LIGNIN MODIFIED PHENOLIC SYNTAN - A CONTRIBUTOR TO OUR BIO-BASED SOLUTIONS

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Abstract. Bio-based chemicals are considered to play a central role in our transition towards a bio-based and circular economy and contribute to a more sustainable leather manufacturing process with reduced environmental impact. One of the logical steps in this direction is to increase the renewable contents of existing leather chemicals. Towards this end we've developed a patent-pending technology for the production of new types of polyphenolic syntan products , in which industrial lignins are used during the chemical conversion process to replace part of the phenol used in the production of otherwise 100% petro-based polyphenolic retanning chemicals. We have shown that our innovative technology is compatible with most of the industrial lignins (kraft, soda, organosolv, hydrolysis) from different origins (soft/hard wood, grass, straw). The obtained polyphenolic products have tanning power and are suitable to be used as retanning agents for various types of leather rendering good organoleptic properties with additional added value of increased bio-based content and improved biodegradability that can contribute to decrease the effluent treatment load. Moreover, these products can be tailor-made to meet low emission (low free phenol, low free formaldehyde) requirements.

1 Introduction

In order to contribute to a more sustainable leather manufacturing process and leather value chain, in 2016 Smit & zoon started its own designing process of new products through the Bio-Based innovation platform. As a logical first step, answers to several key questions have been looked for: What is Bio-Based? What is renewable? Which term and method do we use to define the Bio-Based content in the Bio-Based platform? What is biodegradable? How do our current products perform? What is our vision for future products? In the process of answering these questions and guided by the Cradle-to-Cradle (C2C) Certified™ program, Material Reutilization Score (MRS) was used to obtain deeper insights into the formulation and environmental performance of our leather chemicals and treated as the basis for the design of new generation bio-based chemicals. Three main focus areas are setting the tone of current activities in the Bio-based platform: 1. Increasing the renewable contents of the existing product groups; 2. Smart valorization of industrial side streams from biological origin and 3. Improving the general biodegradability of leather chemicals. While focusing on such topics, it is well-understood that a proper balance needs to be found between cost, sustainability and performance. In the mean time, leather's end of life scenario plays a role and needs to be revisited.

Many polyphenolic macromolecules are routinely used in the manufacturing of leather. These water soluble compounds are either of natural origin such as tannins and lignosulfonates or of largely petro-chemical nature such as phenolic syntans.[1,2] The use of petro-chemical building blocks in the manufacturing of phenolic syntans not only contributes to their relatively high Carbon Footprint (CF)[3] but also poses harmful emission risks. Improvements in syntan's petro-chemical nature are expected to eliminate these problems and contribute to a more sustainable leather value chain. In one study carried out following the C2C methodologies, Material Reutilization Scores (MRSs) of different groups of leather wet-end chemicals have been calculated and compared.[4] MRS takes into account the combined effect of the renewability and biodegradability of chemical ingredients in a product. The preliminary results indicate that improvements in syntan's MRS is likely to generate bigger positive impacts compared to other wet-end chemicals e.g. natural oil-based fatliquors. To this end, a priority area in our bio-based

research platform is to improve the bio-based content of syntan products. Lignin, a natural polyphenol being the most abundant natural aromatic resource is well-known for its role in woody biomass to give resistance to biological and chemical degradation due to its hydrophobic nature and insolubility in aqueous systems. Derived from natural lignin, lignosulfonate presents sulfonate groups that make it water soluble is by far the only type of lignin used as such in leather making processes. As the most important source of bio-based aromatics, the valorization of lignin streams that are currently mostly used directly for producing process energy has become an increasingly important topic for the bio-based and circular economy. In this paper, the first examples of using water insoluble industrial lignins as phenol replacements for the manufacturing of phenolic syntan are discussed.

2 Materials and methods

2.1 Materials

Lignin contains three different structural components/monomers:p-coumaryl, coniferyl and sinapyl alcohol in p-hydroxylphenyl (H), guaïacyl (G) and syringul (S) units, respectively (see Figure 1).[5] The cross-linked structure of lignin is very complex and can vary a lot depending on the specific species, the season, the geological region/climate and the age of the plant. Generally speaking the H/G/S composition strongly depends on the type of plant: hardwood mainly contains G and S, soft wood mainly G and grass species contains all three.

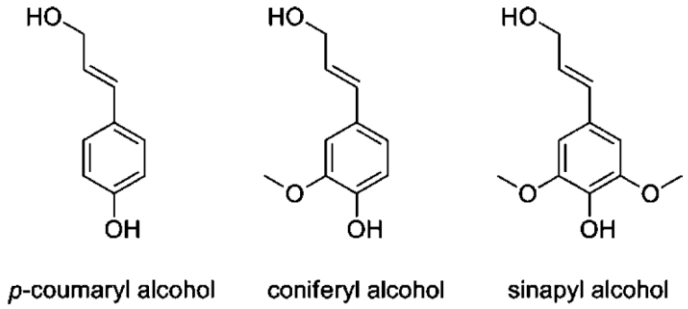

Fig. 1. Building blocks of lignin (adapted from Ref. 5).

Table 1 presents an overview of most of the different lignin types used in this study, they vary not only in their origin/biomass feedstock, but also in the type of pretreatment applied prior to lignin separation. It is worth noting that as a result of these variations, each specific type of lignin may present different composition of functional groups: namely varying contents of phenolic, aliphatic and carboxylic hydroxyl groups. In addition to those listed in the table, some lab-scale prototypes have also been tested. All lignins used in this study have similar physical form as a (dark) brown powder.

Table 1. Types of lignin used in this study, their origin and typical characteristics.

Type of lignin	Pretreatment Chemistry	purity	Ash	Mw (g/mol)	origin
Kraft	Alkaline	high	low	≤ 6000	soft & hard wood
Soda	Alkaline	high	low	≤ 6000	grass/straw
hydrolysis	Acid	moderate	low	n.a.	wood
organosolv	Acid	Very high	low	≤ 2000	wood

Depending on the type of applications either pickled calf pelt, chrome-tanned calf wet-blue (WB) or glutardialdehyde-tanned wet-white (WW) are used as starting materials for leather trials.

2.2 Methods

The synthesis of lignin modified syntan follows a modified procedure largely based on the traditional synthesis of phenol-aldehyde condensates or phenol-urea-aldehyde condensates.[1,6] Depending on the type of lignin chosen, lignin is added in its original powder form after phenol sulfonation. Afterwards the condensation with different aldehydes or mixture of aldehydes took place with or without the addition of urea at elevated temperatures. After termination of the polymerization, the pH of the reaction mixture is adjusted to obtain a clear liquid product. The product can be further processed, for example by spray-drying, to obtain a powder product.

The molecular weight (Mw) of the lignin and lignin modified phenol-urea-formaldehyde polymer is measured by alkaline gel permeation chromatography (GPC) according to the procedure described by Gosselink et al.[7]

GPC analysis of representative samples based on different types of lignins following varying polymerization procedures are carried out at neutral pH using a PSS MCX column combination medium and the elution curve is recorded using a UV-detector at 280 nm. Standard used for calibration of the molar mass distribution are sodium polystyrene sulfonates with a molecular weight range of 891 to 976000 dalton.

Shrinkage temperature (Ts) tests are performed according to IUP 6. Ready biodegradability test of chemicals is done following an in-house Manometric Respirometry method based on OECD 301F. Free phenol is determined by an in-house method using Emerson's reagent and detected by UV-Vis spectroscopy.[8]

Free formaldehyde is determined by an in-house method using acetylacetone and ammonium acetate and detected by UV-Vis spectroscopy at 412 nm. Free glyoxylic acid is determined by an in-house titration method using hydroxylamine.

3 Results and Discussion

3.1 Incorporation of lignin to the product

All the lignins listed in the previous section can be used for the preparation of lignin-phenol based polycondensates. However, every lignin type requires (slight) modifications on the synthesis procedure and results in syntans with different product characteristics (e.g. Mw, viscosity) and different effects on leather. The maximum lignin:phenol ratio (w/w) also varies per lignin type.

There are strong indications that lignin is participating in the polycondensation reaction and not just incorporated in the final product in a sulfonated form: 1. The amount of sulfuric acid used in the reaction is either in very slight excess to even not enough to completely sulfonate the phenols used. In either case the sulfuric acid concentration seems to be too low[9] to allow lignin sulfonation or phenolation under the applied experimental conditions. Only after the initiation of the polycondensation reaction with the addition of the aldehydes the slow dissolution of the insoluble lignins is observed when viscosity build-up becomes obvious eventually leading to almost total dissolution of all insolubles. 2. Even when the amount of sulfuric acid used is not even enough to sulfonate all the phenol the lignin dissolution at the end of the condensation procedure is still observed. 3. A somewhat higher Mw is obtained when products are made following similar procedures but replacing the 100% phenol with a combination of phenol and lignin. 4. Comparison of alkaline GPC results on the original lignin and the product with lignin incorporated in the chemical recipe clearly shows Mw build up after the synthesis with no exact overlap of any peak values.
Theoretically there are probably several chemical reactions taking place at the same time. First of all, lignin does contain phenolic hydroxyl groups , which would be the most obvious possibility for lignin to act just as a phenol to participate in the polycondensation reaction. Secondly, lignin can also be

phenolated under acidic conditions and eventually resulting in its incorporation into the polymers. A third possibility is the self-condensation of the phenyl propane subunits of lignin under such conditions.[9] In Fig.2 the most obvious possibility of lignin participating in the polycondensation reaction is illustrated.

Fig. 2. Possible crosslinking sites on lignin and on the polymer (indicated by the red arrows).

For most of the prototypes the emission profile of the lignin modified polymers has been checked and can be controlled via optimized synthesis procedure to minimize the free monomer contents. The free phenol content is generally below the detection limit of 20 ppm. Depending on the type of aldehyde used in the reaction, the product can be made free from formaldehyde.

3.2 Tanning effect of the lignin modified prototypes

The obtained prototypes display tanning effect in stabilizing the fiber network, which was demonstrated by their ability to raise the shrinkage temperature (Ts) of hides. This has been tested in two ways: on pickled pelt following the traditional tanning procedure and on glutardialdehyde pre-tanned wet-white leather.

Following a typical tanning procedure starting from pickled pelt, one of the lignin-phenol-aldehyde condensates is applied with an amount of up to 70% (w/w) based on pelt weight in combination with a dispersing syntan as an auxiliary. The measured Ts of the obtained leather is 75°C.

When the same lignin-phenol-aldehyde condensate is applied on WW leather pre-tanned with glutardialdehyde that typically displays a shrinkage temperature of 68-70°C at up to 30% (w/w) based on shaved weight, a maximum increase of Ts of 12 °C has been recorded. It was also seen that the higher the amount applied, the higher the Ts of the obtained leather will be.

3.3 Retanning effects of the lignin modified prototypes

We have demonstrated that the obtained lignin-phenol-aldehyde prototypes are suitable to be used as retanning agents for both chrome-tanned and chrome-free leather rendering good organoleptic and physical properties. When a typical usage of up to 30% (w/w) based on shaved weight is applied in the retanning stage, pronounced effects in improvements in the grain tightness, grain smoothness and fullness of the crust can be expected.

In some cases when specific types of lignins are incorporated in the product, the treated leather may display very unique, nice and soft touch.

3.4 Biodegradability of the lignin modified prototypes

Biological degradation of lignocellulosic biomass is essential for the closure of the ecological carbon cycle.[7] It is known that the biological degradation of wood results in lignin degradation by enzymes under the influence of environmental factors such as light, temperature and humidity.[10] In our study the degradation of a lignin-phenol-urea-aldehyde syntan (with a lignin:phenol ratio of 3:4) has been compared with that of a similar, traditional urea containing but 100% petro-based phenolic syntan: an increase of the BOD_5/COD of 400% was obtained. Our most recent developments show that with higher lignin:phenol ratio there are still room for further improvements.

4 Conclusions

Various industrial, water insoluble lignins from different origins can be used to prepare polyphenolic (re)tanning agents with higher bio-based contents. Compared with otherwise 100% petro-based phenolic syntans, the lignin-modified syntans can be made with a mixture of lignin and phenol that contains a majority of lignin (w/w). The bio-based syntans display tanning effects in its capability of raising the shrinkage temperature of leather or hide. When used in the retanning stage, they render leather improved grain tightness, grain smoothness and fullness. Lignin modified syntans can be further tailor-made to meet low emission requirements and contribute to improvements in waste water quality due to its higher biodegradability. We hope to show you that our innovative technology not only facilitates a novel way of utilizing and upgrading bio-based industrial side-streams, but also offers truly added value in upgrading leather qualities and contributing to minimizing the environmental impact of leather making process.

In addition to the lignin-based polymers, the quickly developing project portfolio within the bio-based platform manifests that Smit & zoon is making steady steps towards a largely sustainable leather value chain by 2025.

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