



# **Biocomp 2016**

The 13<sup>th</sup> Pacific Rim Bio-Based Composites Symposium  
Biobased composites for a sustainable future  
November 14<sup>th</sup> to 16<sup>th</sup>, 2016 - Concepción - Chile

**ABSTRACTS**

[www.biocomp2016.cl](http://www.biocomp2016.cl)  
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## ORGANIZATION

### Steering Committee

- **James Hague** - Australia
- **John Wolodko** - Canada
- **Changtong Mei** - China
- **Fu Feng** - China
- **Philip Humphrey** - United States
- **Shigehiko Suzuki** - Japan
- **Warren Grigsby** - New Zealand
- **Yusuf Hadi** - Indonesia
- **Paridah MD. TAHIR** - Malaysia
- **Chunping Dai** - Canada
- **Roger Rowell** - United States (Chair)
- **Alex Berg** - Chile

## WORKING GROUPS

### General organization

- **Chair: Alex Berg** - Chile

#### Members

- **Chunping Dai** - Canada
- **Roger Rowell** - United States
- **Shigehiko Suzuki** - Japan
- **Philip Humphrey** - United States

### Technical support

- **Chair: John Wolodko** - Canada

#### Members

- **Paridah MD TAHIR** - Malaysia
- **Alex Berg** - Chile
- **Changtong Mei** - China

### Recruitment

- **Chair: Yusuf Hadi** - Indonesia

#### Members

- **Warren Grigsby** - New Zealand
- **Roger Rowell** - United States
- **Philip Humphrey** - United States

### Social program

- **Chair: Roger Rowell** - United States

#### Members

- **Alex Berg** - Chile

## KEYNOTE SPEAKERS

### PLENARY SESSION

**Andreas Michanickl, University of Applied Sciences Rosenheim, Germany.**  
“Wood-Based-Panels and Composites – Challenges and Perspectives for the Future”.

**Shigehiko Suzuki, Shizuoka University, Japón.**  
“Elements of wood-based material research from lamina to nano”.

**John Wolodko, Alberta Innovates, Canadá.**  
“An Overview of Materials R&D Activities in Alberta’s Bioresource Sector”.

**Warren Grigsby, SCION, New Zealand.**  
“Interfacial Adhesion Behaviors within Natural Fiber Composites: A View at Fiber Level”.

**James Hague, Australian Forest Research Company Pty Ltd, Australia.**

**Andreja Kutnar, University of Primorska, Eslovenia.**  
“Traditional and Innovative Wood-Based Bioproducts”.

**Juan Matos Lale, Unidad de Desarrollo Tecnológico, Chile.**  
“Eco-Friendly Methodology for the Synthesis of Graphene-Based Catalytic Membrane Reactors”.

**Danny García Marrero, UCSC, Chile.**  
“Polycarboxylated Flavonoid Oligomers as Functional Additives for Polylactic Acid-, Polystyrene-, and Polyethylene-Based Composites”.

**Roger M. Rowell, University of Wisconsin – Madison, USA.**  
“From Academic to Commercial: Story of Acetylation of Wood”.



### SUNDAY, NOVEMBER 13<sup>TH</sup>

- 17:30 - 18:00 Registration (UDT)
- 18:00 - 20:00 Welcome drink (UDT)

### MONDAY, NOVEMBER 14<sup>TH</sup>

08:00 - 09:00 Registration

09:00 - 09:40 Opening ceremony  
**Alex Berg** - Executive Director Technological Development Unit, UDT.  
**Carlos González** - Vice-rector of Research and Development, University of Concepción.  
**Roger M. Rowell** - Professor Emeritus of the University of Wisconsin, Madison, United States.

09:40 - 10:30 **PLENARY SESSION**  
**Andreas Michanickl**, University of Applied Sciences Rosenheim, Germany.  
**"Wood-Based-Panels and Composites - Challenges and Perspectives for the Future"**.

10:30 - 11:00 Coffee

11:00 - 11:40 **SESSION 1: BIOCOSITES I**  
**Keynote: Shigehiko Suzuki**, Shizuoka University, Japan.  
**"Elements of wood-based material research from lamina to nano"**.

**SESSION 2: ADHESIVES AND BONDING**  
**Keynote: Warren Grigsby**, SCION, New Zealand.  
**"Interfacial Adhesion Behaviors within Natural Fiber Composites: A Ciew at Fiber Level"**.

11:40 - 12:05 The Use of X-Ray Computed Tomography in Bio-Composite Research.  
 José Couceiro, Luleå University of Technology, Sweden.

Mechanical Performance of Glue Joint in Structural Hardwood Elements.  
 Peter Niemz, ETH Zurich, Institute for Building Materials, Switzerland.

12:05 - 12:30 A New Biobased Composite Material Using Bark Fibres *Eucalyptus*.  
 Cecilia Fuentealba, Unidad de Desarrollo Tecnológico, Chile.

Environmental friendly natural resins from polyphenolic extracts: Perspectives and challenges  
 Jorge Santos Ucha, Unidad de Desarrollo Tecnológico, Chile.

12:30 - 12:55 Changes in Mechanical and Surface Properties of Medium Density Fiberboards and Particleboards with Accelerated Aging Test.  
 Sahriyanti Saad, Shizuoka University, Japan.

Wood-Straw Composites Bonded with Urea Formaldehyde Glue Modified by Ethanol.  
 Emilia-Adela Salca, Transilvania University of Brasov, Romania.

13:00 - 14:00 Lunch

14:00 - 14:40 **SESSION 3: BIOCOSITES II**  
**Keynote: Andreja Kutnar**, University of Primorska, Slovenia.  
**"Traditional and Innovative Wood-Based Bioproducts"**.

**SESSION 4: BIOPLASTICS**  
**Keynote: Danny García Marrero**, UCSC, Chile.  
**"Polycarboxylated Flavonoid Oligomers as Functional Additives for Poly(lactic Acid)-, Polystyrene-, and Polyethylene-Based Composites"**.

14:40 - 15:05 Continuous Wood Surface Densification - Chemical Treatments to Reduce the Set-Recovery.  
 Benedikt Neyses, Luleå University of Technology, Sweden.

Lignin-Ester Derivative as Matrix for Composites Elaboration by Press Moulding.  
 Jalel Labidi, University of the Basque Country, Spain.

15:05 - 15:30 Wood preservatives utilising low-value olive production products in Slovenian Istria.  
 Matthew Schwarzkopf, University of Primorska, Slovenia.

Bio-Based Polymer Pellets and Films Derived from Agro-Industrial Residues.  
 Jesús Serrano, Center for Advanced Polymer Research (CIPA), Chile.

15:30 - 15:55 Performance of Medium Density Fibreboards Prepared with Recycled Fibers.  
 Byung-Dae PARK, Kyungpook National University, Republic of Korea.

Supercritical Impregnation of Cinnamaldehyde into PLA Films to Develop Antimicrobial Food Packaging Materials.  
 Carolina Villegas Vallejos, University of Santiago de Chile, Chile.

15:55 - 16:40 **COFFEE & POSTER SESSION**

16:40 - 17:05 Electrospun Nanofibers Using Whole Microalgal Biomass: A Novel Sustainable Approach in the Field of Biobased Composite Materials.  
 Sivashunmugam Sankaranarayanan, Universidad de La Frontera, Temuco, Chile.

Adhesive Forces Acting Between the Components of Wood-Plastic Composites on Molecular and Macroscopic scale.  
 Bernard Effah, Stellenbosch University, South Africa.

17:05 - 17:30 Novel Biocomposite Based on Chitosan - *Sphagnum magellanicum* Fibers.  
 Gustavo Cabrera, Centro de Investigación, Desarrollo e Innovación (CIDI), Grupo Hijuellas, Chile.

A novel hydrocolloid wound dressing based on pectin, starch and bioactive extracts of Chilean native plants.  
 Constanza Sabando, Center for Advanced Polymer Research (CIPA), Chile.

20:00 **PARRILLADA (CHILEAN BARBECUE - Club House Victoria)**  
 Free for full registration participants. Others attendees \$30.000 / USD 45

## TUESDAY, NOVEMBER 15<sup>TH</sup>

09:30 - 10:10	<b>SESSION 5: FIBER REINFORCED PLASTICS</b> Keynote: John Wolodko, Alberta Innovates, Canada. "An Overview of Materials R&D Activities in Alberta's Bioresource Sector".	<b>SESSION 6: BIOCOMPOSITES RESEARCH IN INDUSTRY</b> Keynote: James Hague, Australian Forest Research Company Pty Ltd, Australia.
10:10 - 10:35	Study of Macro Algae and Mollusc Wastes as Secondary Fillers in Novel Wood-Plastic Bio-composite Particleboard. Claudia Echeverria, University of New South Wales, Australia.	Industrial experience regarding natural and low emission adhesives Esteban Ramirez, Innovation Manager, Research and Development, MASISA S.A.
10:35 - 11:00	Experimental study of the effect of organic powder in a composite matrix of Fiber Reinforced Plastics (FRP). Katherine Sanhueza, Universidad de La Frontera, Chile.	Cellulose microfibrilles: From the laboratory to industrial scale. Dr. Eduardo Izquierdo, Director Research and Development COMASA S.A., Forestal y Papelera Concepción.
11:00 - 12:20	<b>COFFEE &amp; POSTER SESSION</b>	
12:20 - 12:45	Novell Compounding Process for Utilizing TMP-Fibers in Wood-plastic Composites. Oliver Mertens, University Hamburg, Germany.	Adaptation and transference of high standard timber frame construction. Carla Chávez, Polo Madera Program, Universidad de Concepción, Chile.
12:45 - 13:10	Steam Explosion as a Treatment of Hemp Fibers ( <i>Cannabis Sativa L.</i> ) for Production of Composite Materials. Thibaud Sauvageon, Université de Lorraine, France.	"WOODEN CONNECTION" Embracing territories through architecture and design Susana Herrera, Factoría.
13:10 - 14:30	Lunch	
14:30 - 15:10	<b>SESSION 7: CARBON BASED MATERIALS</b> Keynote: Juan Matos Lale, Unidad de Desarrollo Tecnológico, Chile. "Eco-Friendly Methodology for the Synthesis of Graphene-Based Catalytic Membrane Reactors".	<b>SESSION 8: MODIFIED WOOD COMPOSITES</b> Keynote: Roger M. Rowell, University of Wisconsin - Madison, USA. "From Academic to Commercial: Story of Acetylation of Wood".
15:10 - 15:35	Elucidating the role of ammonia-based salts on the preparation of cellulose-derived carbon aerogels Luis E. Arteaga, Unidad de Desarrollo Tecnológico, Chile.	Esterified Lignin as Hydrophobic Agent for Use on Wood Products. René Herrera Díaz, University of the Basque Country, Spain.
15:35 - 16:00	Synthesis of Visible-Light Response TiO <sub>2</sub> and its Application to Carbonized Board. Sung-Phil Mun, Chonbuk National University, South Korea.	Surfactant Properties of Alkenyl Succinates Derived of Lignins. Nacarid Delgado, Unidad de Desarrollo Tecnológico, Chile.
16:00 - 16:25	Coffee	
16:25 - 16:50		Microencapsulation of Polyphenols Extracted from <i>Pinus radiata</i> bark. Tomás Kappes R., Universidad de Concepción, Chile.
16:50 - 17:20	<b>POSTER AWARDS AND CLOSING CEREMONY</b>	

# POSTER SESSION

## ADHESIVES AND BONDING

### AB01

SECOND GENERATION AMINO RESINS  
JOÃO FERRA  
EURORESINAS - INDÚSTRIAS QUÍMICAS SA - PORTUGAL

### AB02

ENGINEERED WOOD PRODUCTS MADE WITH 100% BIO-BASED ADHESIVES: NEW APPROACHES TO DESIGNING ADHESIVES FOR WOOD PANEL MANUFACTURE  
WARREN GRIGSBY  
SCION - NEW ZEALAND

## BIO-RESOURCES

### BR01

INFLUENCE OF TREE HEIGHT IN THE CHEMICAL COMPOSITION OF THE LIPOPHILIC EXTRACTS FROM THE *Eucalyptus Nitens* BARK  
NICOLÁS GONZÁLEZ  
UNIVERSIDAD DE CONCEPCIÓN - CHILE

### BR02

FILMS BASED ON FUNGAL BIOMASS DERIVED CHITOSAN  
GUSTAVO CABRERA  
CENTRO DE INVESTIGACIÓN, DESARROLLO E INNOVACIÓN (CIDI), GRUPO HIJUELAS - CHILE

### BR03

ANTIMICROBIAL ACTIVITY OF MODIFIED/UNMODIFIED POLYFLAVONOIDS AND LIGNIN FROM PINUS RADIATA OBTAINED UNDER PILOT-PLANT SCALE  
DANILO A. ESCOBAR  
UNIDAD DE DESARROLLO TECNOLÓGICO - CHILE

### BR04

GROWING UP IN DIFFERENT ALTITUDE: CHANGES IN THE GROSS CALORIFIC VALUE AND ELEMENTAL COMPOSITION OF *Abies religiosa* WOOD  
RICARDO MUSULE  
INSTITUTO DE BIOTECNOLOGÍA Y ECOLOGÍA APLICADA, UNIVERSIDAD VERACRUZANA - MEXICO

### BR05

ESTIMATION OF WASTE MEDIUM DENSITY FIBREBOARD GENERATION FROM DIFFERENT SOURCES FOR ITS RECYCLING IN KOREA  
JEONGKWAN ROH  
KYUNGNAM NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY - REPUBLIC OF KOREA

### BR06

PRELIMINARY STUDY OF FRACTIONATION AND PURIFICATION OF STILBENOIDES FROM EXTRACT OF *Vitis vinifera* (PINOT NOIR) GRAPE CANE BY ADSORPTION ON MACROPOROUS RESINS (XAD-7)  
SEBASTIAN RIQUELME  
UNIDAD DE DESARROLLO TECNOLÓGICO - CHILE

### BR07

CARACTERISATION OF NETTLE FIBERS PRODUCED BY STEAM EXPLOSION  
PAOLA NAVARRETE  
LERMAB - UNIVERSITÉ DE LORRAINE - FRANCE

### BR08

PRODUCTION OF FIBERS FROM METAL-RICH PHYTOREMEDIATION HEMP  
THIBAUD SAUVAGEON  
UNIVERSITÉ DE LORRAINE - FRANCE

### BR09

BACTERIAL POLYHYDROXYALKANOATE FOR ELECTROSPUN FIBER PRODUCTION  
FRANCISCA ACEVEDO  
UNIVERSIDAD DE LA FRONTERA - CHILE

## BIOPLASTICS AND BIOCOSITES

### BB01

COMPOSITE PANELS MADE FROM TETRA-PAK AND POLYETHYLENE WASTE MATERIALS  
EMILIA-ADELA SALCA  
TRANSILVANIA UNIVERSITY OF BRASOV - ROMANIA

### BB02

DYNAMICS OF SMALL MOLECULES IN METAL-ORGANIC FRAMEWORKS (MOFs) STUDIED BY <sup>2</sup>H AND <sup>13</sup>C SOLID-STATE NMR  
HAIYAN MAO  
NANJING FORESTRY UNIVERSITY - CHINA

### BB03

EFFECT OF DIFFERENT POLYMER BLENDING ON THE MECHANICAL PROPERTIES OF POLYPROPYLENE BASED WOOD PLASTIC COMPOSITE  
HIKARU KOBORI  
SHIZUOKA UNIVERSITY - JAPAN

### BB04

SELF-BONDED COMPOSITE FILMS BASED ON CELLULOSE NANOFIBERS AND POLYLACTIC ACID MICROFIBRILS.  
EDUARDO ROBLES  
UNIVERSITY OF THE BASQUE COUNTRY UPV/EHU, ESPAÑA.

### BB05

GREEN COMPOSITES OF RESIDUAL MICROALGAE BIOMASS: ADVANCES IN MICROALGAE BIOMASS BIOREFINERY FOR BIODIESEL PRODUCTION  
SIMONET TORRES  
CEDENNA, UNIVERSIDAD DE SANTIAGO DE CHILE - CHILE

### BB06

THERMAL AND MECHANICAL CHARACTERIZATION OF COMPOSITES BASED ON A POLYMERIC MATRIX OF POLYLACTIC ACID, POLYETHYLENE GLYCOL AND TALC  
IVÁN RESTREPO  
UNIDAD DE DESARROLLO TECNOLÓGICO - CHILE

### BB07

EFFECT OF ACTIVATION AND MAGNETIZATION ON THE ADSORPTIVE REMOVAL OF METHYLENE BLUE ONTO OAT HULL BIOCHAR  
MARÍA EUGENIA GONZÁLEZ  
UNIVERSIDAD CATÓLICA DE TEMUCO - CHILE

### BB08

BIOCOSITES WITH FORESTAL RESIDUES OF TZALAM (*Lysiloma latisiliquum*) AS REINFORCEMENT  
CANCHE-ESCAMILLA G  
CENTRO DE INVESTIGACIÓN CIENTÍFICA DE YUCATÁN - MEXICO

### BB09

DEVELOP AND CHARACTERIZATION OF BIODEGRADABLE COMPOSITE TO USE IN FOREST INDUSTRY  
CATALINA CASTILLO SEPÚLVEDA  
UNIDAD DE DESARROLLO TECNOLÓGICO - CHILE

### BB11

CHARACTERIZATION AND APPLICATION OF A NATURAL POLYMER AS A THERMAL INSULATION BIOMATERIA  
JUAN PABLO CÁRDENAS RAMÍREZ  
UNIVERSIDAD DE LA FRONTERA - CHILE

### BB12

MECHANICAL AND PHYSICAL PROPERTIES OF HEMP FIBER-MAT REINFORCED POLYETHYLENE FILM COMPOSITES  
HEIKKO KALLAKAS  
TALLINN UNIVERSITY OF TECHNOLOGY - ESTONIA



## **NEW ANALYTICAL TECHNIQUES, PROPERTIES AND TESTING**

### **NA01**

*In-situ* MOISTURE CONTENT AND DENSITY MEASUREMENTS IN SURFACE DENSIFIED WOOD USING DUAL X-RAY ABSORPTIOMETRY IN MEDICAL CT-SCANNING  
JOSÉ COUCEIRO  
LULEÅ UNIVERSITY OF TECHNOLOGY - SWEDEN

## **PROCESSING TECHNOLOGIES**

### **PT01**

RESISTANCE OF SMOKED GLUED LAMINATED LUMBER TO SUBTERRANEAN TERMITE ATTACK  
TITLE  
Y. S. HADI  
BOGOR AGRICULTURAL UNIVERSITY - INDONESIA

### **PT02**

INFLUENCE OF VENEER DENSIFICATION UPON THE PROCESS OF PLYWOOD PRODUCTION  
EMILIA-ADELA SALCA  
TRANSILVANIA UNIVERSITY OF BRASOV - ROMANIA

### **PT03**

ANAEROBIC DIGESTION OF CHICKEN MANURE: EFFECT OF SUBSTRATE CONCENTRATION ON THE BIOGAS YIELD  
CONSTANZA BEATRIZ ARRIAGADA GAJARDO  
UNIVERSIDAD DE CONCEPCIÓN - CHILE

### **PT04**

A NEW METHOD TO SELECT WOOD SPECIES SUITABLE FOR SURFACE DENSIFICATION  
BENEDIKT NEYSES  
LULEÅ UNIVERSITY OF TECHNOLOGY - SWEDEN

### **PT05**

EFFECT OF SUPERCRITICAL IMPREGNATION PROCESS ON THYMOL RELEASE FROM PLA FILMS FOR FOOD PACKAGING APPLICATIONS  
ALEJANDRA TORRES  
UNIVERSITY OF SANTIAGO DE CHILE - CHILE

### **PT06**

ENZYMATIC GRAFTING OF PINE BARK TANNINS, A STRATEGY FOR THE SURFACE MODIFICATION OF LIGNOCELLULOSIC MATERIALS  
DANIEL MARTÍNEZ  
GRUPO BIOSUV, DEPARTAMENTO DE INGENIERÍA QUÍMICA,  
UNIVERSIDAD DE VIGO - SPAIN

## **SUSTAINABILITY, ECONOMICS, MANAGEMENT AND MARKETING**

### **SE01**

EXERGOCHEMICAL ANALYSIS OF HEAT AND POWER PRODUCTION FROM MUNICIPAL SOLID WASTE GASIFICATION  
YANNAY CASAS LEDÓN  
UNIVERSIDAD DE CONCEPCIÓN - CHILE





**KEYNOTES**

## PLENARY SESSION

### WOOD-BASED-PANELS AND COMPOSITES – CHALLENGES AND PERSPECTIVES FOR THE FUTURE

Andreas Michanickl – University of Applied Sciences Rosenheim, Germany

#### **General - State of the art**

Wood based panels have been produced on an industrial scale since the end of the 19<sup>th</sup> century. Plywood is the first product that gained considerable importance as board material and as moulded parts long before polymers were invented. Fibre insulation boards and hardboards have been produced since the beginning of the 20<sup>th</sup> century. Particleboard followed in 1941. Waferboard started in 1955 followed by Oriented Strand Board (OSB). The industrial production of Medium Density Fibreboard (MDF) started in 1965. Since about 1980 we have seen modern Wood Plastic Composites (WPC) coming up in North America, later in Europe, Asia and other continents. In the last years we saw the first production of wood fibre mats and wood fibre boards for insulation and construction purposes with high thicknesses using a dry process with continuous steam injection technology. For a couple of years we have observed that Laminated Veneer Lumber (LVL) and I-beams from different types of material have become increasingly important in Europe, a long time after their development and production on large scale in North America. Also wood composite materials made from sawn timber are still showing considerable growth. In this context glue laminated timber, known since about 1860, and cross laminated timber, today also used for the construction of multistorey houses, have to be mentioned. These are only some examples. Besides this a wide range of wood composites and engineered wood products have been produced for many years for all types of applications. It can be stated that wood based panels and other wood composites are well established as green and sustainable products.

#### **Challenges of the wood based panel industry**

The classical existing wood based panels as Plywood, PB, MDF and OSB will be also needed and therefore produced in the next decades. But the challenges and the required R&D of this industry will be different to the past.

First of all the high level of development needs to be considered. After decades of intensive R&D the production of wood based panels takes place on a very high technological level. Without doubt further improvements are possible. But progress will be more difficult, more costly and less dramatically as in the past.

Over the last decades the production capacity of wood based panel mills steadily has been increased in order to decrease production costs and to increase competitiveness. Production technology has made considerable progress. Today there are particleboard mills with production capacities of about 1 million cubic meters per annum, MDF and OSB mills with capacities of up to 750.000 cubic meters per year. With regard to energy supply most of these mills are self-sufficient.

All this requires extremely large amounts of raw materials. Procurement and distribution logistics for such mills are some of the biggest challenges. Technically bigger capacities are possible. Nevertheless a lack of raw material already can be observed in various countries. Some big mills around the globe are out of production despite having the latest production technology due to a lack of raw material or too high prices for its procurement. The creation of even bigger production sites is unlikely considering the economical and of course environmental aspects.

The focus of development today and in the future will be not more increasing production capacities in order to decrease costs as it has been the last decades. Of course one focus will remain the further optimisation of production technology in order to decrease the consumption of resources. Another focus will be ensuring raw material supply. The collection and utilization of waste wood might get increasingly important where natural resources are limited.

But more than ever before all types of logistical aspects especially with regard to interactions with suppliers and customers will gain even more importance. To ensure this, modern ERP-Systems (Enterprise resource and planning systems) connecting all players along the value chain will become indispensable. These will enable the production and delivery of standard and even small and exceptional lots in very short times. For some factories this is already state of the art.



### **Challenges of the existing products**

Plywood, Particleboard, MDF, OSB and also WPCs have been produced for many decades. But with regard to a resource saving green economy they also have some disadvantages.

First of all it can be stated that they are only pre-products which are subject to various further processing steps, which need lots of electric energy and cause waste. In most cases they have to be packed and shipped to the place of further processing.

Furthermore the variety of forms is limited. Wood based composites mostly have panel or sheet form. Three-dimensional shapes are very limited and very expensive. Only small and medium production numbers are possible.

Another problem could be seen in their weight. Particleboard and MDF are heavy compared to natural wood. Their production requires a lot of limited raw material. The weight of particleboard has increased over the last two decades due to the increasing utilisation of waste wood. This has only a poor quality compared to fresh wood and does not allow the production of particles of the same quality as from fresh wood.



**Pictures 1 and 2:** Three-dimensional shapes from classical wood based composites are very limited and very expensive. Only small and medium production numbers are possible.

The utilisation of waste wood might be seen as advantageous with regard to raw material price but the more waste material is processed the more the weight of the final product is increasing and the more thermal and electrical energy, resin, machinery, maintenance and transport for procurement and distribution are needed. It also can be observed that the quality of waste wood is steadily decreasing along with the increasing demand and more and more material has to be sorted out, resulting in an increase of the before mentioned cost factors.

### **Challenges of the global society**

Despite the green and sustainable character of wood composites, research and development with regard to the existing and new materials made from wood is still necessary. The world's population is still growing. Consumerism is still growing. Wood is a renewable resource but its availability is limited. On the one hand modern forest tree breeding and forest management allow increasing the forest production but on the other side a decrease of arable land, an increasing demand of food and renewable raw materials can be observed. Wood also is increasingly used for the production of many other products and for the production of energy on industrial scale. Pellets are only one example.

## PLENARY SESSION

### WOOD-BASED-PANELS AND COMPOSITES - CHALLENGES AND PERSPECTIVES FOR THE FUTURE

#### Perspectives for R&D and new products

It can be stated that new wood composite materials have to fulfil new requirements. As already mentioned in the future the available resource wood has to be used in a more efficient way. We have to make more from the same amount of material to satisfy the increasing demand of a growing population and to enable the utilisation of wood in new applications. This means to increase the utilisation efficiency mainly by developing new production processes and new products.

Products do not only have to be green and sustainable. For their production, further processing, transport, utilisation and recycling as less renewable resources should be used as possible. Also this has to be considered. The whole life cycle should have the lowest ecological impact possible.

New production processes for the production of resource saving furniture also might be applicable for the production of other consumer goods and vice versa. The requirements for goods made from wood today are the same as for goods which are not yet made from wood or other renewable resources.

Today there are already three dimensional components made from natural fibres for the production of furniture and automobiles on the market. Also hybrid materials are already available. These are light and resource saving. Nevertheless they are still subject to further processing such as surface coating and mounting connection means.



Picture3: Furniture structure made from natural fibre and natural binder. (Picture: BASF)

Another disadvantage of these - compared to classical wood based panels already quite advanced materials - can be seen in the utilisation of natural fibres from flax or hemp. These fibres have good strength properties but they are very expensive and their availability is limited with regard to industrial processes. Due to the length of these fibres also processing is challenging. In this context fibres from wood might be more interesting. But with regard to such new production processes the production of wood fibres needs to be adapted to such applications.



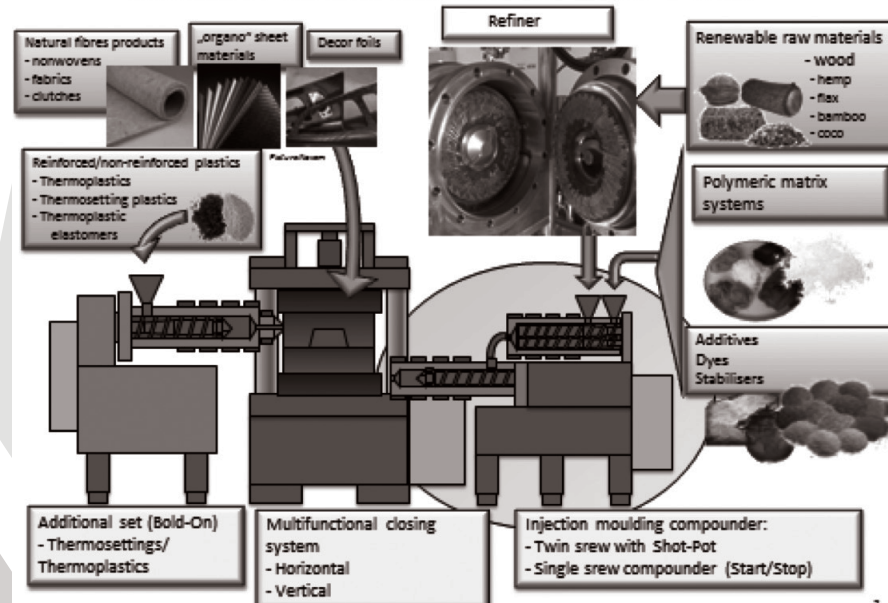
**Picture 4:** Three dimensional, structural very thin hybrid material mainly made from natural fibres with plastic reinforcement structure presented by Johnson Controls.

At the University of Applied Sciences in Rosenheim research is going to produce multifunctional, structural off-tool parts with final surface ready to assemble by using only one single process.

Picture 5 shows the scheme of a new pilot plant at the University of Applied Sciences in Rosenheim for the production of such multi-functional natural fibre based composites. The planning, design and production of this plant has taken place in the last two years. Now it is in the start-up phase and first trials are being done.

These include the utilisation of wood fibres and also non-wovens made from wood and other natural fibres. Of course also standard materials can be used. Parts produced with this technology can be used in a wide range of applications. The automobile and furniture industry are only two examples.

### Scheme of the MUNACU Trial Plant



**Picture 5:** Scheme of the "MUNACU" (Multi-functional natural fibre based composites) trial plant at the University of Applied Sciences Rosenheim.

## KEYNOTES

S1

### ELEMENTS OF WOOD-BASED MATERIAL RESEARCH FROM LAMINA TO NANO

Shigehiko SUZUKI, Dr.

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Demand for wood-based panels in Japan is steadily recovered after the Great East-Japan Earthquake, which occurred in 2011. The Act on Feed-in Tariffs for renewable energy enforced in 2012 targets solar, wind, hydro, geothermal, and biomass power generation. The power purchase price of woody biomass was classified into four stages: 40, 32, 24, and 13 J-Yen/kWh for unused wood, general wood, and construction waste wood, respectively. Shortages and increasing prices of wood chips may impact the panel industry, a problem raised at the time of the FIT introduction. In standardization activity, the Standard for CLT was established in JAS and “Structural MDF” was added to the JIS Fiberboard. By introducing some statistics of timber products and panel products, current situation is discussed first.

As the second topic, this paper discusses and introduces our research work focussing on the transition of element size from lamina in glue laminated timber (GLT) and nano for a future potential material. We have worked on technical issues of wood-based material as a main direction regarding to lamina, veneer, strand, particle, fiber, fines (wood powder) and nano materials. Some of which were already concluded and some are currently in progress.

Relating to “lamina”, the study is/was focused on durability performance of glued laminated timber (GLT) and cross laminated timber (CLT) as its use for structural application. Evaluating method for the durability of CLT is one of the most important issues for us. A plywood project for utilizing Japanese cedar (sugi) was conducted as a study on “veneer” element. *Eucalyptus grandis* veneer was chosen for the reinforcement of this plywood. A three-layer wood-based panel, called J-OSB, was introduced as a panel which can utilize recycled wood for core layer and strand from sugi for the surface layers. Another study on the utilization of bamboo for oriented strand-board (OSB) manufacture has also been conducted regarding to research works focusing on “strand” element. Many kinds of researches on “particle” were done relating to the production parameters. As one of the topics, temperature and vapour pressure behaviour during hot pressing are discussed. Durability performance of wood-based panel products is still a main topic in our research group. As a study on “fiber”, the effect of wood species and clearance of the defibrator disc on fiber properties and length distribution was examined.

We conducted research on the use of “fines (wood powder)” in wood plastic composite (WPC) production. Improvement of the compound was discussed as part of the utilization of low quality forest residue material. CNF research has attracted attention mostly in wood science. As a new research on nano-scale, we are focusing on potential of fibrillated surface and cellulose nano fiber (CNF) as a binder. It showed that the addition of those nano scale elements enhanced the mechanical properties of wood flour or fiber board. A wet-pulverizing with disk mill is also effective to form nano-scale morphology on the fiber surfaces for this purpose.





# Biocomp 2016

The 13<sup>th</sup> Pacific Rim Bio-Based Composites Symposium  
Bio-based composites for a sustainable future  
November 13<sup>th</sup> to 15<sup>th</sup>, 2016 - Concepción - Chile

## KEYNOTES

### S2

## INTERFACIAL ADHESION BEHAVIORS WITHIN NATURAL FIBER COMPOSITES: A VIEW AT FIBER LEVEL

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### Overview

The interactions between adhesives, resins and polymers with fibers at the adhesion interface is critical to the performance and durability of natural fiber composites. Moreover, using natural fibers or wood, high interfacial strain of this interface can occur during moisture-induced swelling of these substrates which can lead to adhesive bond failure and poor performance [1]. Bondline infiltration and fiber cell wall penetration are examples of macroscale behaviours of polymeric resin or plastic components which contribute to adhesive bond formation and reinforcement of fiber-adhesive interfaces (Figure 1). Fundamental insights of wood composite processing have resulted from the application of various microscopy techniques to visualize interfaces between resin and wood fiber [2]. Qualitative and quantitative information characterizing wood fiber-adhesive interactions during panelboard manufacture has determined how adhesives and resins become distributed on fiber during application and contribute to bonding on panel consolidation. Furthermore, differences can arise between adhesive types, use of renewables and be influenced by temperature and moisture content when processing composite products. Adhesive or resin migration into fiber cell walls can also modify the properties of cell walls. Visualisation of interfacial behaviors within natural fiber plastic composites and laminates has revealed resin or polymer cell wall infiltration and interactions variously impact moisture-induced cell wall property changes at molecular- and macro-scale. This paper will provide some perspectives on visualizing fiber-adhesive interactions in different wood and natural fiber composite products and how observations have been used to understand interfacial behaviours between synthetic and biopolymers and natural fibers and may be applied to improve composite processing.

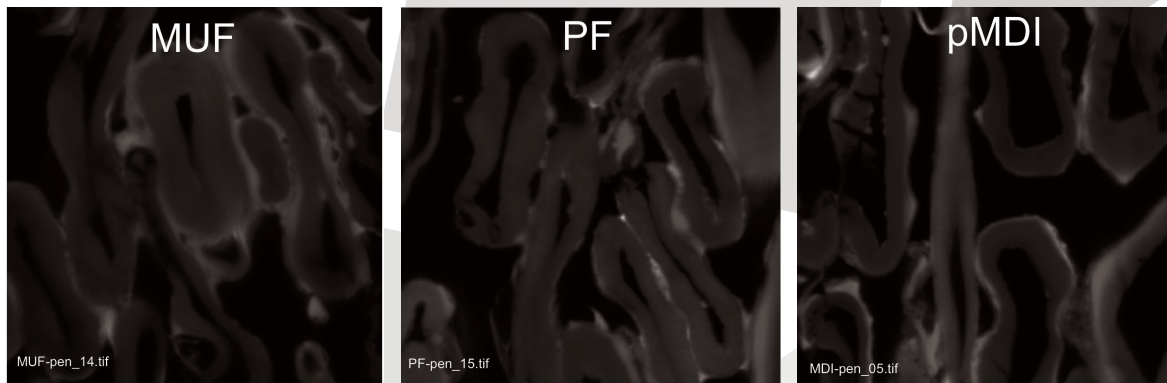


Figure 1. Examples of fiber-adhesive interfaces within cross-sections of MDF panel sections prepared with various resins (MUF, left; PF, centre; and pMDI, right). Where the adhesive is green and wood fiber is red.

### A view at the fiber level

The influence of adhesive type on fiber-adhesive interactions has been evaluated in medium density fiberboard (MDF) manufacture using mechanically blending [2,3]. The extent of resin movement into the wood cell was found to be a function of temperature and fiber moisture content at pressing. Both higher moisture content and temperature led to greater urea formaldehyde (UF) resin penetration of the fiber wall [3]. In contrast, isocyanate- (pMDI) and phenolic-based (PF) resins exhibit relatively lower rates of resin penetration when similarly pressed at high mat moisture contents (Figures 1,2). Melamine urea formaldehyde (MUF) resin had an intermediate level of resin penetration. Using these findings, the impact of a high free urea content in UF resin,



typical of current EO systems, was evaluated through using differing UF resin syntheses [3]. Typical E1 and E0 UF resin formulations having high final urea contents were found to have relatively greater resin penetration behaviour than using UF resin without a final urea charge. The results of this work offer opportunities for resin design as well as how resin chemistry and plasticization of wood components within the fiber cell wall may impact fiber-adhesive interfaces. Furthermore, study outcomes may contribute to the understanding the inherent differences between UF and MDI resin performance and usage in MDF manufacture where the latter is typically associated with lower panel resin loading for a given performance compared to UF resin.

Through synchrotron-based X-ray fluorescence microscopy (XFM), Br-labelled phenol-formaldehyde (BrPF) penetration into wood cell walls has been mapped and quantified (Figure 3) for plywood bondlines [4]. Five BrPF adhesives with differing average molecular weights (MWs) were evaluated with resin mobility from the bondline and cell wall infiltration found to reduce with greater molecular weight. Nanoindentation of cell walls was performed at 0% and 78% RH to assess the effects of BrPF infiltration on cell wall hygromechanical properties. Results revealed, for the same resin weight uptake, lower MW BrPF adhesives were found to be more effective at decreasing moisture-induced mechanical softening of the wood cell wall. This greater effectiveness of lower MW phenolic adhesives likely resulted from their ability to decrease moisture sorption sites and mechanically restraining wood polymers during swelling.

Natural fiber reinforced resin and plastic composites can have applications in exterior environments where moisture sensitivity of the fiber component can lead to loss in composite performance. Through microscopy, a method was developed to observe the interfacial behaviours between the plastic matrix and fiber, quantify the extent of fiber and composite swell, and relate this to macroscale performance [5]. A poly(lactic acid)/wood fiber

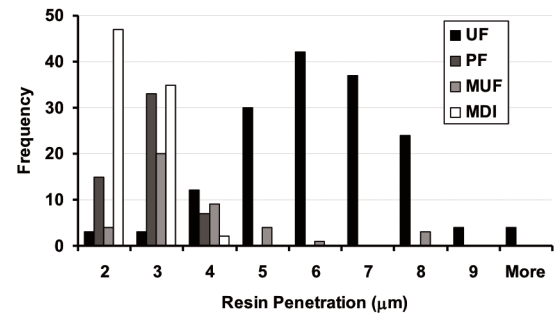


Figure 2. Frequency distribution of individual measurements of resin penetration of MDF fiber wood cell walls for UF, MUF, MDI and PF resins. Panel pressing undertaken at >18% mc.

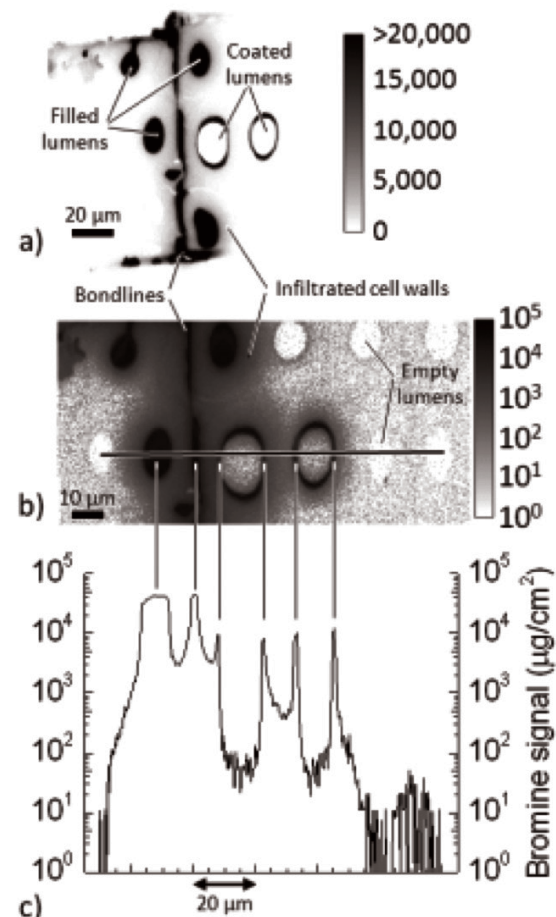


Figure 3. An XFM image of Br signal intensity of a Br-labeled PF adhesive-wood bondline revealing the extent of resin migration from the bondline and infiltration of wood cell walls. Viewed using a) linear scale and b) logarithmic scale. In c) the profile across the bondline and multiple cells is displayed. All units are in µg/cm<sup>2</sup>

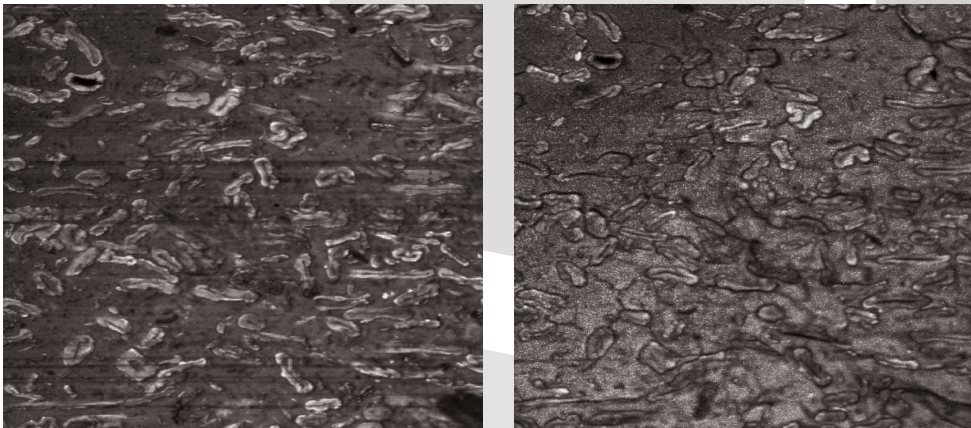
## KEYNOTES

### S2

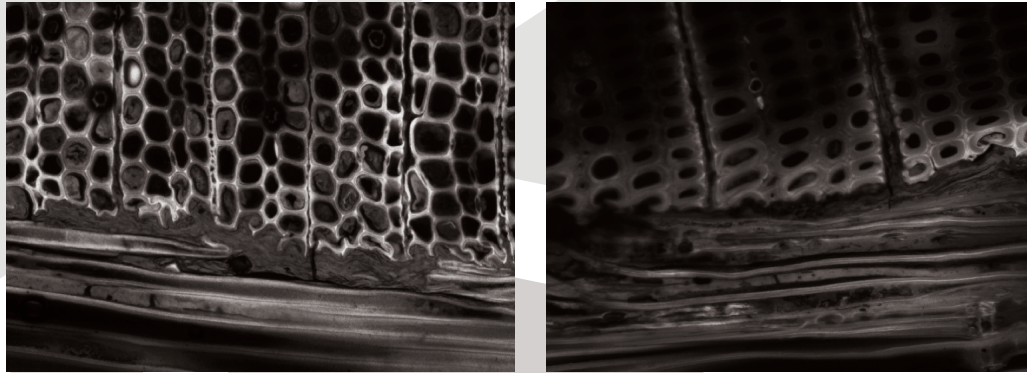
#### INTERFACIAL ADHESION BEHAVIORS WITHIN NATURAL FIBER COMPOSITES: A VIEW AT FIBER LEVEL

composite was subjected to 100 day wet-dry cycling and microscopy images periodically acquired across the composite cross-section (**Figure 4**). Analysis revealed fiber swell was the main driver for composite dimensional swell and the propagation of cracks within the composite. Collapsed fibers were found to swell an average 9% resulting in composite swell in the dimension of the general alignment of this fiber collapse. It was also determined water uptake and drying led to irreversible, differential swell between the matrix and fiber and the creation of voids. Composite swelling also led to a fractured polymer matrix with cracks generally propagating from fibers.

With increasing interest in the commercial utilisation of renewables to partially- or fully-substitute petrochemical components in adhesive, resin and plastic formulations it is necessary to know the fiber-adhesive interphase characteristics of such materials. Potential adhesive components such as starch, protein, tannin and lignin have been visualised on wood fibers [6]. A range of interfacial behaviors were observed across these bio-components which had varied mobility on the fiber surface and ingress into the fiber cell wall. As with synthetic systems, an implication of these observations is that these bio-components may similarly impart such behaviors when incorporated in adhesives and resins. Given its ready availability and with much work already undertaken integrating lignin into phenolic resins, we have been investigating the inclusion of lignin to design totally biobased adhesive systems [7]. Through visualizing fiber-adhesive interphase characteristics of this polyphenolic, the inherent attributes of lignin have been further developed into the bio-based adhesive system Ligate™ for use in engineered wood products and paperboard packaging [8]. The Ligate™ technology which does not use formaldehyde or any petrochemicals in its manufacture has comparable interfacial behaviours as synthetic adhesives (**Figure 5**) and been evaluated in an initial mill-scale plywood trial.



**Figure 4.** Confocal microscopy images of a PLA/MDF fiber WPC composite. The original WPC specimen dry (left) and after 100 days of soaking followed by 8 weeks of drying (right).



**Figure 5.** Fluorescence microscopy images of plywood bondlines with the Ligate resin without filler (left) or with an optimal filler content (right). Where the adhesive is red and wood fiber is green.

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## KEYNOTES

### S3

## TRADITIONAL AND INNOVATIVE WOOD-BASED BIOPRODUCTS

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### Abstract

This presentation will deliver description of traditional and innovative wood based products and their crucial role in the global carbon cycle and the fight against climate change. Special emphasize will be given to the need for efficient resource use of wood resources, including reuse and upgrading of waste wood. The environmentally preferred option to maintain wood materials in a maximum quality level by reuse in solid form, therefore extending the carbon storage duration, will be presented.

The presentation will be delivering key findings of the recently published monography "Environmental Impacts of Traditional and Innovative Forest-based Bioproducts" [1].

### Introduction

Many policy strategies and actions directly impact the forest product industry. For example, Europe is setting course for a resource-efficient and sustainable economy. The goal is a more innovative and low-emissions economy, reconciling demands for sustainable agriculture and fisheries, food security, and the sustainable use of renewable biological resources for industrial purposes, while ensuring biodiversity and environmental protection. The term being use to address this is bioeconomy. The bioeconomy comprises those parts of the economy that use renewable biological resources from land and sea – such as crops, forests, fish, animals and micro-organisms – to produce food, materials and energy. It is an essential alternative to the dangers and limitations of our current fossil-based economy and can be considered as the next wave in our economic development. The need for efficient and effective use of renewable resources is directing development of new technologies and processes as well as developing of new markets for renewable based materials and products.

### Climate change and forest products industry

Forests play a crucial role in the global carbon cycle and the fight against climate change. Forest biomass is currently the most important source of renewable energy. The demand for wood, and for wood fuel in the context of increasing renewable energy demand, is a strong stimulus for increasing forest growth and productivity and for improving management practices more wood and residues could be harvested and mobilised while demand for forest products is growing for material and energy uses as a way to reduce carbon emissions by substituting products that cause higher emissions. Wood products can contribute to climate change mitigation as they act as a carbon pool during their service lives, as they withdraw CO<sub>2</sub> from its natural cycle, as wood products can substitute for more energy-intense products after their service life, as they can substitute for fossil fuels if they are incinerated. Since increased harvest reduces carbon sinks, there is the need for speeding up production rates and developing forest raw materials with new properties. Forests of the future will be increasingly dedicated to producing fibres, timber, energy or customised needs, which will have considerable impacts on the provisioning of a broad range of public goods.

### Wood products

Besides the solid wood products the new industrial processes that extend the size and modify the properties of natural wood, and the need to use manufacturing residues and lower grade trees to produce more versatile and more consistent products have resulted in numerous materials known as engineered wood products [2]. Sandberg [2] delivered an overview of engineered wood products and discuss the additives used to form them. Furthermore, the forest products ranges from established forest products (building materials, paper and wood energy), potential large



volume bioproducts (liquid biofuels), high value added products (biomaterials, and new chemicals, pharmaceuticals). It is illustrated that key challenges differ between 'old' bioproducts, such as wood where progress is connected with design development and incremental improvement of industrial processes - and 'radical' innovations of new materials and substances, which involves new market development [3].

### Reuse and upgrading of waste wood

Efficient resource use is the core concept of cascading (Figure 1), which is a sequential use of a certain resource for different purposes [4]. This means that the same unit of a resource is used for multiple high-grade material applications (and therefore sequestering carbon for a greater duration) followed by a final use for energy generation and returning the stored carbon to the atmosphere. Intelligent concepts for reuse and recycling of valuable materials at the end of single product life will reduce the amount of waste to be landfilled. According to some recent projects there is great potential to expand wood recovery for uses beyond energy and particleboard production. Many solutions have been proposed to simplify and automate contaminant detection and then sorting and cleaning of the contaminated materials.



Figure 1: Concept of cascade use of wood.

### Conclusion

The forest products can be use for a larger number of application. The demand for more environmentally sustainable products and energy is making the wood resources an important part of the bioeconomy. The demand for renewable-sourced materials will drive innovation in the forest-based sector, which will support more jobs and strengthen the economy. The forest-based sector offers many opportunities for new products, processes and systems that only well supported and executed research can identify and create value from.

### Acknowledgements

The author is pleased to acknowledge the support of the COST Action FP1407 and WoodWisdom-Net+ and the Slovenian Ministry of Education, Science, and Sport of the Republic of Slovenia for their support of the What We Wood Believe and Cascading Recovered Wood projects; European Commission for funding the project InnoRenew CoE under the Horizon2020 Widespread-2015 program, and infrastructure program IP-0035.

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## KEYNOTES

S4

### POLYCARBOXYLATED FLAVONOID OLIGOMERS AS FUNCTIONAL ADDITIVES FOR POLYLACTIC ACID-, POLYSTYRENE-, AND POLYETHYLENE-BASED COMPOSITES

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#### ABSTRACT

Poly(lactic acid (PLA)-, polystyrene (PS)-, and polyethylene (PE)-based blends were prepared with *Pinus radiata* modified/unmodified bark polyflavonoids. Esterification with maleic anhydride (20 °C, 24h) of such polyphenol was performed in order to diversify functionalities in view of envisaged applications. Rheological, morphological, thermal, and mechanical properties of the blends were studied. Polyphenols affect the processability parameters in a high extent. Polymer-matrix type affects dramatically the granule morphology, and the dimensional features of the polyflavonoid particles. On the other hand, polyphenol-composition affects the blends thermal behavior significantly. The decreasing of decomposition temperature ( $T_d$ ) in function of the polyphenol-content was remarkable on PLA-based blends. The mechanical properties were significantly affected by the polyflavonoids-content. Polyphenols increased the elasticity modulus (E) in PS-, and PLA-based blends as described in previous works. However, polyflavonoids degrade the E-values on PE-based blends in a high extent. Bark modified polyflavonoids from radiata pine might be used successfully for the designing of functional thermoplastic composites.

#### Introduction

Polyphenols are secondary metabolites of great relevance in nature. Among other members of the polyphenols group, polyflavonoids and lignin are highly abundant in vascular plants [1]. The utilization of polyphenols in materials engineering has been limited by physicochemical properties (e.g. low miscibility in thermoplastics, limited solubility in organic solvents, and lack of functional groups prone co-polymerization).

In view of tailoring properties, as well as for improving miscibility with thermoplastics chemical modification of certain polyphenols has been reported. In fact, esterification of polyflavonoids with five-member cyclic anhydrides provides several advantages for material design: (1) non side-chain products are obtained during the derivatization reaction, (2) cyclic anhydrides are more reactive than linear-chain counterparts which enable derivatization reactions at room temperature, (3) unsaturated carboxylic chain from the polyphenol derivatives is a desirable functionality for several kinds of polymerization pathways (e.g. radical, ionic, and coordination), (4)  $\alpha$ - $\beta$  unsaturated polycarboxylic acid derivatives are considered biologically active compounds against a wide range of bacteria and fungi, and (5) the unsaturated polycarboxylic moieties might improve the miscibility between polyphenols and selected thermoplastics.

This work reports the preparation and characterization of several blends based on commercial thermoplastics (PLA, PS, and PE), and polyflavonoids. Rheological, morphological, molecular, thermal, and mechanical analyses were performed. The effect of the chemical modification of polyphenols (esterification with maleic anhydride) was evaluated. The new thermoplastic-based materials are expected to play an important role beyond the traditional PLA-, PS-, and PE-uses.

#### Experimental

##### Materials

*Poly-lactic acid (PLA)*: partially crystalline PLA (Polylactic acid) Ingeo™ Biopolymer 3251 grade supplied by NatureWorks® Co. LLC, USA.

*Polystyrene (PS)*. Styron 484 supplied by Dow™ Chemical Co., Europe GmbH (Switzerland).

*Polyethylene (LDPE)*. Low density polyethylene supplied by HANWHA (South Korea).





*Polyflavonoids (T).* Non-water soluble radiata pine bark polyflavonoids (PRI) pilot-plant feedstock extracted with methanol/water solution (1:20, w/v) at 120 °C was used [1].

### Methods

*Modified polyphenols with maleic anhydride.* Esterification of polyphenols with maleic anhydride was described elsewhere [3].

*Blends formulation.* Blends based on PE, PLA, and PS were prepared at 110, 170, and 240 °C, respectively. The time of mixing ( $t_{mix}$ ) in the rheometer was 15 minutes.

Table 1. Composition of thermoplastic-based blends prepared on the rheometer.

Blend-type	Composition (wt. %)			Blend-code
	TP	T	TM	
TP-T	99.0	1.0	-	(PLA <sub>99</sub> /TI <sub>1</sub> ) (PS <sub>99</sub> /TI <sub>1</sub> ) (PE <sub>99</sub> /TI <sub>1</sub> )
	97.5	2.5	-	(PLA <sub>98</sub> /TI <sub>2</sub> ) (PS <sub>98</sub> /TI <sub>2</sub> ) (PE <sub>98</sub> /TI <sub>2</sub> )
	95.0	5.0	-	(PLA <sub>95</sub> /TI <sub>5</sub> ) (PS <sub>95</sub> /TI <sub>5</sub> ) (PE <sub>95</sub> /TI <sub>5</sub> )
TP-TM	99.0	-	1.0	(PLA <sub>99</sub> /TM <sub>1</sub> ) (PS <sub>99</sub> /TM <sub>1</sub> ) (PE <sub>99</sub> /TM <sub>1</sub> )
	97.5	-	2.5	(PLA <sub>98</sub> /TM <sub>2</sub> ) (PS <sub>98</sub> /TM <sub>2</sub> ) (PE <sub>98</sub> /TM <sub>2</sub> )
	95.0	-	5.0	(PLA <sub>95</sub> /TM <sub>5</sub> ) (PS <sub>95</sub> /TM <sub>5</sub> ) (PE <sub>95</sub> /TM <sub>5</sub> )

TP: thermoplastic (PLA: poly-lactic acid, PS: polystyrene, PE: polyethylene), T: unmodified radiata pine polyflavonoid (tannin), TM: modified radiata pine polyflavonoid (degree of substitution: 3).

*Preparation of the blends.* In a specific order components were added in a rheometer. PLA and polyflavonoids were mixed for 2 min in a mixer and loaded into the chamber (time mixing,  $t_{mix}$ : 0).

*Cold-blend processing.* Blends were ground in an electric mill (IKA, Basic MF10) and 30 g compression molded on a LabTech LP20-B press (T: 175 °C, t: 5 min, p: 32 bar).

*Rheology (torque rheometer).* Measurements were carried out in a torque rheometer (Brabender 50 EHT, Germany) with roller blades. The rotor speed was 50 rpm, and the free volume of the chamber was 20% of the total volume.

*Particle size distribution.* Morphology of the blends was assessed by confocal fluorescence microscopy as previously described [3].

*Thermal stability (TGA).* Thermogravimetric analysis was performed on a NETZSCH TGA instrument (TG 209 F3 Tarsus, Germany).

*Mechanical testing.* Selected laminate samples were cut with a die (gage length 60 mm, width 1.5 ±0.2mm) and kept in a chamber oven overnight, and the Young's modulus (E) were determined. Universal tensile testing machine (SmarTens 005, KARG Industrietechnik, Germany).

### Results and Discussion

*Rheology (processability features).* Modified (TM), and unmodified polyflavonoids (T) reduced the torque values during the mixing regardless the thermoplastic-type (Table 2). The dramatic influence of polyflavonoids on rheological behavior is expected considering that such oligomers are highly polar compounds in comparison to the studied thermoplastic polymers (PE, PS, PLA). It is worth to notice that chemical modification decreased significantly the torque value regardless the polyphenol-, and the polymer-type. The result can be interpreted based on the fact that esterification with maleic anhydrides yields highly polar unsaturated carboxylic acid moieties hindering chain-chain interaction between the polyphenol derivatives, and the polymers.

## POLYCARBOXYLATED FLAVONOID OLIGOMERS AS FUNCTIONAL ADDITIVES FOR POLYLACTIC ACID-, POLYSTYRENE-, AND POLYETHYLENE-BASED COMPOSITES

Table 2. Maximal torque-value associated to the thermoplastic-melting for polyphenol-based blends (tmix: 15 min).

Loading (wt. %)	Polyphenol	
	T	TM
PE (100)	45 ±7	
1.0	45 ±3	40 ±5
2.5	42 ±4	36 ±3
5.0	21 ±5	12 ±2
PS (100)	100 ±11	
1.0	36 ± 4	34 ±4
2.5	31 ±9	38 ±2
5.0	20 ±6	31 ±4
PLA (100)	40 ±6	
1.0	37 ±5	33 ±6
2.5	34 ±6	32 ±4
5.0	30 ±3	29 ±2

T: polyflavonoid (tannin), TM: modified polyflavonoid. N= 3  
PLA: poly-lactic acid, PS: polystyrene, PE: polyethylene

The differences in torque-values can be also explained considering that the viscoelastic properties of polyflavonoids dramatically change during the esterification with anhydrides [3].

Polyphenol-type affects dramatically the rheological behavior mainly in PS-based blends. Apparently a drastic reduction of the viscosity in function of the polyflavonoid-loading is suggested.

### Particle size distribution.

Confocal fluorescence microscopy enabling polyphenols quantification in a wide range of experimental conditions. In fact, morphological and structural pattern of polyphenolic macromolecules might be assessed this way. The technique acquires special relevance for polyphenol-based materials due that the morphological characterization of phenolic particles distributed on the plastic-matrix is hardly assessed [3].

Considering that polyflavonoid-based blends are colored composites, the evaluation of fluorescence emission pattern was performed based on the fact that PE, PS, and PLA

are not active-fluorescent polymers. Such advantageous features was taken in advance in order to study the morphology of polyflavonoid-particles dispersed on thermoplastics.

Maximal intensity projection of selected blends is shown (Figure 1).

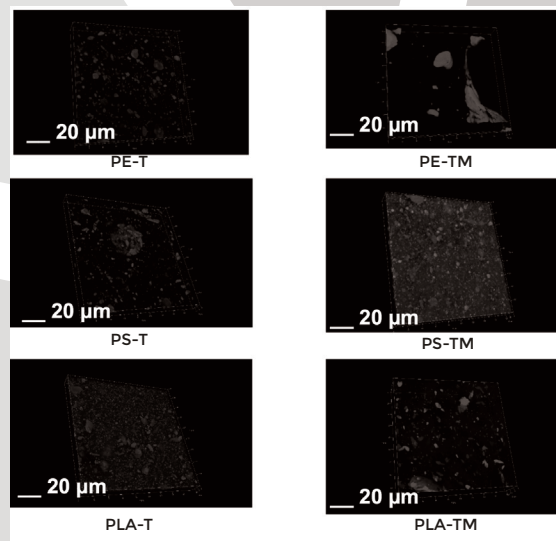


Figure 1. Maximum intensity projection of selected thermoplastic-based blends (tmix: 15 min). Note: imagen of the corresponding TP98/P2 blend is shown. T: polyflavonoid (tannin), TM: modified polyflavonoid, PE: polyethylene, PS: polystyrene, PLA: polylactic acid

It is worth to notice that a wide range of particle shapes were observed in function of the polyphenol-, and the thermoplastic-type. Modified polyflavonoid particles show a certain agglomeration on the PE-matrix. The results can be explained considering the dramatic differences on polarity between polyphenols and PE. However, polyphenols dissolved on PS-, and PLA-polymers show an apparent good dispersion features regardless the polyphenols-type.

The result suggests that a longer period of mixing (tmix: >15 min) might be required in order to establish better dispersion of polyflavonoids particles on the PE-matrix.

**Thermal stability.** TGA analysis (DTG) reveals a significant effect of the polyphenol-, and thermoplastic-type on the thermal behavior (Figure 2).



Decomposition temperature (Td) oscillated between 340 and 500 °C, and was strongly associated to the thermoplastic-type. Blends prepared with PE show the highest thermal stability between 450-500 °C. Regardless the polyphenols-type, and blend-composition PLA-derived blends show the lowest thermal resistance.

The low thermal resistance of modified polyphenols-based blends is also expected. The  $\alpha$ - $\beta$  unsaturated carboxylic moiety in derivatives enable early thermal decomposition as consequence of decarboxylation (Td: 170-180 °C), as well as the ester-cleavage at low temperatures [3].

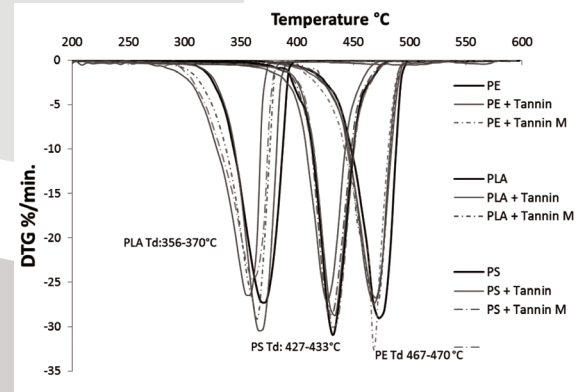


Figure 2. DTC (first derivate from the TGA-trace) of selected blends. N=3 T: polyflavonoid (tannin), TM: modified polyflavonoid, PE: polyethylene, PS: polystyrene, PLA: polylactic acid.

In general, the results establish that chemical modification of polyphenol remarkably affects the thermal resistance of high polarity blends, regardless the miscibility trends.

**Mechanical testing.** Effect of the polyphenol-type on the elasticity modulus was investigated. E-values of thermoplastic-based blends seems to be highly dependent of composition (Table 3). An increased amount of polyphenols additives affect the elasticity modulus in a different manner for every kind of thermoplastic. T-, and TM degrades the E-modulus in a high extent, excepting for PLA-based blend.

Table 3. Elasticity modulus (E) of thermoplastic-based blends prepared with polyphenols ( $t_{mix}$ : 15 min).

Loading (wt. %)	Polyphenol					
	T		TM		T	
	(PE) 230 ±56		(PS) 1850 ±176		2750 ±337	
1.0	231 ±39	1605 ± 234	1605 ± 234	1550 ±178	2200 ±286	2650 ±198
2.5	220 ±32	1650 ±219	1650 ±219	1380 ±211	2350 ±298	2870 ±217
5.0	200 ±18	1690 ±197	1690 ±197	1710 ±163	2400 ±271	2790 ±218

T: polyflavonoid (tannin), TM: modified polyflavonoid, PE: polyethylene, PS: polystyrene, PLA: polylactic acid.

From the practical point of view modified-, and unmodified-polyflavonoid building-blocks (loading: 1-5 wt.%) are highly recommended for the designing of PLA-, and PS-based composites.

Polyflavonoids, show poor performance as functional additives in term of flexural features on PE-based blends. The behavior can be explained considering the high content of polar functional groups on such building-blocks [2,3]. In addition, the results point out that TM seems to be highly desirable additives for PLA-based materials design. The suggestion is done because esterified derivatives exhibit apparently better miscibility on the COOH-containing polymer (PLA).

## KEYNOTES

S4

### POLYCARBOXYLATED FLAVONOID OLIGOMERS AS FUNCTIONAL ADDITIVES FOR POLYLACTIC ACID-, POLYSTYRENE-, AND POLYETHYLENE-BASED COMPOSITES

#### Conclusions

Polyethylene-, polystyrene-, and poly(lactic) acid-based blends were successfully prepared with *P. radiata* polyflavonoids building-blocks (1-5 wt.%).

Modification of radiata pine polyphenols is a viable strategy in order to improve the performance on polystyrene-, and poly(lactic) acid based-blends as consequence of a better processability features. However, polyflavonoid derivatives strongly affected the PE-based composites performance.

Chemical structure of the polyphenol's grafting influences: (1) the processability during the melt-blending, (2) the miscibility of the components, (3) the thermal resistance, and (4) the flexural performance.

The image-processing data based on confocal fluorescence microscopy was successfully utilized in order to estimate the polyphenol particles morphology, and in consequence enabling miscibility predictions between polyphenolic additives, and thermoplastics. The processability parameter in term of torque-value and time of mixing seems to be affected by the functional group composition at the molten state. The modified polyphenols showed higher compatibility features as consequence of a dramatic reduction of particle volume on PS-, and PLA-based blends. Despite that polyphenolic additives affected the decomposition temperature ( $\Delta T_d$ :  $<15^\circ\text{C}$ ) regardless the polyphenol-content, polyflavonoids can be used as functional additives for selected applications. Modified polyphenols via esterification with maleic anhydride might be preferably used on PS-, and PLA-based blends. The interaction between target functional groups from the additives, and the thermoplastic-matrix dictates the behavior of the blends.

#### Acknowledgments

D.E. García like to thank Comisión Nacional de Investigación Científica y Tecnológica (CONICYT, Chile, Project FONDECYT 11150056), and Basal Project (PFB-27) for the financial support. The authors would like to acknowledge to Mrs. Corina Silva, and Mrs. Carmen Pradenas for their technical assistance. In addition, authors also like to thanks to Germán Osorio, and Joanna Tereszczuk (Center for Advanced Microscopy, CMA Bio-Bio), from Concepción University for the technical assistance regarding confocal microscopy and image-processing, respectively.

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# Biocomp 2016

The 13<sup>th</sup> Pacific Rim Bio-Based Composites Symposium  
Bio-based composites for a sustainable future  
November 13<sup>th</sup> to 15<sup>th</sup>, 2016 - Concepción - Chile

## KEYNOTES

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### AN OVERVIEW OF MATERIALS R&D ACTIVITIES IN ALBERTA'S BIORESOURCE SECTOR

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#### Abstract

Over the past decade, there has been an increasing interest in utilization of bio-based feedstocks for "green" materials, chemicals and alternative energy. This has been driven primarily by a growing focus on sustainable practices and reduced environmental impact by public, government and industry stakeholders. The province of Alberta offers significant potential to be a leader in the bio-based economy due to its existing energy/petrochemical infrastructure, and strong agriculture and forestry sectors. This presentation provides an update of various research efforts taking place in the province, and highlights major initiatives in bio-based materials.

In the first part of the presentation, an overview is provided of Alberta's resource landscape from both a forestry and agriculture perspective, and its potential in advancing the bio-based economy. A brief summary of current R&D activities from a variety of research teams in the province is provided including the development and application of nano-crystalline cellulose (NCC), thermosetting bio-composites and engineered wood panels, lignin utilization, and novel bio-polymers. In the second part of the presentation, a number of studies by the author and co-workers on the properties of bio-fibre based thermoplastic composites are highlighted. These studies focus on the mechanical behaviour and durability of various thermoplastic polymers (including polyethylene, polylactic acid and starch blends) reinforced with a variety of bio-based fibres derived from both forest and agricultural feedstocks (including wood pulp, industrial hemp and other locally grown natural fibre options) [1-4].

In general, fiber type and fiber fraction were both shown to affect the mechanical properties and durability of thermoplastic composites exposed to various environments including water immersion, soil burial and UV exposure [1,2]. In terms of monotonic properties, increasing fiber content typically resulted in composites with increased elastic modulus but reduced elongation and impact strength. Tensile strength was shown to vary depending on fiber type and fraction. Similarly for moisture absorption tests, increasing fiber fraction resulted in an overall increase in total water uptake of the samples, regardless of fiber type. The majority of the natural fiber composites took at least 12 months to reach equilibrium moisture content (saturation). Degree of mechanical degradation was seen to depend on a number of factors including fibre type, polymer type and exposure environment (water immersion, soil burial and UV exposure). Generally, there was a noticeable decrease in mechanical properties over time with environmental exposure for all natural fibre composites studied. Of the fiber types tested, composites made from chemically pulped wood had both the best short-term mechanical properties and long-term durability compared to other natural fiber types tested. Based on microstructural examination, this increased performance was attributed to the wood pulp's finer fiber structure and uniformity which allows for better dispersion, and less moisture or biological attack.

Another area of study focussed on the behaviour of bio-fibre composites under fatigue loading. Fatigue is an important consideration in many design applications where cyclic or reversed loading occurs (e.g. automotive, consumer goods, etc.). For natural fiber composites, there has been a great deal of work on static (monotonic) mechanical properties, but very limited studies related to fatigue. In the author's work [3], the fatigue properties of hemp reinforced high density polyethylene (HDPE) composites were investigated experimentally, and a new model was developed to predict the fatigue-life response of these materials. Overall, the addition of hemp



fibers slightly improved the fatigue strength of the polymer matrix, however, adding hemp fibers did not change the sensitivity (slope) of the developed fatigue life curves. The observed fatigue failures varied from a ductile-brittle mode for the unreinforced HDPE, to a brittle type of failure for the reinforced composites. The fatigue strength after water absorption was also found to be lower than the fatigue strength of both the unreinforced matrix polymer and the dry hemp-HDPE composites. This was attributed to the hydrophilic nature of the natural fibers which resulted in a reduction of fiber and interfacial strength in the composite.

Finally, the effect of different pulping methods (mechanical and chemical pulping) on the properties of pulped fibre thermoplastics was assessed for a variety of fibre feedstocks (both wood and non-wood) [4]. Overall, the addition of pulped fibre to high density polyethylene (HDPE) improved both the tensile strength and modulus (stiffness) of the polymer. When “specific” mechanical properties were considered (which accounts for the density of the material options), pulped hardwood and flax composites appeared to be viable alternatives to E-glass composites. This is due to the fact that the density of natural fibres is approximately 40-50% less than glass. As a result, natural fibres are excellent candidates for replacing glass-fibre in applications where lightweight is required (e.g. transportation). In addition to the technical evaluation, a preliminary economic evaluation was performed to assess the cost-performance of each fibre and pulping method. Overall, thermo-mechanically pulped (TMP) hardwood had the best composite performance per cost (in terms of specific strength and specific modulus) relative to all other material options tested including glass-fibre composites (the existing industry standard). In addition to its cost-performance, hardwood pulp is also readily available at commercial scale which is a significant advantage over agricultural based fibre feedstocks. This analysis provides manufacturers with preliminary data to select natural fibre composites that will maximize part performance at the lowest cost.

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## KEYNOTES

S7

### ECO-FRIENDLY METHODOLOGY FOR THE SYNTHESIS OF GRAPHENE-BASED CATALYTIC MEMBRANE REACTORS

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#### INTRODUCTION

Carbon-based structures characterized by a polygonal cell distribution are commonly named random networks [1,2]. On the other hand, well defined, molecular and therefore nanometric networks such as fullerenes [3], nanotubes [4] and graphene [5] have been some of the most remarkable discoveries in the area of carbon research in recent years. Another ill-defined type of randomly carbon network is that corresponding to the microporous structure of activated carbons (AC). So, three carbonaceous network structures can be considered according to the dimension: the molecular (fullerenes, nanotubes, graphene), the micro (microporous carbon), and the macro (macroporous carbon). Although in the case of carbon materials, synthetic routes for both molecular-networks and micro-networks have been extensively investigated [3,6], few studies exist regarding the synthesis and characterization of random networks of carbon [7-11]. This work presents the synthesis and characterization of 2D and 3D polygonal random networks of carbon (RNC) from the controlled pyrolysis of saccharose in absence or presence of KOH.

#### METHODOLOGY

The synthesis, the topological definition, the activation and characterization of RNC have been reported in previous works [7-10]. In a typical synthesis 2 g of D(+)-saccharose was placed inside a 50 mL Pyrex beaker and dissolved in 1 mL of water or in 1 mL of aqueous solution (34 wt%) KOH and stirred at 80°C until a viscous and light brown solution was observed. The solution is left in rest until achieving the recrystallization of the saccharide. Then, the sample was submitted to two consecutive heat treatments. First, at low temperature inside a vacuum oven at 130°C, for 10 min. The second one in a ceramic muffle under N<sub>2</sub> flow at 450°C. The carbonaceous macro-networks were denoted as A<sub>NW-1</sub> and A<sub>NW-2</sub>, for the saccharose dissolved in water or in KOH solution, respectively. Different temperatures and times under N<sub>2</sub> or CO<sub>2</sub> flow were used for the activation of porous framework [9]. Characterization of A<sub>NW-1</sub> and A<sub>NW-2</sub> was performed by N<sub>2</sub> adsorption-desorption isotherms, XRD, XPS, RAMAN, FTIR, EPR, SQUID, NEXAFS and XANES.

#### RESULTS AND DISCUSSION

Fig. 1 shows the optical images of the bi-dimensional (2D) macroscopic RNC obtained in presence of KOH (A<sub>NW-2</sub>). The topological properties of the 2D-RNC are significantly different from other 2D cell structures [7,8]. The polygonal distributions of the macro-networks from the A<sub>NW-1</sub> (Saccharose + H<sub>2</sub>O) and A<sub>NW-2</sub> (Saccharose + KOH) showed the pentagon was found to be the most abundant polygon in the 2D RNW. In previous works [8,9] we showed the activation of the present RNC can be easily achieved by physical activation under CO<sub>2</sub> flow or by pyrolysis under N<sub>2</sub> flow, with BET surface areas up to 850 and 981 m<sup>2</sup>.g<sup>-1</sup> [9].



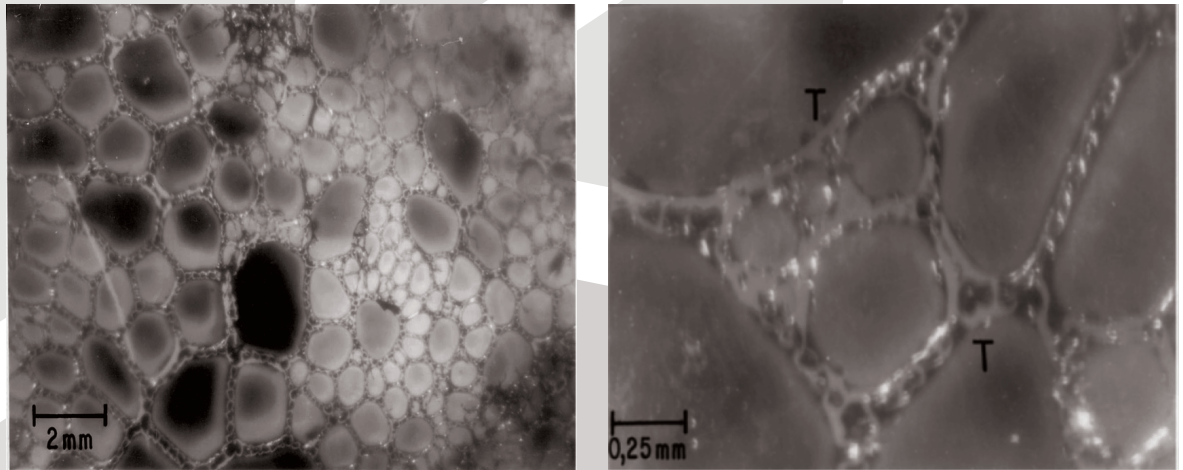


Fig. 1. Images of the 2D carbonaceous macro-network film from the  $A_{NW-2}$  sample adhering to the pyrex beaker. (Left): Typical random pattern showing the predominance of five-sided cells. (Right): A subsection showing the presence of "T" type vertices with internal angle  $\theta = 180^\circ$ .

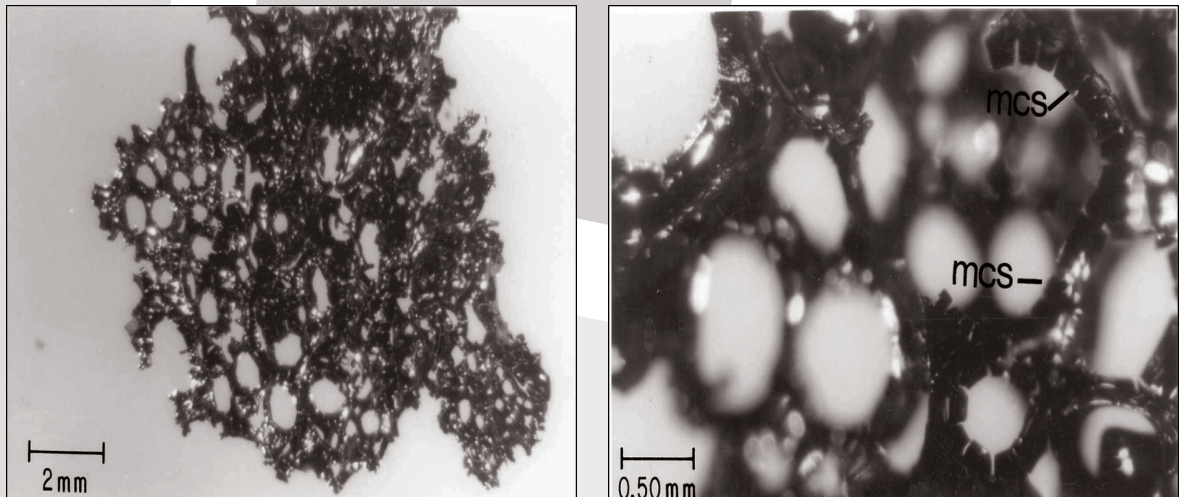


Fig. 2. Image of bulk carbonaceous macro-network from the  $A_{NW-2}$  sample. (Left): 3D random structure of a subsection of the sponge. (Right): Subsection showing macrocoil shapes (mcs).

In addition, a similar randomly structure to that in the films was found in the three-dimensional (3D) random network of carbons in the shape of irregular sponge balls were obtained as shown the Fig. 2. An assembly of carbonaceous grains with different sizes composed the sponges where the carbon grains developed into a continuous of 3D-RNC in the form of tubes with coiled shapes. The formation of coils was attributed to the diffusion of  $K_2O$  nanoparticles within the carbonaceous matrix. It can be seen from Fig. 3 (left) that filaments interconnect the structure in the 3D-RNC. An interesting resemblance with exfoliated graphite or graphene oxide can be seen from the SEM image in Fig. 3 (right) for the  $A_{NW-2}$ .

## ECO-FRIENDLY METHODOLOGY FOR THE SYNTHESIS OF GRAPHENE-BASED CATALYTIC MEMBRANE REACTORS

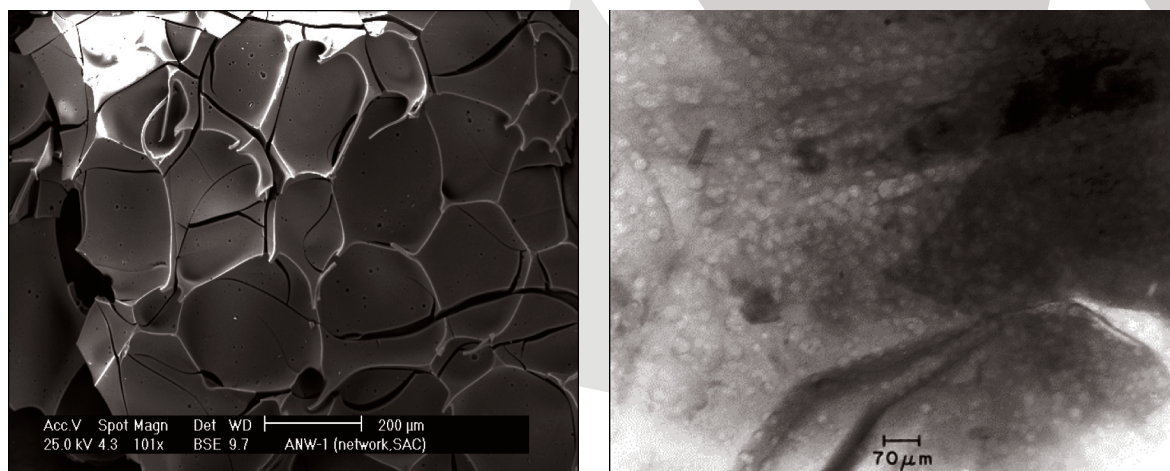


Fig 3. SEM images of random networks of carbon (RNC). (Left):  $A_{NW-1}$  (Right):  $A_{NW-2}$ .

The XRD pattern from Fig. 4 (left) shows graphite is the main crystalline phase in the RNC. However, RAMAN spectra in Fig. 4 (center) shows interesting shifts to lower frequency when RNC is prepared in presence of potassium. It can be seen that D-band and G-bands for  $A_{NW-2}$  were shifted down to 1361 and 1582  $\text{cm}^{-1}$ , respectively. The G peak at 1582  $\text{cm}^{-1}$  fits very well with that reported for graphene [12] where G peak is due to the doubly generated zone center  $E_{2g}$  mode [13]. So, the present work reports by the first time an easy and eco-friendly alternative methodology to prepare graphene-based materials from the controlled pyrolysis of saccharose in presence of KOH instead of  $\text{KMnO}_4$  commonly used by the Hummer method [14].

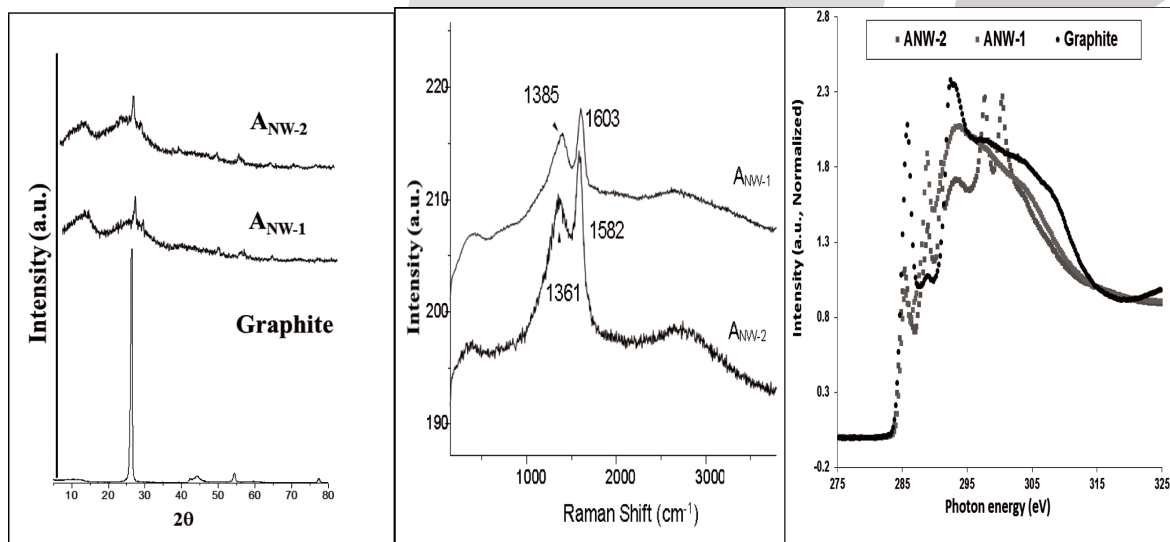


Fig. 4. (Left): XRD patterns. (Center): RAMAN spectra. (Right): C K-edge NEXAFS, for  $A_{NW-1}$  and  $A_{NW-2}$  samples.

The graphene-based structure in  $A_{NW-2}$  sample proposed above has been confirmed by the C K-edge near NEXAFS spectra in Fig. 4 (right). This spectrum showed important differences with respect to high-ordered pyrolytic graphite and with  $A_{NW-1}$ . It can be seen that  $A_{NW-2}$  samples showed an additional peak about 291.2 eV theoretical predicted [15] and ascribed to the lowest-energy



C 1s  $\rightarrow$ s\* excitation. It is remarkable to note the appearance of additional resonances between 297.8 and 300.6 eV in the shape of a very symmetric and double peak with 2.8 eV in difference. These peaks can be ascribed to a Stone-Wales structural defect [15,16]. This defect is created by rotating two carbons by 90 degrees, with a formation energy of about 5 eV [16]. The consequence of this rotation is the appearance of two five-rings and two seven-rings in agreement with the polygonal cell distribution in this sample, which showed an important contribution of pentagons and heptagons to the network of carbon [7-11].

Additional characterization by XPS showed important differences with respect to graphite. Finally, EPR and SQUID analysis suggested RNC develop para/diamagnetic behavior that strongly depend of synthesis and activation conditions [10].

### CONCLUSIONS

The controlled pyrolysis of saccharose is a single method to obtain simultaneously graphene-based 2D films and 3D sponge balls. These materials can be included within the random networks of carbon (RNC). RAMAN and NEXAFS confirmed the presence of graphene structure, and the presence of structural defects was attributed to the pentagon as the most abundant polygon in the films.

### ACKNOWLEDGMENT

J. Matos thanks to the Chilean Basal Project Chilean Basal Program PFB-27.

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## KEYNOTES

S8

### FROM ACADEMIC TO COMMERCIAL: STORY OF ACETYLATION OF WOOD

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#### Abstract

Acetylation of wood is done by reacting a softwood or hardwood with acetic anhydride at an elevated temperature. It is usually done without a catalyst and the reaction is carried out under nitrogen at or near the refluxing temperature of the anhydride. In many cases, the limiting factor in the reaction is the rate of penetration of the anhydride into the wood, especially in thick limber. By product acetic acid is removed under vacuum, recovered and sent back to the anhydride supplier for conversion back to acetic anhydride using the ketene process. The acetylated wood has very high dimensional stability, high decay resistance and good resistance to ultraviolet radiation with little change in thermal properties. Dry strength and stiffness of acetylated wood is about the same as controls but wet strength and stiffness are much higher in acetylated wood as compared to non-acetylated wood.

#### Introduction

The acetylation of wood was first performed in 1928 in Germany by Fuchs [1], using acetic anhydride and sulfuric acid as a catalyst. Fuchs found an acetyl weight gain of over 40%, which meant that he decrystallized the cellulose in the process. He used the reaction to isolate lignin from pine wood. In the same year, Horn acetylated beech wood to remove hemicelluloses in a similar lignin isolation procedure [2]. Tarkow first demonstrated that acetylated balsa was resistant to decay in 1945 [3]. Tarkow was also the first to describe the use of wood acetylation to stabilize wood from swelling in water in 1946 [4].

While laboratory acetylation of wood has been practiced for nearly a century, the commercialization of acetylated wood has been met with several challenges. The first patent was granted in 1930 in Austria on acetylated wood. Koppers Company may have made the first earnest, albeit short-lived, attempt at entry into the acetylated wood market in the 1960's. They used a process of first solvent drying wood in a reactor followed by reaction with acetic anhydride in the same reactor. This was followed by efforts in Russia and Japan (Diaken) in the 1970's and 1980's. In the late 1980's and early 1990's, ACell, in Sweden, were granted many patents and built two pilot plants: One for solid wood using microwave technology and one for acetylating fibers. Accsys Technologies, which had acquired technologies developed earlier at Stichting Hout Research (the Netherlands) and Scion (New Zealand), launched trial quantities of Accoya®, an acetylated pinus radiata, into the market and began full commercial scale production in Arnhem, the Netherlands in 2007. This was followed in 2012 with Eastman Chemical Company introducing Perennial Wood™ using acetylated southern pine produced at its pilot facility in Kingsport, Tennessee. In 2014, Eastman stopped the production of Perennial Wood™ [5].

#### Acetylation Chemistry

All woods contain acetyl groups: softwoods, 0.5 – 1.7% and hardwoods, 2 – 4.5%. Adding acetyl groups in the cell wall results in major changes to the properties and performance of the acetylated wood.

Acetylation is a single-addition reaction, which means that one acetyl group is on one hydroxyl group with no polymerization (Figure 1). Thus, all the weight gain in acetyl can be directly converted into units of hydroxyl groups blocked.



Figure 1: Reaction of acetic anhydride with wood.

Isolated lignin reacts faster with acetic anhydride as compared to hemicelluloses and holocellulose [6] [7] Kumar and Agawal reported that at an acetyl weight percent gain of 13.5, 86.4 % of the lignin



was acetylated, 21.6 % of the hemicelluloses and 9.3% of the cellulose [6]. Reacting wood at 120 °C with acetic anhydride and no catalyst, at an acetyl weight gain of 16 to 19%, theoretically about 90% of the lignin is esterified, and 25% of the holocellulose [8]. It is assumed that 100% of the hemicellulose hydroxyl groups are substituted and no cellulose hydroxyl substituted. There may be a small amount of hydroxyls esterified on the surface hydroxyls in the amorphous regions of cellulose.

**Properties of acetylated wood**

Moisture and dimensional stability

**Table 1** shows the change in volume in wood from green to dry to acetylated. The elastic limit

**Table 1:** Change in volume in wood from green to dry to acetylated.

Green vol cm <sup>3</sup>	OD Vol cm <sup>3</sup>	Change %	Ac WPG	OD Vol cm <sup>3</sup>	Change %
38.84	34.90	-10.1	22.8	38.84	+10.1

of cell wall is not exceeded and the bulked acetylated wood is back to the wood's original green volume. From green volume to dry results in about a 10% loss in wood volume and the acetylation brings the wood volume back to that of the original green wood. The bulking of the cell wall back to near its green volume is the mechanism of dimensional stability. Since the water molecule is smaller than the acetyl group, water is able to access some hydroxyl groups in the acetylated wood.

The equilibrium moisture content (EMC) is reduced as the level of acetyl weight gain increases.

**Table 2** shows the reduction in EMC as a function of acetyl weight gain.

**Table 2:** Equilibrium moisture content of acetylated pine.

Weight Percent Gain	EMC at 27C°		
	30% RH	65% RH	90% RH
0	5.8	12.0	21.7
6.0	4.1	9.2	17.5
10.4	3.3	7.5	14.4
14.8	2.8	6.0	11.6
18.4	2.3	5.0	9.2
20.4	2.4	4.3	8.4

**Table 3** shows the dimensional stability of both control and acetylated solid pine and fibreboard made from acetylated fiber.

**Table 3:** Dimensional stability of acetylated wood (solid wood, 21.6 WPG, fiber 22.7 WPG, 24 hour water soak)

	EMC	S	ASE
Solid Pine Control	21.7	13.8	----
Acetylated	8.4	4.2	69.3
Pine Fiberboard (5% phenolic resin) Control	20.2	21.3	----
Acetylated	3.4	2.1	90.1

S = Swelling coefficient, ASE = Antishrink efficiency

## KEYNOTES

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### FROM ACADEMIC TO COMMERCIAL: STORY OF ACETYLATION OF WOOD

#### Decay resistance

As the level of bonded acetyl increases, resistance to decay increases to both brown- and white-rot fungi (Table 4). There is a significant decrease in fungal attack at an acetyl level of approximately 10% which means that many of the hydroxyl groups that are required for a fungus to recognize wood as a food source have been modified. As the acetyl level reaches 15%, the attack by white-rot fungi has stopped and very little attack occurs with brown-rot fungi. At an acetyl level of about 18%, there is no attack by either brown-or white-rot fungi.

Table 4: Resistance of Acetylated Pine to Decay Fungi in ASTM D-2017-71 Soil Block Test (Brown-rot = *C. trabeum* White-rot = *T. versicolor*, ASTM D 1413, American Society for Testing and Materials. ASTM Standard method of testing wood preservatives by laboratory soil-block cultures (1976).)

Acetyl Weight Gain (%)	Weight Loss After 12 Weeks	
	Brown-rot Fungus (%)	White-rot Fungus (%)
0	61.3	7.8
6.0	34.6	4.2
10.4	6.7	2.6
14.8	3.4	<2
17.8	<2	<2

Figure 2 shows the control sample (A) before the 12 week soil bottle test using a brown-rot fungi (see Table 4). After 12 weeks, the control sample is covered with fungal mycelium (B) and the cell wall was destroyed (C). After the same length of time, in the same experiment, the sample acetylated to 19 WPG showed no weight loss but there was evidence of mycelium growth (D). This shows that the acetylated wood was not toxic to the fungus, the fungus just could not recognize it as a food source.

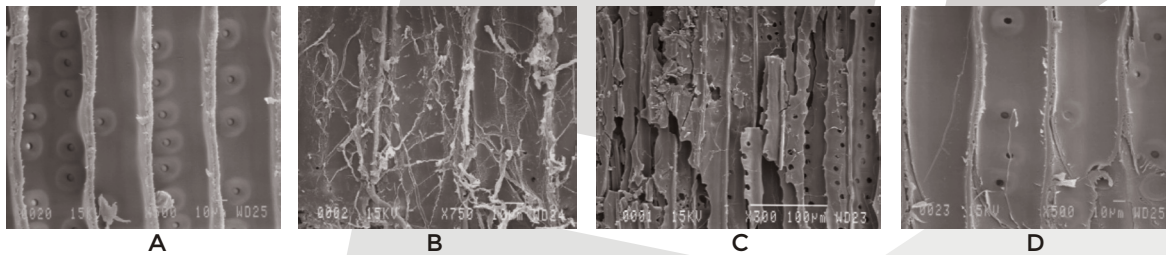


Figure 2: Control pine before (top, left) and after 12 week soil block test with brown-rot fungi top right and bottom).

The key to fungal resistance can be seen in Table 5. Control and particleboards made from different levels of increasing acetyl content were placed in a fungal cellar in Uppsala, Sweden [9]. The samples were evaluated at different times, up to 36 months, to determine the level of attack and to measure sample thickness. The first sample check was done at 2 months and already the control had swollen and there was a moderate fungal attack. At the same inspection time, the acetylated sample at 7.3 weight percent gain (WPG) was swollen but there was no evidence of fungal attack. By 6 months, the control samples were badly swollen and destroyed as a result of fungal attack.

At 3 months, the acetylated sample at 7.3% showed the first signs of fungal attack and was still swollen. This sample continued to be attacked and was destroyed at 12 months. At 4 months, the sample at 11.5% was swollen but no fungal attack was noted. After one more month, this sample showed the first signs of fungal attack. This trend, of a sample first showing swelling before any fungal attack, leads to the conclusion that swelling must take place before any fungal attack takes



place. This shows the importance of cell wall moisture being required before fungal attack can take place.

**Table 5:** Fungal cellar tests of aspen flakeboards made from control and acetylated flakes.

WPG Rating at Intervals (months)

0	2	3	4	5	6	12	24	36
7.3	S/2	S/3	S/3	S/3	S/4	--	--	--
11.5	S/0	S/1	S/1	S/2	S/3	S/3	S/4	--
13.6	0	0	0	0	S/0	S/1	S/2	S/4
16.3	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0

Nonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria. 2Flakeboards bonded with 5 percent phenol-formaldehyde adhesive. Rating system: 0 = no attack; 1 = slight attack; 2 = moderate attack; 3 = heavy attack; 4 = destroyed; S = swollen.

**Table 6** shows the results of acetylated wood after 300 days in three different types of soil. The compost soil has mainly brown-rot fungi, the sandy soil has mainly soft-rot fungi, and the forest soil has mainly white-rot and soft-rot fungi.

**Table 6:** Results of in-ground tests on control and acetylated pine.

Sample	Weight Loss in:		
	Compost	Sandy Soil	Forest Soil
Control	74±9	50±16	27±24
Acetylated	1±0	1±0	0

### Strength and stiffness

**Table 7** shows the strength and stiffness properties of control and acetylated pine. There is considerable loss of wet strength and wet stiffness in non-acetylated wood as compared to acetylated wood. There is a loss of over 60% in wet strength in non-acetylated wood while acetylated only drops 10%. There is a loss of over 35% in wet stiffness of non-acetylated wood while acetylated wood only loses less than 9% in wet stiffness. Acetylation has been shown to slightly increase the strength properties of fiberboards and flakeboards. Strength properties of wood are very dependent on the moisture content of the cell wall. The fact that the EMC and fiber saturation point of acetylated wood are much lower than that of unmodified wood alone accounts for their difference in strength properties [5].

**Table 7:** Strength properties of acetylated solid pine wood.

Sample	Dry Strength MOR N/mm <sup>2</sup>	Wet Strength MOR N/mm <sup>2</sup>	Dry Stiffness MOE N/mm <sup>2</sup>	Wet Stiffness MOE N/mm <sup>2</sup>
Pine	63.6	39.4	10,540	6760
Acetylated Pine (19WPG)	64.4	58.0	10,602	9690

## KEYNOTES

S8

### FROM ACADEMIC TO COMMERCIAL: STORY OF ACETYLATION OF WOOD

#### Conclusions

In acetylated wood, reductions in hygroscopicity are due to substitution of hydroxyl groups with an acetyl group which is less hygroscopic as compared to the hydroxyl group. Increased dimensional stability in acetylated wood is due to the bulking of the cell wall back to its original green dimensional so the cell wall cannot expand very much more (because of the elastic limit of the cell wall). Decay resistance of acetylated wood is due to the lowering of the cell wall moisture content becoming too low to support fungal attack so the initial enzymatic attack does not take place. Dry strength properties are not significantly changed in acetylated wood as compared to non-acetylated wood and acetylation results in greatly improved wet strength and wet stiffness properties.

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# Biocomp 2016

The 13<sup>th</sup> Pacific Rim Bio-Based Composites Symposium  
Bio-based composites for a sustainable future  
November 13<sup>th</sup> to 15<sup>th</sup>, 2016 - Concepción - Chile





**ORAL**

## SESSION 1-1

### THE USE OF X-RAY COMPUTED TOMOGRAPHY IN BIO-COMPOSITE RESEARCH

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X-ray computed tomography (CT), which was introduced in the medical field in the early 1970s, is also a powerful tool for the non-destructive measurement of dynamic processes in wood [1]. For more than 20 years, medical CT has been used in wood research at Luleå University of Technology. The uniqueness of the CT equipment allows processes such as drying, modification, water absorption, internal and external cracking and material deformation to be studied in temperature- and humidity-controlled environments. The data recorded by the CT during the process is converted into two or three dimensional images that, for instance, can show dynamic moisture behaviour in wood drying and crack formation.

This paper gives an overview of the possibilities of using CT in bio-composite research, and shows examples of applications and results that can be particularly difficult to achieve using other methods. A specific focus is on studies on wood products that use combinations with materials such as metal and especially on how to deal with the difficulties that this entails.

The practical application of the result is that CT-scanning, combined with image processing, can be used for non-destructive and non-contact three-dimensional studies of exterior construction elements during water sorption and desorption, to study parameters such as swelling and shrinking behaviour, delamination phenomena and crack development.

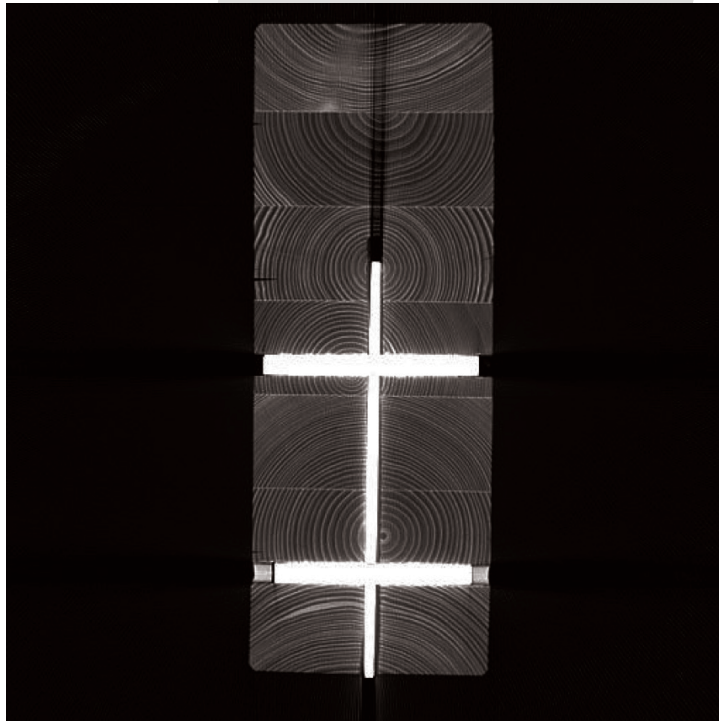


Fig.1 - Cross-sectional view of a glulam beam of Norway spruce with an aluminium plate anchored with two aluminium dowels. The lower dowel is sealed with a silicone sealant. The grey scale of the image indicates density: high density materials, like aluminium, are white, whereas low density is represented by black pixels.

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## **A NEW BIOBASED COMPOSITE MATERIAL USING BARK FIBRES** *Eucalyptus*

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*Eucalyptus nitens* and *Eucalyptus globulus* are among the commercially most important forest species in Chile. There has been a steep rise in *Eucalyptus* plantations in recent years, the total cultivated area being 704,078 hectares in 2010 to 828,728 hectares in 2014. The main problem associated with this situation is the post-process waste generation. In this context, *Eucalyptus sp.* bark contrary to *Pinus radiata* bark has disadvantages in handling, storage, disposal and use as fuel, becoming an undesirable by-product. However, bark *Eucalyptus sp.* have competitive advantages, principally due to their high fiber content and morphology. The present work reports an alternative to add value to this lignocellulosic raw material.

Fibers, produced from bark, were used to develop a competitive thermal insulation building board in terms of cost and thermal conductivity, besides of environmental and social benefits. The current ecological tendencies to develop sustainable green materials [1], [2] and the new regulations about thermal insulation in construction field in Chile provide better scopes for its development.

Bark eucalyptus was supplied from a wood chipping facility and treated mechanically. The results shows that the use of a hammer mill is highly efficient with a high fiber yield of 90% and the product with a high specific area, adequate for obtaining a homogeneous board. Another aspect considered in this study was the fiber moisture content accounting both the behavior of the bark in the milling process and the content of fibers/particles below 20 mm considered as a process residues. Therefore, a fiber moisture content between 20% - 30% (dry basis) and the utilization of a hammer mill was selected.

The thermal insulation board was made using a commercial phenolic resin as fiber binding agent and a steam pressing process to consolidate the board. The dependency of thermal conductivity with the density of the board was measured. The results obtained indicate that the thermal conductivity is directly proportional to the board density, with experimental values within 0.05 to 0.07 W/mK for board densities within 100 and 300 kg/ m<sup>3</sup>. This values are comparable with the commercial products based on natural fibers.

Due to the inherent nature of bark, a degradability test for fungi damage were also evaluated. The presence of phenolic adhesive in the fiber help to resist this effect as occurs in wood panel.

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### CHANGES IN MECHANICAL AND SURFACE PROPERTIES OF MEDIUM DENSITY FIBERBOARDS AND PARTICLEBOARDS WITH ACCELERATED AGING TEST

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Medium density fibreboard and particleboard panels are commonly used for building or exterior application in Japan. For such kind of that application, panels expose to relative humidity change over a long time which lead to degrade surface properties and mechanical properties of the panel. It is well known that reducing properties can cause shortening service life of panel and affect durability performance of the product itself. Therefore, evaluation of strength and surface roughness change under aging test are necessary to have a better understanding of those behavior and determine correlation of the those both mechanical and surface roughness change. Two types of commercially manufactured panels, medium density fiberboard (MDF) and particleboard (PB) were used as panel specimens. Each panel type consist of two sort panels which different in adhesive type. Specimens were prepared to be 50 mm wide and 300 mm long with five replications. All specimens were subjected to relative humidity (RH) change condition called wet-dry cyclic treatment for fifteen cycles under laboratory-controlled conditions. Each cycle consisted of wet state in 60°C and 90% RH for 120 hours then followed by dry state in 60°C for 48 hours without humidity control. Mechanical properties, elastic constant ( $E_d$ ) and loss tangent ( $\tan \delta$ ) values of (2,0) vibration mode were determined using a vibration non-destructive method. Surface roughness parameters, average roughness ( $R_a$ ), mean peak-to-valley height ( $R_z$ ) were measured quantitatively using surface profiler at three designated points on specimen. All parameters for both mechanical and surface roughness were measured before and during cyclic treatment.

The test results shown that  $E_d$  value of all panels decreased along the cyclic treatment with the different extent. Among the panels, MDF panel which is bonded with MDI resin has little change of  $E_d$  compared to the value before exposure. Value of  $\tan \delta$  increased during treatment for all panels with the exception of PB with MDI resin which showed almost unchanged after fifteen cycles. Roughness values changed as they are exposed to cyclic treatment.  $R_a$  was found increased during successive cycle, however no remarkable difference between first and complete cycle were found in case of MDF which is bonded by MDI. Correlation between  $\tan \delta$ , which correspond to internal loss of the board, and  $R_a$  was well presented of MDF with MUF resin.

## MECHANICAL PERFORMANCE OF GLUE JOINTS IN STRUCTURAL HARDWOOD ELEMENTS

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### 1 INTRODUCTION

Adhesive bonding is an essential task in modern timber engineering. The spruce is since 100 years and more Europe's most important wood resource for timber engineering. Consequently, the testing standards focus mainly on this wood species. A transfer of these standards onto other wood species is, due to the material's complexity, only of limited application. New approaches have thus to be employed to verify the load bearing capacity of glue joints in other wood species. The European beech (*Fagus sylvatica* L.) is the most common broad-leafed tree species in Switzerland. It has good mechanical properties of which the timber engineering can profit. The focus of this presentation therefore was on the failure mechanisms of glue joints in beech wood, realized with different, commercially available adhesive systems.

### 2 MATERIAL AND METHOD

The fracture toughness of cracks within the bond line, crack propagation at the glue joint and wood fibre and adhesive bridging after failure were investigated with different methods. Fig. 1 show the Arcan test. Also shear strength and delamination were tested. [2,3,4]

### 3 RESULTS

Joints of phenol resorcinol formaldehyde (PRF) showed constantly good results, the determined characteristics generally lay in the same range (fig 2-4) as for beech wood.

Polyurethane (PUR) has good fracture mechanical properties, but these cannot be activated in beech wood joints. The weakest link of PUR joints in beech is the adhesion. The gained results indicate that if the adhesion can be optimised through adequate priming or adhesive formulation, this adhesive system will be a versatile alternative to conventional adhesive systems.

The nanoindentation is capable to show the effects of external factors on the glue joints and allows the comparison of different adhesives. It could for example be shown what previously was assumed: Moisture cycles under controlled conditions as well as outdoor weathering have a positive impact on the adhesion of PUR onto beech wood (on the microscopic scale), with Terminally conducted standard tests on industrially produced elements

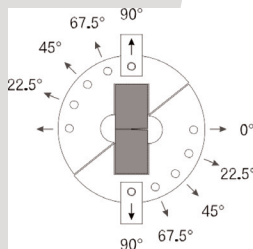


Fig. 1: Arcan Test

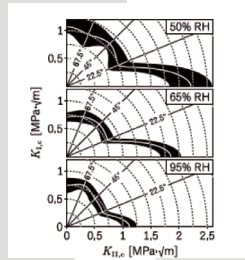


Fig. 2: Fracture toughness  $K_{Ic}$  of PUR for different RH

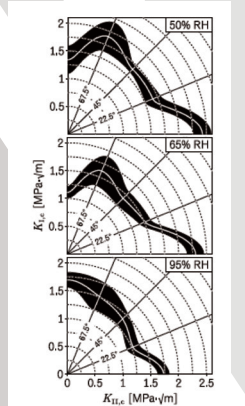


Fig. 3: Fracture toughness  $K_{Ic}$  for PRF and different RH [1]

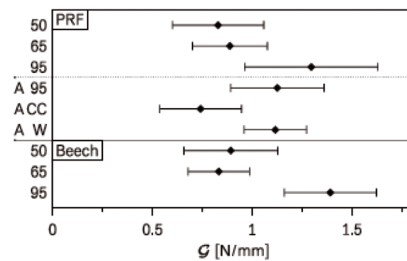
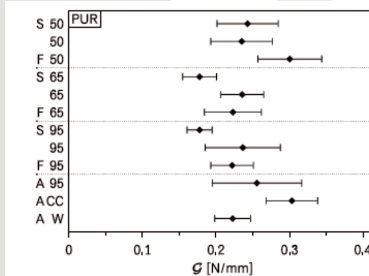


Fig. 4: Fracture energy G for PRF and 1-C PUR [1]

## SESSION 2-1

### MECHANICAL PERFORMANCE OF GLUE JOINTS IN STRUCTURAL HARDWOOD ELEMENTS

made of ash wood (*Fraxinus excelsior L.*) illustrated the difficulty of these tests: none of the investigated adhesive system of six in total was able to full the requirements of the standards EN 301 (fig 5.). Only the PRF was able to achieve the demanded tensile shear strengths. The same results we got for delamination tests according EN302-2. Priming can improve significant the shear strength and reduce the delamination.

#### 4 CONCLUSIONS

Only the PRF was able to achieve the demanded tensile shear strengths. In what extent these standard tests estimate the quality of such elements will the future show, since just such ash wood elements are already realized in Swiss timber constructions.

#### ACKNOWLEDGEMENT

The project was founded from the Swiss National Foundation (NFR66) and the Swiss Federal Office for Environment FOEN

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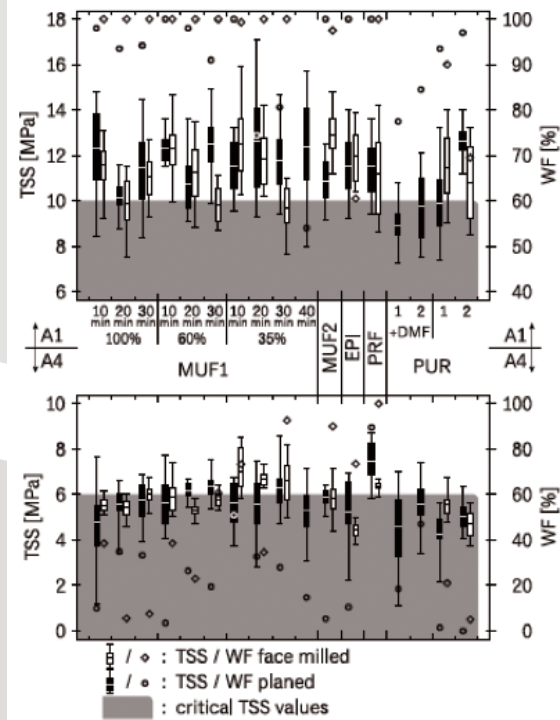


Fig 5: Results for the Tensile shear strength (EN 302) for ash wood and different adhesives [1]





## ENVIRONMENTAL FRIENDLY NATURAL RESINS FROM POLYPHENOLIC EXTRACTS: PERSPECTIVES AND CHALLENGES

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Nowadays wood panels are mainly manufactured with thermosetting synthetic resins, most of them based on formaldehyde. However, environmental and health considerations are leading to increasingly severe standards regarding the allowed formaldehyde emissions from wood boards. This fact, coupled with the increasingly higher cost of petroleum-based resin, has intensified the search for alternative resins based on natural materials for the formulation of wood adhesives. The use of polyflavonoid tannins is one such alternative, not only to prevent the use of formaldehyde but also to reduce its release from wood panels (Pizzi 2006; Kim 2009).

In this study we review the principal techniques of characterization/formulation of bioadhesives based on tannins. We highlight the potential application of extracts obtained from industrial lignocellulosic wastes (chestnut shell, chestnut bur and *Eucalyptus* bark). Our main interest is complete removal of formaldehyde from adhesive formulations. For this, hardener alternatives to formaldehyde were used: tris(hydroxymethyl)nitromethane (TRIS), glyoxal (GLY) and hexamethylenetetramine (HEX). The influence of hardener type and concentration, as well as pH, on adhesive gel time and pot-life was studied. A comparative structural characterization of the adhesives was performed by <sup>13</sup>C-NMR spectroscopy. Thermomechanical analysis (TMA) tests were carried out as an indication of the final strength of the adhesive systems. Particle boards of type 2 for interior use (EN 312) were manufactured with adhesives based on chestnut shell tannins, alone or mixed with chestnut bur/or eucalyptus bark tannins. Free formaldehyde was determined and boards prepared with TRIS, GLY and HEX tannin adhesives were classified as E0 (J.Santos *et al*, 2016).

These results reveal new challenges in the study of interactions between condensed tannins and hydrolysable tannins; curing reaction at low temperature, greater water resistance of bioadhesive-derived wood products and the possibility of obtaining lower-viscosity purified extracts for specific applications are also topics for further study.

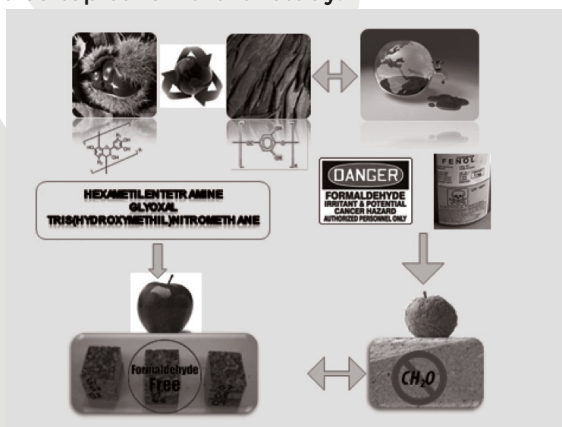


Fig.1 - Environmentally friendly wood adhesives based on chestnut (*Castanea sativa*) shell tannins

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## SESSION 2-3

### WOOD-STRAW COMPOSITES BONDED WITH UREA FORMALDEHYDE GLUE MODIFIED BY ETHANOL

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The development of particleboards is going slower by the lack of wood. The cereal straw is one of the most perspective raw materials in the world, which can replace wood in the manufacture of wood composites and particleboard in particular. The chemical composition of straw and wood is similar. The stocks of straw increase annually. A major obstacle to use straw in the manufacture of particleboard is the fat-wax surface layer of the straw with adhesive coatings properties that prevents achieving satisfactory adhesive bonding between straw particles using traditional UF glues [2]. It appears that the fat-wax surface layer of straw particles can be destroyed by ethanol in the process of bonding it by the modified UF glue [1]. The aim of this study was to investigate the influence of UF glue modified by ethanol on the properties of wood-straw boards.

Wood and straw particles of approximately 2% moisture content, a commercial UF resin with a solid content of 64% and viscosity of 92 s were used in this study. Ammonium chloride was used as a hardener, and 96% solution of ethanol was used as a modifier. Three-layers wood-straw boards with density of 650, 750 and 850 kg/m<sup>3</sup> and the ratio between the layers of the board 20:60:20 (external:internal:external) were manufactured. Herewith, the wood particles for the outer layers were mixed with unmodified UF glue. The wood and straw particles were mixed at the ratio of 35:65% with additional modified UF glue to form the inner layer of board. The glue consumption in the board's layers was 14% of the mass of absolutely dry particles. Wood-straw boards were pressed at the temperature of 170 oC and pressure of 2.2 MPa.

The experimental values of modulus of rupture (MOR), internal bond (IB), thickness swelling (TS) and water absorption (WA) of wood-straw boards (which were determined according to standards EN 310, EN 319, EN 317) are shown in Table 1.

Table 1. Properties of wood-straw boards

Property	Density of boards, kg/m <sup>3</sup>		
	650	750	850
MOR, MPa	11.63 (1.31)	13.40 (2.43)	17.67 (1.32)
IB, MPa	0.33 (0.042)	0.36 (0.018)	0.39 (0.019)
TS (24 h), %	14.34 (2.28)	13.73 (4.20)	10.87 (2.44)
WA (24 h), %	81.48 (17.9)	74.47 (13.83)	53.42 (17.58)

As can be seen, the modification of UF glue with the 96% ethanol improves the basic properties of wood-straw boards. In particular, MOR increased by 53%, IB increased by 33%, and water absorption and thickness swelling of the boards decreased to 10%. The resulting wood-straw boards have improved mechanical performances compared to standard requirements of EN 312-2. Thus, is possible to expand the raw material base for particleboards manufacturing by involving the agricultural waste, such as straw is and therefore to save the wood materials.

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## **CONTINUOUS WOOD SURFACE DENSIFICATION - CHEMICAL TREATMENTS TO REDUCE THE SET-RECOVERY**

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The hardness of the outer surface of solid wood can be improved by densification, and this opens up new fields of application for low-density species. So far, surface densification relies on time- and energy-consuming batch processes, and this means that potential advantages over more expensive hardwood species or non-renewable materials are lost. Using fossil-based plastics or applying wood densification processes with a high energy consumption has an adverse effect on the environment.

In a previous study, the viability of a high-speed continuous wood surface densification process was tested. By adopting a roller pressing technique, the surface of solid Scots pine boards could be densified at speeds of up to 80 m/min [1].

Even though the general viability and potential of such a process was proven, several problems need to be solved before it can be implemented industrially. One of the most crucial problems is to reduce the moisture-induced set-recovery of the densified wood cells, and this has to be done at the same speed as the actual densification process. For this reason, the aim of the present study was the integration of the roller pressing technique with different pre- and post-treatment methods to reduce the set-recovery.

Aqueous solutions of hydrogen peroxide and sodium hydroxide were used as pre-treatment agents to activate the wood surface prior to densification. Cactus juice was used as a post-treatment impregnation agent immediately after the densification. The densification stage functioned as the 'hot' stage of a modified hot-cold bath process. After the impregnation stage, the cactus juice polymerized to mechanically stabilize the compressed wood cells.

The results showed that the set-recovery could be reduced by using the described treatments. Future work will focus on integrating all the process steps into a fully continuous and automatic process.

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## SESSION 3-2

### WOOD PRESERVATIVES UTILISING LOW-VALUE OLIVE PRODUCTION PRODUCTS IN SLOVENIAN ISTRIA

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Within the Slovenian region of Istria, the olive growing and olive oil production industry is strong. This industry has a long history and the olives grown here have high levels of biologically active compounds including a variety of phenolic compounds. Using materials generated by this industry in potential wood preservative systems would not only valorize low value materials and stimulate rural economies, but would also provide an alternative to currently used oil-based preservative systems. The objective of this study was to produce an oil treatment for use as a wood preservative and assess its efficacy in reducing leaching, weathering effects, and fungal growth. This project is an ongoing and is a joint collaboration between the University of Primorska, the BioComposites Centre at Bangor University, the Norwegian Institute for the Bioeconomy (NIBIO), and the Biotechnical Faculty of the University of Ljubljana.



## **PERFORMANCE OF MEDIUM DENSITY FIBREBOARDS PREPARED WITH RECYCLED FIBERS**

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A lot of wood furniture that had been made of medium density fibreboard (MDF) is expected to generate huge amount of MDF wastes after its lifetime use all over the world. Thus, this study attempted to isolate recycled fibers from MDF panels using two different processing methods (refiner and hammer mill) after pre-treatment, to characterize the isolated recycled fibers using various techniques, and to investigate their performance of recycled MDF with different recycled fiber contents. The nitrogen analysis results showed the presence and removal of urea-formaldehyde (UF) resins in the recycled fibers. Mechanical properties of recycled MDF such as modulus of rupture (MOR), internal bond (IB) strength and nail withdrawal resistance showed maximum values at 10% recycled fiber content and then decreased thereafter as the recycle fiber content increased. This result indicates that the recycled fibers are stiffer than virgin fibers owing to the cured resin in the fibers.

## SESSION 3-4

# ELECTROSPUN NANOFIBERS USING WHOLE MICROALGAL BIOMASS: A NOVEL SUSTAINABLE APPROACH IN THE FIELD OF BIOBASED COMPOSITE MATERIALS

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Value added products from sustainable sources are one of the accepted alternatives [1] for the on-going petroleum products and that can be produced in bulk to satisfy the overall world's demand [2]. Microalgal biomass is a renewable source, which can be efficiently and productively cultivated in less space without competing with agricultural crops. Nanofibers are nothing but fibric material with the diameter range from micrometer to sub microns (or) nanometers. This kind of modification greatly increases the specific surface area, flexibility in surface, functionality and mechanical performance compared to the normal form of the material. Electrospinning is one of the most attractive technique for nanofibers preparation because of its simplicity, reproducibility, cost effectiveness and scope for large variety of starting materials [3]. Recently, the use of biopolymers to replace the role of commercial polymers in nanofibers preparation methods has gained attention. In the current study, a novel attempt to use the whole microalgal biomass for the development of electrospun nanofibers was performed.

Crude *Scenedesmus almeriensis* biomass was dispersed in acetone and then 10% polyethylene oxide solution (in water) was added to the medium. The obtained suspension was taken in a syringe and continuously sprayed on the aluminium foil sheet folded on the collector drum in the electrospinning unit (Fig. 1 A). The operating condition was fixed as +25 KV; -3 (to) -4 KV with the flow rate of 1.5 to 2 mL/h. Scanning electron microscope (SEM) image of the obtained nanofibers are given in Fig. 1 B and C. The formed nanofibers are in between 200 - 250 nm. Further studies are in progress to optimize the best operational conditions.

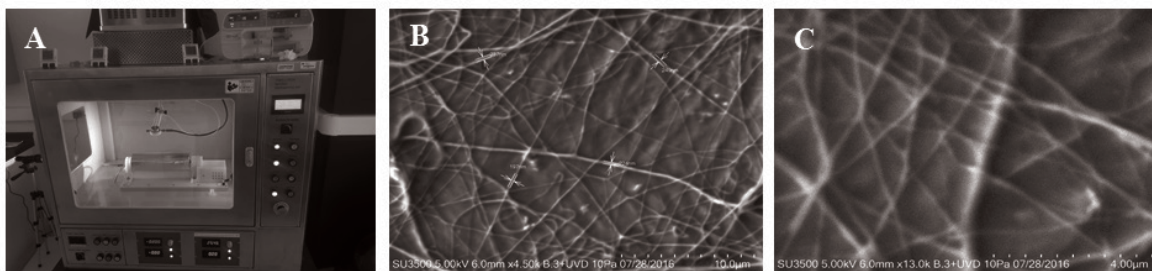


Fig. 1 (A) - Electrospinning unit, (B & C) - SEM images of *Scenedesmus almeriensis* derived nanofibers

### Acknowledgements

This research was funded by CONICYT through FONDECYT Posdoctoral Project 3160392 and FONDECYT Project 11140127.

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## NOVEL BIOCOMPOSITE BASED ON CHITOSAN - *Sphagnum Magellanicum* FIBERS

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Chitosan is a family of natural polysaccharides mainly composed by glucosamine units  $\beta$ -(1-4) linked having different acetylation extension. Such polymers have unique properties that make them interesting as biomaterial such as biodegradability, biocompatibility, low toxicity, polycationic nature in acid media and good film forming properties as well. It is known the ability of chitosan to trap heavy metals and also their binding properties that allow them to absorb other toxic compounds such as dyes, pigments and phenolic compound [1]. On the other side, peat moss (*Sphagnum magellanicum*) fibers are commercial available as low cost material. They are mainly used in substrate mixture for ornamental, fruit or vegetable plants growth in nurseries due to their high water retention capacity. The absorption properties from other peat mosses had been previously reported. Biocomposite materials have the advantage of combining the properties from different compounds they are built up. In present work biocomposite materials based on Aegla chitosan - *Sphagnum magellanicum* are presented. Different amount of fiber (0.25, 0.5, 0.75, 1.0, 1.5 and 2 wt %) were mixed with chitosan dissolved in acetic acid to prepare membranes using the dye casting method. The membranes were further crosslinked with epichlorohydrine, neutralized with a mixture of ethanol (70% v/v) - NaOH (1 % w/v) and washed to remove the excess of reagents and sodium hydroxide. Membranes from each biocomposite were prepared and characterized by FTIR, SEM, TGA-MS and DRX. The swelling capacity for each mixture at pH 2, 7 and 10 were carried out. Some of these results are presented in figure 1 A - B.

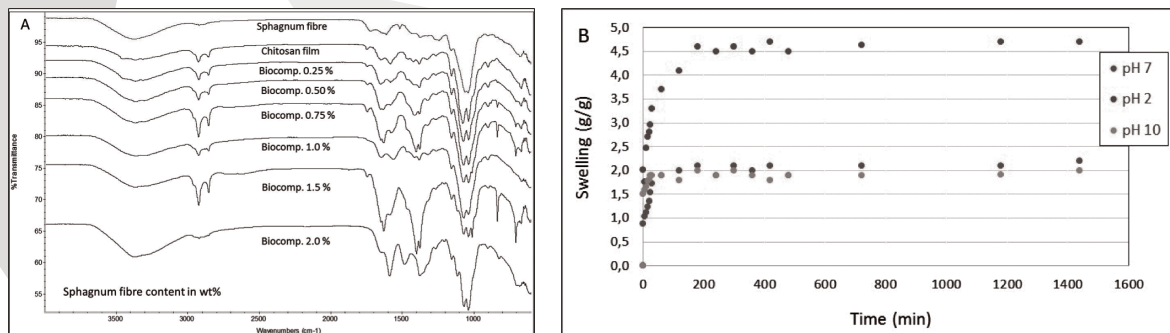


Fig.1- FTIR of chitosan and biocomposites (A) and swelling capacity of biocomposite 2 wt% (B).

The incorporation of *Sphagnum* fiber to chitosan matrix improves the swelling capacity of biocomposite membranes. The higher swelling capacity was observed at pH 2. According the thermogravimetric analysis biocomposites showed similar peak decomposition temperature than pure chitosan. A composting test was also carried out in order to compare the biodegradability of such composites and results will be presented.

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## LIGNIN-ESTER DERIVATIVE AS MATRIX FOR COMPOSITES ELABORATION BY PRESS MOULDING

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The huge global attention about damaging effects of commercial synthetic polymers on the environment due to their non-renewable nature and its high use has increased in recent years, creating a big demand of development of eco-friendly biomass based products. Lignin, one of the main structural components of lignocellulosic biomass and its abundance being the second most abundant macromolecule in nature, can offer a large amount of organic material that could be used in the production of biopolymers. Lignin by itself presents some disadvantages for plastics production due to its rigidity, fragility and its poor film forming ability as well as difficulty during processing due to its high softening point ( $T_g$ ) [1]. However, its chemical structure provides high potential for chemical modifications. Chemical modification of hydroxyl groups like esterification could be the best alternative to increase its range of applications in the polymer industry area, lowering the glass transition point of lignin and increasing its thermoplasticity [3], highly desirable for current industrial polymeric processing technology. This study was focused on the isolation of lignin from Spruce and the synthesis of lignin-ester derivatives using a long aliphatic chain (12 carbons) to obtain a reduction of its softening point and make it a thermoplastic product, capable of being processed by press moulding. The main objective was to produce a fully environmental-friendly material. For that the used of cellulose acetate as reinforcement was aimed to provide better consistency to the final material and triethylcitrate (TEC) as plasticizer was used in different concentrations. The new physicochemical properties of lignin after chemical modification like molecular weight, hydrophobicity and thermal properties, as well as the thermal, mechanical and morphological behavior of elaborated composites were evaluated.

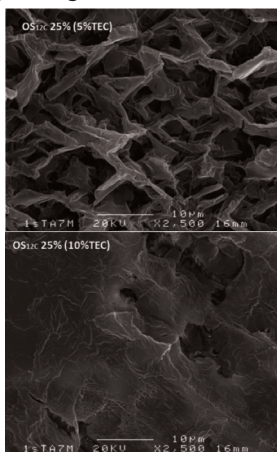


Fig. 1- SEM micrographs of composites.

	$\sigma$ (KPa)	$\epsilon$ (%)	$E$ (MPa)
<b>5% TEC</b>			
OS <sub>12C</sub> 5%	707.0 ± 57.0	1.5 ± 0.2	53.7 ± 9.4
OS <sub>12C</sub> 10%	968.5 ± 36.2	1.0 ± 0.4	86.1 ± 5.9
OS <sub>12C</sub> 25%	1429.0 ± 74.0	1.6 ± 0.3	111.9 ± 7.6
<b>10% TEC</b>			
OS <sub>12C</sub> 5%	317.0 ± 57.9	1.7 ± 0.1	57.3 ± 1.4
OS <sub>12C</sub> 10%	756.2 ± 30.8	6.0 ± 1.3	45.1 ± 4.3
OS <sub>12C</sub> 25%	946.8 ± 51.2	4.0 ± 1.1	47.1 ± 4.1

Table 1. Average values of tensile strength, elongation at break and Young modulus of composites.

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## BIO-BASED POLYMER PELLETS AND FILMS DERIVED FROM AGRO-INDUSTRIAL RESIDUES

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Agricultural residues represent a renewable, cheap and abundant source of raw materials for multiple purposes. This possibility is particularly attractive in an international perspective by the scarce availability and the environmental effects caused by burning fossil fuels. Agricultural residues are wasted or burned in most cases. Nevertheless, this kind of biomass can be processed to obtain products with high added value under a green chemistry concept, showing good perspectives as feedstock for biomaterial production. One possible way to generate these high added value polymeric products from agricultural residues is the solvolysis (Fig. 1.a), a chemical conversion method that allows to process high amounts of biomass to obtain a viscous product (Fig 1.b) [1], converting lignocellulosic wastes into highly reactive black liquor that can be used for the preparation of environmentally friendly polymeric products for the chemical industry [2]. Our recent studies have revealed that by the solvolysis of milled corn stover (Fig. 1.c) it is possible to produce a black viscous liquid that can act as a plasticizer for potato native starch to obtain a thermoplastic material, which can be subjected to polymer processing equipment with a view of developing biomaterials and bio-products. In this work we have established operating parameters for proper upscaling to pilot production of pellets and tubular blown films from evaluation of the thermoplastic material.

The methodology of the experimental study encompassed the evaluation of raw materials, premixes, blends, pellets and tubular films formed. In this context, corn stover was subjected to a solvolysis process to obtain a dark bio-based plasticizer. The black liquid was mixed at room temperature with starch at different compositions, obtaining premixes capable of being processed in a torque rheometer under certain conditions of temperature and time and at constant rotational speed. Control samples of a starch-glycerol mixture were also studied. From the results obtained (maximum torque, mixing energy, stickiness) the most suitable composition and its optimum processing conditions were chosen for upscaling to pilot level. Selected materials were tested by Fourier Transform Infrared Spectroscopy (FT-IR), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC), in order to identify their functional groups and thermal properties.

At pilot scale, pellets of the selected materials (Fig. 1.d) were obtained by extrusion processes (Fig. 1.e), and then used in a film blowing machine to conform bio-based films (Fig. 1.f). Mechanical properties of the final products (tensile and dart impact tests) have been considered.

This study allowed detecting the functional groups present in the materials and their thermal properties, as well as studying their mixing rheological behavior. Furthermore, it was possible to identify processing parameters to obtain pellets and film at a pilot scale, and to determine the mechanical performance of the final products under tensile and impact solicitations.

Therefore, it is clear that the bio-based plasticizer is able to provide the native starch with suitable properties to transform it into pellets and tubular blown films, and that the upscaling to industrial production of both products is feasible and may be studied in further investigations.

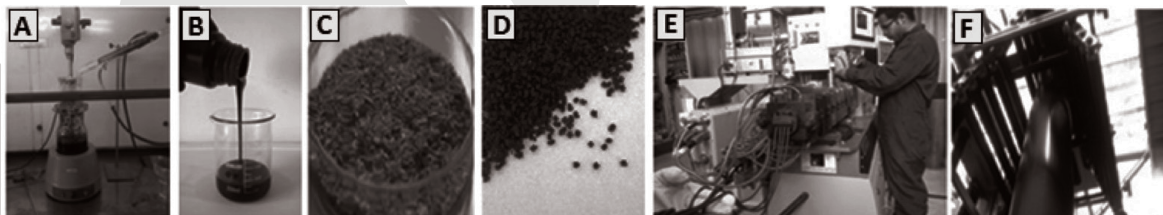


Fig.1 -Bio-based pellets and films obtained from agro-industrial materials. (a) Solvolysis process. (b) Bio-based plasticizer. (c) Corn stover. (d) Bio-based plasticizer/starch pellets. (e) Extrusion process. (f) Blown film extrusion process.

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### SUPERCritical IMPREGNATION OF CINNAMALDEHYDE INTO PLA FILMS TO DEVELOP ANTIMICROBIAL FOOD PACKAGING MATERIALS

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In the last years there has been an increasing interest in the development of renewable materials with biodegradable properties in an attempt to contribute to the sustainable development and to reduce the environmental impact associated with petroleum-based plastics [1]. Poly (lactic acid) (PLA) is one of the most important commercially available bio-based and biodegradable thermoplastic polyesters. This bioplastic can offer a sustainable alternative for food packaging across a wide range of commodity applications in response to consumer's demands and market trends in the use of renewable resources [2]. On the other hand, during the last years the research on the development of active materials with antimicrobial and antioxidant properties has increased with the purpose to protect food from oxidative reactions and microbial growth [3,4].

There are several techniques for incorporating additives or active substances in plastic films. One of the most used in the packaging industry is the extrusion process. However, this process has disadvantages such as the possible volatilization or degradation of the active agent(s) because of the high temperature values used during the plastic processing. So, the supercritical solvent impregnation (SSI) represent an alternative at this process. The supercritical impregnation process offers important advantages as controlling the solvent power of the fluid by small changes in pressure and temperature and also avoids the use of organic solvents. This type of impregnation technique uses a non-toxic and inert media, commonly CO<sub>2</sub>, as solvent to incorporate the additive or active compound in the polymeric matrix [5].

In this work, supercritical solvent impregnation has been tested for the incorporation of active compounds into biopolymer materials for antimicrobial food packaging. Cinnamaldehyde (Ci), with proved antimicrobial activity, was successfully impregnated on poly (lactic acid) (PLA) using supercritical carbon dioxide (scCO<sub>2</sub>). Impregnation tests were carried out under two pressures conditions (9 and 12 MPa) and three depressurization rates (0.1, 1 and 10 MPa min<sup>-1</sup>) in a high-pressure cell at constant temperature (40 °C). The aim of this work was to study the influence of different conditions of supercritical solvent impregnation method on the thermal, mechanical and structural properties.

Results showed that all the studied conditions permitted to impregnate cinnamaldehyde, at concentrations between 8 to 13 % w/w. Characterization of films revealed strong modifications in thermal, and mechanical properties of impregnate biopolymer films, resulting on a more flexible, less brittle and more resistant material compared to neat PLA.

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## ADHESIVE FORCES ACTING BETWEEN THE COMPONENTS OF WOOD-PLASTIC COMPOSITES ON MOLECULAR AND MACROSCOPIC SCALE

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Increasing environmental concerns have necessitated the search for new materials with high performance at affordable costs. Wood-plastic composites (WPCs) are a relatively new material class that cover a broad range of composite materials utilizing an organic resin binder (matrix) and fillers composed of cellulosic material. Despite the variability in their mechanical properties, natural fibers offer many advantages when compounded with plastic materials. The interaction between the fiber and matrix is one of the determining factors for the formation of composites. However, poor fiber-matrix interfacial adhesion is the result of surface incompatibility between hydrophilic natural fibers and non-polar polymers. Since the wood component of a wood-plastic composite is hydrophilic and the plastic is hydrophobic, a compatibiliser is often used to improve interfacial bonding of the two different phases [1-2].

The polymer matrix of WPCs is mostly low density polyethylene (LDPE), or other polyolefines. Most of them can be obtained from recycled plastic and pose therefore an environmentally friendly material source. There are 559 alien invasive species (AIS) in South Africa of which 383 are plants which are causing damage worth billions of Rands to South Africa's economy every year [3]. These species need to be cleared from public land and can therefore be regarded as waste materials, which also makes them environmentally friendly raw materials. Many analytical methods have been used to study the microscopic and macroscopic mechanical, physical and chemical properties of WPCs. One of these methods is Chemical Force Microscopy (CFM), which is an extension of the Atomic Force Microscopy (AFM), in which the tip is modified with specific functional groups to provide information about the chemical composition of the surface [4]. CFM can therefore be used to analyze and quantify the chemical interactions between the different components in WPCs on the molecular scale, which helps to explain physical and mechanical properties of the macroscopic composite material.

In this study, the molecular interaction forces of a three component wood plastic composite (WPC) system were investigated with Atomic Force Microscopy (AFM), using chemically modified tips. The adhesive forces determined on a molecular scale were compared to macroscopic tensile properties of blended WPCs samples. Wood from six different tree species was compounded with low density polyethylene (LDPE) and three different compatibilisers: two commercial types, namely EVOH and PE-g-MA and one developed from thermally degraded polyethylene (dPE). The adhesive forces were determined between all individual components with AFM and the tensile strength was determined for all different WPC blends. EVOH proved to be very sensitive to its binding partners, especially the wood species. Composites containing PE-g-MA as compatibiliser had higher tensile strength and were less sensitive to the wood species. Composites containing dPE as compatibiliser had a consistently high tensile strength comparable to PE-g-MA for all the wood species. The results of the study show that dPE is an effective adhesion promoter in WPC systems and invasive wood species can be incorporated into WPCs; however, the choice of compatibiliser is vital, as it affects the interaction forces and the mechanical properties of the composites. A strong positive correlation was found between microscopic adhesive force and macroscopic tensile strength.

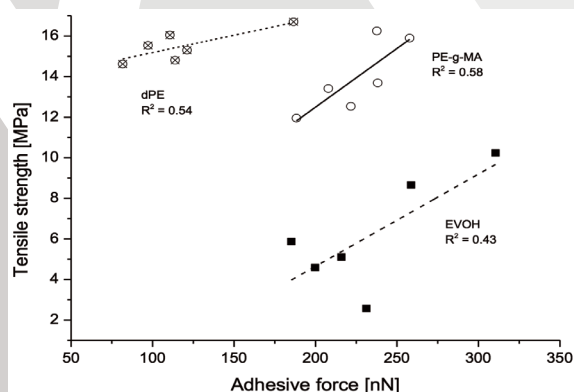


Figure 1: Correlation between tensile strength of WPCs and adhesive force of compatibiliser coated tips and wood surfaces.

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## SESSION 5-1

### STUDY OF MACRO ALGAE AND MOLLUSC WASTES AS SECONDARY FILLERS IN NOVEL WOOD-PLASTIC BIO-COMPOSITE PARTICLEBOARD

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Research Scope: Waste Materials/ Wood-Plastic Bio-composites/ Marine Bio-fillers/ Low Carbon Building Materials

#### Summary

This research studies locally sourced waste materials for the development of a novel low-cost non-toxic environmentally sensitive bio-composite panel for architectural applications. For this purpose 4 waste materials have been selected which blend mixture it is unprecedented until date.

#### 1-Introduction

In the quest for the development of high performance, low carbon, low cost novel green building materials, transferring wastes into resources prospects the ultimate sustainable outcome from the Industrial Ecology perspective.

The Government of Australia integrates this concept on December 2014 releasing the Waste Avoidance and Resource Recovery Strategy 2014-21 (WARR), establishing a multi-sector framework for reducing waste generation while keeping materials circulating within the economy [1].

In this context wastes materials such as Copper Chrome Arsenic (CCA) treated timbers as well as other treated timbers, plastic films and mixed plastics which in 2015 were listed amongst the six environmental priority wastes by the New South Wales Environment Protection Authority (NSW EPA).

Moreover, these waste materials in the Sydney Metropolitan Area from the Commerce and Industry (C&I) waste stream bulk correspond to 14.5% for post-consumer timber and 12.8% for mixed plastics. All together represents the 27.3% corresponding to 367,650 tons per year [2].

Therefore the objective of this study is to examine the potential use as well as the recovery routes of these two priority wastes as the main raw material for the development of a new generation of high performance environmentally sensitive Wood-Plastic Bio-composite (WPBC) for architectural applications.

#### 2-Materials Selection Criteria

Thermoplastic such as polypropylene (PP) has been selected as the polymer matrix for its low toxicity as well as its excellent hydrophobic, thermal and insulating properties.

Wood waste flour (WF) has been selected as the main filler for structural strength as well as to provide thermal and acoustic insulation.

Marine bio-wastes such as seaweed (Sw) and seashell (Ss) have been selected in their function of secondary fillers for structural strength, mould resistance and fire retardant properties due to high salt as well as high calcium carbonate content respectively, in order to improve the composite overall performance at a low cost.

Nonetheless Wood-Plastic Composites (WPC) have been extensively researched in the past decades, this hybrid mixture is unprecedented until date, presenting an opportunity for innovation in the bio-composite field with new enhanced properties.

#### 3- Experimental

The Fillers/Matrix blend is prepared to 60/40 weight ratio with the particle size sieved to 20 and 40 mesh respectively. Secondary fillers are incorporated to the blend as 10 and 20 % weight ratio. The selected materials are subject to a 4 step process in order to manufacture a final bio-composite panel: particle size reduction, mixture preparation, hot-pressing and slow cooling for mold disassembly.



#### 4-Results

A series of WPBC panels have been prepared and tested for moisture absorption as well as for mechanical performance as per ASTM D1037. Additionally SEM micrographs (Fig.1) have been captured from the top surface as well as from the fracture surfaces for microanalysis. Details of the composite microstructure, the particles morphology as well as the adhesion between matrix/fillers interphases have been examined.

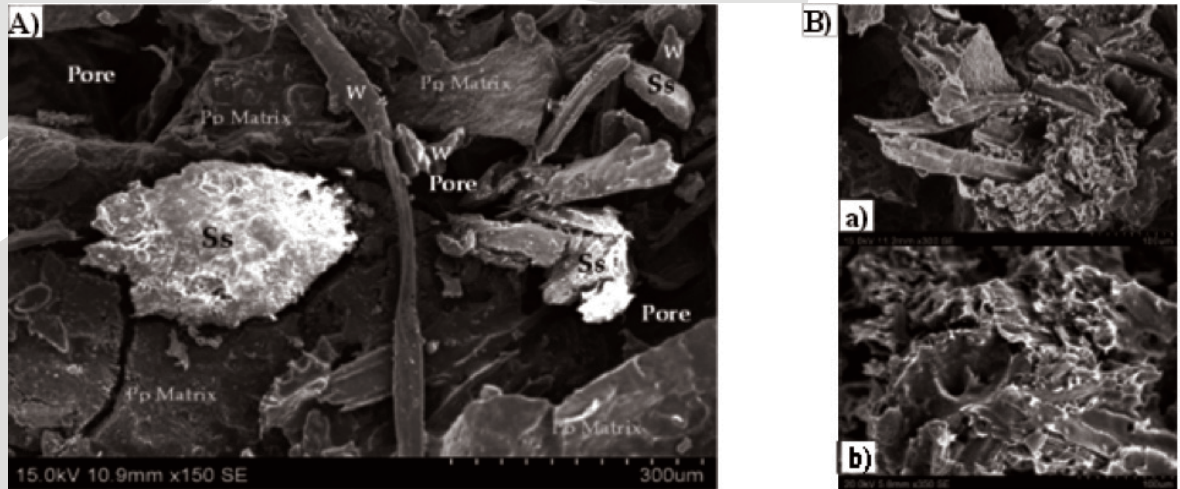


Figure 1. WPBC Panel Matrix/Fillers interphase microstructure SEM analysis: A) Internal bond at 300µ; B) Fracture surface at 100µ: a)WPPpSsSw Panel, b)WPPpSsSw+MaPp Panel.

According to mechanical tests MOR and MOE values were as per MDF standards. As expected incorporating MAPP coupling agent to 3% weight ratio significantly improved the filler/matrix adhesion improving the mechanical performance to 300%. Incorporating the secondary marine bio-fillers indeed improved the mechanical properties of the prototype panel. For moisture absorption test all specimens presented low thickness swelling of 0.6-4.6 % as well as low water absorption values of 27.8-36.8%.

These results suggest the proposed novel bio-composites indeed achieved an enhanced performance being most suitable for high moisture environments applications.

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## SESSION 5-2

### EXPERIMENTAL STUDY OF THE EFFECT OF ORGANIC POWDER IN A COMPOSITE MATRIX OF FIBER REINFORCED PLASTICS (FRP)

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The potentiality of the abundant source of algae fibers and particles, residues of the biofuel production [1], allows to an opportunity to develop a new materials with better mechanical properties.

This paper presents the results of the experimental study of a bio-polymer subjected to a tension load. The objective of this paper it found a better combination between an organic material and a polyester resin to optimize the mechanical behavior of the matrix. The organic material it a microalgae named *Botryococcus brauni*, obtained from the residual process of the biofuel production. In the case of the polyester resin, the study considers a PALATAL P4 (BASF, Santiago, Chile) to create the optimized bio-resin. The raw material, microalgae, used to develop the reinforcement of the polyester resin has been obtained through the process of hydrolysis ( $H_2SO_4$ -MeOH) and lipid extraction ( $CHCl_3$ -MeOH). The experimental program consider specimens that contain 5% in weight microalgae and 95% of polyester resin

The results shows that the mechanical properties in tension of the specimens with a 5% of microalgae increase the maximum stress in a 40%, respect to the neat polyester resin. In the case of the strain, an increment of a 124% it reach respect to the strain of the neat resin. The improvement of the mechanical behavior it due to the carbon contained in the microalgae, mainly. The content of the carbon in the microalgae it around of 30-40% of weight. By the other side, the content of the proteins and lipids in the microalgae it help to improvement the strains and total displacement of the specimen tested.

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## NOVELL COMPOUNDING PROCESS FOR UTILIZING TMP-FIBERS IN WOOD-PLASTIC COMPOSITES

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Commercially available Wood-plastic composites (WPC) as one group of bio-based composites usually consist of wood particles (WP), a thermoplastic matrix and additives. WP displays a low aspect ratio. It acts as a filler and increases the stiffness of the composites but does not improve the tensile strength [1]. Because of low cost and adequate processability, it is mainly used as wood source in WPC materials. In order to improve strength, a growing interest came up by using thermomechanical pulp fibers (TMP) in polymer matrices [2]. TMP-fibers display high aspect ratios and have the potential to provide reinforcement effects to the material [3]. TMP-fibers are usually produced via a refining process for medium density fiber boards (MDF). Moreover, high yields are obtained through TMP refining, resulting in a cheaper fiber compare to e.g. chemical pulps [4]. The TMP process conditions obtain most of the lignin on the fiber surface which possess a better interface for bonding to the hydrophobic nature of polyolefin matrix [5]. For the application of TMP-fibers in WPC some difficulties occur regarding the processability with continuous WPC compounding technologies such as extrusion. TMP-Fibers have low bulk density, a non-free flowing behaviour and tend to form bridges and agglomerates which makes a constant feeding into the extrusion process and a resolving difficult [3]. For industrial scale processing generally continuous feeding technologies are required [6]. For compounding of wood fibers or flour, dry material is required to keep the vapour evaporation during the process to a minimum in order to achieve good composite properties. To date, most investigations on fiber based WPC use laboratory scale technologies to avoid the feeding problem [6]. Others used pelletizing technologies to densify the fibers in order to achieve a controlled feeding into the extruder. But a significant reduction in fiber length is observed due to high shear forces during pelletizing resulting in decreasing reinforcement capability [7]. In order to solve the feeding problem and to eliminate fiber agglomeration as well as a drying step, we developed a novel on-step compounding process for TMP-fiber based WPC. A "12 pressurized disc-refiner was used in order to defibrate wet wood chips as well as melt neat polymer granulates (PP and HDPE) and compound it together in one process step. Fiber/polymer content was set from 50-50% and 70-30% (w/w) without any additives. The material after process show a typically TMP-fiber with chopped polymer particles which were inseparable connected to the fiber. In a further step we pelletized and dried the compound and produced injection molded test specimen. For reference commercially wood flour with PP and HDPE were compound via a twin-screw extruder. The mechanical properties revealed comparable results to the reference. It is shown that process is a promising way to produce TMP-fiber and compound it with thermoplastic polymers in one step.

### Keywords:

WPC, Compounding, TMP-fibers, Refiner

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## SESSION 5-4

### STEAM EXPLOSION AS A TREATMENT OF HEMP FIBERS (*Cannabis Sativa L.*) FOR PRODUCTION OF COMPOSITE MATERIALS

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Steam explosion was described by several authors to be an effective method for the separation of fibers from lignocellulosic biomass [1]. Steam process involves four stages [2]: steam penetration into the fibers, degumming, fibrillation and cellulose degradation. The control of the process is essential in order to make an efficient treatment without altering the cellulose fiber. Several parameters can be modified to change the severity of the treatment (temperature (T), time (t), soda concentration in impregnation liquid (C)).

Composite materials were prepared with hemp fibers (20%) and polypropylene (80%), with a twin screw extruder, and with two different rotation speeds: 250 and 750 rounds per minute. The output was 3000 grams per hour. Several groups of fibers were processed:

- Untreated fibers
- Carded untreated fibers
- Exploded fibers (conditions A : T = 190°C, t = 3 min, C = 0 %)
- Exploded fibers (conditions B : T = 210°C, t = 5 min, C = 6 %)

Mechanical tests (tensile strength) were made with a dynamometer to characterize the different samples. The best results of Young's modulus were obtained with exploded fibers (conditions A). The lignin relocation on the fibers surface after steam explosion could cause a better adhesion between the matrix and the fibers.

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#### Key words

Hemp fibers, steam explosion, composite materials





## ELUCIDATING THE ROLE OF AMMONIA-BASED SALTS ON THE PREPARATION OF CELLULOSE-DERIVED CARBON AEROGELS

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The effects of using  $(\text{NH}_4)_2\text{SO}_4$  as a carbonization promoter for producing cellulose-derived carbon aerogels (CAG) was studied. The effects of pretreatment on the textural, morphological, and chemical properties of pristine cellulose nanofibers (CNF) were analyzed through  $\text{N}_2$  adsorption, scanning electron microscopy (SEM), X-ray diffraction (XRD), elemental analysis, inductively coupled plasma optical emission spectrometry (ICP-OES), and Fourier transform infrared spectroscopy (FT-IR). Furthermore, the thermal behaviors of raw CNF and those impregnated with  $(\text{NH}_4)_2\text{SO}_4$  were investigated by coupling thermogravimetric analysis with mass spectrometry (TGA-MS). The results suggested that the pretreatment did not cause any morphological/structural changes in the nanofibers. However, the presence of  $(\text{NH}_4)_2\text{SO}_4$  affected their pyrolysis by favoring intermolecular dehydration, thereby reducing the formation of levoglucosan and increasing the carbon yield during pyrolysis. Interestingly, above certain impregnation level, the concentration of sulfate-derived species in the gas phase increased. This phenomenon was attributed to an excess of salt within the fiber structure and on their surfaces. Consequently, the levoglucosan-to-carbon route was inhibited, and the mechanisms of intra- and inter-molecular dehydration, chain scission, and crosslinking reactions were affected, leading to a reduced char yield. The chemical effects of ammonia-based salts is elucidated supported on the interpretation of MS signals and kinetic modeling results.

## SYNTHESIS OF VISIBLE-LIGHT RESPONSE TiO<sub>2</sub> AND ITS APPLICATION TO CARBONIZED BOARD

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TiO<sub>2</sub> has been attracted a great deal of interests as photocatalyst due to its redox capability under ultraviolet (UV) irradiation as well as non toxic material. These exclusive properties of TiO<sub>2</sub> lead a wide-ranging applications such as degradation of organic compounds, deodorization, and anti-bacterial treatment. Many scientists have been conducted researches to apply TiO<sub>2</sub> onto variety of materials. A crack- and twist-free carbonized board has been developed from medium density fiberboard (MDF), plywood, and wood panels. The carbonized board showed outstanding performance on formaldehyde removal, but poor performance on aromatic volatile organic compounds. To improve the performance of carbonized board, we have attempted to combine photocatalyst, TiO<sub>2</sub>, and carbonized board. TiO<sub>2</sub> supported carbonized boards were prepared by one-step and two-step methods [1,2], and both sample showed excellent toluene removal performance under UV light. The objective of this study was to develop visible-light response TiO<sub>2</sub> on carbonized board for using in indoor condition that uses usually visible-light. To have photocatalytic activity under visible-light, metal doping is one of the solutions. Therefore, we have conducted to synthesize visible-light response TiO<sub>2</sub> using the metal doping method. Titanium tetrapropoxide (Ti-tip), cobalt nitrate, and iron nitrate were used as a precursor materials for metal doped TiO<sub>2</sub> synthesis. A 5 mol% of cobalt nitrate or iron nitrate was mixed with 50% diluted Ti-tip in isopropanol (IPA) and then spread on the surface of MDF. The metal doped Ti-tip treated MDF was carbonized in electronic furnace at 800°C for 2 h. The XRD results showed that crystal form of metal doped TiO<sub>2</sub> was similar to rutile form of TiO<sub>2</sub>. Based on SEM-EDS images, metal doped TiO<sub>2</sub> was well distributed on the surface of carbonized board. Toluene removal test was conducted by modified 20 L chamber system with commercially common fluorescent lamp as light source. Metal doped TiO<sub>2</sub> carbonized board showed 100% toluene removal performance under visible-light at 15 h. No significant difference between cobalt and iron doping on toluene removal test. However, it was slower than TiO<sub>2</sub> supported carbonized board under UV light. For the future study, XPS and DRS analysis will be conducted to understand characteristics of synthesized metal doped TiO<sub>2</sub>.

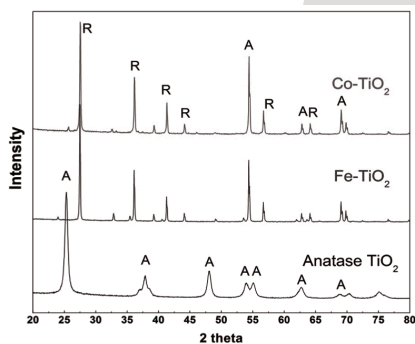


Fig.1 - XRD results of synthesized metal doped TiO<sub>2</sub>.

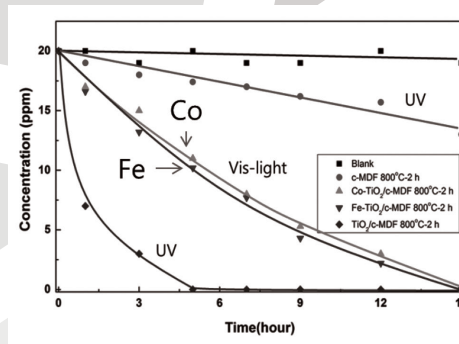


Fig.2 - Toluene reduction performance of different types of TiO<sub>2</sub> supported carbonized board.

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## ESTERIFIED LIGNIN AS HYDROPHOBIC AGENT FOR USE ON WOOD PRODUCTS

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Lignin from Spruce and Eucalyptus wood was isolated by organosolv process, and subsequently was chemically modified using a long aliphatic chain (12C) of lauroyl chloride as reagent [1], to obtain a hydrophobic lignin derivative to be used as protective agent on wood products (Figure 1). Each esterified lignin was applied on wood veneers by two different methods. First method was to apply as coating using for that a press moulding (current industrial processing technology) at two different conditions [2]. The second method consisted in impregnation using acetone as solvent and immersing the samples during different periods of time. The chemical modification of lignins was confirmed by FTIR, GPC and DSC resulting in an increase of its molecular weight and great reduction of glass transition temperature, allowing to process lignin by press moulding besides improving the solubility in acetone.

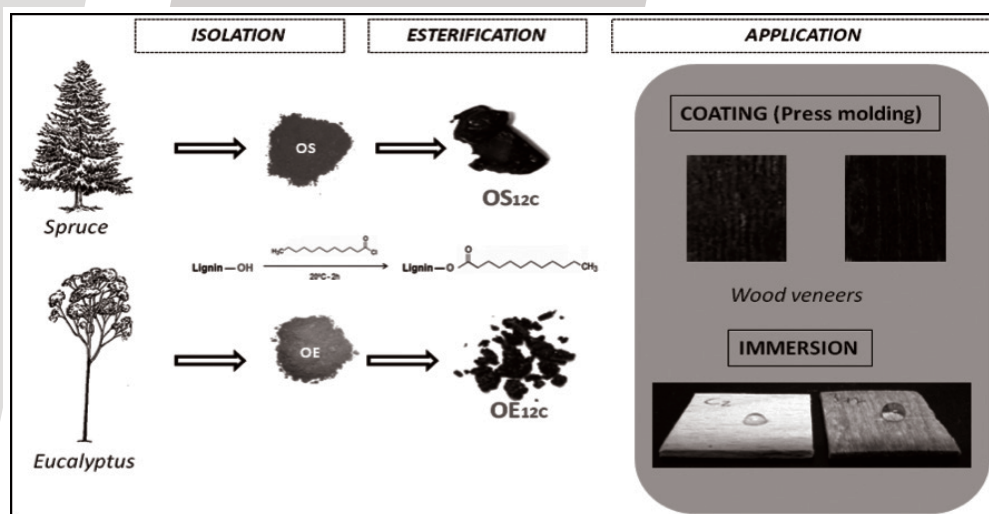


Figure 1: Graphical abstract of process.

The wood hydrophobicity ( $WCA \approx 140^\circ$ ), oleophobicity ( $OCA \approx 120^\circ$ ) and stability against water and oil dramatically increase after treatments observed by dynamic contact angle analysis. Besides, the efficiency of treatments over time was confirmed by accelerated aging test.

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### SURFACTANT PROPERTIES OF ALKENYL SUCCINATES DERIVED OF LIGNINS

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After cellulose, lignin is the second most abundant biopolymer in the vegetable world. Lignin is founded in the cell walls of plants and represents 15-40% by dry weight of plant biomass.

Since lignin is a natural phenolic polymer, it is used in various fields and there are a variety of potential products obtainable by chemical modification, including surfactants [1]. The limited supply and increasing cost of surfactants for different applications have led to the study of renewable resources as alternative sources, based on the biomass feedstock readily available and inexpensive. In this regard, the technical or commercial lignins are of great interest because they represent a byproduct in the production of pulp industries for papermaking, which usually is burned to generate power and recover the reagents used in the process; however, this byproduct can be harnessed for obtaining aromatic derivatives of industrial interest [2].

To enhance surfactant properties of lignin is necessary to change existing functional groups in order to change its hydrophilic-lipophilic balance (HLB). Therefore, the chemical modification of lignin was performed by an acylation reaction with alkenylsuccinic anhydrides (C<sub>9</sub>, C<sub>12</sub> and C<sub>16</sub>), by microwave assisted controlling the reaction parameters. The characterization was carried out by Fourier Transform Infrared Spectroscopy (FTIR). In the FTIR spectra of lignin derivatives it was observed decreased band corresponding to the characteristic hydroxyl groups of the biopolymer (where the reaction occurs), and the appearance of the band associated with the carbonyl groups of carboxylic ester and acid incorporated into structure by ring opening of the anhydride. On the other hand, the evaluation of surfactant properties showed that all the derivatives decreased surface tension of water a greater proportion than the starting lignin. The surfactant character of the derivatives obtained increases with the number of carbon atoms in the chain alkenyl anhydride incorporated due to the hydrophobic effect that makes the derivative migrate to the surface instead of remaining within the solution.

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## MICROENCAPSULATION OF POLYPHENOLS EXTRACTED FROM *Pinus radiata* BARK

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*Pinus radiata* bark extract contains several polyphenolic compounds with bioactive properties. Previous studies in our laboratory have shown a potent *in vitro* antioxidant activity of these extracts [1]; these properties, coupled with the lack of toxicity of the extracts, suggest a potential use in phytopharmaceutical applications. However, the direct application of the pine extracts in oral pharmaceutical formulations is limited because of their instability in the digestive tract environment. To overcome this limitation, the microencapsulation process promises to be the solution to allow oral intake.

The objective of this study was to stabilize phenolic extracts obtained from *Pinus radiata* bark by microencapsulation, using the spray drying method and to evaluate the influence of the polysaccharide type on the physical and chemical characteristic of the particles.

The microparticles were elaborated using alginate and maltodextrin as encapsulating agents in different proportions (0, 25, 50, 75 and 100%); the selection of these polymers was due to their proved high encapsulation efficiency and metabolic safety in the host organism. Water was used as the solvent, with an initial charge of 10% extract in a laboratory spray dryer (Büchi B-290). The obtained particulates were characterized in their size distribution (Microtracks 3500, based on laser diffraction), morphology (visualized by scanning electron microscopy (SEM)), process yield (mass %), encapsulation efficiency (total phenols by Folin Ciocalteu), antioxidant capacity (DPPH), residual moisture and density.

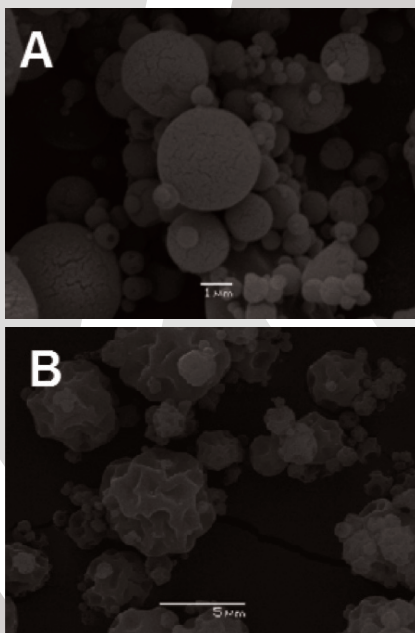


Figure 1 - SEM images of alginate and maltodextrin microparticles

Images obtained by SEM of microparticles containing *P. radiata* bark extract, elaborated using (A) alginate and (B) maltodextrin as encapsulating polymer.

The results were spherical monodisperse microparticles (Figure 1), with smooth or rough surface, depending upon the predominant excipient (alginate or maltodextrin), respectively. The average diameters range varied from 1.01 and 4.03  $\mu\text{m}$  depending on the evaluated proportions. While the process yield range was 58.5 to 72 depending on each combination; which was better than reported levels for pilot scale production [2]. The encapsulation efficiencies ranged from 73.76 to 92.68%. Residual moisture and density ranged from 1.53 to 8.84% and 0.378 to 0.444 g/mL respectively. Measurements had variation coefficients of less than 3%, except for the size distributions, due to the production method of the microparticles by the spray dryer technique.

Thus, we conclude that is feasible to produce microparticles with high entrapment efficiency levels of phenolic extracts of *Pinus radiata* bark and with consistent characteristics of size for future oral administration in salmon.

### Acknowledgments

The authors thank to the Project InnovaCorfo12IDL2- 13353 for the funding for this research.

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**POSTER**

## **SECOND GENERATION AMINO RESINS**

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Project 2GAR is promoted by Euroresinas, involving as partners Faculdade de Engenharia da Universidade do Porto, Instituto Politécnico de Viseu and Associação Rede de Competência e Polímeros. The project aims to introduce novel properties in the formaldehyde-based resins ("amino resins") produced by the company. This allows Euroresinas to assume a more competitive position in existing markets and penetrate into new markets, both national and international. The project assumes three fundamental objectives: a) provide amino resins with higher storage stability, so as to allow transportation by boat to international costumers; b) provide the resins with the necessary resilience and elasticity for producing flexible panels based on cork granulate; c) incorporate a significant amount of nature-based raw materials in amino resins.

The project is based on a strong interaction between all partners along all its execution phases, taking advantage of both the individual competences and the synergies generated by joint work, as already demonstrated in previous projects. It is intended to end the project with the production of new formulations in industrial reactor, followed by application, by final clients, in production of wood and cork composite panels (wood-based panels and composition cork).



**AB02**



**Biocomp 2016**

The 13<sup>th</sup> Pacific Rim Bio-Based Composites Symposium  
Bio-based composites for a sustainable future  
November 13<sup>th</sup> to 15<sup>th</sup>, 2016 - Concepción - Chile

**ENGINEERED WOOD PRODUCTS MADE WITH 100% BIO-BASED ADHESIVES: NEW APPROACHES TO DESIGNING ADHESIVES FOR WOOD PANEL MANUFACTURE**

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Scion is developing a 100% bio-based adhesive technology for engineered wood products (EWP) providing products that are green, sustainable and do not use formaldehyde. This new adhesive technology uses ingredients from forestry and agricultural processing residues including lignins and proteins. These feedstock ingredients are altered in a chemical process so that their formulation together provides suitable adhesive properties and performance. Efforts have focused on using lower value ingredients and understanding the relationships of ingredient purity and chemistries to adhesive and panel performance. Discussed is the suitability of the bio-adhesive technology for three EWPs: medium density fibreboard, particleboard and plywood. Minimum performance requirements can be met for all three products including strength and water resistance, together with negligible formaldehyde emissions which are below the background emissions of wood.

## INFLUENCE OF TREE HEIGHT IN THE CHEMICAL COMPOSITION OF THE LIPOPHILIC EXTRACTS FROM THE *Eucalyptus Nitens* BARK

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Industrial processes of the forest industries generate large amounts of waste material, in particular bark. The vast majority of these industries burn the bark to produce energy, which is used by the industry or simply sold. This combustion process has low efficiency and a damaging effect for the used equipment, due the high quantity of resins present in the bark. *Eucalyptus Globulus* (*E. Globulus*) and *Eucalyptus Nitens* (*E. Nitens*) are widely cultivated by the forest industries and have acquired a great importance in Chile due to its fast growth, making up 33% of the total forest plantations in the country in 2014 [1]. For this reason, it is interesting to obtain chemical products of commercial interest from the eucalyptus bark, improving its use, prior to being used as fuel.

The aim of this study was to characterize lipophilic extracts obtained from *E. Nitens* bark. A lipophilic-compounds extraction protocol from *E. Nitens* bark was formulated; determining the influence of tree height in the extraction yields and chemical characteristics of the bark extracts.

Bark from three *E. Nitens* trees aged between 10-12 years, with similar height (34,666±2,516 m), was sampled from "Forestal Comaco" Industries. These trees were sectioned into five equidistant cuts along each tree. After debarking, drying and grinding of the samples, the lipophilic components of the ground bark were extracted by Soxhlet extraction with dichloromethane. Subsequently, the extracts were qualitatively characterized by GC-MS analysis.

An extraction protocol, for *E. Nitens* bark lipophilic compounds was successfully elaborated. Extraction yields showed a rising profile correlated with tree height, obtaining higher yields in the superior cuts of the tree (0,85 % at the top of the tree) than in the bark obtained from the bottom (0,51 % on the tree stump). The values were comparable with lipophilic extracts obtained from *E. Globulus* by Domingues [2]. Finally, the lipophilic extracts of *E. Nitens* were chemically characterized, obtaining greater amounts of sterols and triterpene acids (compounds of commercial interest) in the bark from the top of the tree, than from the bottom. Among the identified compounds were found: lupane, oleanane and ursane triterpenic derivatives and sterols such as  $\gamma$ -sitosterol and stigmasta-3,5-dien-7-one, which were found in the top of the trees in 145%, 32%, 159%, 115% and 226% more than in the bottom, respectively; besides  $\beta$ -amyirin which was found only in the top of the tree. These findings were consistent to the compounds described by Domingues who analyzed the inner and outer *E. Nitens* bark separately [3]. The named compounds possess anti-inflammatory, anti-cancer and anti-tumor properties, among others [4], which could potentially be used for the formulation of a phytodrug.

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## FILMS BASED ON FUNGAL BIOMASS DERIVED CHITOSAN

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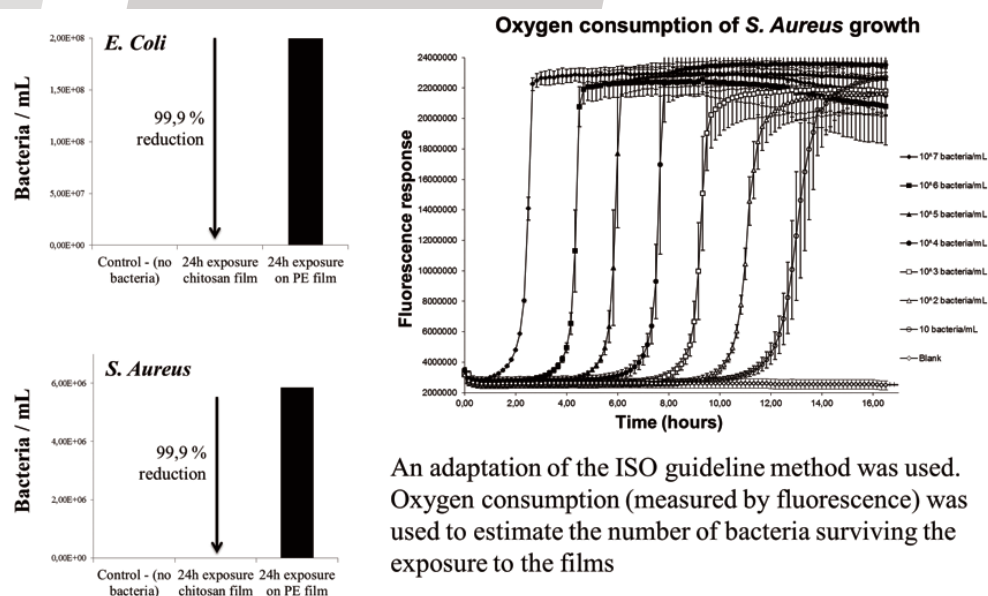
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Contemporary environmental consciousness sturdily encourages the development of biodegradable materials instead of synthetic polymers used for packaging purpose. Chitosan, mostly extracted from crustaceans, has long been used in the preparation of edible films, and as a carrier of several functional. The aim of this work was to evaluate the properties of films prepared from a commercially available fungus-derived chitosan (Kionutrime CsG, Kitozyme). Kionutrime CsG and crustacean-derived chitosan (Sigma) films of different composition were prepared by casting, and their chemical and mechanical properties were comparatively studied. Glycerol was used to facilitate processing and increase films flexibility.

Results showed that Kionutrime CsG based films have slightly higher thickness and lower water uptake rate than crustacean-derived chitosan films and showed a significantly lower tensile strength and elongation-at-break. These mechanical properties are correlated with a lower molecular weight (MW visc) and temperature of decomposition (TGA analysis) of the chitosan molecules in Kionutrime CsG. The antimicrobial activity against two different bacterial strains (*E.coli* and *S. Aureus*) under dynamic contact conditions (for 24h) was evaluated using PET film as control (Figure 1).



No living bacterial cell was detected after the exposure on the chitosan film

Fig. 1- Antimicrobial activity of chitosan based films against two different bacterial strains (*E.coli* and *S. Aureus*) under dynamic contact conditions.

A clear antimicrobial effect was observed on Kionutrime CsG films. A partial dissolution of chitosan molecules on the surface of the film in contact with the exposure medium is likely involved in the observed bactericide effect. Additional works are underway to improve the mechanical and chemical properties of fungal chitosan based films.

## ANTIMICROBIAL ACTIVITY OF MODIFIED/UNMODIFIED POLYFLAVONOIDS AND LIGNIN FROM *Pinus radiata* OBTAINED UNDER PILOT-PLANT SCALE

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### ABSTRACT

Polyflavonoids from *Pinus radiata* were extracted under pilot-plant scale conditions at 120°C during 120 min as described by Bocalandro *et al.* (2012). Extractions were carried out in a reactor (volume 4 m<sup>3</sup>) using a methanol/water solution (1:20, w/v). Once the polyflavonoid extract had been obtained, it was evaporated under vacuum (absolute pressure: 0.05 bar) to remove the methanol, thus obtaining two fractions (1) the water-soluble (TS), and (2) the water-insoluble (TI) one obtained after decanting. Lignin (L) from *P. radiata* was extracted by the Acetosolv process in acid media (García *et al.*, 2016). Polyflavonoids and lignin were modified with maleic anhydride by several synthesis pathways (20 °C, 24h). Physicochemical properties of derivatives were analyzed by spectroscopy methods (FT-IR, <sup>1</sup>H- RMN). Anti-microbial activity was studied using aerobic mesophilic (AM) isolated from a Chilean food- processing industry. Minimum Inhibitory Concentration (MIC) was calculated, and the results expressed in part per million (ppm). The water-insoluble polyflavonoids fraction (TI), and modified TI showed the major antimicrobial activity. The others modified/unmodified polyphenolic (TS, and L) building-blocks showed low antimicrobial activity.

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## GROWING UP IN DIFFERENT ALTITUDE: CHANGES IN THE GROSS CALORIFIC VALUE AND ELEMENTAL COMPOSITION OF *Abies religiosa* WOOD

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Nowadays, wood energy is an important natural and renewable resource that has been used since the beginning of civilization [1, 2]. Therefore, it is important to measure the caloric value of wood in order to know its energy potential. This parameter is closely related to the elemental chemical composition of the material [3, 4]. It has been reported that the elemental composition of some trees changes along the different sites of growth and their respective environmental conditions (for example at different altitudes in meters above sea level, masl) [5, 6]. Consequently, the aim of this study was to evaluate whether the gross calorific value (GCV) of wood and its elemental composition changes significantly along different altitudes. We used *Abies religiosa* wood as a model study. Wood samples from six trees at six different altitudes within a range from 3,000–3,500 masl (36 trees) were collected and analyzed: GCV and elemental composition (percentages of carbon, oxygen and hydrogen). We found that the GCV changed significantly at different altitudes and also the elemental composition. Our results indicate that *A. religiosa* wood which grew at 3,100, 3,300 and 3,400 masl have more energy amount than wood which grew in 3,200 and 3,500 masl. For that reason, we conclude that the energy quality from this kind of wood changes significantly in relation to the altitude.

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## ESTIMATION OF WASTE MEDIUM DENSITY FIBREBOARD GENERATION FROM DIFFERENT SOURCES FOR ITS RECYCLING IN KOREA

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Recycling of waste medium density fibreboard (wMDF) panels is very important in the viewpoint of raw material acquisition and environmental issue. Recycling of wMDF panels requires to estimate the amount of wMDF panels generated, to establish ways of collecting and sorting them, and to develop technology of isolating recycled fibers from them. This paper was conducted to estimate the amount of wMDF and to come up with a reasonable ways of collecting wMDF in Korea. Most of wMDF panels were generated from urban solid wastes and industrial wastes, including urban solid waste and construction wastes. The analysis these solid wastes showed that wMDF, particleboard, solid wood, and plywood were 39.5%, 19.7%, 17.1% and 5.7%, respectively. It was also estimated that the total wMDF panels were 988,554 tonnes per year in Korea, including 144,864 tonnes from MDF mills, 125,808 tonnes from furniture industry, 15,396 tonnes from building materials, and 702,065 tonnes from solid wastes. These results indicate that about 10% of raw wood chips for MDF production could be replaced when about 60% of wMDF from MDF mill and furniture industry.



## PRELIMINARY STUDY OF FRACTIONATION AND PURIFICATION OF STILBENOIDS FROM EXTRACT OF *Vitis vinifera* (PINOT NOIR) GRAPE CANE BY ADSORPTION ON MACROPOROUS RESINS (XAD-7)

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### ABSTRACT

The interest on phenolic compounds, especially stilbenoids and procyanidins, has risen up in the last two decades due to their benefits on human health. Residues from wine industry have been the focus of many studies searching for such metabolites all around the world. Grape canes, obtained after annual pruning of vines, is a waste estimated in more than 120.000 tons per year only in Chile. They contain much higher levels of stilbenoids than grape, wine and other winemaking residues [1].

In this work, we report the extraction at pilot plant scale of Pinot noir grape canes, using a 750 L reactor and 80% ethanol/water (v/v) mixture as solvent. Qualitative and quantitative determination of stilbenoids and other phenolic compounds, mainly procyanidins, were performed by HPLC-DAD-ESI-MS/MS. Other chemical constituents, including carbohydrates, organic acids, metals, and lignin were also detected and quantified. The dry extract obtained under optimal conditions (T: 80°C, t: 100 min, solid/liquid ratio 1:10) showed a yield of 2.4 g of stilbenoids per kg of dry grape cane, with a total stilbenoid concentration of 5.45%.

In addition, the purification of the obtained extract to separate stilbenoids and procyanidins from lignin and carbohydrates was evaluated by using a macroporous XAD 7 resin at different ethanol proportions in the eluent. Stilbenoid concentration in the product was increased to 46.6% and 49.9% eluting with 20 and 40% of ethanol, respectively.

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### Acknowledgments:

CORFO Grant 14IDL2-30156, Proyecto Basal PFB-27, CONICYT

## CARACTERISATION OF NETTLE FIBERS PRODUCED BY STEAM EXPLOSION

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The current development of natural fibers and bio-based materials are motivated by legislation as well as customers demands for more sustainable and environment-friendly products. Nettle is a well-known plant and is generally considered as a weed. Recently, the scientific community showed a renewed interest in this plant for phytotherapeutic uses and for fibers production (figure 1).

In this work, individual nettle fibres were produced using a steam explosion process [1,2]. The steam explosion parameters were set to 210°C and 5 minutes and 210°C and 2.5 minutes after a maceration step using H<sub>2</sub>O or 5% NaOH.

The yields before and after carding process were determined. Unitary fibres percentage was obtained and morphological properties (diameter and length) and distribution were measured. Mechanical properties (tensile strength and elasticity modulus) were obtained by standard methods. These values have been compared to three different industrial cotton fibres. Around 2% of lost production was detected after carding process. The unitary fibers percentage was almost 100% with a texture very similar to that of cotton. Almost all unitary fibres presented a diameter lower than 30 µm. The tensile strength and elasticity modulus showed an important variability. Nevertheless, the mechanical properties of the nettle fibers have displayed values comparable to those of the cotton fibers (figure 2 et 3). Utilizations of these fibers in the fields of textile and composite will be considered in future works.

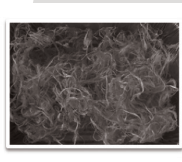


Fig.1 Nettle fibers obtained by steam explosion method.

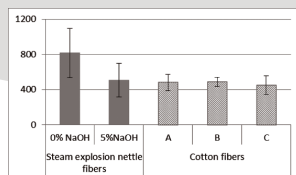


Fig.2 Nettle fibers and cotton mechanical resistance (MPa)

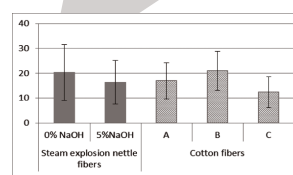


Fig.3 Nettle fibers and cotton elasticity modulus MOE (GPa)

### Key words

Nettle fibers, steam explosion, unitary fibers.

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Acknowledgements The authors gratefully acknowledge the financial support of the Newfibre project, through regional (Région Lorraine) and European (FEDER) funds.



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## **PRODUCTION OF FIBERS FROM METAL-RICH PHYTOREMEDIATION HEMP**

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Phytoremediation constitutes a sustainable approach for polluted soil clean-up and or pollutant stabilization in the soil. However, there are some concerns about the utilization of metals-rich biomass and about fate of heavy metals after biomass disposal. In this study, the production of fine fibers from phytoremediation metal-rich hemp was studied using steam explosion treatment.

The main goal of this work was to determine the heavy metals distribution in the fractions of the process (fibers, liquid effluents). Utilization of the fibers for material application is discussed.

## BACTERIAL POLYHYDROXYALKANOATE FOR ELECTROSPUN FIBER PRODUCTION

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Electrospinning is a technique for production of polymeric fibers with diameters in the nano- and micrometer range, offering high flexibility in terms of material choice. A number of diverse polymeric materials have been electrospun, including synthetic and natural polymers [1]. Electrospun fibers have shown great applicability for novel materials in packaged foods, tissue engineering, wound healing, bioactive molecules delivery, as well as sensor, filtration, composite reinforcement, and nanoelectronic applications [1]. Polyhydroxyalkanoates (PHAs) are biopolyesters synthesized by microorganisms. The diversity of structure of PHA depends on the bacterial species and growth conditions [2]. These well-known biosynthetic and biodegradable bioplastics have been used for the development of diverse applications [3]. *Burkholderia xenovorans* LB400 is a model bacterium for degradation of aromatic compounds. LB400 cells grown on glucose are capable to synthesize poly(3-hydroxybutyrate) (PHB) [4]. The aim of this study was to produce electrospun fiber from bacterial PHB for industrial applications. Strain LB400 was grown in M9 minimal medium using two different carbon sources i.e. xylose and mannitol (10 g L<sup>-1</sup>) and 1 g L<sup>-1</sup> NH<sub>4</sub>Cl. Cells were freeze-dried and PHB was extracted with chloroform and dried at room temperature. Biopolymer-based films were used to produce fibers by electrospinning under an applied voltage adjusted at 25 kV, a flow rate of 0.5 mL h<sup>-1</sup> for biopolymer solution and a rotor speed of 25 rpm, under room conditions (25°C, 50% relative humidity). The nanofibers were collected on an aluminium foil at a distance of 25 cm. Fiber diameter and morphology ( $Y_d$  and  $Y_m$ ) were analyzed by scanning electron microscopy (SEM).

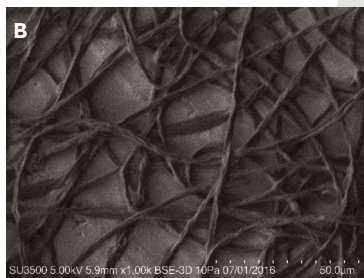
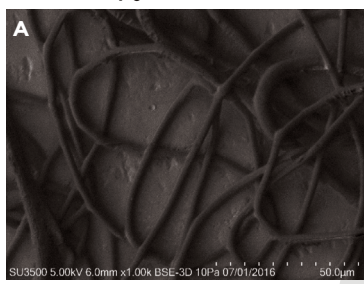


Fig. 1. SEM micrographs of electrospun microfibers using different carbon sources as substrate for LB400 bacterial growth.

A) PHB produced from xylose. B) PHB produced from mannitol.

Bead free fibers using both PHBs were obtained (Figure 1). The fiber diameter ( $Y_d$ ) and morphology ( $Y_m$ ) using PHB from xylose was around 2.6  $\mu\text{m}$  and 0.9625, respectively, whereas using PHB from mannitol the  $Y_d$  was lower (2.2  $\mu\text{m}$ ) and  $Y_m$  of 0.9875. As shown in Figure 1, the surface morphology of both microfibers seems to be different even though to be produced from the same polymer. The results indicate that the carbon sources determine the fiber structures and properties. Further studies should be performed for analyzing the physicochemical and mechanical properties of these PHB-based microfibers which may open up novel applications.

### Acknowledgments

This research was supported by funding from CONICYT through FONDECYT (11140127 & 1151174), USM (131342 & 131562), Red RIABIN and CNBS.

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## COMPOSITE PANELS MADE FROM TETRA-PAK AND POLYETHYLENE WASTE MATERIALS

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The utilization of different household wastage is one of the biggest problems all over the world. Waste from plastics industry is portraying more important problem with a significant increase in countless production lines of plastics based material last several decades. Plastics waste materials have their relatively long period of degradation. It was estimated that polyethylene would degrade less than 0.5 % in 100 years, and 1 % if exposed to sunlight for 2 years before biodegradation [1]. The cardboard and paper packaging such as Tetra-Pak have been on the market and their popularity substantially increased. Cardboard and paper packaging represent the largest proportion of household waste composition by weight.

Therefore, the aim of the study was to produce panels from different waste such as Tetra-Pak and polyethylene particles and determine basic engineering properties of the samples. Three types of waste particles, namely Tetra-Pak (Fig 1, a), PE films (FPEF) (Fig 1, b), candy PE wrappers (CPEW) (Fig 1, c) were used as raw material to manufacture composite panels. All particles were dried to reach 10 % moisture content in a laboratory oven prior they were manually mixed based on ratios. Composite panels (Fig 1, d) were pressed at the temperature of 200oC and pressure of about 3.5 MPa and the duration was 1.2 min/mm. The target density of composite panels was 900 kg/m<sup>3</sup>.

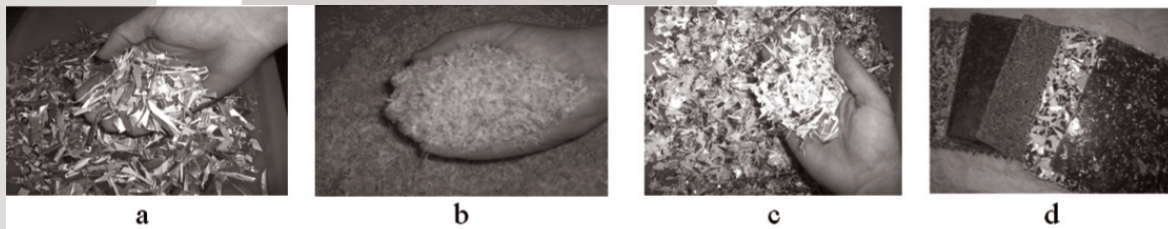


Fig.1. Raw materials and composite panels: a) Tetra-Pak; b) FPEF; c) CPEW; d) Composite panels

The results showed that the highest modulus of rupture (MOR) value of 15.5 MPa was determined for the samples having 40 % Tetra-Pak and 60 % CPEW particles. MOR values of the panels decreased with decreasing content of CPEW in the samples. The increased content of Tetra-Pak particles in the samples also resulted in reduction of their strength characteristics and dimensional stability. Properties of the samples considered in this work satisfied minimum requirements of typical particleboard stated in EN standards. Therefore, the findings of this study showed that waste packaging materials such as Tetra-Pak particles, FPEF and CPEW can be used as raw materials for value-added composite production. Such utilization of waste packaging materials and the production of such panels have a significant influence with high ecological impact.

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## DYNAMICS OF SMALL MOLECULES IN METAL-ORGANIC FRAMEWORKS (MOFs) STUDIED BY $^2\text{H}$ AND $^{13}\text{C}$ SOLID-STATE NMR

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MOFs (Metal-organic frameworks) are a type of new hybrid porous materials, consisting of metal ions and organic linkers [1]. MOFs possess potential applications in various sectors such as separation, gas storage, catalysis and controlled drug delivery [2,3]. Solid-state NMR (Nuclear Magnetic Resonance) is a unique tool of investigating this potential material which allows to obtain detailed information about the guest dynamics due to structural particularities of different MOFs as well as host-guest interaction.

Here we report solid-state NMR study on MIL-53(Al) and CPO-27-M (M=Ni and Co) to follow the guest dynamics after adsorbing different relative amounts of small molecules, e.g., deuterated acetone [ $(\text{CD}_3)_2\text{CO}$ ] and  $\text{CO}_2$ , respectively [4,5]. Deuterium ( $^2\text{H}$ ) SSNMR is performed to follow the dynamic features of [ $(\text{CD}_3)_2\text{CO}$ ] in MIL-53(Al). Deuterium is a quadrupolar nuclei and the detailed analysis of the observed characteristics line shapes of adsorbed species allowed us to get motional information. In CPO-27-M (M=Ni and Co) MOFs  $^{13}\text{C}$  enriched  $\text{CO}_2$  is adsorbed with respect to the metal atom.  $^{13}\text{C}$  wide-line NMR spectra were recorded at variable temperature to follow the dynamic behaviour, host-guest interaction and adsorption process of the gas molecules in the adsorbed state. The presence of paramagnetic  $\text{M}^{2+}$  makes the NMR characterization complicated and the paramagnetic effects i.e., shift of spectral lines and line broadening is observed. Two different scenarios are observed when  $\text{CO}_2$  is adsorbed in CPO-27-M (M=Ni and Co) which indicates that dynamics of adsorbed species are different though these MOFs are isostructural.

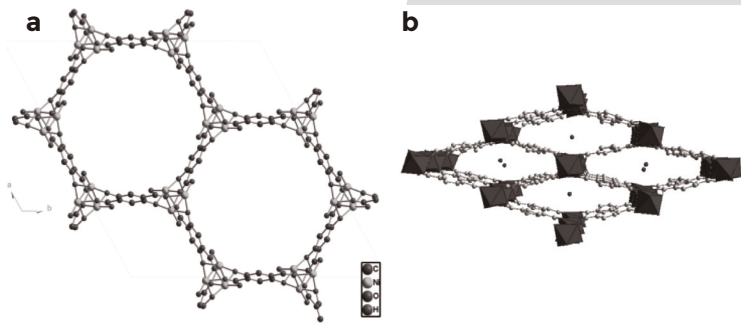


Figure 1. Crystal structure of a) CPO-27-M and b) MIL-53(Al)

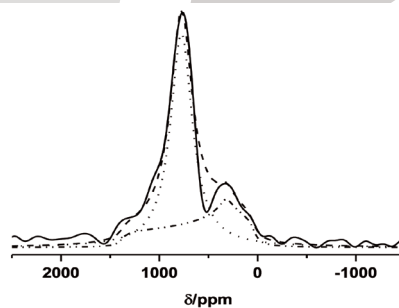


Figure 2.  $^{13}\text{C}$  static spectrum with simulation for  $0.5 \text{ CO}_2/\text{Ni}$  recorded 223 K. The dotted and dashed-dotted lines represent the mobile and rigid components of the spectrum. The dashed lines represent the sum of the two components.

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## EFFECT OF DIFFERENT POLYMER BLENDING ON THE MECHANICAL PROPERTIES OF POLYPROPYLENE BASED WOOD PLASTIC COMPOSITE

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Wood-plastic composites (WPC), which is made from wood flour, polymer and additives improves some mechanical properties such as tensile strength and stiffness compared to pure polymer. However the remarkable reduction of impact resistance is one of the critical drawbacks of WPC for many applications. Although a lot of investigations about impact strength of WPC has been reported, only few studies are focused on the improvement of impact strength [1]-[3]. In this research, the effect of different polymer blending on the impact strength of WPC was investigated to clarify the effect of interfacial adhesion in the composites.

Polyethylene (PE), polyvinyl butyral (PVB) and elastomers were added into PP based wood flour composite in order to improve impact strength. Several experimental conditions including addition of different kind of compatibilizers were tested to evaluate the relationship between interfacial adhesion condition and mechanical properties of composites.

In the case of PE blended composite, mechanical properties decreased with increase of PE content. At 20 wt% PE, no remarkable effect of the compatibilizer and mixing procedure on the mechanical properties was found. On the other hands, addition of elastomers improved the impact strength without any decrease of bending and tensile properties. However, the properties of PP and PE based WPC with elastomers were still lower than that of PP based WPC.

In the case of PVB blended composite, further decrease of impact strength was observed. Bending and tensile strength were also lower than PP based WPC. These results suggest that PVB did not act as adhesive between PP and wood flour. Addition of elastomer improved the impact strength whereas decreased bending and bending properties of the composites. In terms of impact strength, elastomers were found to be most effective among three candidate additives.

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## SELF-BONDED COMPOSITE FILMS BASED ON CELLULOSE NANOFIBERS AND POLY(LACTIC ACID) MICROFIBRILS

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Cellulose nanofibers and poly(lactic acid) microfibrils, two biobased polymers were used to elaborate new films and their properties were evaluated. Cellulose nanofibers were obtained using high pressure homogenization while poly(lactic acid) microfibrils were obtained from a commercial partner. The objective of the present work is to evaluate a new approach to the symbiosis that the most abundant biopolymer (cellulose) [1] and the most popular synthesized bio-based polymer (PLA) [2] to give more applications and therefore open new markets, thus increasing the demand for these polymers in the industry, which will promote a decrease in their production, in particular for PLA, making them more competitive in the global markets. The results obtained confirmed the good affinity of these two polymers as well as the complementary properties that they contribute with as composites.

Self-bonded composite films with different composition were fabricated by hot pressing and their properties were evaluated. Mechanical properties at tension were measured with a universal testing machine; water vapor permeability was evaluated with a thermohygrometer and surface tension with sessile drop contact angle method. Furthermore, paper standards and thermal properties of the composites were also analyzed. The results presented show an important characterization of these composites as basis for further applications. Native cellulose (Cellulose  $\alpha$ -II) fibers were defibrillated using a Niro Soavi Panda homogenizer by high pressure homogenization ~1000 bar during 90 min (1:10 w/v) and then kept in freezer for their preservation. Cellulose nanofibers and PLA fibrils were mixed inside a beaker at 20 000 rpm with a paper blender, then the suspension was sonicated during 15 min to allow PLA oligomers to defibrillate from the main fibril and enhance the bonding with CNF. Water was extracted with a paper forming vacuum device and hot pressed at 110 °C for 5 minutes (185 kPa) with a Siempelkamp hydraulic press. The ratio between CNF and PLAmf was 100/0, 75/25 and 50/50 (referred as 100C, 75C and 50C respectively).

Figure 1 presents SEM images of the elaborated composites surface with 300x magnification, as well as an image of the breaking edge after tearing burst essay with a 55x magnification. The surface of 100C film presents the traditionally smooth surface of nanocellulose-based films; some rugosities can be observed and are attributed to the non-stick paper used during hot-pressing. When PLA microfibrils are added to the films, there is an evident anisotropic distribution, with entanglements and an increase in the pores due to entanglements, overlapping and the low compatibility of the composite films which leads to a porous rough material.

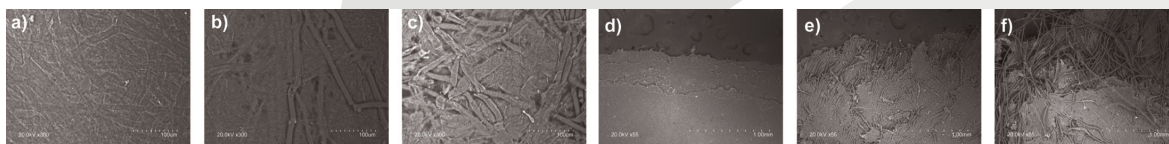


Fig.1 - SEM images of film composites a) and d) correspond to 100C, b) and e) to 75C and c) and f) to 50C; first row presents images of the surface of the composites and second row corresponds to fracture region after mechanical tests

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## GREEN COMPOSITES OF RESIDUAL MICROALGAE BIOMASS: ADVANCES IN MICROALGAE BIOMASS BIOREFINERY FOR BIODIESEL PRODUCTION

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Currently, the scientific are exploring new energy sources that are more environmentally friendly, renewable and sustainable. Our fossil fuel reserves are rapidly being depleted and significant environmental problems have been associated with the greenhouse effect generated by combustion gases, deterioration of the ozone layer, and global warming. A global concern is observed, for example: At the Paris climate conference (COP21) in December 2015, 195 countries adopted the first-ever universal, legally binding global climate deal. A great deal of scientific research has focused on the search for alternative fuels, sources of renewable energy, and fuels with lower combustion gas emissions. One of the most promising alternatives for replacing fossil diesel fuel is biodiesel and microalgae biodiesel. Currently, biodiesel production from microalgae is still at laboratory and pilot scale, this production of biodiesel generates a depleted biomass waste, otherwise known as residual microalgae biomass (RMB). The new concept development in this work was the biorefinery of microalgae. The main goal was the use RMB in biocomposite materials. Microalgae biomass of *Nannochloropsis gaditana* was used for biodiesel production by direct transesterification process. The chemical composition of the remaining RMB showed a high content of protein, for this reason, the RMB was a suitable alternative for green composites. The RMB was used in composites with Poly(butylene adipate-co-terephthalate) (PBAT), the composites were prepared by extrusion and injection molding, the content of RMB was 10, 20, 30% wt. The compatibilization between the matrix and RMB was studied for plasticization with glycerol and urea, and other method was used silane treatment. The biocomposites were characterized using FT-IR and thermogravimetric analysis, and their mechanical properties were compared, including tensile, flexural and impact strength (Fig. 1). The effect of RMB on the morphology of the polymer matrix was analysed by scanning electron microscopy and confocal laser scanning microscopy. The RMB can be used for the production of new "green composites" and new concept of material like film with microalgae for garbage bag or agriculture mulch film.



Figure 1: Residual microalgae biomass (a); Residual microalgae biomass plasticized with glycerol and urea (b); Green composites PBAT/RMB (80/20 wt) (c) and Green composites tested in Instron (d).

### ACKNOWLEDGMENTS

This research received financial support from CONICYT-FONDECYT Chile Grant 11121591 and Desert Bioenergy S.A. (from Innova-CORFO).

## THERMAL AND MECHANICAL CHARACTERIZATION OF COMPOSITES BASED ON A POLYMERIC MATRIX OF POLYLACTIC ACID, POLYETHYLENE GLYCOL AND TALC

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### ABSTRACT

New trends and market demands for the plastics industry requires polymeric materials with suitable thermal and mechanical properties preferably from renewable sources and biodegradables, thus, biopolymers have been established as an alternative for replacing existing synthetic polymers as part of the new engineering materials. Polylactic acid is a commercially available bio-based material obtained from renewable sources such as starch and sugar. It is one of the most widely used bioplastics due to its optical, mechanical and barrier properties, and good processability by conventional transformation techniques of thermoplastics [1]. PLA is classified as GRAS (Generally Recognized as Safe) by the FDA (American Food and Drug Administration), therefore have been used in fields such as medicine, environmental science and in food packaging applications.

Currently, PLA have a wide range of applications in food packaging industry of which are lately focused on PLA thermoformed used in containers for fresh fruit and vegetables [2,3]. However, many investigations have been carried out on the properties and applications of PLA because some properties still have been found do not reach the required characteristics for many potential applications [4]. Between some issues restricting the use of PLA is its poor technical performance compared with many conventional polymers, in this context, some strategies have been adopted to improve properties of PLA include blending with other bioplastics and/or the incorporation of additives such a filler to produce composite materials.

This study was based on development and characterization of a composite material based on a polymeric matrix of PLA and additives of PEG and microparticles of Talco. The composite was prepared by melt extrusion using twin screw extruder in a system of PLA/PEG/Talco with different composition ratios varying from 6 to 25 % w/w of additives.

The thermal properties of composites were evaluated using a differential scanning calorimetry (DSC). In comparison with pure PLA, glass transition temperature (T<sub>g</sub>) for all composites were shifted to lower values indicating the plasticizing effect of the PEG, independent of the presence of the talc particles. Opposite behavior was observed for cold crystallization temperature (T<sub>c</sub>) demonstrating a nucleating effect of talc particles in the polymeric matrix. Thermogravimetric analysis (TGA) results showed that the thermal stability of the composites decreases with increasing additives content in the matrix. Regarding the tensile test analysis, results show that the elastic modulus of the matrix of PLA is affected by incorporation of the additives, thus, as increase content of additives to PLA decrease elastic modulus, indicating higher rigidity of the PLA/PEG/Talc composites, however there was an increase in tensile strength for all composites.

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## EFFECT OF ACTIVATION AND MAGNETIZATION ON THE ADSORPTIVE REMOVAL OF METHYLENE BLUE ONTO OAT HULL BIOCHAR

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Thermochemical conversion of lignocellulosic biomass has been considered as a viable option to produce intermediate liquid streams for biofuels and biochemical. Biochar can also be used as a precursor of value-added activated carbons. Recent studies have shown that steam activation and magnetization of biochar greatly enhances the surface area and porous structure, and thus the sorption capacity for water contaminants [1].

In this study the relationship between physicochemical properties of biochar-based activated and magnetized carbons and its adsorption was investigated using methylene blue.

Activated biochars were produced from biochar obtained through pyrolysis of oat hull by chemical activation with KOH after and before pyrolysis. A factorial design  $2^3$  with 4 central replicates was used to study, the effect of KOH/oat hull or KOH/biochar mass ratio (2, 1.25, 0.5), temperature (400°C to 600°C) and residence time (1 to 3 h), were evaluated. After activation, all samples including commercial activated carbon were magnetized using the co-precipitation method.

The activated biochars and magnetized biochars obtained were characterized in terms of specific surface area, total pore volume and pore size distribution. FTIR was used for the identification of functional groups in the products. The structure of activated and magnetized biochars were analyzed by using SEM. Moreover, an elemental analysis of samples was performed. Also, the adsorptive properties of activated and magnetized biochars were tested using methylene blue dye.

The results show that activated biochar from agricultural wastes increased its surface area from 49 m<sup>2</sup>/g to 386 m<sup>2</sup>/g. Moreover, porosity is influenced by all factors (temperature, residence time and KOH impregnation ratio) evaluated. In terms the adsorption capacity, the experimental data indicated that the adsorption isotherms are well described by the Freundlich equilibrium isotherm equation.

The optimum conditions resulted in activated biochar obtained from biomass activation and subsequent magnetization, with an adsorption capacity of 229 mg g<sup>-1</sup>, while the BET surface area and total pore volume corresponded to 299,75 m<sup>2</sup> g<sup>-1</sup> and 0.245 cm<sup>3</sup> g<sup>-1</sup>, respectively. This study demonstrates that high surface area activated biochar can be prepared by chemical activation of biochar with KOH as activating agent.

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### Acknowledgements

This work was supported by FONDECYT Project N° 3140630 and 1150707.

## BIOCOMPOSITES WITH FORESTAL RESIDUES OF TZALAM (*Lysiloma latisiliquum*) AS REINFORCEMENT

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Biomposite is a family composite materials, in which a natural fiber such (as wood fiber/flour, kenaf fiber, sisal, etc.) is mixed with polymer from nonrenewable [polyethylene (PE), polypropylene (PP), etc.] or renewable [poly lactic acid (PLA), poly hydroxyalcanoatos (PHA), etc.] resources. Compared with the traditional synthetic fillers, natural filler present lower density, less abrasiveness, lower cost and they are renewable [1]. Forest residue can be a source of natural fiber. This residue is generated during cutting of the trunks of trees for wood products and by the forest industries such as sawmills or primary processing industries and manufacturers of processed wood products. In the Yucatan Peninsula, the timber industry is based on some common tropical species such as Tzalam (*Lysiloma latisiliquum*) due to its abundance and it is easy to saw (Lopez and Tamarit, 2005). Tzalam wood is used in the manufacture of staves, furniture, tool handles, cabinets, etc. It is a source of forest residue because its branches are very thin for use in the above applications.

In this paper, the branches of Tzalam were dried and milled in a knife mill and 40-60 mesh fractions was extracted with methanol and its chemical composition and thermal properties were determined. The extracted and unextracted samples were mixed with PP in a mixing chamber to obtain the composite and it was characterized by determining their mechanical and thermal properties.

The chemical composition of Tzalam residues was similar to other timber species. It presented a total content of 19.9 % and 56.5 % of lignin and holocellulosa, respectively. It has been reported that the bark is rich in tannins, which were extracted with methanol to see the effect on the properties of biocomposite. Figure 1 show the TGA and DTGA curves of Tzalam residues. It can observe in the TGA curves three decomposition zones due to: 1) loss humidity, 2) hemicellulose and initial cellulose decomposition, and 3) decomposition of cellulose and lignin. The maxima decomposition temperature (peak at DTGA curve) was of 350°C. These results are similar to those reported in the literature in which it is indicated that the biocomposite with natural fiber must be processed at temperatures no higher than 200°C, due to its low initial decomposition temperature. The composite obtained with Tzalam wood, results in more rigid material and an increase for Young modulus of 50% was obtained with respect the PP matrix. The use of coupling agent results in a better interface between the fiber and matrix a higher tensile strength for this material.

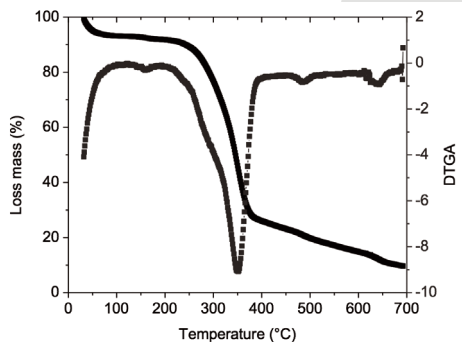


Figure 1. TGA and DTGA of Tzalam residues

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## DEVELOP AND CHARACTERIZATION OF BIODEGRADABLE COMPOSITE TO USE IN FOREST INDUSTRY

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The forest industry it is one of the most important in Chile and represent an 8.7% of total exports [1]. To maintain the plant production in nurseries, large extensions of land, abundant application of chemicals products and a proper watering are required, among others processes than increase the production cost. Making the obtention of plants (by cuttings) a difficult task to achieve, especially due to the cost associated to the process and restrictions to prevent environmental pollution. The use of somatic embryos is an alternative for clonal propagation by cuttings [2] and a source of material to generate artificial seeds [3] as a technique economically-viable. Maintaining the genetic, reducing the costs, space and time required to produce a plant, would allow the forestry industry increase his production. The aim of this study is develop a biodegradable composite to use as a capsule for artificial seeds, giving an alternative solution to Chilean forest industry. Through a reactive extrusion process, biocomposites (C1i, C2i and C3i) were prepared based on chemically modified corn starch and a matrix of biodegradable resins. An evaluation of the materials was realized to determine the parameters, as well as the thermal, mechanical, and rheological features.

The samples were analyzed by Differential Scanning Calorimetry (DSC) in a NETZSCH 204 F1 Phoenix® heated from 25°C to 250°C at a rate of 10°C/min, the Thermo Gravimetric Analysis (TGA) was done in a NETZSCH TG 209 F3 Tarsus® heated from 30°C to 600°C at a rate of 10°C/min with a nitrogen flow rate of 10 mL/min. Melt Flow Index (MFI) was evaluated in triplicate in a INSTRON (model MF20), preheated 7 min at 165°C with 2,16 Kg load, while Capillary Rheology were tested with a temperature of 170°C and a shear rate 100-4000. The tensile properties of the specimens were determined following ASTM D-638 standard, in a computer-controlled KARG testing machine (model Smar tens 005) with a load of 5 KN/10 min with a speed of 10mm/min.

TGA results showed a decomposition of the material with a 10% of weight loss, when the temperature is between 280°C and 301°C, while the DSC reveal that the melting temperature of the samples is 162-164°C, indicating an extremely reduced decomposition of the samples under processing conditions caused by the difference over 120°C of the melting point and decomposition temperature, assuring the quality of the material after the process of blend. The MFI values 10.98 (g/10min) (C1i), 15.43 (g/10min) (C2i) and 15.52 (g/10min) (C3i) indicates that even though there is a high percentage of organic matter (40-30%) the fluency will allow a correct processing of biocomposites, getting a perfect filling of the mold cavity during the injection [4]. The traction test indicates an elastic modulus for the samples of 240-263 MPa.

The studied blends present optimum mechanical and thermal properties to use the biocomposite in the generation of biodegradable capsules for artificial seeds. The analysis of the results allows to conclude that materials will maintain their properties and functionality after the all process of manufacturing.

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## CHARACTERIZATION AND APPLICATION OF A NATURAL POLYMER AS A THERMAL INSULATION BIOMATERIAL

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Buildings are known for their high energy consumption, and therefore as relevant actors as climate change contributors.

This is the reason why one of the most important challenges in the future is the reduction of their energy demand throughout the life cycle. Thermal insulation materials play a significant role improving the energy efficiency of buildings and therefore many studies focus their efforts in developing low environmental impact materials.

In this context, the aim of this work was to study a natural polymer and its application as a thermal insulation material. The natural polymer was chemically, physically and mechanically characterized. In addition, a composite material blended in a mold using the natural polymer and sprayed with Polyurethane (PU) was used to evaluate possible applications. Morphological studies of natural polymer showed an interesting natural porous structure (Fig. 1) with a smooth surface similar to those found in closed cell insulation materials and an excellent compatibility with PU foam. This composite showed good thermal stability, an excellent thermal conductivity for a natural insulation material, high density, and good compressive strength. The natural polymer in a PU matrix like a block type showed to be an appropriate thermal insulation material, being an excellent opportunity to reduce the environmental impacts of these type of insulating foams.

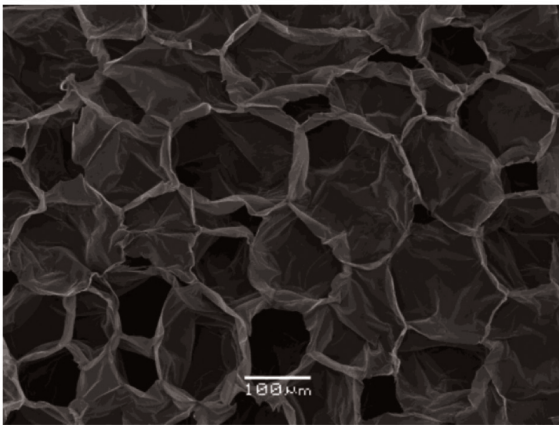


Fig.1 - SEM micrograph of cross section



## MECHANICAL AND PHYSICAL PROPERTIES OF HEMP FIBER-MAT REINFORCED POLYETHYLENE FILM COMPOSITES

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Thenatural fiber composite materials have many advantages, such as environmental-friendliness, recyclability, economical-efficiency, healthiness and good mechanical properties.

These composites have got a lot of attention in the industrial applications, such as automobile industry, aerospace and construction industry. These kinds of materials are certain to be a very extensive use in the future. However the main problem is the incompatibility between the hydrophilic natural fibers and hydrophobic thermoplastic and thermoset matrices. Some physical and chemical treatments can enhance the adhesion between fiber and the matrix.

This research investigates the effects of fiber modification, mechanical properties and physical properties of hemp fiber-mat reinforced polyethylene (PE) film composites. In this research nonwoven hemp fiber mat (see Fig. 1) was used as reinforcement material and acetic anhydride modified PE film (see Fig. 1) was used as matrix material. Surface treatment of hemp fiber-mat was investigated as a means of improving the fiber/matrix interfacial strength and mechanical properties of hemp fiber-mat reinforced PE film composite. The hemp fiber-mat was modified with sodium hydroxide and silane (3-Aminopropyl-triethoxysilane). Hemp fiber-mat /PE film composite samples were made with compression molding. Composites mechanical properties were tested with 3-point flexural test, tensile test and compression test. Composites properties were also tested with water soaking test and artificial aging test.

It was found that the water uptake of sodium hydroxide and silane (3-Aminopropyl-triethoxysilane) modified composite was reduced by 14% compared with that of unmodified composites (see Fig. 2) which indicates that silane modification improves the moisture durability of the composite. The mechanical properties of modified samples had different improvements. The tensile stress increased 35% for 3-layer composites, the flexural properties increased 11.5%-123.3%, the compressive strength did almost not increase, but the compressive modulus increased 19%-35.4%. The artificial aging test approved that the chemical modification process can prevent the moisture absorption into the composite.

However, some properties of the hemp fibre-mat/PE film composites were unstable, because the hemp fibres are unevenly distributed in the mat.

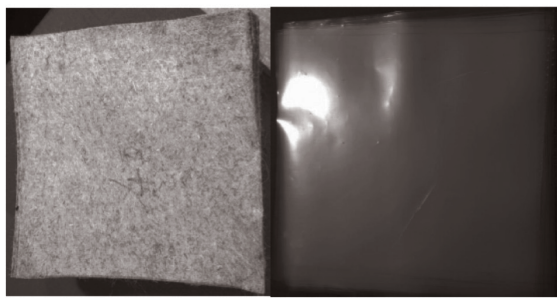


Fig.1 - Hemp mat and PE film

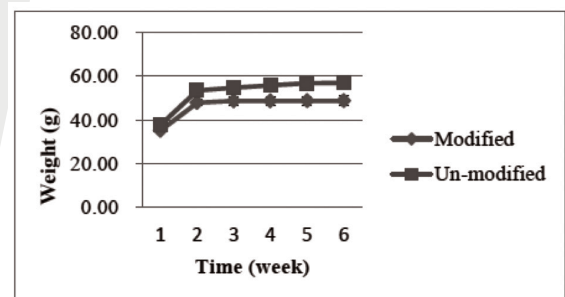


Fig.2 - Average water uptake of 3-layer modified and un-modified composites at 6-week period.

## ***In-situ* MOISTURE CONTENT AND DENSITY MEASUREMENTS IN SURFACE DENSIFIED WOOD USING DUAL X-RAY ABSORPTIOMETRY IN MEDICAL CT-SCANNING**

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There is a considerable interest in developing treatments for densifying wood species which have a low density in order to improve mechanical properties like impact resistance, longitudinal Young's modulus, strength and hardness. The abrasion resistance and hardness of a wood surface can be improved by densifying only a thin surface layer of the wood [1].

A challenge when studying surface densified wood is to be able to study the degree of densification when the moisture content (MC) varies in the wood. Small changes in MC can initiate release of interlocked stresses and cause unwanted set-recovery of the densified wood structure. This process is rapid and difficult to study in-situ, but this is necessary for a better understanding of the phenomenon.

The aim of this study was to investigate, using a dual X-ray absorptiometry (DXA) technique, whether it is possible to detect MC gradients and density-profile variations in surface-densified specimens of Scots pine (*Pinus sylvestris* L.). This technique could contribute to the development of better methods to reduce set-recovery and ensure a higher quality of the surface-densified end products.

The DXA technique for MC estimation involves two consecutive scans at two different X-ray energies. Methods that apply this technique are currently being tested to develop prediction models for MC using either DXA machines or CT-scanners [2]. In the present study, MC was estimated by applying DXA with a medical computed tomography (CT) scanner Siemens Somatom Emotion Duo.

Several MC measurements were made by performing two scans at 80 and 130 kV in a group of surface-densified Scots pine specimens. MC was estimated at different stages, after the specimens had been subjected to conditions that would lead to a change in MC and the formation of a moisture gradient. The division between the CT numbers in the two images was used to create a regression model against the reference measured MC and the  $R^2$  value was greater than 0.95. Predictions for MC were made on a different group of specimens, resulting in a root mean square error of about 2 MC percentage points. The 130 kV level was used to measure the density profile throughout the specimens.

The estimation of MC using DXA in CT-scanners is a technique still under development. Furthermore, medical CT-scanners have a relatively low range of scanning energies for this goal. Nevertheless, these results show that DXA is applicable using such a range of medical CT scanning energies for in situ MC measurements, as well as for the determination of density profiles of surface-densified wood. The relatively low scatter suggests that, with further refinement, the method could achieve a high level of precision.

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## RESISTANCE OF SMOKED GLUED LAMINATED LUMBER TO SUBTERRANEAN TERMITE ATTACK

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Timber from plantation forests consists of a lot of juvenile wood, which has low resistance to attack by subterranean termites (*Coptotermes curvignathus*). Wood smoke created through pyrolysis contains numerous polycyclic aromatic hydrocarbons that could prevent termite attack. Three-layer glued laminated lumber (glulam) was created using either the same wood species (mangium, manii [*Maesopsis emini*], or sengon [*Falcataria moluccana*]) for all layers or a combination of mangium as the face and back layers and a core layer of manii or sengon. Glulam samples were exposed to smoke from mangium (*Acacia mangium*) wood for 15 days, preserved with imidacloprid, or left untreated. All glulams were tested against subterranean termites according to the Indonesian standard. Gas chromatography revealed that smoke from mangium predominantly contained acetic acid, cyclobutanol, and phenolic compounds. Smoked glulam was more resistant to subterranean termite attack than untreated glulam, but less resistant than the imidacloprid-preserved glulam. Based on the resistance classification in the Indonesian standard, untreated glulam belonged to resistance class V (very poor resistance), and smoked glulam ranked as resistance class III (moderate resistance). Imidacloprid-preserved glulam belonged to resistance class II, corresponding to resistance to subterranean termite attack.

## INFLUENCE OF VENEER DENSIFICATION UPON THE PROCESS OF PLYWOOD PRODUCTION

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The process of plywood production under industrial scale needs optimal parametric schedules in order to achieve the best production line capacity. Out of the parameters involved into the plywood production, the pressing time is the most important one which has to be as short as possible to maximize the process efficiency, but long enough to allow the adhesive curing. Jokerst and Geimer [3] have offered the solution of such production problem by applying the steam injection.

But there are also other efficient methods that may be used to reduce the pressing time during the plywood fabrication. Such new approach refers to the preliminary veneer densification (Fig.1). It appears that both physical and mechanical properties of plywood panels are enhanced when applying veneers densification as a pre-treatment before plywood production [1, 2].

The present study aims to evaluate the influence of veneer densification upon the pressing time of plywood. Veneers made of fast-growing wood species were used for the experiments. The densification was performed in laboratory conditions by using a press under variable parametric schedule. Plywood samples were obtained from both densified and non-densified veneers. Prior to any process step, both veneers with and without pre-treatment and the produced plywood were kept under constant room conditions.

The results showed that such preliminary densification influenced the pressing time of plywood when compared to untreated specimens. Therefore densification allowed the shortening of over-heating time and pressing time as well. Such findings may be used for industrial applications to optimize the plywood production. Moreover, such plywood panels can be further used efficiently for building applications and interior design works.

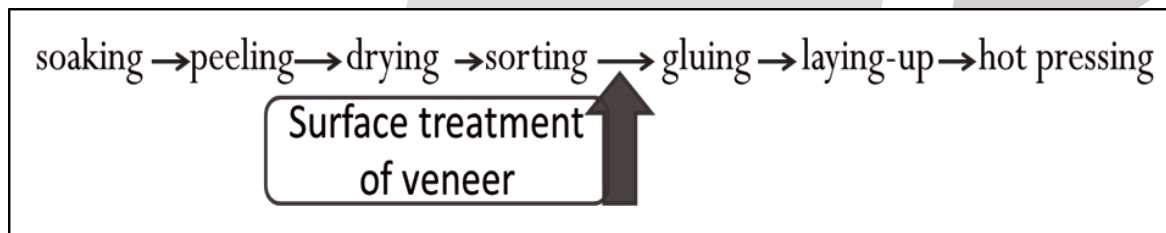


Fig.1. Sub-processes of the innovative plywood manufacturing process

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## ANAEROBIC DIGESTION OF CHICKEN MANURE: EFFECT OF SUBSTRATE CONCENTRATION ON THE BIOGAS YIELD

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The significance of anaerobic digestion (AD) processes has grown within the last three decades, since biogas, a form of renewable energy, can be produced through biological treatment of wastes and wastewaters. Moreover, around  $8.0 \cdot 10^5$  tons of chicken manure are generated in Chile per year; thus  $6.2 \cdot 10^8$  m<sup>3</sup> of biogas can be produced, considering a yield of 80%<sup>1</sup>. The AD of chicken manure bottleneck is the high content of total ammonia nitrogen (TAN) and protein nitrogen, which in turn produces more TAN, reaching inhibitory concentrations for methanogenic bacteria and decreasing the biogas production. The aim of this study was to determine the optimum concentration of the organic matter measured as chemical oxygen demand (COD) in the anaerobic digester inlet stream to reach the maximum biogas production.

A continuous feed two-stage anaerobic digestion system (ADS) was operated to treat chicken manure. The first stage with a working volume of 1.25 L was operated at 55°C and the second stage (working volume of 4.32 L) was operated at 35°C. The ADS was inoculated with biomass from a mesophilic one-stage AD reactor, therefore an acclimation period was necessary. Three substrate concentration were used, 19.49, 30.70 and 43.00 gCOD/L, whereas the organic loading rate remained constant at 7.17 gCOD/L-d. The biogas flow was measured by liquid displacement and the biogas composition was determined by a gas chromatograph.

A maximum biogas and methane production of 10.80 L<sub>biogas</sub>/d and 5.29 L<sub>CH<sub>4</sub></sub>/d, respectively were obtained at the end of the 2<sup>nd</sup> period using an inlet substrate concentration of 30.70 gCOD/L (Fig.1). The inlet TAN concentrations were 1.33, 2.04 and 2.44 gTAN-N/L at the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> period, respectively. During all periods, the TAN produced by protein degradation did not exceed 15% of the feeding TAN concentration, which was predicted by previous studies<sup>2</sup>.

Finally, the ADS operation demonstrates that a high substrate concentration inhibits the biogas production, mainly by the high TAN content; also, the optimal inlet concentration to reach a maximum methane production in a two-stage ADS fed whit chicken manure is 30.70 gCOD/L.

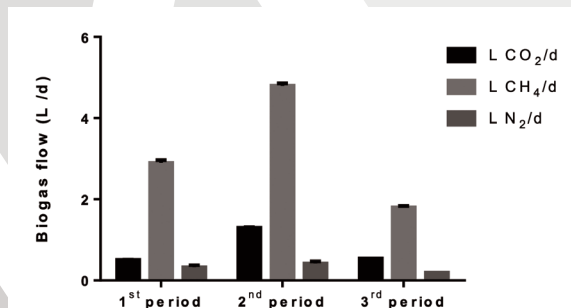


Figure 1. Biogas flow in a continuous feed two-stage anaerobic digestion system. During the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> periods the inlet concentration were 19.49, 30.70 and 43.00 gCOD/L respectively, with a constant organic loading rate.

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## **A NEW METHOD TO SELECT WOOD SPECIES SUITABLE FOR SURFACE DENSIFICATION**

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Surface densification improves many properties of solid wood. This opens up new applications for low-density species e.g. flooring or wooden structures, and adds value to these species. Research into the surface densification of wood has been focused mainly on Scots pine, Norway spruce, aspen and poplar. In order to propagate the use of surface densification techniques, it is necessary to find more wood species that have a particularly high potential for an increase in value through such a treatment.

The purpose of this study was to select wood species, which are suitable for surface densification and being used in a specific product, by applying a systematic and quantifiable selection method. The method that was presented in detail in an earlier work is designed around a workflow consisting of multiple stages, takes into account weighted selection criteria and provides a quantified ranking of the most suitable species [1].

The results suggest that several species such as alder, basswood, cedar, and obeche that have not been considered for surface densification may be suitable candidates. Aspen, poplar and pine were confirmed as suitable by being among the top scoring species in the ranking.

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## EFFECT OF SUPERCRITICAL IMPREGNATION PROCESS ON THYMOL RELEASE FROM PLA FILMS FOR FOOD PACKAGING APPLICATIONS

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Nowadays, one of the biggest driving forces for innovation in food packaging has been the increasing demand by consumers for safe, high quality, minimally processed and extended shelf life [1]. Active Packaging (AP) technologies are being developed as a result of these driving forces. Antimicrobial (AM) packaging is one of the most interesting and promising components of AP, which potentially allows industry to combine the preservative functions of AM agents with protective function for foods.

Today, new trends in food packaging involve the use of biopolymers in order to develop eco-friendly materials and simultaneously propose new techniques to give specific properties to these materials [2]. Antimicrobial (AM) packaging is one of the most interesting and promising components of AP, which potentially allows industry to combine the preservative functions of AM agents with protective function for foods. On the other hand, the demand for the use of natural additives has produced a clear increase in the number of studies based on natural extracts such as essential oils (EOs), which are categorized as Generally Recognized as Safe (GRAS) by US Food and Drug Administration. Among the EOs, thymol (major component of thyme and oregano essential oils) has been widely used as active component in antimicrobial packaging. It is very important to know the mass transport rates of an active substance from packaging to food in order to design an efficient active packaging [3].

Additionally, one of the problems that currently occur in the preparation of active packaging with essential oils by the traditional methods is related to the volatilization or degradation of the active agent(s) because of the high temperature values used during the plastic processing [4].

Because of this, the aim of this work is the supercritical impregnation of thymol in PLA films at 12 MPa and different depressurization rates (0.1, 1 and 10 MPa min<sup>-1</sup>) at a constant temperature (313 K), in order to obtain a polymeric material with potential to be used as active food packaging. The impregnation process allowed the preparation of PLA films containing thymol at concentrations varying from 13 to 21 w/w %. An important decrease of glass transition temperature (T<sub>g</sub>) was obtained, because of a plasticizing effect of thymol.

Simultaneously, a phenomenological mass transfer model has been used to describe the mass transfer of thymol from the polymer to different food simulants, obtaining diffusion coefficients values ranged between  $0.8 \cdot 10^{-13}$  to  $7.0 \cdot 10^{-11}$  m<sup>2</sup>s<sup>-1</sup>.

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## ENZYMATIC GRAFTING OF PINE BARK TANNINS, A STRATEGY FOR THE SURFACE MODIFICATION OF LIGNOCELLULOSIC MATERIALS

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Low durability against the attack of pathogen agents and high hydrophobicity are the main drawbacks for the use and valorization of wood. Therefore, in order to take advantage of many properties of lignocellulosic materials, the modification of their physicochemical properties is a mandatory step [1].

In the present study, condensed tannins (CTs) from *Pinus radiata* bark were chemically modified with propylene oxide in order to provide new chemical functionalities as a wood modifier [2]. Both condensed tannins, and hydroxypropylated tannins (HPTs) were used for beech (*Fagus sylvatica*) wood surface modification assisted by laccase enzyme (51003). Laccase was used as catalyst to promote the grafting of the tannins onto wood surface [3].

FT-IR mapping, and Confocal Fluorescence Emission Microscopy of the treated samples confirmed the grafting of polyphenols onto wood surface. The enzymatic treatment reduced the leaching of CTs (27 %) and HPTs (44%). In addition, the CTs, and HPT-treated samples increased their superficial hydrophobicity in terms of lower water uptake.

The results highlighted that the enzymatic grafting of CTs on wood surface is a useful tool for the functionalization of lignocellulosic materials. Chemical modification of CTs seems to be a convenient strategy to develop new properties on wood for a wide range of technologies.

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## EXERGOECONOMIC ANALYSIS OF HEAT AND POWER PRODUCTION FROM MUNICIPAL SOLID WASTE GASIFICATION

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### Abstract:

A municipal solid waste (MSW) gasification system integrated with a heat and power combined cycle (CHP) was studied using exergoeconomic analysis. In order to evaluate the potentialities of MSW for CHP, a comprehensive gasifier model was developed and calibrated using experimental data. The exergy destruction cost, total production cost, relative cost difference, exergoeconomic factor and thermoeconomic cost of electricity were studied through a modeling approach. Moreover, a sensitivity analysis was carried out in order to have a good insight into system performance, focusing on gasifier temperature ( $750 < T < 950^{\circ}\text{C}$ ) and equivalence ratios ( $0.2 < \text{ER} < 0.3$ ).

Results showed that waste-based integrated combined cycle (WICC) efficiencies were favored at higher gasifier temperature and lower equivalence ratio (ER). Similar tendency was observed for the total production cost ( $C_{\text{tot}}$ ), exergy destruction cost ( $C_{\text{D}}$ ) and environmental cost ( $C_{\text{env}}$ ). Specifically, above  $850^{\circ}\text{C}$ , the total production cost ( $C_{\text{tot}}$ ), exergy destruction cost ( $C_{\text{D}}$ ) and environmental cost ( $C_{\text{env}}$ ) were reduced, leading to a positive economic framework. The higher exergy losses correspond to gasifier, which amounted nearly 60% of the whole system due to the effect of chemical reactions and heat transfer in this stage.

The thermoeconomic cost of electricity (TCOE) using MSW as feedstock varied between 0.07 and 0.13 US\$ kWh<sup>-1</sup>, which was competitive and comparably lower than the electricity price in the Chilean market (0.121 US\$ kWh<sup>-1</sup>).

### Keywords

MSW gasification, exergy efficiency, exergoeconomic valuation, electricity price.





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