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**International Conference on** 



November 10-11, 2016 Alicante, Spain

### Workshop (Day 1)



## **Sustainable Bioplastics**

November 10-11, 2016 Alicante, Spain

#### Avantium renewable chemistries update

We have recently announced the completion of the JV with BASF named Synvina.<sup>®</sup> It's goal is to develop world-leading positions in FDCA and PEF by building an upto 50ktpa plant at the BASF's Verbund site in Antwerp and to license the technology for industrial scale production. Synvina<sup>®</sup> will use the YXY process<sup>®</sup> developed by Avantium for the production of FDCA.

There are two projects in an earlier phase which we are able to share more details of.

- Zambezi process 2G sugar biorefinery and
- Mekong process to produce bio based monoethylene glycol (bio-MEG)

The Zambezi process has great potential to provide sugars from non-food biomass for chemical and bio-polymer applications. Zambezi has several advantages over other 2G technologies: static biomass, avoidance of pretreatment, high purity glucose products, near quantitative yield, produces clean lignin and is feedstock flexible.

The Mekong process is one-step, high atom efficiency process which is competitive with the oil based MEG. The current commercial route to bio-MEG is a multistep low atom efficiency process, making bio-MEG too expensive, especially in a low oil environment. With bio-MEG demands estimated to reach 3 million tonnes in the next few years and the wider MEG market some 10x this volume, the potential for the technology is enormous.

The current status and perspectives of Zambezi and Mekong will be discussed further in the talk.

Alan A Smith

Avantium Renewable Chemistries, Netherlands

#### **Biography**

Alan looks after Business Development for Avantium Renewable Chemistries, picking up projects from the incubator stage to when it's time to seek collaborations. For the past 13 years he has been working in a role in business development in the Chemical Industry and before that spent over a decade running R&D projects.

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### Scientific Tracks & Abstracts (Day 1)



## Sustainable Bioplastics

November 10-11, 2016 Alicante, Spain

### Characterization and biodegradation of lactate-based polymer biosynthesized from renewable carbon sources

Seiichi Taguchi, Ken'ichiro Matsumoto, Toshihiko Ooi, Camila Utsunomia, Ryosuke Kadoya and Kenji Takizawa Hokkaido University, Japan

) iologically synthesized polyhydroxyalkanoates (PHAs) are attractive materials as bio-based alternatives of petroleum-Biologically synthesized polyhydroxyalkanoaces (11116) are activated to be a microbial platform carrying evolutionarily engineered PHA synthetic enzymes that confer high enantioselectivity and broad substrate specificity toward monomeric constituents. The finding of an engineered PHA synthase with lactate (LA)-polymerizing activity (lactate polymerizing enzyme, LPE) was a major breakthrough to achieve the microbial production of the diverse polymers, particularly LA-based polymers. Polylactic acid (PLA) is most widespread bio-based polymer due to its superior transparency and processability. Our microbial processes produce LA-based polymers from renewable resources via one-pot fermentation. In this talk, topics for the engineering approaches to synthesize new biopolymers will be introduced together with the polymer biodegradation. Especially, combination of metabolic engineering and enzyme engineering are very powerful toolboxes for this purpose. Recently, using analytical GC-MS, we established the quantitative metabolite analysis procedure to address the rate-limiting step for synthesis of LA-based polymers. This new analytical system actually provided us with improved production of PLA-related polymers. This strategy should be applicable to a wide range of PHA-producing systems. It should also be noted that the unusual substrate specificity of LPE was found to be applicable for the synthesis of PLA-related polymers incorporating even other 2-hydroxyalkanoate (2HA) monomers; glycolate and 2-hydroxybutyrate. This finding further expands the structural diversity in microbial polyesters. Xylose utilization was also effective for production of PLA-related polymers with respect to realizing the value chain system from raw biomass to valueadded biomaterials.

#### Biography

Selichi Taguchi has completed his PhD from The University of Tokyo and was promoted as a Professor of the Graduate School of Engineering, Hokkaido University, in 2004. In 1997, he had visited to join as a Research Scientist at the Institute of Molecular and Cellular Biology of Immune System, Luis-Pasteur University. He also worked at the Polymer Chemistry Laboratory of RIKEN as a Senior Research Scientist. His current main research focuses are on the creation of novel biological catalysts that can be adapted to the desired environment or biosystem. He has published more than 150 papers in reputed journals.

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# **Sustainable Bioplastics**

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#### Market development of kaneka biopolymer PHBH

**Kenichiro Nishiza** Kaneka Belgium N.V., Belgium

Mainly due to its bio-based and biodegradable character, PHA (Polyhydroxyalkanoate) materials are gaining clear interests in the field of polymer industries. In this presentation a specific co-polymer of 3-hydroxybutyrate-co-3-hydroxyhexanoate ("PHBH"), is described as produced by Kaneka Corporation. PHBH is a 100% plant-based and biodegradable polymer to offer flexibility in films, heat resistance in solid products. While maintaining the key characteristics of polyolefin materials, the polymer can be converted to its compounds in a variable range from soft to hard. Moreover, the printability and heat-sealability are of high quality and suitable for biodegradable packaging. PHBH holds OK compost and OK compost HOME certifications, which guarantee biodegradation in an industrial and a home composting system and PHBH biodegrades under anaerobic conditions. It also meets the ASTM D7081 which is the standard specification of marine biodegradabilities draw attention as a low environmental load material. For example, PHBH is tested as garbage bags for anaerobic digestion facilities. The employed raw materials are biomasses such as plant oils, which are renewable resources. Through kaneka's fermentation technology, the polymers are accumulated in the bodies of microorganisms and further refined and extracted. PHBH based materials are generally converted by standard polymer processing techniques such as injection moulding, blow moulding, etc. In addition, we would like to introduce several marine biodegradable applications which can contribute to reducing marine pollution by plastics.

#### Biography

Kenichiro Nishiza has completed his Master's degree of Synthetic Chemistry and Biological Chemistry from Kyoto University Graduate School of Engineering, and has joined Kaneka Corporation in 2005. He has been working at the Cooperate R&D of Kaneka in the research field of Reactive Polymer Processing from 2005 to 2011. Now, he is the Technical Service Specialist Biopolymer of Kaneka Belgium, and has been developing new PHA applications in European market.

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## **Sustainable Bioplastics**

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Novel bio-based elastomeric polymer based on semi-interpenetrating poly(3-hydroxyalkanoate)s and sunflower oil using a trithiol as crosslinking agent

Carine Mangeon<sup>1</sup>, France Thevenieau<sup>2</sup>, Estelle Renard<sup>1</sup> and Valérie Langlois<sup>1</sup> <sup>1</sup>Université Paris Est, France <sup>2</sup>Groupe Avril, Paris

Poly(3-hydroxyalkanoate)s (PHAs), have been suggested as green substitutes to replace petroleum-based commodity polymer because of their biodegradability, biocompatibility and versatility. Although PHAs are very promising material in the field of eco-friendly plastics, their intrinsic brittleness and narrow processing temperature window limit their range of application. As a consequence, many attempts have been made to develop PHA with better mechanical and thermal properties. In recent years, much attention has been focused on the development of polymeric materials from vegetable oils, a sustainable resource. Their competitive cost, worldwide availability and built-in functionality (ester functions and in saturations) make them attractive to reinforce various types of polymers. In this study, we reported a unique approach to toughen PHAs by increasing their elongation at break and enhancing their thermal stability using sunflower oil (SO). The strategy consisted of synthesis of a bio-based semi-interpenetrating (semi-IPNs) network by crosslinking sunflower oil and triméthylolpropane tris(3-mercaptopropionate), a trithiol using "click" thiol-ene reactions into linear PHA polymer matrix. This functionalization process that is characterized by high yields, high reaction rate and short reaction time was initiated photochemically by ultraviolet light in the presence of a photoinitiator 2,2-diméthoxy-2-phénylacétophénone (DMPA). The resulting semi-IPNs PHA/SO exhibited excellent flexibility and showed relatively good thermal stability. Mechanical analysis results have shown that semi-IPNs with 30 wt% of cross-linked sunflower oil displayed excellent properties with an increase of the elastic modulus (170%) as compared to pristine PHA (7%). Moreover, it has been demonstrated that the thermal stability of the semi-IPNs increased by incorporation sunflower oil into PHA matrix. Moreover, a single glass transition temperature for the semi-IPN containing sunflower oil up to 30% was observed with dynamic mechanical analysis (DMA), which suggested good compatibility between sunflower oil and PHA in the network.

#### **Biography**

Carine Mangeon is pursuing her PhD at the East Paris Institute of Chemistry and Materials Science, Thiais, France, since September 2014. Her scientist research deals with the development of new bio-based polymeric materials. The main goal of her study consists in developing and improving the properties of polyhydroxyalkanotaes (PHA) produced from bacterial strains in order to enhance their thermal and mechanical properties. She has published two patents and one publication in this research field.

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# Sustainable Bioplastics

#### Biopolymers based multifunctional composite systems by electrospinning technique

Ilaria Cacciotti

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The formulation and development of multifunctional systems based on biopolymers (e.g. polycaprolactone, polylactide, polyhydroxyalkanoates, etc.) and natural and synthetic additives, both inorganic (e.g., calcium phosphates (CaP), bioglasses (BG), silica and calcium carbonate) and organic (e.g., agro-food byproducts, tannic acid and ascorbic acid), are gaining a lot of interest in order to provide innovative and improved properties, in terms of mechanical reinforcement, antioxidant and antimicrobial features for potential applications in the food packaging and biomedical sectors. In particular, in the food packaging sector the addition of proper fillers to biopolymeric matrices is strongly motivated by the need to improve their mechanical, thermal and gas barrier properties that avoid their industrial employment. Similarly, in the tissue engineering field several efforts are currently devoted to the devise of biomimetic multifunctional composites able to simulate the composition and/or the morphology of the tissue to be regenerated. Electrospinning is a low-cost and versatile technique which able to process several kinds of materials in fibers with large surface area-to-volume ratio and has recently emerged as a very promising approach, due to its ability to generate structures which well mimic those of the native tissue extracellular matrix typical of different biological tissues, and to entrap biomolecules, allowing their controlled release. Moreover, this technique occurs at ambient conditions, and, therefore is very suitable to encapsulate and stabilize thermolabile substances, ensuring their controlled release and their direct interaction with the environment, extending shelf life and food quality, in the case of food packaging applications. In this framework, composite fibrous mats were successfully processed by electrospinning. The obtained systems were fully characterized in terms of microstructural, thermal, and mechanical and biological properties by observation at scanning electron microscopy (SEM), X-ray diffraction, FT-IR spectroscopy measurements, differential scanning calorimetry (DSC), X-Ray diffraction (XRD) analysis, uniaxial tensile tests, and cytotoxicity tests.

#### Biography

Ilaria Cacciotti is an Associate Professor of Biomaterials, Tissue Engineering, and Material Science and Technology. She is the Coordinator for Engineering Area, member of the Research Committee and of the Board of PhD Course in Industrial and Civil Engineering at the Engineering Department of University of Rome Niccolò Cusano. She has graduated in Medical Engineering (Master of Science Award 'Fondazione Raeli'), completed her PhD in Materials Engineering, and has obtained II Level Master's degrees in Forensic Genetics and in Protection against CBRNe events. She has spent research periods at Kyoto Institute of Technology-Piezotech (Japan) and ITRI-Deakin University (Australia). Her research activity is mainly focused on the synthesis and characterisation of nanoceramic, polymeric and composite materials, in forms of particles, spheres, films, fibres, for biomedical and food packaging application. She was awarded with 8<sup>th</sup> CCT Award "Best Oral Presentation for Young Researchers", 10<sup>th</sup> International Award "Giuseppe Sciacca"-Young Students, European Biomaterials and Tissue Engineering Doctoral Award, "Young Researcher Award Elsevier-*Materials Science and Engineering: C*", "Top Cited Author 2011-2012 *ChemEngJ*", "Certificate of Excellence in Reviewing" (MaterChem and Phys 2013).

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# **Sustainable Bioplastics**

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#### Tailoring functional PHA-based materials for biomedical applications

Valerie Langlois

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**P**oly(3-hydroxyalkanoates) (PHAs) constitute a class of natural polyesters produced and accumulated by many bacteria as carbon and energy supply when an essential nutrient is limited. Due to their biodegradability and biocompatibility features, PHAs look promising candidates for biomedical applications especially in the fields of biomedical devices, tissue engineering or biodegradable drug carriers. For the latter application, amphiphilic bacterial PHAs-based diblock or triblock co-polymers have been synthesized and proved to self-assemble into micelles, nanoparticles or polymersomes in aqueous media. In the case of endovascular prosthesis, drug eluting stents are of great interest in the field of interventional cardiology by promising a long-term prevention of restenosis. An adequate drug release control, mechanical response to stent expansion and degradability of the coating are of major importance. The present approach described the potential use of poly(3-hydroxyalkanoate)s as biodegradable and compatible coatings. We also showed that electrospun biocomposite scaffolds based on biocompatible and biodegradable polyesters, such as poly(3-hydroxyalkanoate)s, will hold relevance as temporary supports for human mesenchymal stromal cells development and differentiation with a high therapeutic potential in tissue regeneration processes. Recently, we developed antibacterial biomaterials based on PHAs by different photochemical modifications of the surface.

#### Biography

Valerie Langlois has completed her PhD from University Paris VI. She is now a Deputy Director of the East Paris Institute of Chemistry and Materials Science, France (Université Paris Est, CNRS). Her main scientific interests are related to biodegradable polyesters, their chemical modifications and synthesis of copolymers. Her research activities are devoted to fundamental aspects of biodegradable polyesters in relation with their biomedical applications such as drug delivery systems, tissue engineering or antibacterial materials. She has published more than 80 publications in this research field.

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# **Sustainable Bioplastics**

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#### Biodegradable and compostable materials for packaging applications

**Pilar Villanueva** AIMPLAS, Spain

**B** iodegradable plastic materials can be considered as the main breakthrough of the last two decades in plastics technology. Its use has broadened too many applications as its properties have been improved to meet more demanding requirements. Biodegradable materials are being established as an alternative to conventional thermoplastic materials in a number of applications such as packaging, biomedical, agriculture, etc. However, most of the biodegradable plastics need physical and/or chemical modifications to achieve the requirements for each case of study. Related to this, AIMPLAS is working in different European projects, where new materials have been developed suitable to obtain biodegradable packaging by extrusion technologies directly applicable to conventional industrial processes. Two examples are BIOBOTTLE and BIO4MAP projects.

**BIOBOTTLE Project:** New biodegradable bottles and pouches have been developed for packaging different types of dairy products (fresh milk, pasteurized mild and UHT dairy products), maintaining their shelf life in comparison with traditional packages. The packages developed in the project, fulfill the different characteristics based on thermal, mechanical, microbiological and organoleptic properties depending on the type of dairy product. One of the main challenges of this project was to fulfill the thermal properties to support the sterilization and pasteurization conditions.

**BIO4MAP Project:** The aim of this project was to develop innovative fully biodegradable and recyclable, multilayer, flexible and transparent structures for packaging fresh pasta and different types of cheese that requires customized modified atmosphere (MAP). Different biodegradable thermoplastic materials have been combined, mainly polylactic acid (PLA) and polyvinyl alcohol (PVOH). Packages have been obtained by co-extrusion and thermoforming technologies. With the aim of increasing the barrier against moisture, a biodegradable coating based on natural waxes has been applied to the inner layer of the multilayer structure.

#### Biography

Pilar Villanueva has a Bachelor's degree in Chemical Engineering and has finished her PhD in 2009 within the program "Technological innovation projects and process and product engineering" from the Universitat Jaume I of Castellón. Her thesis was focused on basic research in the development of nanocomposites made of polyethylene and clay nanofillers. She works at AIMPLAS as a Researcher and Extrusion Technician since 2009. She has participated in several national and European projects involved in the development of new biodegradable and compostable plastics for packaging, agricultural applications and household appliances. She is the author of more than 20 contributions to conferences and journals, including an international patent.

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### Sustainable Bioplastics November 10-11, 2016 Alicante, Spain

#### Reconstitution of collagen triple helix in physically crosslinked hydrogels and films

#### Daniel Brannum

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The demand for viable materials to treat medical solutions such as tissue regeneration and bone regrowth in modern day medicine has not yet been met. Though there have been many breakthroughs, in recent decades the advances are unfortunately incremental. Collagen, being the most abundant protein found in the human extracellular matrix has been an attractive option for treatment in these fields. However, properties such as thermal stability, solubility, and reconstitution of hierarchical structure have proven to be challenging. Due to the poor solubility in standard solvents people have heated solution, used organic acids, or even electrospun collagen mats. These methods destroy hydrogen bonding, denaturing the collagen into random coil type polymers. The presented research highlights a benign solvent system that allows for an increase in collagen concentration levels orders of magnitude higher than previously cited in literature. At the same time the collagen solution only temporarily disrupts the hydrogen bonding making it possible to reconstitute the natural triple helix. This method is then used to form physical crosslinked hydrogels and dry films. For additional stability and comparison of mechanical properties, chemical crosslinking through known natural methods, such as genipin and riboflavin, were used. The fundamental understanding of collagen and how to mimic physiological conditions will bring forward new advances in medical applications.

#### Biography

Daniel Brannum is starting his 5<sup>th</sup> year in the Macromolecular Science and Engineering Department at Case Western Reserve University. He has 2 patents pending and multiple papers in preparation. During his time in graduate school, he has received the Bayer Award for excellence in research, dedication, and contribution to the scientific community and earned internship positions at 3 different Fortune 500 companies.

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## Sustainable Bioplastics

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#### Novel bio-based active release materials for biomedical applications

**Tina Modjinou, Valérie Langlois and Estelle Renard** University of Paris-Est, France

Which the increasing scarcity of oil resources and in a period of energy transition due to global warming and the impacts on the biosphere, researches are conducted to find an alternative to petrochemical products. Among these resources, plants have a growing interest since they are an enormous source of complex chemical molecules exploited in different fields such as fragrance, food, cosmetic and pharmaceutical industries. Essential oils, present in plant resources, constitute a non-food valorization of the biomass. The powerful and green process of thiol-ene addition was used to elaborate bio-based networks from eugenol loaded with two phenolic compounds as active release materials. Carvacrol, a phenolic monoterpenoids present in thyme or oregano, and tannic acid, a polyphenol family tannins (glucose polyester) known for their antibacterial and antioxidant activities have been embedded in the cross-linked eugenol based network to increase its antibacterial properties. Their antibacterial and antioxidant activities have been evaluated and promising properties have been demonstrated since derived materials led to a tremendous inhibition of the adhesion of *Staphylococcus aureus* and *Escherichia coli*. Systems proceeding by diffusion (carvacrol) or by diffusion and immobilization (tannic acid) of antibacterial and antioxidant moieties have been obtained. Moreover, in the case of tannic acid, the materials present the advantage of having a sustainable antibacterial and antioxidant activities over time since an oxidative coupling reaction between phenol groups leads to the trapping of tannic acid in the network.

#### Biography

Tina Modjinou has done her graduate studies (PhD) from East Paris Institute of Chemistry and Materials Science, France (Université Paris Est, CNRS) under the supervision of Professor Estelle Renard. Her PhD work focused on the chemical modification strategies for biodegradable/biocompatible co-polyester mainly PHAs for medical applications. The main goal of her studies is devoted to the design of new bio-based materials with antioxidant and antibacterial activities and the improvement of theirs properties. She has published 3 papers in these research fields.

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### Workshop





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## **Sustainable Bioplastics**

M Reza Nofar

Istanbul Technical University, Turkey

November 10-11, 2016 Alicante, Spain

#### Extending polylactide applications by overcoming its drawbacks

Despite the profound features of polylactide (PLA) such as being originated from biomass and its biodegradability, PLA has several drawbacks that limit its use in different applications. A series of these drawbacks could be according to its glass transition temperature (Tg = around 60°C) and its very slow crystallization kinetics. In applications where the service temperature require to be below 60°C, PLA behaves as a very brittle polymer, whereas in those cases where the service temperature should be much wider beyond 60°C, PLA can easily be deflected by heat because the degree of crystallinity is not high enough to provide the required rigidity. Moreover, a series of drawbacks originate from the PLA's melt conditions. Due to the low melt strength of PLA followed by its slow crystallization rate, forming the final products with required shape is not easy. Similar scenario exists in processing of PLA/gas mixture to form high-quality foamed structures. In this work, it is shown that the enhancement of PLA's crystallization kinetics could significantly enhance its processability, formability and foamability, and could widen its service temperature beyond its Tg, and further can improve the mechanical properties of its final products. Furthermore, blending PLA with other biopolymers with high melt strength, high toughness and ductility could improve the melt strength and processability of PLA, compensate its brittleness and enhance its mechanical properties. These approaches provide new routes to extend the PLA's usage in much wider commodity applications.

#### **Biography**

M Reza Nofar has completed his PhD from University of Toronto and Postdoctoral studies from McGill University and Polytechnique Montreal. He is currently an Assistant Professor at Istanbul Technical University, Turkey. His research interests could be listed as Polymer Processing, Manufacturing of Innovative Biopolymeric Systems, Multiphase Polymer Blends and Composites, Multifunctional Nanocomposites, Micro/Nanocellular and Micro/Nanofibrillated Systems. So far, he has been the recipient of several Canadia National/Provincial and Institutional Scholarships and awards. He has contributed his research output as 1 authored book, 2 book chapters, 1 patent, 28 refereed journal articles, and over 50 refereed conference papers.

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### Scientific Tracks & Abstracts (Day 2)



# Sustainable Bioplastics

November 10-11, 2016 Alicante, Spain

### Potential natural additives and agro-industrial by-products in biopolymer formulations for active food packaging

María Carmen Garrigós, Ana Cristina Mellinas, Marina Ramos and Arantzazu Valdés University of Alicante, Spain

The addition to natural additives and/or agro-industrial by-products discarded from food processing operations is an innovative trend in polymer science with clear application in active food packaging. A variety of natural compounds have been proposed for incorporation to polymer matrices to improve the packaging's functionalities as well as food quality and safety. The demand for the use of natural additives in polymer formulations has produced in recent years a clear increase in the number of studies based on natural extracts from plants, essential oils or agricultural waste products as well as their original compounds (including phenolic acids, tannins, proanthocyanidins and flavonoids) for food packaging applications. Their action is essential in preventing food oxidation, off-flavors development, nutritional losses, spoilage from food-borne bacteria and organoleptic deterioration by microorganism proliferation. The use of biopolymers such as poly(lactic acid), PLA; poly( $\varepsilon$ -caprolactone), PCL; bio-polyethylene, bio-PE; starches; gelatines, caseinates, etc., offer an attractive approach for the development of sustainable materials. These biopolymers can be excellent carriers for active compounds in food packaging applications. In this speech, the potential of some natural bioactive compounds and agro-industrial by-products and their incorporation into different biopolymer materials will be presented as a result of the research performed by the authors.

#### **Biography**

María Carmen Garrigós has done her PhD in Chemistry from the University of Alicante (2003). She is an Associate Professor in Analytical Chemistry at the University of Alicante from 2015. She is the Author of 38 research papers published in journals related to Analytical Chemistry, Food Technology and Polymer Science. The main research areas are: Chemical modification of biopolymers; Natural additives for active packaging; Edible films; TPUs obtained from vegetable oils; Valorisation of agro-food residues; Carbohydrate-based advanced biomaterials; Extraction and encapsulation of bioactive compounds; and Quality control methods and multivariate analysis for food authentication.

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# **Sustainable Bioplastics**

November 10-11, 2016 Alicante, Spain

### Design of nanocomposites by interfacing biopolymers with metal oxides and metal organic frameworks (MOFs)

#### Nathalie Steunou

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) iopolymer-based materials have received increasing attention for potential applications in energy, medicine and environment Biopolymer-based materials have received increasing attention for potential origin is related to their chemical complexity and selfassembly properties, for which no synthetic equivalent is usually available, together with their large abundance and nonfossil origin, two key aspects for the synthesis of green materials. The development of bio-elastomers usually requires their reinforcement by appropriate fillers that enhance the mechanical properties and impart new physico-chemical properties (catalytic, optical, magnetic, gas separation, etc.). In this presentation, we will focus on functional nanocomposites prepared by assembling biopolymers with different types of inorganic fillers including metal oxides, polyoxometalates and metal organic frameworks. First, by combining gelatin with a large range of polyoxometalates of different charge density, bio-elastomers with tunable mechanical properties were prepared by a complex coacervation process. Due to cost-effectiveness, ease of preparation and biocompatibility, these nanocomposites may present great potential as modified electrodes for detection as well as drug carriers or scaffolds for tissue engineering. More recently, our interest was also devoted on composite membranes prepared by combining porous metal polycarboxylate based MOFs and biopolymers for gas separation application. An approach integrating advanced characterization tools was developed at the colloidal level to characterize the microstructural and physico-chemical properties of these materials. Indeed, one critical issue of this family of materials concerns the chemical and thermodynamic compatibility between polymers and inorganic particles that drive both the polymer microstructure (degree of crystallinity, cross-link/entanglement density, confinement effect, etc.) and the dispersion of nanofillers.

#### **Biography**

Nathalie Steunou is a Professor at the Institute of Lavoisier from the University of Versailles St Quentin-en-Yvelines-Université Paris Saclay, France since 2010. She was an Assistant Professor for about 11 years at the Pierre-and-Marie-Curie University in the Laboratory Chimie de la Matière Condensée de Paris. She has acquired a strong expertise in the Chemistry of Hybrid Materials based on metal oxides, metal organic frameworks and biopolymers for different applications in the domains of energy, environment and medicine. She is co-author of more than 60 papers.

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## **Sustainable Bioplastics**

November 10-11, 2016 Alicante, Spain

### Dynamic metabolic control analysis on *Cupriavidus necator* predicts effects of environmental conditions on PHB production from glycerol

Chenhao Sun, Colin Webb and Konstantinos Theodoropoulos The University of Manchester, UK

C tatement of the Problem: Utilisation of glycerol from the ever-expanding biodiesel industry is deemed as a promising Solution for the sustainable manufacturing of value-added chemicals. In one such novel fermentation processes, glycerol is utilised by bacterial strain. Cupriavidus necator DSM 545 to synthesise poly(3-hydroxybutyric acid), a bioplastics with the potential to replace its petrochemical counterparts in many applications. To improve PHB batch production via means of model-guided process or genetic engineering, insights into the behaviour of cellular metabolism under dynamic fermentation environments is essential. The purpose of this research is, therefore, to demonstrate how metabolic fluxes can be reconfigured in response to environmental or genetic changes. Methodology & Theoretical Orientation: A dynamic flux control analysis (DMCA) approach was used in this study. It comprises generation of time-series flux distributions over batch fermentation using dynamic flux balance analysis (DFBA), a constraint-based stoichiometric modelling approach. Based on the flux distributions profiles, metabolic control analysis (MCA) calculated flux control coefficients to quantify the relative changes of metabolic fluxes in response to changes in system variables such as enzyme activities and metabolite concentrations. Findings: We calculated control coefficients of PHB flux with respect to factors such as TCA activity, glycerol concentration and oxygen level. The degree of control of PHB synthesis fluxes was not fixed, but rather changed with metabolic state and environmental condition during the fermentation. Furthermore, the control coefficients were able to provide qualitatively correct predictions of the change of PHB synthesis in response to perturbation in oxygen level during the fermentation. Conclusion and significance: DMCA could generate quantitative description of the interaction between PHB synthesis pathway and system variables. We envisaged the possibility of developing a process control scheme for PHB production based on metabolic control coefficients.

#### **Biography**

Chenhao Sun joined Professor Konstantinos Theodoropoulos's research group in 2013 and has since been working on PHB production using Cupriavidus necator DSM 545 from glycerol. His research focused on using combined computational-experimental approaches to gain an in-depth understanding of the metabolism of the strain associated with PHB synthesis, and hence providing hints as to how PHB productivity can be improved via genetic or process engineering means. He has created Matlab programs to perform dynamic flux balance analysis and dynamic flux control analysis on bioreactor experiment data and yielded positive results.

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## **Sustainable Bioplastics**

November 10-11, 2016 Alicante, Spain

#### Biocomposites reinforced with nanocellulose/graphene hybrid nanofillers

Sarah Montes<sup>1</sup>, Germán Cabañero<sup>1</sup>, H Grande<sup>1</sup>, Jalel Labidi<sup>2</sup> and Ibon Odriozola<sup>1</sup> <sup>1</sup>IK4-CIDETEC, Spain <sup>2</sup>University of the Basque Country, Spain

In the last few decades, the development of green composites has gained increasing attention, mainly due to the global awareness of environmental issues. This fact has resulted in the emergence of sustainable and environmentally friendly green materials, which are renewable, recyclable or biodegradable. Cellulose is considered the most abundant renewable polymer on Earth. Nanostructures such as microfibrillated cellulose (MFC) and cellulose nanocrystals (CNCs) can be extracted from this naturally occurring polymer by mechanical and chemical methods, respectively. CNCs have been extensively investigated in the preparation of polymer biocomposites, especially those based on biodegradable polymers, due to their good mechanical properties and reinforcing capability, abundance, low weight and biodegradability. As well as reinforcing nanomaterial, CNCs have been recently reported to effectively stabilize graphene aqueous dispersions prepared by liquid phase exfoliation of graphite, obtaining a nanocellulose-graphene hybrid nanomaterial. This hybrid nanomaterial was used in the preparation of green composites based on two different polymeric systems. On the one hand, a hydrophilic matrix such as polyvinyl alcohol, PVA, in which the biocomposite was prepared by direct incorporation into PVA of, previously exfoliated graphene with cellulose nanocrystals. As a result of the combination of graphene and nanocellulose in PVA, a synergistic effect was obtained. On the other hand, a fully bioderived green composite based on polylactic acid, was also prepared. The investigation of the optical, thermal and mechanical properties of the new green composites will be presented.

#### Biography

Sarah Montes has got her degree in Polymer Chemistry and has done her Master's in Applied Chemistry and Polymers from the University of The Basque Country. Currently, she is a Scientific Researcher at IK4-CIDETEC, specialized in the development of polymeric composites/nanocomposites, especially bio-based polymers and in the characterization of polymeric materials. She has been the Coordinator of the ECLIPSE European Project. She is the author and co-author of 5 scientific papers and 2 patents.

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# **Sustainable Bioplastics**

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#### Thermal characterization of vegetable tannin reinforced TPU-based bio-composites

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The aim of this study was to investigate the use of vegetable tannin as a potential reinforcement material in polymer composites for the production of footwear sole material. For this purpose, the acorn cups and the waste of acorn obtained after the tannin extraction was used as the reinforcement materials for thermoplastic polyurethane (TPU) based composites. Alkali treatments were applied for modifying the surface of acorn cups and pulps to increase the compatibility between the filler and polymer matrix. The preparation of the composites with different filler loadings (10, 20 and 30 wt%) was performed via hot melt extrusion. The effect of surface modification on the thermal and morphological characteristics of the biocomposites was investigated in terms of Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) analyses. The FT-IR results showed that the vegetable fillers were incorporated into the polyurethane matrix successfully and partial structural modifications were occurred as a result of the alkali treatments. Although the thermal resistance of composite materials at low temperatures was found slightly lower than the TPU, higher thermal resistance values were obtained at higher temperatures. Overall results showed that the homogenous dispersion of vegetable fillers within the polymer matrix was achieved successfully and the obtained bio-composite materials were found to be a good candidate to use as bio based footwear sole material.

#### **Biography**

Fatma Erdogan has graduated in Mechanical Engineering in 2014 and is pursuing her Master's from Ege University in Material Science and Engineering. Her areas of interests are Polymeric Composites, Biocomposites and Polymer Materials. She is also interested in biomedical materials, biomedical structures and their finite element analysis.

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# Sustainable Bioplastics

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### Towards a biomass based polymer industry: Synthesis, characterization and process optimization of bioderived renewable polyesters

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The polymer industry is likely to encounter environmental problems arising from excessive usage of petrochemical sources and will therefore be required to shift towards bio-based processes. Polyesters represent an exciting area for renewable feedstocks to be considered due to their wide variety of applications. Interesting carbohydrate-derived monomers for polyesters include 2,5-furandicarboxylic acid (FDCA) which is a high value derivative from hydroxymethyl furfural (HMF), itself obtained from the dehydration of C5 and C6 sugars. 1,5-pentanediol (PTO), a potential product from the hydrogenation of furfural is a hydration product from hemicellulose. Also, succinic acid (SA) can be obtained from fermentation. Despite the imminent growth of the biomass derived polymers, the process engineering research for these polymerizations is scarce, which limit their industrial use. Herein this work, we have successfully synthesized poly(1, 5-pentylene succinate) (PTS), poly(1,5-pentylene 2,5-furandicarboxylate) (PTF) and poly(1,5-pentylene 2,5-furandicarboxylate-co-1,5-pentylene succinate) (PTFTS) by a two-step process involving polycondensation and azeotropic distillation. 1H NMR confirmed the polyesters' structure and GPC was used to measure molecular weight. The thermal properties were determined by DSC and TGA. Also, the kinetic parameters of differential rate equations were estimated. Finally, we performed the simulation in ASPEN Plus<sup>™</sup> for different configurations and solved a multiobjective optimization polyesterification problem by the -constraint method to obtain the optimum operation conditions and evaluate the performance in terms of sustainability indicators. To the best of our knowledge, this is the first time a comprehensive work involving synthesis, characterization and process optimization has been presented for this type of polyesters.

#### **Biography**

Mónica Lomelí-Rodríguez has obtained her degree in Chemical Engineering from Universidad Iberoamericana México in 2008 and Master's degree in Advanced Chemical Engineering from King Abdullah University of Science and Technology (KAUST) in Saudi Arabia where she focused in combustion technology and kinetics at the Clean Combustion Research Center in 2011. She has been working as a Process Development Engineer with the Innovative Plastics Division of SABIC before enrolling Tony Lopez's Research Group in Catalysis for Sustainable Chemistry in the University of Liverpool. Currently, she is pursuing her PhD in Biomass Derived Polyesters Synthesis and Reaction Engineering.

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## **Sustainable Bioplastics**

Dawn A Smith

Scion, New Zealand

November 10-11, 2016 Alicante, Spain

#### Advances in the use of bio-based resources in polymer products

Scion's biomaterials and bioproducts research focuses on supporting New Zealand, international manufacturers and brand owners with innovative technologies that utilize sustainably-derived, bio-based resources. Increased bio-based content into products is promoted by legislation as well as consumers and brand owners who are demanding sustainability and renewability claims as well as excellent product performance. New Zealand is not set up for refining petroleum to chemicals and polymers and heavily relies on imported plastics and polymers. One possibility to reduce this dependency is to partially replace them with sustainably produced New Zealand biomaterials. Therefore, we have developed leading expertise in extrusion processing of biomass, biopolymers, fillers, novel bio-based additives and fiber addition. We continue to expand our capability, adding new manufacturing technologies to our processing portfolio. A good example is 3D printing, a rapidly developing and highly disruptive manufacturing technology that is expected to change much of the way business is done. This presentation will outline some of Scion's products, materials and technologies targeting the use of bio-based resources resulting in new functionalities such as lighter weight, water resistance, durability, or enhanced biodegradation. By building on features designed by nature, we aim to develop sustainable products that will meet the demands of the global market place.

#### **Biography**

Dawn A Smith is the Research Leader of Polymers and Composites at Scion in Rotorua, New Zealand, where she has been working for the past six years. Scion is the New Zealand government-owned research institute that specializes in science and technology development for forestry, wood product, wood-derived materials and other biomaterials. Her team has expert capabilities in polymer synthesis, characterization and compounding of polymers, with a focus on renewable systems. She has worked for nine years in a Biomedical Device Industry in R&D and new product development (CIBA Vision/Novartis). She has done her PhD in Polymer Science from the Institute of Material Science, University of Connecticut, USA.

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### Sustainable Bioplastics November 10-11, 2016 Alicante, Spain

#### **Properties of hydrochloric chitosan solutions modified with nano-calcium phosphate complex**

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Tature itself uses materials like cellulose to provide the structure of plants, chitin as the exoskeleton of several insects and molluscs, collagen for mechanical support in connective tissues and so on. At present, the socioeconomic situation of the modern world has raised the interest in renewable materials to use in regenerative medicine. Hard tissue of the human body is very important. The skeletal system provides support and gives shape to the body and provides a network for all soft tissues. The most common problems with hard tissues are bone fractures, defects or diseases in addition other various problems which need to be cured. Bone consists of 69% calcium phosphate (mainly hydroxyapatite), 21% collagen, 9% water and 1% other constituents. It has a composite nature which is built up of mainly ceramic (hydroxyapatite) and polymer (collagen), with a complex hierarchical microstructure very difficult to imitate which gives most of the superior mechanical properties to bone. Biomaterials as an artificial bone are classified into surface-active materials such as hydroxyapatite (HAp), and resorbable materials such as ß-tricalcium phosphate (ß-TCP) and bioactive and biodegradable material as a chitosan and its derivatives. The composition of biomaterials as a ceramics, polymers and/or composite materials, with all advantages and drawbacks, are developed to be used for bone problems. When all these properties of polymers, ceramics are considered producing composite materials have a reasonable approach. In this studies composition of chitosan and/or calcium phosphates are derived from the junction of two or more different materials, containing organic and inorganic materials, including characteristics like bioactivity and biodegradability and biocompatibility with human tissues. The chemical characteristics of chitosan and nano B-TCP/HAp complex are showed by FTIR studies and can be seen the main peaks of energy vibration of both components organic/inorganic exist in the material complex, also can be seen a good stability of the nano-ceramic formation in the chitosan salt solution by potential zeta and ceramic particles size range from 12.8 to 58 nm. In this study, a new method of preparation of calcium phosphates ceramics from micro size to nano size using a common commercial calcium phosphates is also shown, the process consist in a simple dissolution process of the calcium phosphates in acid, however this solution was used to dissolve the chitosan creating a hydrochloric chitosan solutions modified with nano-calcium phosphate complex. These materials can be used in future for medical applications as a base for scaffolds production and as implants in regenerative medicine.

#### Biography

Luciano Pighinelli is currently an Associate Professor of Toxicology and Genetics Research Program at Lutheran University of Brazil and is an Assistant Professor of Research Program in Materials Engineering at the Lutheran University of Brazil. He has done his Doctorate in Biomaterials area for Regenerative Medicine and Tissue Engineering at the University of Innsbruck-Austria, in co-operation with the Institute of Biopolymers and Chemical Fibers in Lodz, Poland. He has several papers and patents in the field of Regenerative Medicine and Radiotherapy. Currently, he is developing research in biomaterials area and biodegradation of polymers used in regenerative medicine and drug-delivery. His research interests are in the field of Biomaterials and Tissue Engineering: bioactive ceramics; scaffolds for bone and tissue repair; musculoskeletal tissue engineering: bone; cartilage; articular joints; calcium phosphate-based drug delivery devices; and ceramics for orthopedics.

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# Sustainable Bioplastics

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#### Innovation trend on sustainable bioplastics: The case of furanoate

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n order to be sustainable, a polymer has to follow eight criteria, which blend sustainable objectives, business consideration and environmental concerns related to their life cycle. One of these criteria imposes that source, manufacture, transportation and recycle, by using renewable energy. In this view, practically no sustainable polymers are present on the market today. The great and growing interest in sustainability is driving the development of "biobased" materials, i.e. obtainable from renewable sources, which could be or not biodegradable and that are characterized by minimum waste production, transport efficiency and controlled after-use disposal and/or recycling. Taking into consideration that poly(ethylene terephthalate) (PET) dominates the packaging scene, due to its competitive chemical-physical, barrier and mechanical performance-to-cost ratio, the interest of researchers and industry is surely versus biobased PET-like polyesters. Considering the actual scenario, in particular, the academic as well as industrial interest is oriented to i) find biosourced alternatives to produce PET reducing petroleum dependence and carbon dioxide emissions, and ii) synthesize new polyesters produced from 2,5-furandicarboxylic acid as monomer.Poly(ethylene 2,5-furandicarboxylate) (PEF), due to its similarity with the well-known poly(ethylene terephthalate) (PET), is one of the most promising renewable-based polyesters, with chemical, thermal, and mechanical properties very similar to those of PET, which renders it a reliable alternative to this latter polymer. In particular, PEF exhibits significantly improved barrier properties compared to PET: in specific, amorphous PEF exhibits an 11X reduction in oxygen permeability, a 19X reduction in carbon dioxide permeability, and a 2.1X reduction in water permeability as compared to amorphous PET. Accordingly, very recently, Avantium produced to the industrial scale PEF bottle for soft drinks, water, and alcoholic beverages. Poly(alkylene 2,5-furandicarboxylate)s can be therefore potentially considered a genuine alternative as sustainable bioplastics, but more research has to be performed to assess their environmental impact through the life cycle analysis (LCA) study.

#### Biography

Valentina Siracusa was graduated in Industrial Chemistry at University of Catania (Italy). She completed her PhD and post-PhD study working on the synthesis and characterization of innovative polyesters. From 2006, she is Associate Professor in Chemistry for Engineering at Catania University. She collaborates to European Projects on several researches such as recycle, ambient, food packaging, and graphene. Actually, she collaborates with national and international research groups on biopolymers materials used in the food packaging field, with also Lyfe Cycle Assessment study. She is author of more than 70 publications and guest editor of international journals.

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