Innovative organosolv treatment to enhance self-adhesive properties of wood, first results of OS-WOOD project

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Context and objectives

Green defibering methods are nowadays strongly investigated in order to convert vegetal biomass into new uses. Main studied application for defibering aim to increase digestibility to fermentescible sugars for biorefinery processes or as a pulping-type treatment to extract the cellulose. Recently, steam explosion has received strong attention for its ability to bring self-adhesion thanks to lignin strong redeposits on the fiber surfaces. Organosolv (OS) treatments also deserve to be investigated for similar purpose. Organosolv defibering is a process based on a mixture of water and a miscible organic solvent. Contrary to steam explosion, a significant part of the lignin can be extracted in a high purity form, so affording a valuable by product. Moreover, a biobased solvent called gamma-valerolactone (GVL) was extensively studied for biorefinery purposes. The scientific question which is addressed in this project is to know if any conditions of GVL organosolv treatment allows the deposits of lignin droplets in the fiber surface and if autoadhesive properties are enhanced by chemical and morphological changes.

Material and methods

Fagus sylvatica, also known as European beech, was used as wood material. It was ground and sieved into 1-2 mm particles using RTetsch ZM 200 machine. Solvent gammavalerolactone (GVL) is non-toxic, environmentally friendly, soluble in water, non-volatile, having a high boiling point (207 °C). GVL is a stable chemical that is not susceptible to decomposition and oxidation at standard temperature and pressure, making it a safe substance for large-scale storage, transportation and other applications (Lê et al 2016). It is characterized by high selectivity to lignin, and the ability to recycle without significant losses (Jiang et al 2016).

Beechwood particles underwent GVL/water organosolv treatment in 800mL closed reactor (Parr), under varying process conditions (temperature, duration, catalysis by sulphuric acid catalyst or no), then were separated into pulp and black liquor by vacuum filtration and carefully water washed. Lignin was precipitated from liquor by water anti-solvant addition (5 volumes/volume of liquor). Dried pulped fibers were weighted to assess the yield of extraction, and Klason lignin. Morphological and structural features of the fibers were studied by scanning electron microscopy (SEM) after the surface was metallized, on a JEOL JSM–IT200 instrument. Most promising samples were finally subjected to board pressing. First particles at a moisture content of 10% samples were compacted using moulds with geometric dimensions of 8 × 8 × 10 cm. The pressing was carried out using a hydraulic press Joos LAP 150 at a temperature of 200 °C at a maximum pressure of 15 N/mm2. which were evaluated for cohesion strength following NF EN 319 standard. The tests were performed on a universal testing machine (Zwick/Roell) under standard loading conditions.

First results and discussion

A selection of weight assessments are summarized in Tab. 1. According to final yield, treatments are sorted in three groups: those which achieve low or mild impact, strong impact (harsch), and intermediate on starting wood weight. Most influent factors are the concentration of acid catalyst and solvent ratio. Harsch and intermediate conditions also allow the extraction of lignin which can be isolated (data non shown). Harsch condition led to high loss of solid fibers and could be attractive in a "lignin first" strategy. Replacing GVL by ethanol lowers the lignin ratio in the fibers as shown by Klason method.

Tab. 1 : résultats pondéraux des traitements organosolv

Treatment intensity[1]	Sample nb	Solvent ratio	Temp (°C)	Duration (min)	H_2SO_4 (mM)	Yield (%)	Klason lignin (%)
	nativ						18
mild	OS4 OS5	GVL, 65% GVL, 65%	150 170	5 5	0 0	99 92	n.d
harsh	OS1 OS7	GVL, 65% GVL, 65%	150 170	45 5	50 25	5 20	n.d
intermediate	OS2 OS8 OS10 OS14	GVL, 65% GVL, 35% GVL, 35% EtOH, 35%	150 170 190 170	5 5 5 5	50 25 0 5	38 30 50 61	n.d n.d 8 14.

[1]experiences have been sorted in three groups following yield (high loss of biomass gives low yield)

FT-IR data help to confirm the relative loss of lignin according to the samples. Lignin specific bands (1593 cm^{-1}, 1505 cm^{-1}, 1453 cm^{-1}) are dramatically reduced when intermediate and harsh conditions were applied. Syringyl groups seems to be more preserved than Gaiacyl ones (Fig. 1).

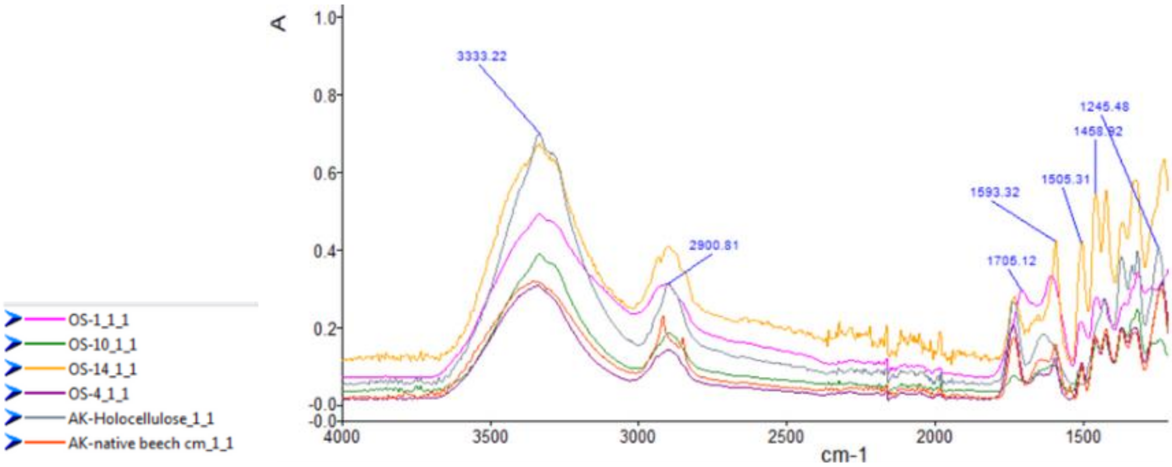


Fig. 1 : spectres en moyen infrarouge des échantillons traités après normalisation au plus grand pic.

Scanning electron microscopy

A detailed image of the sample surface was obtained using SEM, suitable for the detection of changes at the microstructural level. The analyzed samples included natural beech wood as a control and the treated OS10. As shown in Fig. 2, the surface of native beech chips is characterized by a complete structure of cell walls despite mechanical deformations that occurred during the grinding process are visible. In contrast, SEM images of samples subjected to organosolv treatment show varying degrees of destruction of the lignocellulose matrix (Fig. 3). The SEM images of the OS-10 sample particularly shows numerous spherical lignin droplets with a diameter of 0.5 to 2 microns deposited on the fiber surface, which is similar to one literature data (Xu et al 2007) devoted to ethanol organosolv, but has never been observed with GVL. Their presence mainly on the outer layers of the cell wall indicates the migration of lignin from the inner part of the matrix during pulping. At the same time, cell wall destruction and the formation of a porous structure are observed, accompanied by fiber separation, which confirms the effective removal of part of the lignin and hemicelluloses. There was also a partial melting of the surface, instead of lignin droplets in the areas of thermal damage. In addition, the morphological characteristics of the OS-10 samples are largely like the results obtained after a steam explosion. We can conclude that like SE, organosolv treatment show that part of the lignin recondenses on the surface of the fibers. The mild treated samples, on the contrary, retains a morphology close to the native wood and demonstrates minimal changes in the cellular structure.

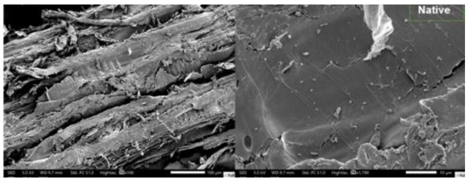
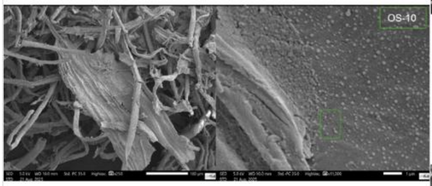


Fig. 2 : SEM microscopy of native beech



Erreur ! Source du renvoi introuvable.
Fig. 3 : SEM photo of OS10 GVL treated beech

Board pressing and self-adhesive properties

For native wood, the cohesion value was not detectable contrary to OS-10 samples which withstood a cohesion strength (F_t) of the order of 0.02 MPa the highest strength among the studied variants. This is obviously a very low value according to standard requirements (0.5 MPa) which indicates the limited binding properties of the structure under these processing conditions. However, density of our panels was assessed around 0.55 instead of 0.65 for commercial particle boards and we have not achieved optimization of board pressing.

Conclusion

We have demonstrated the chemical and morphological changes of GVL-treated beech wood. Lignin droplets were accordingly observed at the fiber surface. It is rather encouraging results because we have shown an enhancement of self-adhesive properties wood particles as expected and we can assume the link between the surface modification of fibers and the ability to promote adhesion, although it's a rather weak effect.

References

Auxenfans T, Crônier D, Chabbert B, Paës G (2017) Understanding the structural and chemical changes of plant biomass following steam explosion pretreatment. Biotechnology for Biofuels, 10:36.

Jiang Z, Zhao P, Hu C (2016) Controlling the cleavage of the inter- and intra-molecular linkages in lignocellulosic biomass for further biorefining: A review. Bioresource Technology, 215:1-12.

Lê HQ, Zaitseva A, Pokki JP, Ståhl M, Alopaeus V, Sixta H (2016) Solubility of organosolv lignin in γ-valerolactone/water binary mixtures. ChemSusChem, 9(19):2939-2947.

Nair LG, Agrawal K, Verma P (2023) Organosolv pretreatment : An in-depth purview of mechanics of the system. Bioresources and Bioprocessing, 10:50.

Pandey KK (1999) A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. Journal of Applied Polymer Science, 71(12):1969-1975.

Rodrigues Gurgel da Silva A, Errico M, Rong BG (2018) Techno-economic analysis of organosolv pretreatment process from lignocellulosic biomass. Clean Technologies and Environmental Policy, 20(7):1401-1412.

Xu Y, Li K, Zhang M (2007) Colloids and Surfaces A: Physicochemical. Engineering. Aspects 301:255-263.

Zhao X, Cheng K, Liu D (2009) Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. Applied Microbiology and Biotechnology, 82(5):815-827.