functional printing has gained a large interest for the manufacturing of electronic components. It stands aside to silicon technologies and specifically targets markets of large area devices (screens, photovoltaics) and flexible electronics (RFID antennas, sensors, smart textiles).

In this work, inkjet printed silver layers are characterized depending on the printing conditions and the required post-printing annealing. The evolution of their microstructure, electrical and mechanical properties is investigated as a function of the annealing temperature. The correlation of the measurements with theoretical models supports the experimental methods that were developed. The knowledge of the printed silver layers assets and the optimization of the printing process lead to the design, fabrication and characterization of flexible electronics devices: a 17 GHz band-pass filter printed on plastic, a flexible vacuum micro-sensor working on the Pirani principle, and a 250 µm thick membrane switch for keyboards. Finally, all printed RF capacitors were realized by stacking Barium Strontium Titanate dielectric and silver printed layers.

These prototypes exhibit performances near the state-of-the-art and suggest new opportunities for printing technologies. This thesis offers a thorough study of inkjet printed silver layers and assess their potential for the manufacturing of flexible devices.

Other members of the jury

Panagiota MORFOULI, Professor, Grenoble INP-Phelma ♦♦ Reinhard BAUMANN, Professor, Chemnitz University of Technology (Allemagne) ♦♦ Yvan BONNASSIEUX, Professor, École Polytechnique, Palaiseau ♦♦ Mohamed SAADAOUI, Doctor, École des Mines de Saint-Etienne

Etzael ESPINO PEREZ

December 11, 2014 - Environmental Science

Ph.D. title

Development of renewable nanocomposites for packaging by the functionalization of polysaccharide nanocrystals

Supervision

Sandra DOMENEK, Associate Professor, AgroParisTech ♦♦ Julien BRAS, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

The creation of nanocomposites is one of the promising technologies for adapting the mechanical and barrier properties of biobased and biodegradable polymers to the requirements of commodity products such as food packaging.

The Panagro project aimed at the creation of fully organic nanocomposites by the distribution of cellulose nanocrystals (CNC) inside polylactide (PLA). Compatibility between nanocharges and polymer is one of the challenges in the development of nanocomposites. The Panagro project proposed rise to this challenge in designing the cellulose nanocrystals surface with a double functionality, insuring compatibility and modifying barrier properties of the nanocomposites towards organic vapours.

Two versatile surface grafting methods respecting the principles of green chemistry were developed and aromatic molecules were grafted using ozone activation, radical initiation and grafting of the surface in aqueous solvents, or using the reactants as solvents be in situ solvent exchange. The increase of compatibility of PLA and CNC was evidenced by the increase in rubbery storage modulus of nanocomposites and constant gas barrier properties. The permeability of the aromatic probe anisole was decreased due to the distribution of CNC inside PLA and was in addition decreased by the interaction with the aromatic surface grafts.

Other members of the jury

Éliane ESPUCHE, Professor, Université Claude Bernard Lyon 1 ♦♦ Stéphane MARAIS, Professor, Université de Rouen ♦♦ Youssef HABIBI, Associate Professor, CRP Henri Tudor ♦♦ Philippe ROGER, Professor, Université Paris-Sud 11 ♦♦ Naceur BELGACEM, Professor, Grenoble INP-Pagora ♦♦ Alma ROMAN, Associate Professor, Universidad Autónoma del Estado de Hidalgo, Mexique ♦♦ Alain GUINAULT, Research Engineer, Arts et Métiers ParisTech

Raphaël BARDET

November 14, 2014 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Nanocelluloses as potential materials for specialty papers

Supervision

Julien BRAS, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2

Abstract

The original feature of this work is to investigate the contribution of two families of nanocellulose for their application within specialty papers. It exists two families of nanocellulose, i.e. Cellulose Nanocrystals (CNC) and Cellulose Nanofibers (CNF). It results in different properties in suspension and solid states. CNF with their ability to form entangled network are used as dispersive network for particles. In contrast, the self-assembly properties of CNC are used to obtain iridescent films. First, the films based on nanocellulose were considered as model layers. Then, results were implemented at the industrial scale within the papermaking process. It is proposed to use CNF based coating for saving opacifying pigments in lightweight paper, and manufacturing iridescent pigment to impart anti-counterfeiting properties. These sustainable and cost-effective approaches were then validated at pilot scale and by two patent applications.

Other members of the jury

Bernard CATHALA, Research Director, INRA Angers-Nantes Pays de la Loire ♦♦ Patrice MANGIN, Professor, Université du Québec à Trois-Rivières (Canada) ♦♦ Étienne FLEURY, Professor, INSA de Lyon ♦♦ Laurent HEUX, Research Director, Cermav

Maïté HURON

October 22, 2014 - Fluid Mechanics, Energy, Processes

Ph.D. title

Kinetic modeling of cellulose enzymatic hydrolysis: influence of substrate type and study of deactivation phenomena

Supervision

Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2 ♦♦

Ning LIN

June 24, 2014 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Cellulose nanocrystals: surface modification and advanced materials.

Supervision

Alain DUFRESNE, Professor, Grenoble INP-Pagora / LGP2

Abstract

The present work focuses on the properties of cellulose nanocrystals, their surface modification and development of advanced materials. Diverse approaches are employed on these nanoscaled substrates aiming to modify their surface properties and extend their use in highly sophisticated applications, such as postsulfation and desulfation, polymer grafting and adsorption, selective oxidation, molecular grafting, and ‘host-guest’ inclusion.

On the basis of surface modifications, properties analysis (for different sulfate group contents) and various nanomaterials derived from cellulose nanocrystals are investigated and prepared, including gradient sulfated nanocrystals, extruded nanocomposites, biocomposite sponges, and supramolecular hydrogels. The effect of gradient degrees of sulfate groups on cellulose nanocrystals to surface chemistry, morphology and physical properties are discussed, particularly four cross-section models are compared for the determination of the surface degree of substitution on cellulose nanocrystals.

A novel strategy involving a double-polymer-layer shield and physical and/or chemical compatibilization of cellulose nanocrystals is proposed, in order to realize both improvement of thermal stability and promotion of compatibility for nanocrystals with non-polar polymeric matrices during processing by melt-extrusion.

With the idea of participating as crosslinking aid for the construction of advanced materials, selectively oxidized cellulose nanocrystals (with oxidized microfibrillated cellulose as comparison) are introduced in alginate for the development of biocomposite sponges with improved mechanical stability or structural stability.

Through the smart design of in situ ‘host−guest’ inclusion between chemically modified cellulose nanocrystals and cyclodextrin, two hydrophilic polysaccharides are combined in supramolecular hydrogels for use as drug delivery.

In a word, this dissertation contributes to the advances of cellulose nanocrystals in the topics of property analysis and application development.

Other members of the jury

Étienne FLEURY, Professor, INSA de Lyon ♦♦ Christoph WEDER, Professor, Université de Fribourg (Switzerland) ♦♦ Jean-Marie RAQUEZ, Researcher, Université de Mons (Belgium) ♦♦ Alessandra DE ALMEIDA LUCAS, Researcher, Universidade Federal de São Carlos (Brazil) ♦♦ Jin HUANG, Professor, Wuhan University of Technology (China)

Jérémy BOUCHER

June 16, 2014 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Study of the possibilities to produce hemicellulosic ethanol in a biorefinery.

Supervision

Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2

Abstract

This thesis deals with the production of bioethanol of second generation. Bioethanol is a sustainable fuel which can substitute gasoline. Nowadays, it is exclusively produced from food resources, which can have harmful fallout on food prices. That is why the development of a second generation ethanol, from lignocellulosic material, is mandatory. Among all the possible ways to produce such ethanol, this study is focused on the production of ethanol from hemicelluloses in a kraft pulp mill using softwood as raw material.

Softwood hemicelluloses are mainly constituted of galactoglucomannanes (GGM). These polymers are made of sugars which can be fermented into ethanol when they are into their monomer form. During the kraft process, cellulose is produced by removing the lignin from wood. The lignin is then burnt to produce energy. The GGM are also degraded and solubilised during the kraft process but their combustion is not very profitable. The aim of this study is to extract these hemicelluloses prior to the kraft process, hydrolyze them into monomers and then ferment them into ethanol.

The efficiency of different extraction treatments was evaluated. The two processes performed in acidic medium, autohydrolysis (hot water extraction) and acid hydrolysis (in the presence of sulfuric acid) are the most interesting. The acid hydrolysis enables the extraction and the hydrolysis into monomers of most of the GGM. The sugars can therefore be fermented directly. The autohydrolysis requires a secondary hydrolysis to achieve the depolymerization of the extracted GGM. This secondary hydrolysis is performed with an acid as catalyst. This two-step treatment shows two advantages: the cellulose is less damaged and the degradation of sugars extracted is reduced. This degradation has to be avoided because the degradation products cannot be fermented and they are known to inhibit the microorganisms used for the fermentation, which is one of the main issues for the production of second generation ethanol.

The direct fermentations of the hydrolysates, performed with a wild strain of Saccharomyces cerevisiae, allow to reach good yields after 24 hours. However, it might be necessary to increase the concentrations in sugars in the hydrolysates prior to the fermentation in order to raise the profitability of the process. Three processes were compared: evaporation, decrease of the L/W ratio and recycling of the hydrolysate. The evaporation is very efficient and enables to remove acetic acid and furfural, which are inhibitors of the fermentation. Recycling the hydrolysate increases the concentrations in sugars, but also their degradation. Reducing the L/W

increases the concentrations in sugars, but also their degradation. Reducing the L/W ratio is also efficient to increase the concentration.
The fermentation of a hydrolysate produced after an autohydrolysis and a secondary hydrolysis and concentrated to reach 100 g/L of hexoses was not successful because of the high concentration in inhibitors. Several strains of S. cerevisiae were acclimatized to this kind of hydrolysate in order to achieve the fermentation.
A complete process to produce ethanol and cellulose from wood chips was developed by taking into consideration industrial constraints. This study is a first step before its implementation in a kraft pulp mill.

Other members of the jury

Ana Paula DUARTE, Professor, University of Beira Interior (Portugal) ♦♦ Carole MOLINA JOUVE, Professor, INSA Toulouse ♦♦ Antoine MARGEOT, Research Engineer, IFP Énergies nouvelles

Oussama EL BARADAI

April 24, 2014 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Elaboration of flexible lithium–ion electrodes by printing process.

Supervision

Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Davide BENEVENTI, CNRS Researcher / LGP2 - Yann BULTEL, Professor, Grenoble INP / LEPMI

Abstract

The work describes the manufacturing of eco-sustainable lithium-ion electrodes without fluoro-based bindings and organic solvent, thanks to the utilization of celluloses derivatives and a conventional printing process.
The main breakthrough in this work is the formulation of water based inks containing either active particles of the anode (graphite) or cathode (LFP and carbon black) and a cellulosic based binding. Thus cellulose derivatives have a binding role of active materials by replacing fluoro-based binding commonly used and insure the cohesion of electrodes printed onto paper separator without affecting electronic conductivity. In this work a new assembling strategy was proposed.
In order to validate this new technique, a lithium-ion battery was manufactured by using a front/back printing strategy of separator with the integration of current collectors during printing stage.

Other members of the jury

Christine VAUTRIN, Professeur, Centre de Recherche sur la Matière Divisée (CRMD) ♦♦ Dominique GUYOMARD, Professeur, Institut des Matériaux Jean Rouxel (IMN) ♦♦ Christophe PIJOLAT, Professeur, Centre Sciences des Processus Industriels et Naturels

Sébastien THIBERT

April 23, 2014 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Study of the front side metallization of silicon solar cells.

Supervision

Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Davide BENEVENTI, CNRS Researcher, LGP2 ♦♦ Nadège REVERDY-BRUAS, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

Energy is one of the main problems of this new millennium. The photovoltaic electricity should have a significant role in the future energy mix.

At an industrial scale, the front side metallization of silicon solar cells is performed by screen printing of a silver paste. This step is critical in production lines because it determines both their cost and their final performance. Consequently, it is necessary to limit the amount of printed silver paste while maximizing the cell efficiency.

The first part of this work is focused on the effects of the printing parameters on these two crucial aspects. To ensure the photovoltaic industry growth, the screen printing process should be replaced in coming years. The seed and plate concept is an innovative solution during which a first layer is printed and thickened by plating. Thanks to its flexibility and low pressure during printing, the flexographic printing process seems particularly well suited to meet the seed layer requirements at an industrial level. The second part of this work focuses on the development of this printing technique.

Other members of the jury

Mustapha LEMITI, Professor, Institut des Nanotechnologies de Lyon ♦♦ Didier GRAEBLING, Professor, Institut des Sciences Analytiques et de Physico-chimie pour l'Environnement et les Matériaux (IPREM) ♦♦ Jean-Jacques SIMON, Associate Professor, Institut Matériaux Microélectronique Nanosciences de Provence (IM2NP) ♦♦ Bernard BECHEVET, Scientific and technical advisor, MPO Energy

Carolina MORELLI-LIPARRELI

April 4, 2014 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Development and study of the properties of films and molded parts of nano-bio-cellulose nanowhiskers and biodegradable polymers.

Supervision

Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2

Frédéric POUYET

March 21, 2014 - Fluid Mechanics, Energy, Processes

Ph.D. title

New conditions of use of ozone for cellulosic pulp bleaching - Development of a green bleaching sequence.

Supervision

Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

In order to obtain white paper, the brown kraft pulp obtained from wood after a chemical treatment has to be bleached. Several chemical reagents can be used, including the efficient chlorinated agents. However, the use of those chlorinated agents leads to the generation of toxic compounds, among other issues. Other reagents such as ozone and peroxide can be used to partially or fully replace them, but the way they react with pulp components was not fully understood and they seemed to inevitably lead to a degradation of the end product.

The aim of this thesis was to design a greener bleaching sequence, giving high quality pulps without the use of chlorinated reagents. This was achieved thanks to a better understanding of the chemical reactions involved in the bleaching of pulp, and more specifically through a better apprehension of the possible reactions of ozone.

Other members of the jury

Stéphane GRELIER, Professor, Université Bordeaux 1 ♦♦ Dmitry EVTUGUIN, Associate Professor, University of Aveiro (Portugal) ♦♦ Göran GELLERSTEDT, Professor, KTH, Stockholm (Sweden)

Research

Research

Director & Managers

Research groups

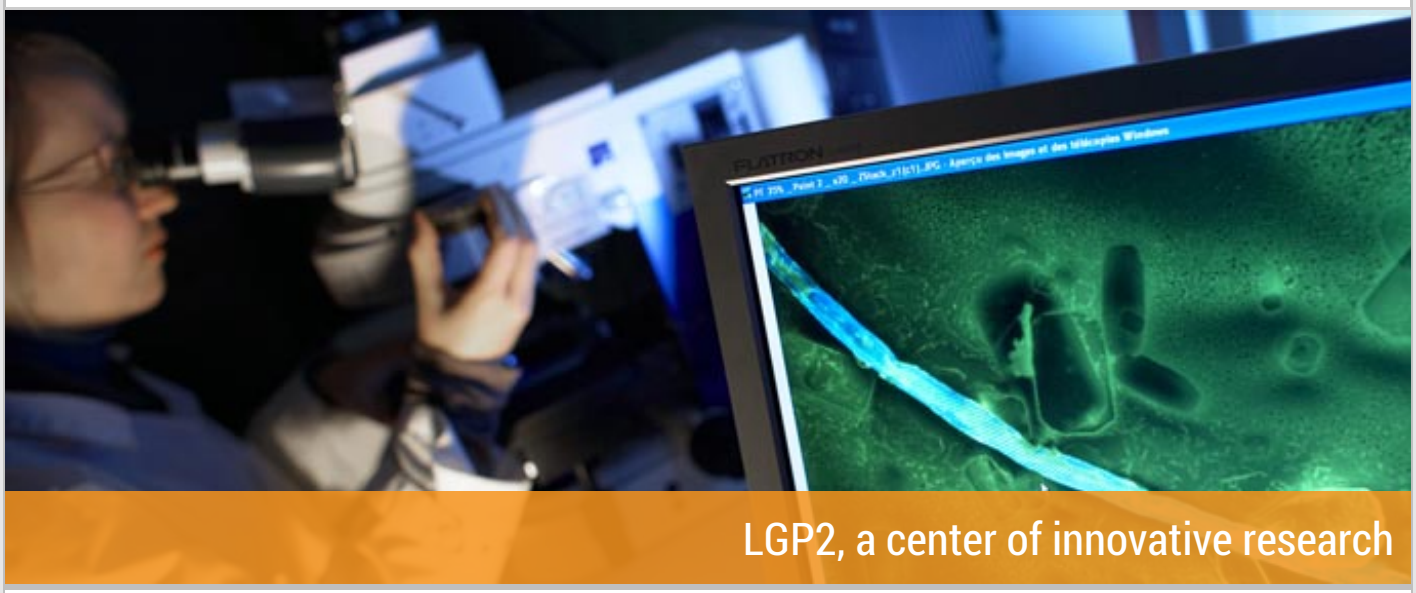
Scientific production

Doctorate, post-doctorate

Partnerships-Projects

Equipments & pilots

Events



LGP2 - Ph.D. thesis defended in 2015

Claire MONOT

December 18, 2015 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Contribution to the study of lignin-carbohydrate complexes (LCCs) in wood. Study of the impact of the different steps of a sulfur-free biorefinery process on these LCCs

Supervision

Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

The valorization of lignocellulosic biomass is nowadays a major issue due to the reduction of fossil resources. Separating each component to valorize them the best way possible is the goal of the pulp and paper biorefineries. The effluent of the mill, called the black liquor, is currently burnt to produce energy, but gasification would increase the energy efficiency. For this, a sulfur-free cooking of wood is necessary, as sulfur inhibits gasification.

Therefore this study first focused on the feasibility of cooking without sulfur, which is more difficult than a conventional kraft cooking containing sulfur. The work was done on softwood which is more difficult to delignify than hardwood. The wood was first pretreated with an autohydrolysis to remove hemicelluloses for further valorization.

The results were conclusive for the production of cellulose for textile applications. To explain the fact that the autohydrolysed wood was easier to delignify than the control wood with kraft and soda cooking, structural differences of wood components were looked for. Lignin did not show major differences whether the wood was prehydrolyzed or not, whereas the complexes between lignin and carbohydrates (LCCs) showed significant differences, which could explain the results obtained.

Other members of the jury

Nicolas BROSSE, Professor, Université de Lorraine, France ♦♦ Ana Paula DUARTE, Professor, Universidade da Beira Interior, Portugal ♦♦ José Carlos DEL RIO, Professor, Instituto de Recursos Naturales y Agrobiologia de Sevilla, Spain ♦♦ Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2, France

Benoît ARNOUL-JARRIAULT

December 17, 2015 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Hemicellulose extraction of paper grade pulp for dissolving pulp production

Supervision

Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

Dissolving pulps, which are composed of 95% cellulose, are the raw materials for the production of regenerated cellulose fibers for textile application and for the production of cellulose derivatives. These products are alternatives to oil based materials. A growing demand in such products is expected in the next decades. Therefore, additional capacities in the production of wood dissolving pulp must be created.

The purpose of this work is to develop hemicellulose removal processes with the aim to convert a softwood kraft paper pulp into a dissolving pulp. Three extraction methods were tested: A cold caustic extraction process (CCE) performed under conventional and unconventional conditions; A process consisting in an acid stage at high temperature (up to 150°C) followed by a hot caustic extraction (A-HCE); An enzymatic hydrolysis using xylanase, mannanase, and cellulase.

Conversion was quite successful with the two first processes. However, 100% of hemicellulose removal was never reached. In order to improve the hemicellulose extraction efficiency, several pre-treatments were tested (refining, steam explosion, TEMPO oxidation). The addition of a refining stage allowed for a reduction of the NaOH concentration during CCE extraction without affecting the hemicellulose extraction efficiency.

The last part of this thesis work focused on the dissolving pulp swelling. A new and rapid test for the characterization of fiber swelling was developed. This method was used as an approach to the assessment of dissolving pulp reactivity in the viscose process in place of the Fock's method.

Other members of the jury

♦♦ ♦♦ ♦♦ ♦♦ ♦♦

Florian MARTOÏA

November 30, 2015 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Nanocomposites and foams from cellulose nanofibrils: rheology during their processing and mechanical properties

Supervision

Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Pierre DUMONT, Professor, INSA Lyon ♦♦ Laurent ORGÉAS, CNRS Research Director, Laboratoire

3SR, Grenoble

Abstract

This study focuses on the use of cellulose nanofibrils (NFCs) as bio-based nano-reinforcement in polymer composites and foams. These renewable materials can be used in place of traditional materials such as for instance to produce sandwich panels. This experimental, theoretical and numerical work aims at optimizing the processing of these NFC-based materials as well as their use properties.

In the first part of this work, the rheology of concentrated NFC suspensions, that behave as thixotropic yield stress fluids, is investigated at macro- and mesoscales using an original rheo-ultrasonic velocimetry (rheo-USV) setup allowing the local flow kinematic to be obtained. We show that the flow of NFC suspensions is highly heterogeneous and exhibits complex situations with the coexistence of wall slippage, multiple shear bands and plug-like flow bands. Using this experimental database, we develop an original multiscale rheological model for the prediction of the rheology of NFC suspensions. The model takes into account the anisotropic fibrous nature of NFC networks as well as colloidal and mechanical interaction forces occurring at the nanoscale. The model predictions prove that colloidal and hydrodynamic interaction forces together with the orientation and the wavy nature of NFCs play a major role on the yield stress and shear thinning behaviour of the suspensions.

In the second part of this work, NFC-reinforced polymer nanocomposite films are processed for a wide range of NFC contents. Using advanced microscopy techniques (AFM, SEM), X-ray diffraction and mechanical tests (tensile and DMA tests), we show that NFCs form highly connected nanofibrous structures with in-plane random orientation, that these connected NFC networks play a leading role on the mechanical behaviour of the nanocomposites and that the elastic properties of nanocomposite films are much lower than those predicted from the micromechanical models of the literature. In light of these observations, we propose an alternative multiscale model in which the main involved deformation nano-mechanisms are those occurring both in the amorphous segments of the nanofibers and in the numerous nanofiber-nanofiber contact zones.

Finally, in a third part, we focus on the influence of the processing conditions, the suspension type and the NFC concentration on the microstructure (using X-ray synchrotron microtomography), the mechanical properties (using compression tests) and the deformation micro-mechanisms (using in situ compression test with X-ray microtomography) of various foams prepared from NFC suspensions by freeze-drying.

Other members of the jury

Tatiana BUDTOVA, Research Director, Mines ParisTech ♦♦ Guillaume OVARLEZ, CNRS Research Director, Université de Bordeaux ♦♦ Jean-Yves CAVAILLÉ, Professor, INSA Lyon ♦♦ Véronique MICHAUD, Professor, EPFL, Switzerland ♦♦ Jean-Luc PUTAUX, CNRS Research Director, Cermav, Grenoble

Marion HUET

November 24, 2015 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Black liquor valorization by hydrothermal processes for energetic and green chemistry purposes.

Supervision

Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Anne ROUBAUD, Research Engineer, CEA

Abstract

This thesis aims to study sulfur free black liquor valorization through two hydrothermal processes: supercritical water gasification and hydrothermal liquefaction. These processes will be compared to the industrial process (evaporation and Tomlinson boiler) with three mains criteria: energetic yield, sodium recovery and phenolic molecules production.

In supercritical conditions, gas formation is competitive with char formation. Fast heating and high temperature permit to increase gas yield, thus energetic yield. However, conversion of phenolic compounds from lignin is low below 500°C, leading to a lower energetic yield than reference. In a continuous process, at high temperatures (700°C) and fast heating, energetic yield should be two times higher than industrial process (simulation at thermodynamic equilibrium). Wood prehydrolysis and softwood lead to a lower conversion of black liquor.

Hydrothermal liquefaction produces a biocrude which can be burnt and phenolic platform compounds. Indeed, lignin is depolymerized into reactive fragments which can be degraded into platform phenolic molecules. Moreover, the recombination of these fragments, leading to biocrude formation, is favored by the carbohydrates derivatives in black liquor. Wood prehydrolysis and hardwood lead to better energetic and phenolic molecules yields.Sodium recovery is satisfactory for both processes. Substitution of Tomlinson recovery by a hydrothermal process is then possible.

Other members of the jury

Maria Jose COCERO, Professor, University of Valladolid, Spain ♦♦ Nicolas BROSSE, Professor, Université de Lorraine, France ♦♦ Frédéric VOGEL, Professor, Institut Paul Scherrer, Switzerland ♦♦ Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Elsa WEISS-HORTALA, Assistant Professor, École des Mines d'Albi-Carmaux, France

Seema SAINI

November 13, 2015 - Materials, Mechanical, Civil Engineering, Electrochemistry

Ph.D. title

Surface modification of cellulose nanofiber to impart active properties for packaging.

Supervision

Julien BRAS, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2

Abstract

The present investigation has developed efficient green strategies for the chemical modification of cellulose nanofibers (CNF) in order to impart antimicrobial activities. Seven different functionalized CNF were produced in this context keeping in mind sustainability and industrial feasibility within new generation packaging field.

First, CNF were designed with cyclodextrin to control the release of natural active molecules. In other strategies, non-leaching contact active antimicrobial surfaces were prepared using natural active molecules or following biomimetic approaches. Results are very promising and allow obtaining efficient antimicrobial surface without any release. High level characterizations confirm surface grafting (e.g. XPS, QCM-D, NMR) and antimicrobial efficiency (S.aureus, E.Coli).

One of the best strategies using antibiotic grafted CNF was produced at lab scale and also implemented at semi-industrial scale. The final idea was to produce medical packages limiting the cross contamination in hospitals.

Other members of the jury

Graziano ELEGIR, Researcher, Innovhub-SSI, Italy ♦♦ Lars WÅGBERG, Professor, KTH Royal Institute of Technology , Sweden ♦♦ Véronique COMA, Associate Professor, Université de Bordeaux ♦♦ Elisa ZENO, Researcher, Centre Technique du Papier , Grenoble

Karima BEN HAMOU

October 24, 2015 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Extraction of structure and properties controlled cellulose nanofibrils: characterization, rheological and nanocomposites applications.

Supervision

Alain DUFRESNE, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Hamid KADDAMI, Professor, Faculty of Science and Technology Marrakech (Morocco)

Abstract

The cellulose nanofibrils (CNF), obtained by TEMPO oxidation of native cellulose microfibrils as colloidal aqueous suspensions, are biosourced nanoparticles having rheological and optical properties well adapted for the conception of new nanomaterials with high performance.

The main purpose of this study was to control and optimize the conditions for preparing these NFCs extracted from date palm tree by examining the oxidation time and the number of passes through the homogenizer. The success of the reaction was demonstrated by FT-IR spectroscopy. The rate of the carboxylic groups has been calculated by conductometric titration and ranged between 221 and 772 mol / g of anhydroglucose. Morphological studies show that oxidized CNFs are very individualized by introducing negative charges on their surfaces that induce electrostatic repulsion forces between the fibrils. Particular attention has been given to the viscoelasticity of oxidized-TEMPO CNF suspensions whose monitoring was carried out by a rheometer ARES-G2TA.

These nanocharges were incorporated in a thermoplastic (PVAc) and nanocomposite materials obtained were characterized by SEM, TGA, DSC, DMA and mechanical testing.

Other members of the jury

Larbi BELACHEMI, Professor, Faculty of Science and Technology Marrakech (Morocco) ♦♦ Étienne FLEURY, Professor, INSA de Lyon ♦♦ Youssef HABIBI, Researcher, Luxembourg Institute of Science and Technology (Luxembourg) ♦♦ Abdelhakim ALAGUI, Professor, Faculty of Science Semlalia Marrakech (Morocco)

Pedro Maximiano RAIMUNDO

October 14, 2015 - Fluid Mechanics, Energy, Processes

Ph.D. title

Analysis and modeling of the local hydrodynamics in bubble columns.

Supervision

Alain CARTELLIER, CNRS Research Director, LEGI ♦♦ Davide BENEVENTI, CNRS Researcher, Grenoble INP-Pagora / LGP2

Abstract

Bubble columns reactors are widely used in chemical and biological engineering due

to their simple configuration with no mobile parts. However, the scale-up rules for such bubble column reactors is still a quite challenging process. In particular, using two-fluid approaches, the current practice relies on an ad-hoc fitting of the bubble size with the column dimension.

To progress in the up-scaling of bubble columns hydrodynamics, experiments have been achieved over a wide range of parameters, with columns diameters from 0.15 to 3m and with gas superficial velocities from 3 to 35cm/s, yielding void fractions up to 35%. To ensure comparable hydrodynamic conditions, almost identical bubble size distributions were produced for all these conditions. In the same spirit, coalescence was blocked. A battery of measuring techniques has been exploited including phase detection optical probes, endoscopic imaging and Pavlov tubes. A new technique has also been developed that provides the mean horizontal diameter of bubbles. That method, which is based on the spatial correlation of the signals from two optical probes located side by side, has been validated in strongly agitated, unsteady bubbly flows at high void fractions.

The database collected on the radial and axial evolutions of local hydrodynamics properties (gas hold-up, bubble size, phasic velocities and their fluctuations...) has led to a clarification of the scaling laws for such systems. In particular, we have shown that the auto-similarity of the flow structure in heterogeneous conditions leads to an entrained liquid flow rate that growths with the column diameter as $D^{2}(gD)^{1/2}$. In other words, the entrainment capability of a bubble column is only set by the column size and does not depend on the injected gas superficial velocity. Furthermore, the heterogeneous character of the flow has been shown to originate from strong concentration gradients that define meso-scale structures: the resulting collective dynamics has a profound impact on the mean relative velocity between phases. Inspired by Simonnet et al. (2008), that dynamics can be well represented by introducing a swarm factor in the drag law. With such an approach, 3D URANS two-fluid simulations become able to reproduce without any ad-hoc adjustment the scale effect observed over the whole range of flow conditions considered here.

Other members of the jury

Evelyne MAURET, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Dominique LEGENDRE, Professor, Université de Toulouse III ♦♦ Romain VOLK, Associate Professor, ENS de Lyon ♦♦ Daniele MARCHISIO, Professor, Politecnico di Torino, Italie ♦♦ Claude DANIEL, Research Engineer, Solvay ♦♦ Frédéric AUGIER, Research Engineer, IFP Energies nouvelles ♦♦ Ann FORRET, Research Engineer, IFP Energies nouvelles

Oleksandr NECHYPORCHUK

October 2, 2015 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Cellulose nanofibers for the production of bionanocomposites

Supervision

Ana Maria BOTELHO DO REGO, Associate Professor, Instituto Superior Técnico (Portugal) ♦♦ Frédéric PIGNON, CNRS Research Director, Laboratoire Rhéologie et Procédés, Grenoble ♦♦ Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2

Abstract

One of the main challenges in the context of biocomposites development is to replace petroleum-based materials with bio-based. Because of their natural origin, relatively high strength and the ability to form transparent products, cellulose nanofibers have a large potential for application in the composite materials.

This work was focused on the optimization of cellulose nanofiber production methods using biochemical and mechanical treatments. Then, the rheological and structural properties of these nano-elements in aqueous media were investigated. Finally, the production of latex-based composites was carried out. The questions of homogeneous dispersion of cellulose nanofibers in the matrix and the interactions between these two components were particularly addressed.

Other members of the jury

Étienne FLEURY, Professor, INSA de Lyon ♦♦ Alain PONTON, CNRS Research Director, Université Paris Diderot ♦♦ Ana Paula DUARTE, Professor, Universidade da Beira Interior (Portugal) ♦♦ Albert MAGNIN, CNRS Research Director, Université Grenoble Alpes ♦♦ Amelia ALMEIDA, Auxiliary Professor, Instituto Superior Técnico (Portugal)

Besma BERRIMA

September 28, 2015 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Structural and chemical study of lignin and its recovery as Alfa macromonomer and/or activated charcoal precurseur

Supervision

Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Sami BOUFI, Professor, University of Sfax, Tunisia ♦♦ Gérard MORTHA, Professor, Grenoble INP-Pagora / LGP2

Abstract

Lignin precipitated from black soda cooking liquor of alfa (Stipa tenacissima) was carefully characterized and valorized following two different approaches: its utilization after chemical modification in view of preparing rigid polyurethane foams and its simple pyrolysis, in order to prepare charcoal. In fact, a comparative study concerning the careful characterization of the hydroxyl functions was realized using several methods and techniques, among which: the conductometric titration differential UV and 13C-NMR spectroscopy.

In the first approach, the precipitated lignin was converted in liquid polyols thanks to a chain-extension reaction with propylene oxide. These formulations were optimized by inspecting the effect of different parameters: lignin/propylene oxide ratio, amount of catalyst, molecular weight of the prepared polyols, hydroxyl index and glass transition temperature. The hydroxyl indexes and the viscosity of the prepared polyols were determined. The rigid polyurethane foams were studied in terms of their density, morphology and mechanical properties.

The lignin was then used as a precursor for the preparation of charcoal without any activation treatment and compared with a commercial homologue. The kinetic of the adsorption was performed and showed that the adsorption equilibrium was reached at about 50 min, and followed a pseudo-first order kinetic model. The adsorption isotherms revealed that lignin-based charcoal retained efficiently metal ions and presented a maximum adsorption capacity varying from 200 to 400 µmol/g. This was true even for concentrations much lower than 20 ppm. The saturated lignin-based charcoal was efficiently regenerated by washing with solutions of EDTA and nitric acid.

These two approaches for the valorization of precipitated lignin from black liquor of alfa cooking gave materials with promising properties. Most cases, materials with properties similar to conventional ones were obtained, which presents a viable option of rational valorization of this industrial abundant and renewable by-product.

Other members of the jury

Souhir ABID, Professor, University of Sfax, Tunisia ♦♦ Étienne FLEURY, Professor, INSA Lyon ♦♦ Latifa BERGAOUI, Professor, INSAT, Tunisia ♦♦ Limam EL ALOUI, Professor, University of Gafsa, Tunisia

Fedia Bettaieb EP KHIARI

September 26, 2015 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Valuation of Tunisian cellulose waste.

Supervision

Alain DUFRESNE, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Farouk MHENNI, Professor, University of Monastir, Tunisia

Abstract

Many cellulosic sources are available in Tunisia in large quantities such as agricultural waste (vine stems) and marine residues (*Posidonia oceanica* leaves and balls). Their valorization presents an interesting activity to produce new products and bio-based biomass materials. The present work deals with the preparation, characterization and application of nanocellulose. In fact, different qualities of nanocellulose, namely cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) were produced and characterized by various methods.

The objective was to better understand the structure and morphology of the nanofibers obtained from both plants. Finally, various nanocomposites were prepared using the cellulose nanocrystals and cellulose nanofibrils as reinforcing element in polyacrylate polymer as matrix. The obtained results were compared with those reported for other sources such as annual plants and wood. It has been shown that nanocellulose from *Posidonia oceanica* and vine stem can be used as a new alternative nanoreinforcing source in nanocomposite applications.

Other members of the jury

Mustapha MAJDOUB, Professor, University of Monastir, Tunisia ♦♦ Étienne FLEURY, Professor, INSA Lyon, France ♦♦ Samir BOUFI, Professor, University of Sfax, Tunisia

Thibaut MARTINI

March 31, 2015 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Study of the ink formulation based on Cu, Zn, Sn S precursors and of the crystallization's annealing for the non-vacuum deposit of photovoltaic layers

Supervision

Anne BLAYO, Lecturer-researcher, Grenoble INP-Pagora / LGP2 ♦♦ Céline MARTIN, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Konstantin TARASOV, Researcher, CEA Grenoble

Abstract

Kesterite (CZTS) is a semi-conductor only made of abundant elements. Its direct bangap between 1.0 and 1.5 eV makes it excellent candidate to replace the currently used absorbers in modules photovoltaic in thin coats.

This thesis describes the fabrication of thin films of CZTS by nanoparticles printing followed by crystallization annealing. Different hydrothermal synthesis of nanoparticles have been developed, some in continuous flow reactor, for a development on a larger scale. The influence of the types of precursors and synthesis conditions on the particles chemical composition was studied and their purity was evaluated.

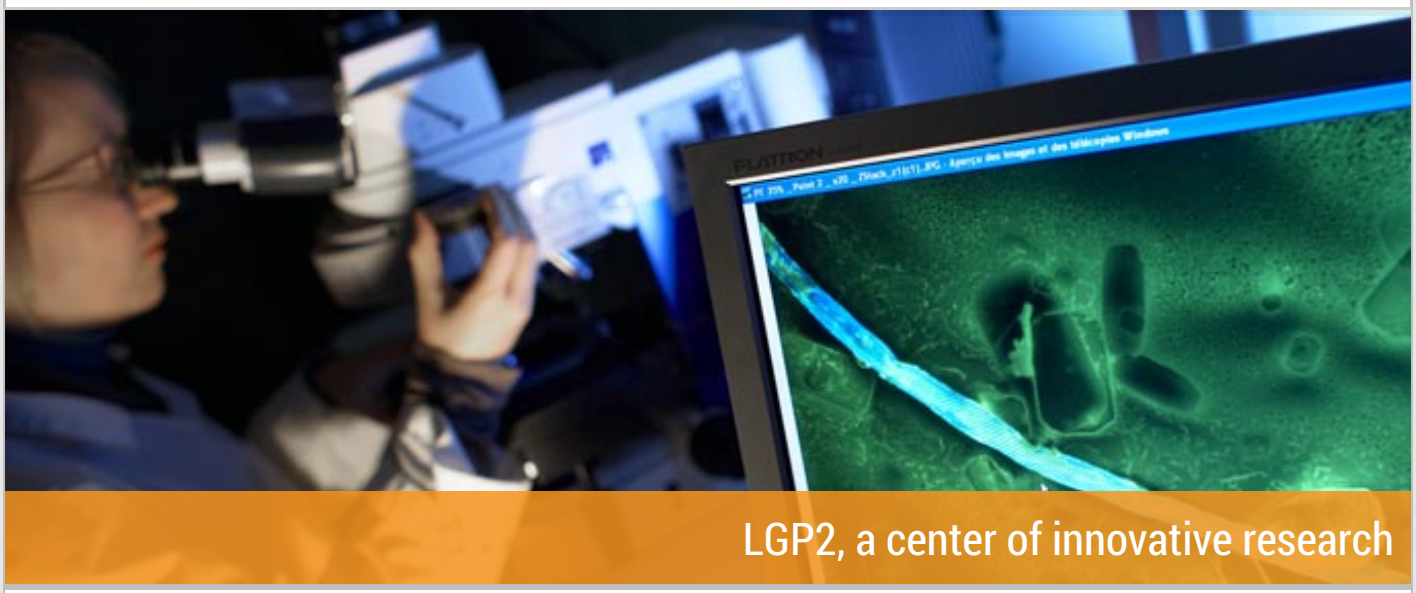
The behavior of the colloidal dispersion is then characterized and three surface functionalizations based on dodecanethiol, dodecyl pyrrolidone and anions sulphides are presented. These stabilizations allow to make an ink-jet and spray ink adapted to the deposit on molybdenum. The printed and dried layers are then annealed in sulfur atmosphere. Annealing of at least 120 minutes is required. However, the growth of the layers is heterogeneous when printed with the nanoparticles stabilized by dodecanethiol and dodecyl pyrrolidone. The presence of carbon in layers, recognizable by spectroscopy Raman, inhibits the growth of the material. Only the thin layers printed by using purified and stabilized by anions sulphides nanoparticles allow the homogeneous growth of the material during annealing.

Other members of the jury

Stéphane DANIELE, Professor, IRCELYON, Lyon ♦♦ John KESSLER, Professor, Institut des Matériaux Jean Rouxel, Nantes ♦♦ Anne DAVIDSON, Associate Professor, Laboratoire de Réactivité de Surface UPMC, Paris ♦♦ Anne KAMINSKY, Professor, IMEP-LAHC, Grenoble ♦♦ Georges BRÉMOND, Professor, INSA Lyon ♦♦ Alain RICAUD, CEO, Screen Solar

Research

Research



LGP2 - Ph.D. thesis defended in 2016

Jennifer MARCON

December 15, 2016 - Fluid Mechanics, Energy, Processes

Ph.D. title

Lignocellulosic pulp: study of a new bleaching sequence with low environmental impact.

Supervision

Gérard MORTHA, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Nathalie MARLIN, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

Chlorine dioxide is the most widely used bleaching agent for the production of bleached chemical pulps. However, its main drawback is the formation of chlorate, which decreases the delignification efficiency, and the reject of COD and toxic chloro-organic molecules (AOX) in mill effluents.

This study focused on the development of a new bleaching stage using chlorine dioxide (D stage) in non-conventional conditions, to reduce the environmental impact and production costs. The work was carried out on several softwood kraft pulps after cooking, taken at different stages of the bleaching sequence. The best results of the novel D stage were obtained for pulps at low kappa number, i.e. at the end of the bleaching sequence. The D stage was optimized and coupled with hydrogen peroxide addition. The same brightness and average degree of polymerization as for conventional D bleaching were obtained. Interestingly, a very important decrease of pollution load (70% of AOX and 20% of COD) was obtained, accompanied by a significant gain of productivity and energy saving (lower temperature and reaction time).

Chemical investigations on the reaction mechanism, carried out by different techniques (ESR, NMR and FTIR spectroscopies, HPAEC-PAD chromatography), allowed to reveal the main features of the reaction mechanism of chlorine dioxide and highlight the structural modifications brought to the pulp residual lignin during the novel unconventional D bleaching stage.

Other members of the jury

Anne-Laurence DUPONT, CNRS Researcher, CRC, Paris ♦♦ Dimitry EVTUGUIN, Professor, University of Aveiro (Portugal) ♦♦ Hervé GALLARD, Professor, University of Poitiers ♦♦ Auphélia BURNET, R&D Engineer, Centre Technique du Papier, Grenoble ♦♦ Lucie BOIRON, R&D Engineer, Munksjö, Apprieux

Jordan PERRIN

December 14, 2016 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Production of pure cellulose from wood by green purification and bleaching process with ozone, for textile and chemical application.

Supervision

Dominique LACHENAL, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Christine CHIRAT, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

Bleaching of wood pulp is still an environmental issue. A new ozone-based TCF bleaching sequence made it possible to produce a bleached dissolving pulp whose properties were comparable to those of a pulp bleached with a conventional bleaching sequence using chlorine dioxide (ECF).

It was noticed that the TCF bleached pulp had better brightness stability. The origin of yellowing is still poorly understood. It was studied here by the implementation of several analytical methods including EPR spectroscopy, UV-Raman spectroscopy for the analysis of aromatic and quinone residues and also fluorescence spectroscopy for the measurement of carbonyl and carboxyl groups. It was shown that the carbonyl groups present on the cellulose are detrimental to the brightness stability, both during accelerated ageing and mercerization. They can be partly eliminated by an alkaline treatment, which in return improves the brightness stability. Addition of hydrogen peroxide allows for a further increase of the brightness stability, but without any extra carbonyl removal. Hydrogen peroxide would have an effect on some conjugated residual chromophores, mainly quinones, involved in the yellowing mechanism. The TCF pulp would possess less quinones than a ECF pulp.

The thesis was supported by ADEME, the French Environmental Agency, and two major players in ozone generation (Xylem and Degremont-Ozonia)

Other members of the jury

Yves QUENEAU, Research Director, INSA Lyon ♦♦ Carlos PASCOAL NETO, Professor, University of Aveiro (Portugal) ♦♦ Ute HENNIGES, Associate Professor, Boku University (Austria)

Julie CHAPELAIN

December 8, 2016 - Fluid Mechanics, Energy, Processes

Ph.D. title

Dispersed air flotation foams for radioactive decontamination of land.

Supervision

Davide BENEVENTI, CNRS Researcher, Grenoble INP-Pagora / LGP2

Fanny HOENG

October 14, 2016 - Materials, Mechanical, Civil Engineering, Electrochemistry

Ph.D. title

Potential of nanocellulose for conductive ink preparation.

Supervision

Julien BRAS, Associate Professor, Grenoble INP-Pagora / LGP2 ♦♦ Aurore DENNEULIN, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

This project aims at developing new conductive inks based on nanocellulose and silver nanowires for transparent and conductive applications. Nanocellulose are nanoparticles extracted from the cellulose and two kinds currently exist : the cellulose nanocrystals (CNC) and the cellulose nanofibrils (CNF).

This project have evaluated on one hand the ability of using tubular rigid CNC as template for producing silver nanorods, prior their formulation into conductive inks. On the other hand, the ability of using flexible and entangled CNF to stabilize commercial silver nanowires, usually unstable in suspension, was investigated.

The results of this project lead to the patented formulation and commercialization of one low silver content conductive ink based on silver and CNC and two conductive transparent ink based on CNF and silver nanowires. Physico-chemical interactions and colloidal stability of such hybrid suspension have been scientifically studied meanwhile printing process adapted formulation have been successfully designed and tested at laboratory scale but also industrial scale.

Other members of the juryBernard CATHALA, Research Director, INRA ♦♦ Orlando ROJAS, Professor, Aalto University, Finland ♦♦ David GETHIN, Professor, Swansea University, United Kingdom ♦♦ Charles NEUMAN, CEO, Poly-Ink

Nagalakshmaiah MALLADI

September 23, 2016 - Fluid Mechanics, Energy, Processes

Ph.D. title

Melt processing of cellulose nanocrystals: thermal, mechanical and rheological properties of polymer nanocomposites.

Supervision

Nadia EL KISSI, CNRS Research Director, Laboratoire Rhéologie et Procédés, Grenoble ♦♦ Alain DUFRESNE, Professor, Grenoble INP-Pagora / LGP2

Abstract

The low thermal stability and irreversible agglomeration issues are limiting the processing of polymer nanocomposites using cellulose nanocrystals as the reinforcing phase. In this context, thermally stable and highly dispersed cellulose nanocrystals were prepared by green processes (aqueous based methods) like physical adsorption and surface modification. These two different extrudable cellulose nanocrystals were used to reinforce hydrophobic polymers. Ensuing polymer nanocomposites had a positive impact on the storage modulus, tensile strength and Young's modulus.

Importantly, no evidence of micro aggregates in the matrix was observed in the scanning electron microscopy images contrary to non-treated cellulose nanocrystals. Both the surface modification and adsorption are water based methods and are industrially viable solutions.

Other members of the jury

Claire BARRES, Associate Professor, INSA Lyon ♦♦ Lazhar BENYAHIA, Professor, Université du Maine, Le Mans-Laval ♦♦ Bruno VERGNES, Research Director, CEMEF, Nice

Marcos MARIANO

September 22, 2016 - Materials, Mechanical, Civil Engineering, Electrochemistry **[Thesis online]**

Ph.D. title

Applications of cellulose nanocrystals:thermal, rheological and mechanical properties of new materials.

Supervision

Alain DUFRESNE, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Nadia EL KISSI, CNRS Research Director, LRP, Grenoble

Abstract

The preparation of composites based on cellulose nanocrystals (CNC) is normally performed using techniques such as melt processing or casting/evaporation. In the last one, impressive mechanical properties can be reached due to the creation of a particle 3D network that is based on new hydrogen bonds between the cellulose nanorods. This process of new H-bond formation normally takes time and is dependent of the nanoparticle size and its volume fraction. Besides, the quality of filler dispersion into the polymeric matrix is also an important parameter to provide the highest surface area and provides an ideal structure for the rigid structure.

This thesis proposes different preparation methods and characterizations to obtain nanocomposites with a simple preparation either by casting-evaporation or melt processing. Nanocomposites materials based on cellulose nanocrystals and amorphous or semi-crystalline polymer as matrix were prepared and characterized. Most of the work has focused on the optimization of their properties and the impact of the processing method, in particular by extrusion or injection molding. The impact of the nanofiller-induced crystallization of the matrix, and the possibility of reorganization of the nanocrystals after processing, were notably addressed.

Other members of the jury Yves GROHENS, Professor, Université de Bretagne Sud, Lorient ♦♦ Christian CARROT, Professor, Université Jean Monnet, Saint-Etienne ♦♦ Jannick DUCHET-RUMEAU, Professor, INSA Lyon

Elsa WALGER

July 22, 2016 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Study of the activation of hydrogen peroxide by the copper(II)-phenanthroline complex for the color-stripping of recovered cellulosic fibers

Supervision

Gérard MORTHA, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Nathalie MARLIN, Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

Today, recovered papers are reused for the manufacture of bright paper after deinking and fiber bleaching, which generally starts with an alkaline hydrogen peroxide stage (H2O2). However, the efficiency of H2O2 is often limited due to its

low reactivity on the azo groups of paper dyes contained in recovered papers. The goal of this study was to improve the removal of these azo dyes by H2O2.
The improvement of H2O2 bleaching has been studied thoroughly in the context of chemical pulp delignification. In particular, the activation or catalysis of H2O2 by copper(II)-phenanthroline complexes (Cu-Phen) was found to be very effective. This inspired a preliminary bleaching study on deinked pulp and dyed pulp, and resulted in significant improvement of dye removal, which gave birth to our project.
The purpose of this work was to determine to what extent copper(II)-phenanthroline could improve the hydrogen peroxide color-stripping of dyed cellulosic fibers, and how. To answer this question, three intermediate issues were addressed: (1) does Cu-Phen alone have an effect on the dye? (2) does Cu-Phen improve the color-stripping of a dyed pulp by H2O2? (3) how does the H2O2/Cu-Phen system enhance the dye-color-stripping efficiency?
This work was thus divided into three studies: (1) the selected dyes and the complex were characterized in the absence of any oxidant and the interactions between the two were examined, (2) the H2O2/Cu-Phen system was applied on two dyed pulps to assess their color-stripping potential and to attempt to optimize it, and (3) the oxidation mechanism was investigated via trials in aqueous solution, with and without cellulose.
Using several analytical techniques (NMR, FTIR, UV-vis and EPR spectroscopy; ESI-MS) and speciation calculations, this work proved that the Cu-Phen complex enhanced H2O2 for the color-stripping of azo dyes, with and without fibers. It also provided evidence that phenanthroline acted as a stabilizer to adjust the solubility, stability and redox potential of copper(II), but may not be indispensable. The substrate (dyes but also cellulose) was strongly degraded by the H2O2/Cu-Phen system. The results of the mechanistic study supported the hypothesis of substrate oxidation by radicals produced via decomposition of H2O2 rather than by hydrogen peroxide itself. This mechanism, strongly dependent on the pH, is probably part of a catalytic cycle.
Finally, along with further research proposed based on our conclusions, this thesis should contribute to the improvement of deinked pulp bleaching as well as wastewater treatment in the pulp and textile industries.

Other members of the jury

Stéphane GRELIER, Professor, Université de Bordeaux ♦♦ Bodo SAAKE Professor, Universität Hamburg, Germany ♦♦ Carole DUBOC, CNRS Research Directeur, Université Grenoble Alpes ♦♦ Béatrice TUCCIO-LAURICELLA, Associate Professor, Aix-Marseille Université

Fanny BARDOT

June 13, 2016 - Fluid Mechanics, Energy, Processes

Ph.D. title

Modification of lignins from lignocellulosic pulps in order to incorporate them into ink formulations

Supervision

Gérard MORTHA, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Anne BLAYO, Lecturer-Researcher, Grenoble INP-Pagora / LGP2

Abstract

The originality of this work is to use lignin, an aromatic macromolecule from lignocellulosic biomass, in replacement of petroleum-based resins for the formulation of inks for food contact packaging applications. Different chemical modifications were carried out on commercial lignins, in order to make them compatible with the ink components. Used reagents and processes were chosen in order to limit the environmental impact of the whole value chain. Chemical modifications were monitored by several analytical techniques such as GPC SEC for the molar mass distribution and NMR and FTIR spectrometry for the monitoring of lignin functional groups. Ink properties were characterized by rheological and colorimetric (CIE L*a*b* system) measurements on printed samples.

Among the significant results, changes in hydrophilic/hydrophobic balance were particularly noticed. Furthermore, the colour gamut of modified lignin-based inks was enhanced, compared to the one of unmodified lignin-based inks. Two applications emerged from this work: (1) formulation of lignin-based bio-sourced inks, which meet most of the industrial requirements, and (2), development of a modified lignin-based coating which improved barrier properties of recycled paperboard.

Other members of the jury

Anne-Laurence DUPONT, CNRS Researcher, Centre de Recherche sur la Conservation ♦♦ Bernard KUREK, CNRS Research Director, INRA, Reims ♦♦ Stéphanie BAUMBERGER, Professor, AgroParisTech ♦♦ Charles BOUCHARD, Doctor, Siegwerk, France

Awatef LAAROUSSI

April 13, 2016 - Fluid Mechanics, Energy, Processes **[Thesis online]**

Ph.D. title

Flexible biocathode manufacturing by printing processes for implantable enzymatic biofuel cells

Supervision

Naceur BELGACEM, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2 ♦♦ Nadège REVERDY-BRUAS , Associate Professor, Grenoble INP-Pagora / LGP2

Abstract

Enzymatic biofuel cells, capable of converting efficiently the glucose from extracellular fluid into electrical energy, are a power source for implantable devices. However, the power output generated by these cells is not sufficient to fulfill the energy required by implantable artificial organs. Therefore, a new packaging architecture design based on flexible materials derived from printing technologies has been explored in order to enhance the power output of this cell.

This work demonstrates the relevance of printing processes such as ultrasonic spray and gravure to develop homogeneous, thin and flexible biocathodes. During this work, a carbon nanotubes / surfactant suspensions were deposited on a hydrophobic flexible substrate (carbon paper). Despite the poor printability of the substrate, flexible active layers were obtained (thickness between 5 and 10 µm).

Other members of the jury

Philippe CINQUIN, Professor, Université Joseph Fourier, Grenoble ♦♦ Latifa BERGUEOUI, Professor, INSAT, Tunisia ♦♦ Roberta BONGIOVANNI, Professor, Politecnico di Torino , Italy ♦♦ Sophie TINGRY, CNRS Researcher, Institut Européen des Membranes, Montpellier

Fanny TRICOT

February 3, 2016 -

Ph.D. title

Rewritable films on flexible substrates

Supervision

Nathalie DESTOUCHES, Professor, Université Jean Monnet, Saint-Étienne ♦♦ Francis VOCANSON, Professor, Université Jean Monnet, Saint-Étienne ♦♦ Didier CHAUSSY, Professor, Grenoble INP-Pagora / LGP2

Résumé

Previous research conducted by the laboratory Hubert Curien developed photosensitive Ag: TiO2 films on glass as support for updatable or permanent patterns. An adaptation of this work to plastic and paper substrates is here proposed to expand the potential application areas at product secure labeling for example. Fabrication techniques of such Ag: TiO2 films compatible with studied substrates have therefore been developed. Two paths have been considered.

The first uses the combination of Sol-Gel chemistry with the EISA method. Deposition processes such as spin coating, inkjet or flexographic printing are used to form a mesoporous film of TiO2 on substrates. Treatments based on solvent extraction or infrared annealing have been devised to release the porosity of the film without damaging the supports. To make films on paper, a silver salt is added to the sol before its coating. In the case of films deposited on plastic, silver is incorporated by soaking the material in a silver salt solution.

The second developed option proposes formulating an aqueous ink jet ink of TiO2 nanoparticles and silver ions by adapting the composition of a commercial suspension of TiO2 with the requirements of the ink jet process. After printing, the ink is dried by infrared annealing. The photochromic behavior under UV and visible light exposures of fabricated films allows them coloring and bleaching reversibly. Sol-Gel films coated on plastic can also be a support for permanent colored patterns realized by irradiation with a visible light of certain intensity.

Autres membres du jury

Roberta BONGIOVANNI, Professor, Politecnico di Torino , Italie ♦♦ Thierry GACOIN, CNRS Research Director, École Polytechnique, Paris ♦♦ Naceur BELGACEM Professor, Grenoble INP-Pagora / LGP2 ♦♦ Philippe BELLEVILLE, Research Director, CEA, Le Ripault

Research

Research

Director & Managers