



INTERNATIONAL SYMPOSIUM ON LIGNOCELLULOSIC MATERIALS

20th and 21st August 2013 - Amerian Iguazú Hotel - Puerto Iguazú – Argentina

The IMAM (Institute of Materials of Misiones, UNaM-CONICET, Argentina) organizes the INTERNATIONAL SYMPOSIUM ON LIGNOCELLULOSIC MATERIALS on the frame of the 13th SAM-CONAMET International Congress. The Symposium is supported by PROVALOR (CYTED Network for the Value-Added Products from Forest and Agroindustrial Residues) and by RIADICYP, the Ibero-American open network for the cooperation among Academia and Industry in the lignocellulosic materials, pulp, paper and recycled fibers.

The Symposium is oriented to academics, researchers, technicians, professionals and industrials which work and research the lignocellulosic materials. The principal aim of the Symposium is to offer a wide scientific and technological scope on the following topics:

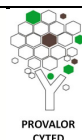
- Paper and board advanced materials
- Composites and nanocomposite materials
- Nanotechnology, micro- and nanocelluloses, and their applications
- Biorefinery of lignocellulosic materials
- Biosynthesis and Deconstruction of lignocellulosic biomass
- Advanced analytical techniques including Surface analysis
- Lignocelluloses, celluloses and papers as smart materials
- Polymers from renewable resources
- Bio-natural adhesives
- Recycling of complex lignocellulosic materials

PROGRAM

The INTERNATIONAL SYMPOSIUM ON LIGNOCELLULOSIC MATERIALS is structured with Plenary lectures, Semi - Plenary lectures, Oral presentations, and Poster presentations. All accepted abstracts will be published on proceedings of this Symposium while full papers will be distributed on a CD indexed with their corresponding ISBN. Additionally, they will be published on the RIADICYP website (open access).

SAM-CONAMET 2013 - FEATURED SPEAKER (PLENARY LECTURE)

Dan Shechtman. Nobel Prize of Chemistry 2011 – Technion, Haifa, Israel and ISU, Ames, Iowa, USA.
“Quasi-Periodic Materials – A Paradigm Shift in Crystallography”





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SAM-CONAMET 2013 - PLENARY LECTURE

Rafael Auras - School of Packaging, Michigan State University, East Lansing, MI. “Development of novel biobased functional polymeric membranes based on thermoplastic cassava starch and poly(lactic acid) reactive blends.”

KEYNOTE SPEAKERS

| | |
|---|--|
| Sabu Thomas | Centre for Nanoscience and Nanotechnology - India |
| Janne Laine | Aalto University- Finland |
| Antonio Aprigio da Silva Curvelo | IQSC, Universidade de São Paulo, Departamento de Físico Química- Brazil |
| Thomas Rosenau | University of Natural Resources and Life Sciences - Austria |
| Antje Potthast | University of Natural Resources and Life Sciences - Austria |
| Pedro Jesus Herrera Franco | Centro de Investigación Científica de Yucatán - Mexico |
| Oscar Leon Manso | NUTRIMENTEC and Fundación CARTIF – Spain |

SAM-CONAMET CONGRESS AND INTSYMLIGNCELLMAT VENUE

Iguazú is located in the northeast part of Argentina, in the Province of Misiones, and has borders with Brazil and Paraguay. It is the City of the Iguazú Falls, in the Iguazú River shared with Brazil.

As a touristic city, it counts with hotels in all the categories as well as hostels and camping sites.

The airport is international and there are flights from/to Buenos Aires and Rio de Janeiro (Brazil).

The Symposium will take place at the Amerian Iguazú Hotel - Puerto Iguazú – Argentina: “Just where 2 rivers and 3 countries meet...”

With its unique location, just a few metres from the Hito Tres Fronteras, Amerian Portal del Iguazú Hotel has a stunning view of the joint of the Iguazú and Paraná rivers. Originally, it was at this point where the outstanding waterfalls were formed but due to an eruption occurred millions of years ago, the waterfalls went backwards to their current position. Therefore, the Hotel is considered to be positioned at a good energy point.

The amazing Iguazú waterfalls, one of the most surprising world wonders, are just 15 km away from the hotel.





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MEMBERS OF THE SCIENTIFIC COMITEE

| | | |
|---------------------------------|------------|-----------|
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| Graciela Beatriz Gavazzo | IMAM | Argentina |
| Mirtha Graciela Maximino | UNL | Argentina |
| Mirta Aranguren | INTEMA | Argentina |
| Celso Foelkel | ABTCP | Brazil |
| Maria Luiza Otero d'Almeida | IPT | Brazil |
| Song Won Park | USP | Brazil |
| Graciela Ines Bolzon de Muñiz | UFPr | Brazil |
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| Francisco López Baldovin | UH | Spain |
| José María Carbajo | INIA | Spain |
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| Kalle Ekman | Stora Enso | Finland |
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| Orlando José Rojas | NCSU | USA |
| Arthur J. Ragauskas | IPST | USA |

ORGANIZING COMMITTEE

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INFORMATION ABOUT SAM-CONAMET CONGRESS AND INT. SYMP. LIGNOCELLULOSIC MATERIALS

<http://www.samconamet2013.misiones.gov.ar/>

THE SUMMARIES OF THE KEYNOTE SPEAKERS OF THE SYMPOSIUM ARE PRESENTED BELOW.





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BIO INSPIRED MICRO AND NANOCOMPOSITES FOR THE FUTURE

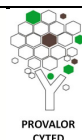
Sabu Thomas

Centre for Nanoscience and Nanotechnology, India



ABSTRACT

Micro and nano bio inspired composite materials are the best future materials for the coming millennium. Cellulose fibers, chitin and starch in different length scales offer outstanding properties like stiffness, toughness and other mechanical properties. Composites from polymers (rubbers and plastics) and reinforcing fibers provide best properties of each. They replace conventional materials in many structural and non-structural applications. Both natural fibers and polymers are light, on combination they give composites of very high strength to weight ratio. In recent years composites made from natural (cellulosic) fibers and organic polymers have gained a lot of interest in construction and automobile industry. Unlike synthetic fibers, natural fibers are abundant, renewable, cheap and of low density. Composites made from natural fibers are cost effective and environment friendly. However, lack of interfacial adhesion and poor resistance to moisture absorption makes the use of natural fibers less attractive for critical applications. However, these problems can be successfully alleviated by suitable chemical treatments. This presentation deals with the use of natural fibers such as pineapple leaf fiber, coir fiber, sisal fiber, oil palm fiber and banana fiber as reinforcing material for various thermoplastics, thermosets and rubbers. The fiber surface modifications via various chemical treatments to improve the fiber-matrix interface adhesion on mechanical, viscoelastic, dielectric rheological ageing and thermal properties will also be discussed. Experimental results will be compared with theoretical predications. The advantages of hybridizing natural and glass fibers also will be scanned briefly. The use of these composites as building materials will be discussed. Finally recent developments in cellulose nanocomposites, chitin nanocomposites and starch nanocomposites will also be presented.





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NANOCELLULOSE: A SUPERIOR MATERIAL DESIGNED BY NATURE

Prof. Janne Laine
Aalto University, Finland



ABSTRACT

During the past decade new technologies originating from nanoscience have emerged and opened opportunities in many fields, including forest products technology. Cellulose is the main constituent in woody plants and the most renewable bioresource. In biosynthesis, cellulose polymers aggregate to form substructures, elemental fibrils (nanofibrils, width of about 5 nm), which in turn aggregate to form cellulosic fibres (width of about 40 µm). Using new effective methods, such as chemical treatments in combination with a high-pressure fluidizer, these fibrils can be disintegrated from the fibres to form uniform nanosized material. A high aspect ratio and specific surface area combined with high strength and flexibility are characteristic for cellulose nanofibrils. Functional hydroxyl groups in cellulose also enable surface chemical modifications, increasing their potential in several applications. These strong, light, tunable nanofibrils have a great potential in special papers, paper coatings, packages and building materials. In addition to the paper and packaging industry, the vehicle, electronics, food product and cosmetics industries can create added value for their products using tailored nanofibrils.



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SOLUBILITY PARAMETERS OF ORGANOSOLV LIGNINS

Antonio Aprigio da Silva Curvelo

Universidade de São Paulo – Instituto de Química de São Carlos

Débora Terezia Balogh and Lísias Pereira Novo



ABSTRACT

The utilization of organic solvents for the production of cellulosic pulps began with the work of Kleinert in 1931. New studies have emerged in the decades of 70 and 80 with the development of ALCELL, Acetosolv, ASAM and Organocell, among others processes. Despite these studies, industrial pulping processes exclusively employ aqueous solutions (Kraft and soda processes) performed in alkaline medium to promote removal of lignin. Alternatively, the dissolution of lignin can be promoted by production of lignosulfonates as in the Sulfite pulping processes.

The increase cost of oil due to the limitations of the reserves associated with increased consumption, promoted the search for renewable sources to supply fuel and chemicals. In this sense, the use of lignocellulosic raw materials are highlighted and led to the rebirth of studies aimed at separating its macromolecular constituents. Associated with the need for fuel, the chemical industry is also seeking alternatives to the production of chemical and, again, the lignocellulosic materials are presented as an alternative source for this supply.

This new scenario has promoted studies of organosolv delignification processes, now in the biorefinery context. The choice of solvent system must consider not only the efficiency of the process but also the subsequent use of the polysaccharides and lignin released in the process. In this sense, this work proposes the use of solubility parameters of lignin as a guide for choosing the most suitable solvent system taking into account the availability of raw materials and the cost of organic solvents.

The solubility parameters were developed by Hildebrand and Scott in 1936 and applied to the study of lignin by the first time by Schuerch in 1952. The limitation of using one-dimensional parameter of Hildebrand was replaced by the introduction of specific parameters for dispersive interactions, dipole-dipole and hydrogen bonding interactions, as proposed by Hansen in 1967.

The solubility parameters for lignins (Hildebrand and Hansen) were determined from the determination of solubility of lignins previously isolated from pulping processes. In 1992 our research group determined the Hildebrand's solubility parameter for lignin from Pine from the yields of the delignification organosolv processes. The obtained value coincided with those reported by Schuerch and Björkman.

Aiming at the application of solubility parameters for studies of organosolv delignification of sugarcane bagasse, we present now the values of the Hansen's solubility parameters for this particular lignin and the extension of these results to the choice of industrial solvents for the isolation of lignins from bagasse sugarcane.





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TOWARDS A BETTER UNDERSTANDING OF CELLULOSE SWELLING, DISSOLUTION AND REGENERATION AT THE MOLECULAR LEVEL

Thomas Rosenau

BOKU University Vienna, Austria

Antje Potthast, BOKU University Vienna, Austria

Kurt Mereiter, Technical University Vienna, Austria

Christian Jaeger, BAM Berlin, Germany

Alfred French, USDA ARS New Orleans, USA

Fumiaki Nakatsubo, Kyoto University, Japan



ABSTRACT

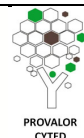
The exact structure of the hydrogen bond networks and the changes of these networks upon swelling and dissolution processes are current ‘hot topics’ in cellulose research. H-bonds are responsible for the allomorphy of cellulose, for the typical properties of cellulose, and for reactivity and chemical behavior. The use of isotopic labeling with modern solid-state NMR techniques in combination with X-ray crystal structure analysis is a powerful approach to obtain solid state and gel structural data of cellulose and cellulose model compounds, so that we now come close to an understanding of cellulose swelling and dissolution on a molecular level, and might even successfully address the old and unanswered question about the special nature of cellulose solvents.

The cellulose model compound methyl 4'-O-methyl-beta-D-cellobioside was the first cellulose fragment analogue found to form two distinct crystal phases, by analogy to the cellulose I and II allomorphs. With the ¹³C-perlabeled form of this compound, novel solid-state NMR experiments that were based on the high degree of isotopic enrichment (>99%) became possible. Protons in hydrogen bonds are detected through the two carbons that are bridged by this proton. The cleavage and re-formation of the complex hydrogen bond network became accessible to detailed analysis for the first time. In the next steps, both ¹³C-perlabeled cellulose (cellulose II) synthesized according to the cationic ring-opening polymerization approach from ¹³CC6-glucose and ¹³C-enriched bacterial cellulose (cellulose I) were subject to similar experiments.

We selected the following cellulose solvents for our studies, which were synthesized in perdeuterated and ¹⁵N-labeled form: NMMO, DMAc, and BMIM acetate. ¹⁵N-labeling allows measuring the defined distance between solvent and the respective cellulose (model) carbon, and thus monitoring approach and action of the solvent.

The studies showed that swelling is a reversible process of 3-4 stages, connected with cleavage of hydrogen bonds mainly to/from OH-6 and OH-2. Dissolution, by contrast, is irreversible and involves in addition H-bonds to/from OH-3. The solvents can be distinguished by (1) the order in which specific H-bonds are broken, (2) the number of distinguishable swelling stages, (3) the number of solvent molecules per anhydroglucose unit, and (4) the solvent distance to the different AGU carbons. In addition to common O-H hydrogen bonds, cellulose solvents also form non-conventional C-H hydrogen bonds involving selectively C-1 and C-3. This C-H hydrogen bond formation might be a prerequisite to cellulose dissolution. In solution (confirmed so far for the solvents DMAc, NMMO and BMIM acetate) the cellulose molecules are surrounded by a layer of tightly bound solvent molecules which are not undergoing dynamic exchange, comparable to primary “solvent shells” known in inorganic chemistry.

All these molecular level data are available for the first time and provide a consistent picture of the molecular mechanisms of swelling and dissolution of cellulose and cellulosic model compounds, which will be presented in this lecture.





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NEW INSIGHTS INTO NATURAL AGING OF CELLULOSIC MATERIALS

Antje Potthast

BOKU University Vienna, Austria

Kyujin Ahn, Myung-Joon Jeong,
Thomas Zweckmair, Manuel Becker,
Ute Henniges, Thomas Rose nau



ABSTRACT

Research on biomaterials is vividly increasing, and more and more biomaterials will eventually re-enter our daily life. But the sustainability of using materials from renewable resources does not necessarily stop at this point. The overall performance and sustainability are linked to the durability of the materials – the longer their lifetime the better the eco-balance. With aging being a natural and inexorable process, means to slow down those aging processes will gain increasing attention, in particular for biomaterials. The prerequisite to placing actions which retard aging is to fully understand it, especially on a molecular level. For lignocellulosic materials we are unfortunately still quite far from having a comprehensive picture of the underlying mechanisms. One reason for this is the fact that we cannot easily reproduce the effects of natural aging by fast artificial aging processes.

In this lecture we present new insights into differences between natural aging and artificial aging of cellulose. Similarities and differences, e.g. with regard to the molecular spots where oxidative processes occur under conditions of natural aging vs. artificial aging, will be explained, and the consequences with regard to life expectancy and possible treatments that counteract aging processes, will be discussed. Novel techniques and new concepts to assess cellulose aging will be presented, one of them considers acetylation reactions during natural aging. Acetic acid is a well-known degradation product of lignocellulosic materials, such as wood or hemicelluloses containing pulps. Also aging of pure celluloses causes formation of small amounts of acetic acid which, in turn, engages in reactions with the cellulosic matrix. We were able to demonstrate that in addition to hydrolysis also surface acetylation occurs under ambient conditions, changing the surface properties of the material, paper in this particular case. In order to quantify the very small amounts of surface acetates, a novel technique based on HS-GCMS has been developed. The new method allows quantification of trace amounts of acetyl (acetate) groups at lignocellulosic substrates without interference from free acetic acid which is omnipresent in such substrates.

Aging of cellulosic materials as a scientific topic has nowadays not only an impact on conservation science, it has its bearing on paper chemistry, general cellulose science and analytical method development, and it influences modern material science to a great deal.



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MICROSTRUCTURE-EFFECTIVE PROPERTY RELATIONSHIPS IN NATURAL CELLULOSIC FIBER REINFORCED POLYMER COMPOSITES

Pedro J. Herrera-Franco
Centro de Investigación Científica de Yucatán, Mexico



ABSTRACT

In recent years, the use of natural fibers for the reinforcement of polymeric matrices has attracted the attention of the composites community. Some of these composites have been based on conventional petroleum synthesized matrices (e.g. polyethylene, polypropylene, etc.) but more recently, because of environmental problems related to their disposal as well as concerns over petroleum availability, biocomposites based on polymeric matrices from renewable resources, such as the PLA, poly(lactic acid), are the most stunning.

It is well known that cellulosic fibers impart polymeric matrix composites high specific stiffness and strength, a desirable fiber-aspect ratio and biodegradability; also, cellulosic fibers are readily available from natural sources and most important, they have a low cost per unit volume basis. One issue that has prevented a more extended utilization of natural cellulosic fibers is the lack of a good adhesion to most polymeric matrices. The hydrophilic nature of natural fibers adversely affects adhesion to a hydrophobic polymeric matrix resulting in "poor" composite strength properties. Different approaches to improve the adhesion between cellulosic fibers and polymeric matrices have been proposed, however, no clear unambiguous mechanism for improving adhesion nor a systematic study that varied the adhesion level to test its effect on composite properties have been offered.

In order to develop the structure-property relationships between fiber-matrix adhesion and the composite mechanical properties, a systematic study that varied the adhesion level to test its effect on the composite properties using a specific fiber-matrix system, namely, henequen fibers (Agave fourcroydes) and a thermoplastic matrix, high density polyethylene was undertaken. The physical and chemical aspects of the fiber surface modification and how such modification was characterized together with their effect on the micromechanical and effective mechanical properties of the composite materials are presented. The results of the study conducted with this fiber-matrix system have shown that there are fundamental differences in both the level of adhesion and in the interfacial failure mode for each fiber-matrix combination when the composites are subjected to different mechanical solicitations. The aim of this presentation is to discuss the relationships between fiber-matrix interfacial shear strength and the static and dynamic mechanical and fracture property data for this composite system.



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IBEROEKA INNOVATION PROJECTS: USE OF THE LIGNOCELLULOSIC WASTES TO OBTAIN FUNCTIONAL EXTRACTS FROM MEDICINAL MUSHROOMS



Oscar León
General Director of NUTRIMENTEC
Technical adviser of CARTIF Foundation, Spain

ABSTRACT

One of the current challenges that is imposed on the scientific-technical and commercial relationships between Ibero-American countries, is to achieve an effective collaboration between countries and enterprises, involving an effective transfer of scientific results and technology from research centers and groups to the enterprises, to achieve a practical and successful application of those results. As an example of this effective collaboration, FUNGIFAR project can be highlighted. It was presented to the Mexico-Spain bilateral call in 2012, and it is being developed in from 2012 to 2014 through a partnership agreement signed by the University of Baja California, CIATEJ and Setas from Baja California (by Mexico) and NUTRIMENTEC Food Technologies and Soria Natural (by Spain), in collaboration with the Foundation CARTIF.

The main aim of this applied research project is to obtain purified extracts with antioxidant, anti-inflammatory, immune-modulating and anti-carcinogenic capacities from medicinal mushrooms grown on modified conditions on a set of lignocellulosic wastes obtained from diverse agro-food sectors, as biomass from crops, spent coffee waste, etc. This would result in a double benefit, the improved obtaining of nutraceutical compounds from cultivated mushrooms, and the complete use of low-value lignocellulosic wastes as substrate for growing mushrooms. By enzymatic hydrolysis of the cell walls of such substrates, after harvesting of mushrooms the digestibility of lignocellulosic residues is improved, allowing its application in the production of biogas, compost, etc.

Thus, although the initial objective of the project was to obtain nutraceutical compounds from medicinal mushrooms, an integral solution was implemented, in which the generation of a viable and profitable use to the agro-food lignocellulosic wastes has been achieved, combining the production of medicinal mushrooms in effective and profitable form with energy production from the final wastes of the substrate.

The results of the project, once finalized, will be patented and marketed in order to capitalize the public investment in R & D, through the obtained funds from the Mexican and Spanish government.

