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WOODCHEM 2013 SCIENTIFIC REPORT

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Introduction

WoodChem 2013 reported over two days the current progress of wood-related chemistry. First session overviewed the career of Prof. Tony Pizzi from Lermab - Université de Lorraine. In session 2, Dr. Ludovic Guinard modelised the forest resources but also quantified their evolution toward our future uses. Session 3 focused on the development of emerging technologies to boost the biorefinery attractiveness to the market, with a keynote from Prof. Jean-Michel Lavoie. The rules and regulation session by Harmen Willemse pointed out the various changes promoted by UE concerning the bio-based economy that will happen in 2016. Session 5 dived deep in the world of chemicals intermediates with talks from Prof. Tatjana Stevanovic and Prof. Alessandro Gandini. A vast review on the valorisation of extractives (small molecules with bio-activity) and lignocellulosic biomass (building-blocks and polymers to design new composites materials like foams, thermoplastics...) was conducted.

1/ The Forest resources

An exhaustive overview of the forest resource and its availability was given by L.Guinard. Wood stock is abundant in the world at about 493,100 Mm³, with a round wood production of 3,355 Mm³ over bark. Wood energy still represents the most common use, achieving almost 60% of the wood production. Each part of trees has specific use like fuel wood, sawing wood. Residues can still be source for lignin, hemicellulose and extractives. The theoretical potential for new harvesting is high at about 800 Mm³ per year. It is defined as the net growth of woody biomass, excluding current industry and the firewood use. However, the part really available is less interesting at about ¼. Fields like Green Chemistry, bio-energy, bio-refinery are amongst the most demanding for wood resources as petroleum substitution. Construction and furnitures, including particleboards are also wood-based. The main drawback to wood could be its unequal quality due to differences between hardwood and softwood, presence of tension wood, knots, bark proportion... Wood plastic composite (WPC) is an example of a new rising and advantageous market for wood. Indeed the production is dramatically increasing since the mid 2000s, especially in the USA, and Europe. WPC are sold at around

63 E/m² in comparison to 250 E/t of raw particle. The competition between energy and material uses for wood will remain a problem in prospect for the next decades. The demand for each sector due to the evolution of our use will be greater and will pressurize on the supply. The situation is expected to end into a wood deficit at least in a few European countries.

2/ Evolution of rules and regulations

H. Willemse presented the CEN as the recognized European standardization body by EU legislation. Standards from the CEN are voluntarily applied within the country. Shared principles are openness, transparency and consensus. Participation includes a national commitment leading to implement European standards. Finally, all standards should reflect the market needs. CEN has mandates on bio-based products (noted M/4XX), requested from the European Commission. It purposes to develop specific standards or study feasibility, and propose a standardization programme. For example, M/430 aimed at bio-polymers and bio-lubricants and was edited by CEN technical body CEN/TC 249, being published in 2012. CEN/TC 411 “Bio-based products” was created in May 2011. Its scopes are standards for bio-based products other than food and bio-mass for energy, covering horizontal aspects (consistent terminology, sampling, certification tools...). It is expected to be published in 2016. French committee has been created in 2012, representing the opinion of stakeholders in France.

3/ Valorisation of small molecules extracted from wood: up to the market

Plants have been used empirically from the prehistory for their properties. In the 20th century, small molecules have been studied for their bio-activity by pharmaceuticals with the purpose of going into the market as proprietary medicinal products. Forest offers a vast source of biochemicals that needs to be further studied. First step consists in a broad screening of each part of the tree (roots, stump, bark...).

Z. Kebbi-Benkeder and co-workers focused on knots because of their high amount in secondary metabolites. They studied 12 species of endogenous European trees including soft-

and hardwoods. Phenols (lignans, flavonoids, stilbenes) were extracted in high quantities by using a traditional lab scale method (consecutive Soxhlet extractions with increasing polarity solvents). After exhaustive characterisation of the extractives, the study highlighted the inter-species variability in secondary metabolites. For example, only conifers (softwood) were containing lignans. A correlation between natural pruning and the extractive amount in knots of hardwoods was observed, suggesting their role in the wood decay resistance. Indeed antioxidant activity from phenols participates in the inhibition of fungi by scavenging free radicals. The influences of age, sampling location, altitude were not studied at this early stage of the project.

P. Saranpää *et al.* extracted stilbene glycosides and aglycones from Norway spruce bark with an ASE (Accelerated Solvent Extractor) or with sonication. Stilbenes glucosides were further hydrolyzed (3 days incubation in a buffer solution) with β -D-Glucosidase. Purification of the hydrolysate on a polymeric resin sorbent gave *trans*-isorhapontigenin and *trans*-piceatannol as major compounds. Fluorescent and UV stability were also carried out. Over 2 weeks, the photoisomerization of *trans*-stilbenes to *cis*-stilbenes was observed. Same result was obtained with UV light but after 30 min, it caused further photocyclization into phenanthrenes. It was found a genetic variation in composition and content of extractives in bark. Indeed, amount in stilbenes is at the highest in the inner phloeme. It is also highest at the crown level and the influences of age and latitude (50 to 67°) were noticed. Northern provenance of trees is correlated to a higher amount in stilbenes ("northern vigour", peatland effect...). Additionally, the antibacterial activity of the purified stilbenes was evaluated on *S. aureus* and *E. coli*. and confirmed, conversely to a bark powder.

If searching for new bioactive molecules is the first step, coming into the market is often the finality. According to B. Holmbom who has experience in this field, it appears very challenging to overcome the numerous obstacles, such as tough regulations. He emphasized the potential of trees as a unique source of protective natural bioactive molecules created by evolution over millions of years. Polyphenols are not the only ones to look after: coniferous trees are rich in resin acids and terpenes, whereas deciduous trees contain some sterols and triterpenoyl alcohols. Holmbom discussed of the development of three products. First are sitosterol and sitostanol discovered during the 50s, submitted to medical assessment in 1987 before being marketed as Benecol® by Raisio Group since 1995. The two molecules can inhibit the uptake of food cholesterol and lower the cholesterol in the blood. It has been incorporated in food like in margarine to make health-promoting "functional" food. HMR lignan from spruce knots (6-29%) is a strong antioxidant that can inhibit the growth of

breast/prostate cancers. Initial research started in 1997 before getting the US-FDA approval as new dietary ingredient in 2004. It reached the market two years later with an industrial scale production. Finally, Abilar® is a fat-based salve containing 10% of spruce resin. This is simply the refined version of an ancient Finnish treatment for chronic wounds. Sum up of these 3 stories, clearing regulations or having a health claim allowed is long and expensive. Benecol® was even submitted to a post-launch monitoring from 2000 to 2009. The paradoxical situation where big pharmaceuticals have no interest in niche market and small companies have no resources to pass safety/clinical testing leads to the decline of approvals or to the best, to a limitation in health claims. In the mean time, regulations in the EU have been gradually tightened, limiting again the pipeline flow. In conclusion, scientists are able to create the essential knowledge base but they need more entrepreneurship to “get down to the real business”.

It seemed rather important for T. Stefanovic to highlight the green side of a project development. She pointed out the need for a more sustainable engineering and green chemistry to minimize environmental harm, and the benefits the wood transformation industry could obtain from it. Life cycling thinking lays on the use of renewable sources of material and energy such as wood. Processes should be designed to minimize energy consumption and material use (atom economy). Therefore it suggests a deeper integration of bio-refineries with these available renewable sources. Waste recycling as well as promoting the material purity should also help to gain value. Application of these principles to the case of yellow birch was reviewed. By-product bark was extracted to exploit the variety of molecules. The evolution of the extraction process tended to use greener solvents (methanol instead of dichloromethane) under sonication to improve phenol selectivity and extraction time. Barks of other commercially important Canadian species were studied for their availability in polyphenolic compounds. Black spruce bark revealed to produce high quantities of phenols (400 mg/g) and flavonoids. This extract also showed the highest antioxidant activity against radical species. Wood extractives, also called non-wood forest products (NWFP) will be further marketed into nutraceuticals, cosmeceuticals, or nutricosmetics for their antioxidant, anti-enzymatic, and antimicrobial properties to promote healthy skin, with anti-ageing effect. Such increase in new natural health products will need enhancement of the sustainability of wood transformation industry coming from green chemistry and engineering.

4/ Functionalization: bio-sourced amphiphilic molecules and polymers

Not only small bio-active molecules grow interest from industrials. Functionalization of small molecules can expand or even create new applications to these molecules. For example, Gérardin and co-workers developed chemical modifications of bio-sourced flavonoids to provide safe and natural antioxidants with improved solubility in lipophilic media. This could have applications in cosmetics or in food industry. The example of Mesquitol was presented. Full identification of this molecule extracted from an invasive Kenyan bush revealed its flavanol structure. Derivatives were synthesized to improve the lipophilicity. Amphiphilic molecules were also obtained in the form of trimodular compounds with amino acids as the intermediate moiety. Despite the first results showing that the compounds were too hydrophilic, it will be modulated by the change of the amino acid moiety. The new derivatives will find applications as surfactants for bioactive emulsions or gelators for smart bioactive gels, *ie* gels that responds rapidly to external stimuli (mechanical, thermal or pH modification).

M. Save also took interest in non-toxic surfactants from sustainable sources but focused on polymers instead of molecular surfactants. She developed a strategy of amphiphilic copolymers where terpenes are the hydrophobic moieties and polymers are the hydrophilic moieties. Natural terpenes were sourced as by-products from the paper industry, resulting from distillation of turpentine. They could be functionalized by thiol-ene click chemistry. Alongside, both synthetic (polyacrylic acid) and natural polymers (dextran issued from saccharose) were investigated. Coupling was attempted by either reductive amination or esterification on the polymer. These molecules allowed exploring the properties of terpenes end-capped copolymers and polyterpenes grafted copolymers. The grafting density of the surfactants and therefore the hydrophilic-lipophilic balance (HLB) could be tuned. The copolymers resulted in efficient stabilizers for direct terpene liquid miniemulsion in water. They also made efficient stabilizer for polystyrene latex synthesis giving stable latex, free of coagulum.

C. Chirat also investigated bio-sourced surface active agents, developed from saccharides and fatty alcohols. Herein the purpose was the conversion of a kraft pulp mill into a biorefinery. The process started with autohydrolysis of woodchips from *Eucalyptus globulus*. Steaming at 150°C and beyond could yield to a partial hydrolysis into acetic acid, thereof inducing hydrolysis into xylose oligomers or monomers. Amphiphilic alkylpolyxylosides (APX) were

synthesized from fatty alcohols (hydrophobic moiety) and the crude hydrolysate saccharides (hydrophilic moiety). This was thought as an alternative to alkylpolyglycoside (APG) obtained from the food sugar glucose (starch sourced). It appeared that the lignin contained in the raw mixture was a contaminant for the transacetalisation but treatment on activated charcoal could remove most of it. It was suggested that the protons (H_2SO_4) were reacting with the lignin benzylic $-\text{OH}$ groups to generate a carbocation instead of catalysing the transacetalization reaction.

5/ Biorefinery : concept and improvements

The purpose of a biorefinery is the separation of the biomass components to produce added value chemicals. J.M. Lavoie estimated the benefits made by an integrated biorefinery.

The processes engaged to valorize biomass depend on the present economy and the competition situations which may occur with other sources. Thermo-processes include gasification, pyrolysis and torrefaction. They lead to the production of heat, electricity or even chemicals. On the other hand, bio-processes are based on fractionation to provide extractives, hemicelluloses and lignins. In addition, cellulose can be further degraded to give sugars and chemicals (ethanol). Nowadays, fractionation of lignocellulose is the only economically viable process to generate chemicals.

Cellulose (42% wt) has to be isolated from the lignocellulosic biomass through existing pulping processes (mechanical, Kraft, Organosolv or steam explosion) before being hydrolyzed to carbohydrates or ethanol (170\$). This step could be performed either in a chemical way (acids) or enzymatically. Hemicelluloses (21% wt) are transformed in a mixture of glucose and xylose. Glucose could be fermented to ethanol (42\$). Xylose can be further chemically converted into xylitol/furfural (67\$) or into ethanol *via* GMOs. Furfural is considered as a gateway to other chemicals (levulinic acid, furans...). Lignin (25% wt) shows a high energy value when burned, but it is also a valuable source of aromatic chemicals for polymers and adhesives. The conversion of lignin is conducted through a successive alkaline depolymerization and a hydrotreatment to gather residual gases (CO_2 , methane), monomers (catechol, 190\$) and oligomers (alcanes, jetfuel, 160\$). Worth of extractives can't be evaluated as it depends on the species. Besides, it will be valuable only if it meets pharmaceutical purity. In conclusion, forest prime residues will be usually transformed into

fibres for the pulp and paper market. Cheap residues are suitable for biofueling with fractionation being a good approach. Highest profits are made on lignin compared to hemi/celluloses, with extractives being considered as a lottery. Thus, in this typical case, biomass could generate up to 600\$. However, these figures don't take into account the energy and hydrogen costs, neither CO₂ recycling cost. Finally, the processes described herein may remain Science Fiction if not integrated further and scaled-up.

Historically, a biorefinery was already running on ABE (acetone-butanol-ethanol) fermentation in 1918. Nowadays, it is gaining interest again as the enzymatic process doesn't compete with food sources to produce chemicals or fuel. This fermentation used cellulose and hemicelluloses separated during an Organosolv process. However the high amount of acetic acid formed could lead to an "acid-crash", in which the cells were not able to switch from the acidogenic to the solventogenic phase, stopping their butanol production. S. Wiesen exposed how butanol production by *Clostridium acetobutylicum* has benefited from two process improvements. Separate hydrolysis and fermentation (SHF) has the most simple set up but generates low yield due to butanol toxicity. Simultaneous saccharification and extractive fermentation (SSEF) lays on *in situ* product removal by liquid-liquid extraction through a membrane ("perstraction"). SSEF on beech wood fibers allowed keeping the butanol concentration under its toxic level, with a 3 folds increased loading. Additionally, the viscosity during the process could be controlled with an automated continuous fiber conveyance.

Not only bacterias like *C. acetobutylicum* could be exploited for fermentation purposes. C. Faulds introduced his fundamental work on filamentous fungi as source of enzymes.

The functional diversity may reach improved delignification and saccharification. The study consisted in identifying which enzymes were active during *in vivo* degradation of lignocellulose and what mechanisms were involved, then providing with an efficient mixture of enzymes. Genome sequencing after automated screening has identified different genes involved in carbohydrates and lignin breakdown. The very specific activity of some enzymes could be further exploited (main-chain vs. side-chain degradation, substrate specific...).

It was suggested that fungal cellulolytic activities involve non-catalytic proteins in addition to oxidative enzymes. In a close future, the degradation mechanisms involved in *Polyporales* species will be certainly established.

Another way of optimizing Organosolv process for lignin extraction was presented by S. Reinhardt. He rationally tailored the conditions of reaction using the method called “design of experiments” (DOE). Parameters such as temperature (160-220°C), reaction time (120-240 min) and ethanol concentration (25-75%) were overviewed with a COST approach (changing one variable at time). The Box-Behnken design requires only 15 experiments to give a thorough picture of the experiment. This framework will allow changing all factors systematically. Optimisation of Organosolv process with DOE tool was successfully run on beech, poplar and pine samples. To meet specifically demand, yields could be optimized for either lignin or cellulose. Furthermore, DOE is reproducible and amenable to up-scaling from 500 mL to 2x15 L reactors.

As seen above, high purity is a crucial parameter to take bio-based products up to the market. F. Schab showed how the company Novasep can provide its clients with both efficient purification and cost matching processes. This company created in Lorraine counts 1200 people, 200 of them working in the R&D department. They manage over 2000 purification systems worldwide, producing 100 different active molecules per year for food, functional ingredients or bio-based industries, for a 300 ME turnover. Indeed Novasep possesses the technological capacity of screening all the separation techniques in use in life science industries, including membrane filtration, chromatography, ion exchange, electro dialysis, adsorption, evaporation or crystallization. Reaching the high purity expected requires a combination of techniques, designed with the help of proprietary modeling tools. Then the process would be fine-tuned at pilot-scale to improve the overall economics. Representative examples of Kraft and Organosolve lignin fractionation, organic acids (succinic, gluconic, and lactic acids), sugars mixture were highlighted. Thus a solution of 99.5% (97% yield) pure sugar monomer can be produced from softwood sugars with appropriate ultrafiltration, demineralization, adsorption, evaporation and separation by sequential simulated moving bed chromatography (SSMB). Further separation with valorization purpose (isolation of C5 and C6 sugars, recovery of byproducts such as hydroxymethylfurfural HMF and furfural) could be designed by Novasep.

6/ Valorisation of paper industry wastes

The ultimate valorization would be that of industrial wastes. T. Auxenfans described the hydrolysis of lignocellulosic biomass from sawdust, an ubiquitous and pre-collected raw material in wood industry. To do so, he treated for short duration oak (hardwood) and spruce (softwood) sawdust with ionic liquids (ILs) before enzyme saccharification with cellulases. 1-Ethyl-3-methylimidazolium methylphosphonate **1** ($[\text{Emim}]^+[(\text{MeO}(\text{H})\text{PO}_2)^-]$) and 1-ethyl-3-methylimidazolium acetate **2** ($[\text{Emim}]^+[\text{CH}_3\text{COO}]^-$) are 2 imidazolium based ILs. On spruce sawdust, it was noted an increase in glucose production up to 3.5 folds after a 40 min treatment with ILs at 110°C. Following enzymatic saccharification on oak sawdust was respectively improved by a factor 4 and 7 when treated with **1** and **2**, with an efficient influence of water as polar anti-solvent used to regenerate the ILs and recover the cellulose fraction. It was suggested that ILs-pretreatment led to a partial deconstruction of sawdust showing an altered surface as well as subsequent lignin extraction, making a better access to lignin structures for cellulases. In addition a combined IL-pretreatment and enzymatic fermentation of sawdust in a one-pot process is currently under development.

Wastewater and sludge also represent an interesting source of profit, after valorisation into chemicals and polymers. E. Paul participated to the Valoria project, as a development of a sludge-to-polyhydroxyalkanoate (PHA) route. Bacteria could produce the linear polyesters PHAs, which show similar physical properties to conventional polyolefins (polypropylene). Their biodegradability could be tuned for various plastic designs. However, its cost would 4 times that of synthetic polymers. Therefore waste and sludge treatment makes way for a cost competitive approach to PHA production. As a result of the project, an on-site implementation of a pilot unit was built. An acidogenic fermentation reactor processing secondary sludge was connected to a solid/liquid separation unit able to clarify an effluent rich in volatile fatty acids (VFA). Next, a biological reactor operated the PHA production under biocatalytic conditions, with a culture selection from the sludge itself. At the end, a downstream processing unit concentrated and dried the PHA-rich biomass. The technical viability of such system was demonstrated. Further development aims at integration to paper industry in order to treat paper mills effluents.

7/ Added value molecules from biorefinery

Bio-refinery can solve environmental or economical issues linked to fossil resources. Lignocellulosic biomass is a renewable feedstock with the second advantage of not threatening the food supply. Molecules of higher value than sugars, ethanol, furfural or hydroxymethylfurfural (HMF) can be obtained under specific conditions.

A. Chappaz *et al.* converted lignocellulosic biomass into levulinic acid which can be a polymer precursor, a chemical intermediate toward bio-active molecules... They modify the acid-catalysed conversion of cellulose to minimize the by-products formation. The selectivity issue was overcome with lower temperatures (<100°C) in strong acidic media such as phosphoric and sulfuric acids. The kinetics of starting materials glucose and cellulose hydrolysis were evaluated under various acidic concentrations.

A. Duwe and co-workers targeted the production of dicarboxylic acids itaconic and succinic acids. They sourced beeches, the most common tree in Germany, and grass silage. The unsaturated itaconic acid has versatile uses as a co-monomer in the production of styrene, acrylonitrile or supplement the production of acrylic acid... An integrated lignocellulosic biorefinery of beech wood and grass silage was built to produce usable sugars by fermentation of the cellulose and hemicellulose. The fungus *Aspergillus terreus* was able to hydrolyse glucose/xylose into itaconic acid. However it revealed very sensitive against a variety of inhibitors contained in the beech/grass hydrolysates. Detoxification was successfully performed on a mixed ions exchanger, increasing the itaconic acid fermentation yield. Conversely, succinic acid fermentation of wood hydrolysate by *Actinobacillus succinogenes* didn't require detoxification. The fermentative production of itaconic and succinic acids is integrated into a pilot plant able to produce the compounds with high yield (respectively 60 and 70%).

8/ New bio-based materials and greener wood treatment

The development of new functional materials based on bio-sourced polymers or bio-sourced building blocks is another strategic research area.

Sugar degradation products furfural and HMF have been precursors for numerous renewable and bio-sourced polymers. A. Gandini reviewed the application of click-chemistry to the

syntheses of furans based polymers. Diels-Alder polycondensation reaction between monomers with furan heterocycles (dienes) and maleimide moieties (dienophiles) is reverted at temperatures above 100°C, leading to a thermo-reversible polymer. Non-linear processes involving multifunctional monomers or crosslinking polymers were also studied. Additionally, vegetable oils were used as initial substrates for the D-A polycondensation. The thermal fragility of the formed adducts can find applications in removable adhesives, self-repairing materials or recycling thermoset materials. Alternatives to petroleum-based syntheses of furan polyesters and polyamides were made with furandicarboxylic acid (FDCA). Fully sustainable polyester was synthesized from renewable FDCA and sugar-based diols.

M. Chemin *et al.* synthesized amphiphilic block copolymers derived from xylan. The first step was the acidic hydrolysis (sulfuric acid) of beech wood hemicellulose into oligosaccharides in a controlled manner. She monitored the reaction on commercial *O*-acetyl-4-methylglucuronoxylan to determine its parameters and suggest a mechanism. Successive depolymerization by the reductive end in alkali media (“peeling”) allowed determining the branching positions. Two different well-defined beech wood xylans containing one or four branching per chain were obtained. The oligosaccharides reducing chain ends were then submitted to reductive amination in aqueous media. They were finally coupled by click-chemistry to vegetable oil-based blocks to provide new bio-based amphiphilic copolymers.

Other bio-based polymers were developed from tannins macropolyols by A. Arbenz *et al.*. They sourced condensed tannins from Gambier, a tree which originates from Asia, but also Quebracho from South America and Mimosa. Condensed tannins are mostly formed of 3-to-8 procyanidins units linked through C4-C6 or C4-C8 bonds with low degrees of polymerization. In order to enhance the reactivity of tannins, phenolic hydroxyls were submitted to oxypropylation under catalytic conditions at high pressure. Optimization of the reaction led to two types of structures depending on the tannin/propylene oxide ratio: a higher tannins concentration provided high PO grafting density of short length PO chains whereas a lower content favored low PO grafting density of longer PO chains length. The oxypropylation process proved to be efficient for condensed tannins of various origins, with no apparent effect from the catalyst. Further development may lead to the synthesis of bio-based thermoplastics.

Tannins extracted from tree bark were used by A. Celzard to prepare 90% natural thermoset resins. Solid foams of various porous structures and physical properties (brittle to viscoelastic, shape-memory) were prepared depending on the formulation.

First generation tannin-based foam showed outstanding fire resistance. Further generations didn't contain volatile formaldehyde (as a cross-linker) or even solvent. Additives like plasticizers (glycerol, PU) could also be added. Three new materials were discovered, inspired from cooking recipes. First is an oil-in-water tannin-based polyHIPEs (polymerized High Internal Phase Emulsions) aka "cured and leached mayonnaise", in which pores are formed by oil droplets. Second is an oil-in-water tannin-based polyHIPE hybrid material standing for "cured and leached whipped cream", in which air was incorporated, adding a second hierarchical degree of pores. A tannin-based solution mimicking the meringue structure, ie only with incorporated air, was also created. Finally, a tannin-based carbon foam showing a vitreous aspect was made from charcoal. A very broad range of new tannin-based materials have been assessed at very low cost. Their structures can vary according to the preparation process, surfactant, pH range, tannins concentration, oil, additives, crosslinker... The unique properties were often improved with respect to standard foams, broadening the range of application.

In anticipation of European standards changes, wood treatments tend to go greener. M. Noel and co-workers have set up a process of wood surface modification in order to improve its dimensional stability, hardness and thus durability. They synthesized seven treatment agents based on environmentally friendly bio-polymers. They are bio-polyesters of polylactic acid (PLA), polyglycolic acid (PGA), polybutylene succinate (PBS) or adipate (PBA). Impregnation of wood with the respective solutions of oligomers differed according to the molecular weight. *In situ* polymerization was also proven. However no "chemical grafting" ie a covalent bonding on hydroxyl groups from wood structure was observed and the new conferred properties are thought to be due to a polymeric chains entanglement. The next generation bio-polymers will be designed by co-polymerisation to fit better the physical and mechanical performances (ant swelling efficiency, fungal resistance, weathering, and hardness) and still remain environmentally friendly.