# Chemical Characterization of Wood-Leather Panels by Means of $^{13}$C NMR Spectroscopy

Tilman Grünewald,[a,c]* Warren Grigsby,[b] Gianluca Tondi,[a] Sven Ostrowski,[a]
Alexander Petutschnigg,[a] and Stefanie Wieland [a]

Intelligent resource usage is one of the most challenging tasks for the wood-based panels industry. With respect to this issue, leather shavings, derived during leather preparation, are a promising new raw material, as they offer not only high availability, but also potentially enhance material properties such as panel fire retardancy. In order to improve the performance of these emerging panel binder materials, an understanding of chemical interactions between the different constituents is crucial. This paper investigates the chemical changes that occur during hot-pressing of wood and leather in combination with lignin by means of solid state $^{13}$C NMR spectroscopy. These constituents, their binary mixtures, and the influences of panel pressing temperature and pressure commonly used in panel production were investigated. The study showed characteristic chemistry and features of these constituents, quantifying the impacts of both heat and pressure on their interactions. Primarily, analysis revealed that lignin readily connects with both the wood and leather components. Lignin induces chemical change within the protein structure of leather, resembling tanning reactions, or protein complexation. By analogy, it was deduced that this interaction also takes place between leather and the lignin-rich wood fibre surface. This effect may be beneficial in industrial-scale production through improving resin binding properties during panel consolidation.

*Keywords: $^{13}$C solid state NMR spectroscopy; Lignin; Wood fiber; Wet blue leather; Chemical connections; MDF*

*Contact information: a: Department of Forest Products Technology, University of Applied Sciences Salzburg, 136a Marktstraße, A-5431 Kuchl, Austria; b: Bioproduct Development, Scion Rotorua, New Zealand; c: Department of Materials Science and Process Engineering, Institute of Physics and Materials Science, BOKU – University of Natural Resources and Life Sciences, Peter Jordan Straße 82, 1190 Vienna, Austria; *Corresponding author: tilman.gruenewald@boku.ac.at*

## INTRODUCTION

Efficiently utilising a material’s inherent properties is an important aspect of materials science and its related fields. This is true for the forest products industry, which has invested considerable efforts to increase both productivity and the efficient utilization of by-products. Research in this field has also been extended to incorporating alternative lignocellulosic materials in lower-grade applications such as wood-based panel production. Examples of such substitutions include straw- and reed-based materials use in medium density fiberboard (MDF) (Han *et al.* 2001), MDF composed of agro-waste products such as bagasse or bamboo (Lee *et al.* 2006), or the use of rice husks as a raw material for particleboard (PB) (Leiva *et al.* 2007). This research has been developed to utilise increasing availability of these materials and to deal with a predicted worldwide undersupply of 100 M m³/yr woody biomass by 2020 (Mantau 2010).

With an annual production of 20 M m³ in Europe (Botting 2011), MDF accounts for a substantial proportion of Europe's overall wood-based panel (Oriented Strand Board (OSB), MDF, and PB) production capacity (65 M m³) (European Panel Federation). Therefore the sourcing of new raw materials with reasonable availability is important within this industry. A promising new raw material for MDF is leather shavings. Potentially over 200,000 tons of leather shavings are generated in Europe per year, and this could provide a considerable resource for the production of wood-based panels (LMC International LTD 1997).

In recent literature, only a few studies on the material use of leather shavings have been reported (Kangaraj *et al.* 2006; Sundar *et al.* 2011). For example Ramaraj *et al.* (2006) describes using leather particles as fillers in ABS plastic, with wet blue leather particles also reported as fillers with PVB polymers (Ambrósio *et al.* 2011). Composites comprising wood fibers and leather shavings have been reported (Lackinger 2009). The structure and mechanical properties of such leather-wood fibre composites have been reported (Grünewald *et al.* 2012; Wieland *et al.* 2013), together with their fire resistance properties (Wieland *et al.* 2012). This combination of properties, especially the fire resistance, is interesting, as the properties are increased to a larger extent than would be expected from the performances of the individual constituents, wood and leather.

While indicative physical properties of the leather-wood fibre panels have been characterized, there is a growing complexity arising within these multi-constituent composites, which may be attributed to a range of component interactions including mechanical, physical, and chemical. To further the understanding and application of leather incorporation with wood fibre, a greater knowledge on these component interactions is required.

The current paper investigates chemical changes that occur during hot pressing and formation of wood-leather panels. The study primarily utilizes $^{13}$C solid state NMR spectroscopy. The chemical change observed between components and within panels is then related to the physical and chemical processes of panel consolidation.

## EXPERIMENTAL

### Materials

Mag. Gerald Lackinger Consulting, Salzburg, Austria specified and provided wet blue leather particles derived from chromium-tanned cattle hide, being produced during the shaving to thickness phase in the leather preparation. The wood fibers were provided by Kaindl, Salzburg, Austria and are a blend of different coniferous species, primarily Norway spruce (*Picea abies*). The lignin powder "Arboform F" was provided by Tecnaro GmbH, Ilsfeld, Germany and is a modified, thermoplastic injection moulding grade lignin. It was used as obtained.

### Sample Preparation

Three constituents – wood, leather, and lignin – and binary mixtures of wood and leather with lignin were investigated before (original) and after the pressing procedure. Each constituent (wood, leather, and lignin) was also treated individually and used as a reference. The detailed list of samples and their treatment is given in Table 1.

**Table 1.** List of Sample Compositions by Weight and Descriptions of their Treatment Undertaken Prior to $^{13}$C-NMR Analysis

| Sample Number | Wood [wt %] | Leather [wt %] | Lignin [wt %] | Treatment |
|---|---|---|---|---|
| 1 | 42.5 | 42.5 | 15 | pT |
| 2 | 100 | 0 | 0 | pT, separated |
| 3 | 0 | 100 | 0 | pT, separated |
| 4 | 0 | 0 | 100 | pT, separated |
| 5 | 100 | 0 | 0 | 0 |
| 6 | 0 | 100 | 0 | 0 |
| 7 | 0 | 0 | 100 | 0 |
| 8 | 0 | 92.5 | 7.5 | pT |
| 9 | 92.5 | 0 | 7.5 | pT |
| 10 | 0 | 92.5 | 7.5 | 0 |
| 11 | 92.5 | 0 | 7.5 | 0 |

The leather shavings were dried to a moisture content of 8% and sieved to <4 mm grid size. The moisture content was gravimetrically determined with a moisture analyser (Kern MLB 50-2). The sieving was carried out with a test sieve of 4 mm mesh size. The leather shavings were mixed with wood fibers in a ratio of 50:50 (w/w) using a laboratory ploughshare mixer.

Lignin powder (15% w/w, calculated on dry mass of fibre/leather) was added as an adhesive binder. In order to retain the integrity of the prepress mats and the forming panels, a mold made from soft board was used to transfer the pre-press mats to the hot press. A temperature of 180 °C and a pressing time of 12 min was used, and this is further referred to as the temperature and pressure treatment (pT, Table 1). The pre-press mat was then pressed to give panels (340 x 250 x 24 mm) and density of 300 kg/m³ using an automated hot press (Hoefer HLOP 280). This treatment of panel pressing applies for the samples, 1-4, 9, and 10. The reference samples without pT treatment were just dry-blended and are not modified in any way.

After conditioning (20 °C/65% R.H.) the panel was manually disintegrated and mixed thoroughly. In a second step, 100 g of material was randomly selected, and from this, 10 g was subsampled and thoroughly milled with the aid of a mortar and pestle. Samples were sealed under vacuum and stored prior to analysis.

Single constituents were mechanically separated from the final panel under an incident light microscope with a magnification factor of 20. This was achieved by taking the disintegrated material (10 g) and selecting wood, leather, or lignin constituents and removing these by the aid of forceps. This selection was aimed at a qualitative distinction of constituents, rather than producing a large quantity of the extracted material.

## $^{13}$C NMR Spectroscopy

Solid state $^{13}$C-NMR analysis was performed on a Bruker Avance 200 spectrometer with a 7 mm HX probe. Samples were packed in a zirconia rotor fitted with a Kel-F endcap. Samples were spun at 5 KHz, and 2048 scans were acquired per spectrum, collecting in the region between -50 ppm and 250 ppm. Optimized Hartmann-Hahn conditions were used to maximize spectral intensity across this region. As the nature of this survey is to compare the peaks only with regard to qualitative changes, any further considerations regarding signal normalization were left aside.

## RESULTS

Modified lignin, wet blue leather particles, and wood fibre were combined together and hot-pressed to give an MDF panel (300 kg/m$^3$). This approach produced viable panels for further analysis. Although higher densities are used in industrial processes, 300 kg/m$^3$ density was acceptable for chemical analysis due to the separability of the constituents, and furthermore, panels of this density had also been used in a prior study (Grünewald *et al.* 2012). Additionally the three components were also combined as binary mixtures and similarly treated under heat and pressure. In order to evaluate any chemical interactions between components, the panels were disintegrated and, together with the binary mixtures, the residues manually separated by identifying each component visually. Separation of components proved straightforward as the integrity of the leather and wood fibre components was retained within the panel.

### $^{13}$C NMR Spectroscopy

Fig. **1** shows the comparison of wood, leather, and lignin, each in its original, untreated form. Each of these constituents is associated with key, characteristic peaks (Table 2). Wood fibre was characterized by the dominant peaks of the cellulose component at 104 ppm (C1) and 72 ppm (C2,3,5), being typical of the species mix used (Puentes Rodriguez *et al.* 2012; Wikberg and Maunu 2004). In the case of leather shavings, the spectrum of leather is defined by the amido-carbonyl peak at 175 ppm together with distinctive aliphatic peaks in the range 20 to 80 ppm (Romer *et al.* 2011). For lignin, this material is defined by the characteristic aryl- (140-150 ppm) and methoxy peaks (50 ppm) (Kringstad and Mörck 1983). However, as this technical lignin had been modified for injection molding, additional peaks attributable to carbonyl (170 ppm) and aliphatics (30 to 40 ppm) are also observed. This may be an indication for either grafted polymer groups to the lignin or simply an added thermoplastic compound that enhances the performance as an injection moulding compound.

Across these three components it was evident that the spectra were readily distinguishable due to their characteristic peaks.

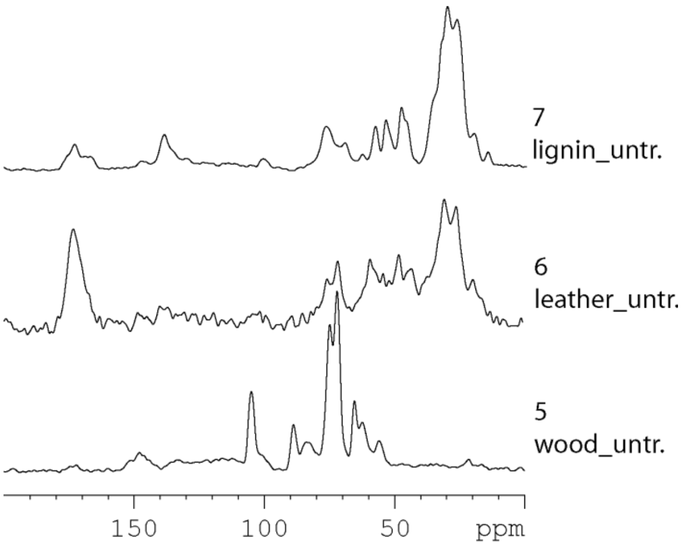

**Fig. 1.** Solid state $^{13}$C NMR spectra of wood (5, bottom), leather (6), and lignin (7, top) in original, untreated form

**Table 2.** Assignment of Chemical Shifts in the $^{13}$C NMR Spectrum (McMurry 2011; Robert 1992; Kringstad, Mörck 1983; Romer *et al.* 2011)

| $^{13}$C NMR shifts [ppm] | Compound |
|---|---|
| 175 | amido-carbonyl |
| 170 | carboxylic acid |
| 150-140 | aryl |
| 104 | C1 cellulose |
| 72 | C2,3,5, cellulose |
| 50 | methoxy |
| 40-25 | aliphatics |

Depicted in Fig. 2 are spectra showing the influence of pressing and heating (pT-treatment) on the wood and lignin binary combination (9 and 11). The parameters of the pressing programme, such as pressure (p) and temperature (T) were similar to those used for MDF panel consolidation. In addition to the pT-treated combination, a comparison of separated wood fibers obtained from the mixture after treatment (2) is also shown.

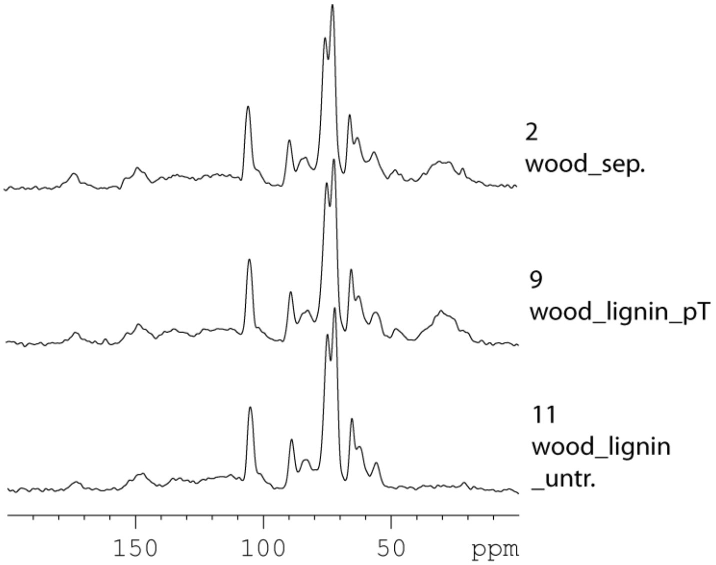

**Fig. 2.** Solid state $^{13}$C NMR spectra of wood-lignin in the untreated form (11), after pT-treatment (9) and separated wood fibre (2)

By comparing the spectra of the wood-lignin before (11) and after pT (9), it can be seen that the heat treatment resulted in an increased presence of peaks in the aliphatic region (30 to 40 ppm). This emergence of aliphatic peaks (9) compared to (11) was likely due to a change in NMR relaxation parameters for this lignin component, indicative of greater molecular rigidity due to an intimate connection between the modified lignin added and wood fiber (Smernik and Oades 2000; Smernik *et al*. 2002). In contrast, sample 11 (added modified lignin powder) exhibited a lower NMR response of the aliphatic peaks and may be due to this sample being in untreated form, being a simple mixture, with the added lignin component remaining physically separated from the wood fibre component. The spectrum of the separated, or extracted, pT wood fibers (2) also showed the aliphatics peaks associated with added lignin, indicative of the presence and intimate connection between the modified lignin and the wood fibers. This may provide direct evidence that the added lignin was at least associated with, or has potentially penetrated the wood fibre cell wall, as indicated by recent studies (Donohoe *et al.* 2008; Hosseinaei *et al.* 2012). This confirms that lignin may bind to lignin-rich MDF fibre surfaces. Modified lignin adhering to fibre surfaces would be sufficient to increase molecular rigidity and result in an observed change in NMR response for the aliphatic moiety of this lignin component in spectra of treated samples (2, 9).

Shown in Figs. 3 and 4 are spectra of various treated binary combinations and the consolidated panel, as well as separated components from these combinations or panel. Fig. 3 shows the leather-lignin binary mixtures untreated and after pT-treatment together in comparison with separated leather and lignin.

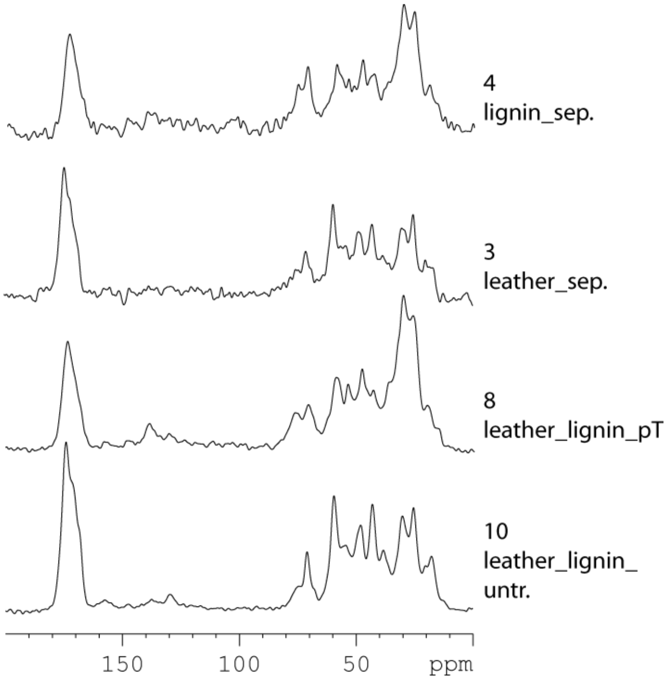

**Fig. 3.** Solid state $^{13}$C NMR spectra of Leather-Lignin in the untreated form (10), after pT-treatment (8) and the separated leather (3) and lignin (4) components

From these spectra, it can be seen that combination and heat treatment resulted in chemical interactions between the components (8). Firstly the amido-carbonyl peak (180 to 170 ppm) broadened on heat treatment with the shoulder at 170 ppm was no longer distinguishable, indicating a change to the proteinaceous component potentially through protein binding or rearrangement (Bicudo *et al.* 2005). An increase in the aliphatic peak (25 to 40 ppm) was observed, which was similarly observed for the modified lignin component in Fig. 2. As suggested above, this increase in the aliphatic peaks was likely due to increased molecular rigidity and lignin binding. Collectively, this, and the change primarily involving the leather amido carbonyl signal suggest interactions between the leather and lignin components, or a further tanning of the leather component. However, it is difficult to definitively deduce any further chemical change, given the little amount (7.5% w/w) of lignin used and the relatively low peak intensity of the lignin aryl carbons (140-150 ppm). Moreover, the lignin methoxy peak (50 ppm), which was broadened, was also complicated by peak overlaps with the protein component. The extracted leather (3) shows a relatively decreased amido-carbonyl, but does not show any significant peak differences in the aliphatic region (25 to 40 ppm) which, anecdotally, would suggest evidence for the presence of lignin as observed with sample 2. Instead, the change in the carbonyl peak may suggest a heat-induced change or rearrangement, although solid state NMR does not readily distinguish protein conformational change (Bicudo *et al.* 2005). Furthermore, the lack of lignin signals in (3) may also be explained by exclusively selecting only pure leather particles with blue spots.

More interesting is the spectrum of lignin particles extracted (4) from the panel. Aliphatic peaks (30 to 40 ppm) can be clearly seen and indicate the presence of the modified lignin together with the leather amido-carbonyl peak (175 ppm) in relatively similar intensity. This indicates the extracted lignin component from the panel was either co-extracted with protein or has become coupled together, despite the lignin being visually pure on microscopy separation.

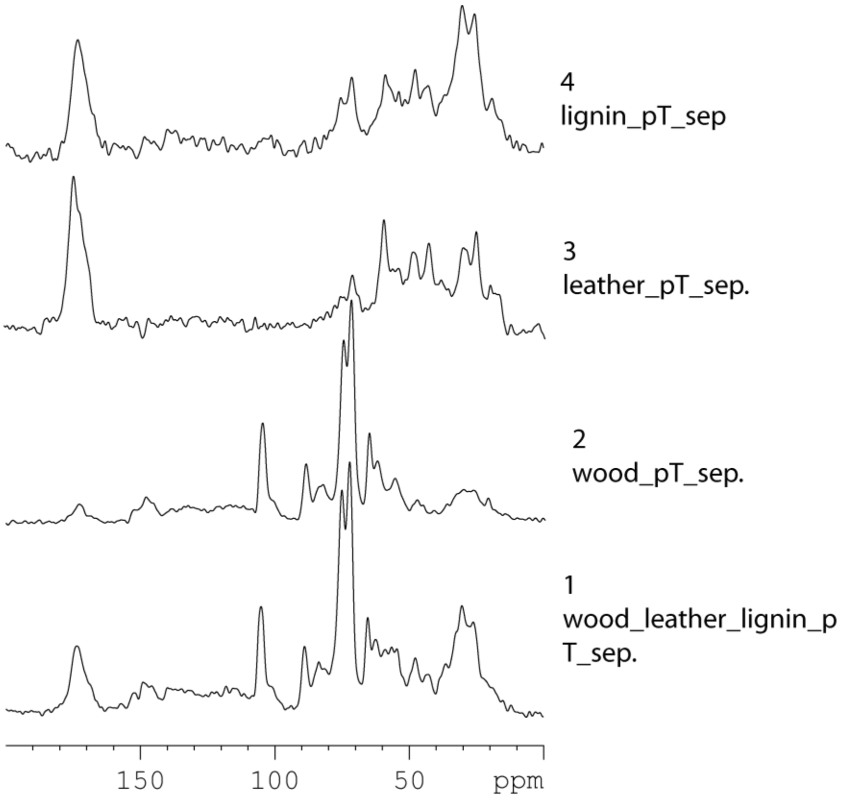

**Fig. 4.** Solid state $^{13}$C NMR spectra of the final complete panel (1) and its respective separated constituents wood (2), leather (3), and lignin (4)

From Fig. 4 it was logically deductible that the extracted components from the panel were chemically similar to the pressure-temperature treated combinations. In the wood sample spectrum it was evident that there was modified lignin associating with the wood fibre component, given the increased presence of the lignin aliphatic peak as observed with the corresponding binary mixture in Fig. 1. While this may suggest that the modified lignin was coupling to fibre, results indicate that the lignin was also associated with the leather component. Generally, the lignin and leather components separated from the panel exhibit comparable chemistries as those of the extracted binary combinations (Fig. 2 and 3). This was particularly evident for lignin whose spectrum indicates this material was also associated with leather as shown in Fig. 3.

## DISCUSSION

NMR spectroscopy indicated changes in the chemistry through association and coupling of wood fibre, leather, and modified lignin components on hot pressing.

This was particularly evident for lignin, with analysis suggesting that this component reacted intimately with the wood fibre in combination under heat and pressure. This was achieved both on binary combination, but also evidenced in the panel. The association of lignin with the wood surface was characterized by a change in the molecular rigidity of the modified lignin. This interaction led to a relative increase to the aliphatic carbon peaks in NMR spectra and was direct evidence for molecular level association (Donohoe *et al.* 2008; Hosseinaei *et al.* 2012).

Results for the direct combination of lignin with leather also revealed an affinity for lignin to couple with leather. Like the wood-lignin interaction, the association of lignin with leather was characterized by changes to key peaks in the NMR spectra. Even with relatively low lignin loading, a change in the protein amido carbonyl peak (175 ppm) was observed together with relative increases to lignin aliphatic peaks. The broad amido-carbonyl peak and the disappearance of a shoulder peak indicate a change in protein structure due to the presence of lignin, possibly resulting from a tanning reaction. This is of particular interest, as it distinguishes a chemical, structural-change from a physical interaction as in the case of wood-lignin. Further proof of this is given by the separated lignin which shows, although visually pure, chemical characteristics associated to leather and the tanning reaction. In analogy this effect should also be visible when mixing leather with wood fibres without any added lignin as the surface of the fibres is rich in lignin.

Based on the presented NMR spectra no clear answer can be given on the nature of the chemical bond that is created due to the interaction. Either a further cross-linking of lignin entities or molecular association is observed. As both contribute to the molecular rigidity of the aliphatics system, the enhancement of the solid state NMR response can be explained. Luo *et al.* (2013) observed this effect in tannin-linoleate systems, but as the unreacted unsaturation was rather evident in these systems, a clear attribution was possible.

This phenomenon is readily studied in the field of plant physiology, specifically tannin- and ligno-protein complexes (Hagerman *et al.* 1998; Zahedifar *et al.* 2002), and also some report on the usage of tannin complexation in tannin-based resins (Luo *et al.* 2013) is known. The artificial complexation of lignin and leather proteins is a novel observation. As supramolecular forces such as complexation are known to increase the performance of adhesives, especially with regard to water resistance, this phenomenon needs further investigation to be able to create a more controlled and effective cross-linking of leather and lignin.

Separation of heat- and pressure-treated samples shows that lignin was associated with leather. Separated leather shows only minor influences of lignin, suggesting that the modified lignin may preferentially associate with wood prior to bonding with leather. During the separation of wood fibers, a reasonable portion of the modified lignin remained on the wood fibers and was difficult to physically separate under the microscope. In contrast, in the case of separated leather, the modified lignin is easily recognizable on the leather scrapes, with physical separation suggesting any bonding with leather was not as strong as for wood. Mostly pure leather was isolated, although any lignin residues were not clearly distinguishable on the leather. This perhaps suggests that lignin preferentially binds with lignin-rich wood than with leather. A possible reason could be the lignin-rich surface of the wood fibres which easily enables the adsorption of the added lignin to the surface.

## CONCLUSIONS

This study has shown that both binary mixtures of lignin with either wood fibre or leather shavings behave similarly when these components are utilized in a pressed wood fibre panel. Heat- and pressure-treated binary mixtures of modified lignin and wood fibre reveal that the lignin adsorbs on the wood fibre surface. This interaction was observed by NMR with an enhancement of the aliphatic signals due to increased rigidity of the modified lignin. Similarly, lignin was also observed to adsorb onto the leather scrapings with NMR, also confirming a chemical interaction between the lignin and leather, akin to tannin or protein complexation. During pressing of a wood panel, comprised of leather shavings and modified lignin, similar interactions between each component were observed. This study has revealed that these components can be mixed in such a way that the interactions of the three components lead to binding of the wood fibre through lignin adsorption and coupling by leather. In conjunction with providing binding of wood fibre, such combinations can provide interesting material properties such as fire retardancy. Further work will be required for a greater understanding of the chemistry of these wood-leather panels and their applicability in regards to other properties such as degradation and end of life cycle.

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