STRUCTURAL ANALYSIS OF WOOD-LEATHER PANELS BY RAMAN SPECTROSCOPY

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Besides other ligno-cellulosic materials such as straw, rice husks, or bagasse, wet blue particles from leather production are a promising new raw material stock for wood-based panels, as they offer not only a high availability, but increase the properties of the panel with regard to fire resistance or mechanical characteristics. A panel with a mixture of 42.5% wood fibers, 42.5% wet blue leather particles, and 15% lignin adhesive was produced, and an inhomogeneous sample was prepared. An area of 9 x 10 mm was rasterized and scanned by means of Raman Spectroscopy. Furthermore, the reference spectra of the constituents, i.e. wood fiber, wet blue leather particle, and lignin powder were recorded. The obtained data were treated and analyzed using chemometric methods (principal components analysis PCA and cluster analysis). An important finding was that the reference data were not directly represented in the panels' spectra, and the correlation matrix of the PCA was not applicable to the panel data. This indicated that chemical changes might take place during the pressing. After processing the panel Raman spectra with the help of PCA and cluster analysis, three distinctive clusters were obtained, discriminating wood, leather, and mixed regions. With the assigned spectral information, it was possible to create a spectral image of the surface.

Keywords: Wet Blue leather; Fiber board; Raman spectroscopy; Heterogeneity; Distribution; Modeling

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INTRODUCTION

Increasing problems with raw material supplies for wood-based panels has triggered recent developments that have been seeking to diversify the material supply. In Europe the demand will exceed the supply within the next five to ten years, mostly depending on the supply scenario. This could result in an undersupply of roughly 100 million m³ of woody biomass in the year 2020. This is explained by the increasing energy use of woody biomass (Mantau et al. 2010). Therefore, different ligno-cellulosic materials such as rice husks (Leiva et al. 2007), straw (Han et al. 2001), or mixtures of bamboo and bagasse (Lee et al. 2006) have been studied. In this paper, we investigate fiberboards made from wood fibers and wet blue leather shavings. These shavings are a by-product of the leather preparation process, generated when a tanned hide is trimmed to its final thickness. Annually, a remarkable amount of 0.2 million tons wet blue shavings (LMC

1997) has been produced in Europe, and hitherto they can only be disposed in a landfill, as they show poor combustion properties. In the last years some attempts have been reported to use the wet blue shavings as a filler in a polyvinyl butyral matrix (Ambrósio et al. 2011; Ramaraj 2006), but, until present, no investigations on the use in a fiberboard are reported, although this invention is protected by an international patent (Lackinger 2009). Bearing the current development of the raw material supply in mind, the discussed leather material could offer a substantial new raw material supply for the wood-based panels industry, such as the MDF industry. As indicated by Lackinger, the dosage of leather improves mechanical properties, such as internal bond and increases the resistance towards fire.

With increasing complexity of the mixed constituents, the strength of the specimen is determined not only by the strength of the single fiber, but also by the interaction between the different fibers. In order to describe this behavior correctly, multi-scale mechanical modeling is a useful approach. Although remarkable efforts have been taken recently to describe composites such as wood, skin, bone, or concrete (Mang et al. 2009), the crucial information, necessary to build those models, is the location of the different compounds, and thus an accurate description of the heterogeneity of a material.

In this paper, the distribution of the constituents in a wood-leather panel is investigated by using Raman spectroscopy and by analyzing the data with chemometric methods, i.e. principal components analysis (PCA) and cluster analysis (K-means clustering), in order to describe the materials composition and structure (Agarwal and Ralph 1997; Musso and Oehme 2008; Gamsjaeger et al. 2011).

Based on this knowledge of the materials structure, physical modeling of the material can be carried out.

EXPERIMENTAL

Materials

Gerald Lackinger Consulting, Salzburg, Austria, provided wet blue leather particles. They are derived from cattle hide and are produced during the shaving to thickness phase in the leather preparation. The wood fibers were provided by Kaindl Salzburg and are a blend of different coniferous species. The lignin powder "Arboform F" provided by Tecnaro GmbH is a modified, thermoplastic lignin with a melting point of approximately 160°C. Its original use is as a plastic in injection molding, but it turned out to be highly suitable adhesive in the fiberboard production.

Sample Preparation

The leather shavings were dried to a moisture content of 8% and sieved to 4 mm grid size. The shavings were mixed with the wood fibers in a ratio of 50:50 using a laboratory ploughshare mixer. Subsequently, 15% of lignin powder, calculated on dry mass, was added as an adhesive. Then a mat was formed and pressed to panels of 24 mm thickness and a density of 300 kg/m³ using an automated hot press Hoefer HLOP 280 at a temperature of 180°C and a pressing time of 12 minutes. After acclimatization at 20°C/65% r.H., a specimen with high heterogeneity was cut out. As the aim of the study

was to determine the applicability of Raman spectroscopy for the description of the panels, a preliminary selection had to be carried out visually. A determination with spectroscopic devices provides new possibilities for the material characterization, such as an automated analysis distribution, which could be helpful for multi-scale modeling. Another very important field of application for this kind of heterogeneity description is the field of online measurement of various parameters. Currently various spectroscopic methods such as FT-IR Raman, NIR, or IR are applied in the wood-based panels industry (Oberkirchner and Petutschnigg 2010; Kandelbauer et al 2010). As described by Kandelbauer, the online determination of quality-influencing properties is a key factor in the assurance of a constantly high product quality.

In the following sections "sample" refers to the sample obtained from the pressed panel. In contrast "constituents" means the raw materials such as wet blue leather, lignin, and wood fiber.

Raman Measurement

As indicated by Vandenabeele et al. (2007), fluorescence is one of the most challenging side effects of Raman spectroscopy with organic materials. Therefore lasers with different NIR wavelengths, such as 1064 nm and 780 nm, were tested since, as Vandenabeele indicates, working in the near infrared region ensures the lowest fluorescence. The final spectra were obtained with a Bruker IFS66 FT-IR spectrometer with Raman module FRA 106 and laser excitation at 1064 nm with a laser spot diameter of 100 micrometers and a laser power of 275 mW. The spectra were recorded with cut-off frequencies of 90 and 3500 cm^{-1} and a resolution of 4 cm^{-1}. For each spectrum, 100 averaged scans were carried out.

The sample was trimmed to fit into the sample holder. Then, using an adjusting mechanism in X- and shims in Y-direction, an area of 9 x 10 mm was rasterized with a grid of 1 mm. After scanning the samples, a transparent PET foil and a black paper were aligned to the sample holder, and the corners of the grid were marked using the laser. Then the samples were scanned and photographed. This procedure is mostly described by Gamsjaeger et al. (2011).

Data Treatment

The spectra were cut off at 120 cm^{-1} for uniformity in the dataset, then the data were vector-normalized and the baseline-offset was corrected using The Unscrambler 9.7 by Camo Software (Kessler 2007; Gamsjaeger et al. 2011).

Data Analysis

In order to distinguish the different constituents wood, leather, and lignin in the panels, reference spectra were recorded and analyzed by using Principal Components Analysis.

As the Raman spectrum reflects the information on the molecular structure of the probed spot, chemically identical structures are grouped within the same cluster. To see whether chemical changes occurred during the pressing, the transformation matrix obtained was applied to the spectra of the panel.

The spectra of the panel were analyzed in a similar way to the single constituents by using a PCA. The PCA is a statistical method to describe a measured dataset. In the chosen approach the Components, which are describing most of the variation, are extracted from the dataset. "The Unscrambler 9.7" extracts this Principal Components with a NIPLAS (Nonlinear Iterative Partial Least Square) algorithm, described in literature (Kessler 2007). Mathematically the PCA is the solution of an eigenvalue problem. The data matrix X is separated into a score matrix T and a correlation matrix P^T. The residuals E are described in a different matrix. This can be described as:

$$X = TP^T + E \quad (1)$$

After extracting the principal components (PCs), a K-means clustering analysis was performed with Euclidian distance measuring (Gamsjaeger et al. 2011). As described in the literature (Backhaus et al. 2008), cluster analysis is a statistical method to assign data into specific groups. The assignment is carried out with the aid of distance measurements and a clustering algorithm. Among these, the k-mean algorithm, a non-hierarchical method, is a useful method.

A limitation of this method, in contrast to Ward's algorithm, is the need to define the number k of clusters beforehand. The idea of k-mean clustering is to create k random centroid points and measure the distance between each object and the centroid. Each object is assigned to the nearest centroid, and the centroid of each cluster is re-calculated. Starting from the new centroid, the before mentioned steps are carried until convergence is reached (Bortz 1999).

Regarding the distance measuring, certain different methods are known. They can be grouped according to the different levels of measurement. Because we deal with metric data, only these distance measurements are taken into consideration. As the relevant information is contained in the distance between the individual, the Euclidian distance measuring seems the most suitable, as it takes larger distances more strongly into consideration.

These clusters were mapped by the use of the surface-fitting tool of Matlab 2009 by Mathworks.

RESULTS AND DISCUSSION

Figure 1 shows the averaged spectra of lignin, wood, and wet blue leather, the constituents. As clearly visible, wet blue shows some rather distinctive peaks, such as can be observed at 2942, 1671, 1449, and 458 cm^{-1}, making it possible to clearly discriminate wet blue against lignin and wood.

Applying the PCA achieves a clear separation of the single constituents by using two PCs. As shown in Fig. 2, PC1 mainly distinguishes wet blue, while PC2 distinguishes wood and lignin.

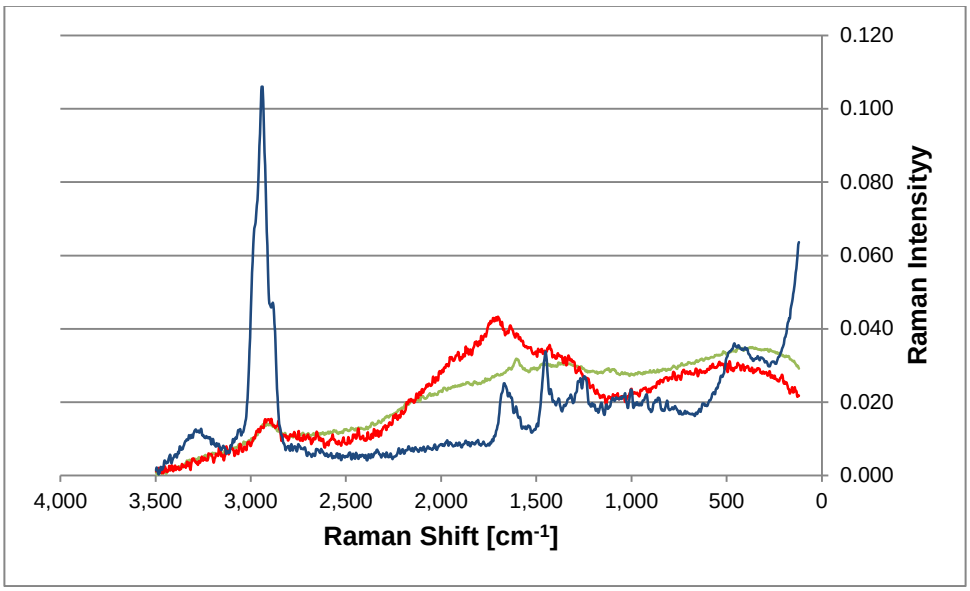

Fig. 1. Averaged Raman spectra of lignin (red), wood (green), and leather (blue)

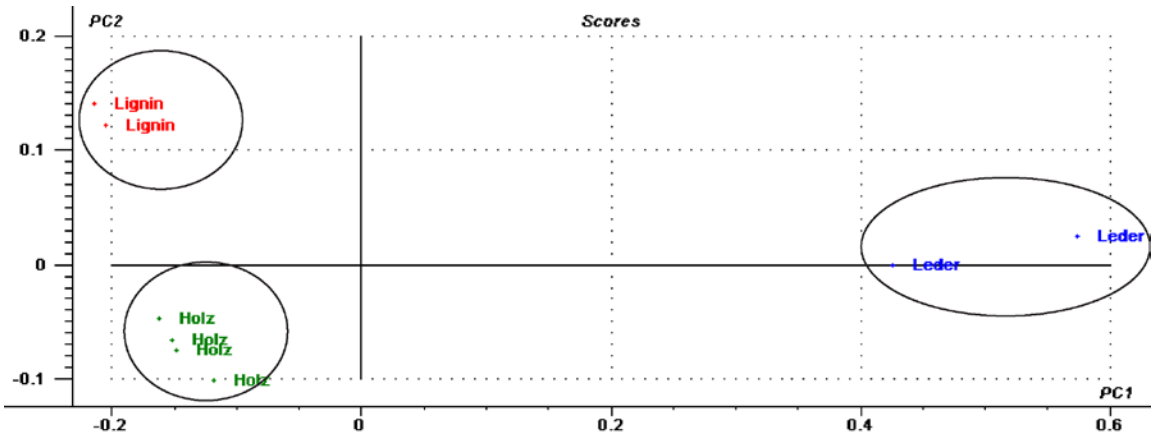

Fig. 2. Principal Components Analysis (PCA) of the single constituents lignin (red), wood (green), and leather (blue)

As the Raman spectrum reflects the molecular structure of the investigated material, it is possible to compare the chemical identity of the compound with that of the single constituents. If the chemical components indeed remain the same in composition, then the clusters should match each other. Applying the correlation matrix P^T, mentioned in "Data analysis" section, of the single constituents to the sample yields no identical clusters, suggesting the occurrence of a chemical change. In order to analyze the sample data, a PCA, considering only the sample data, is employed.

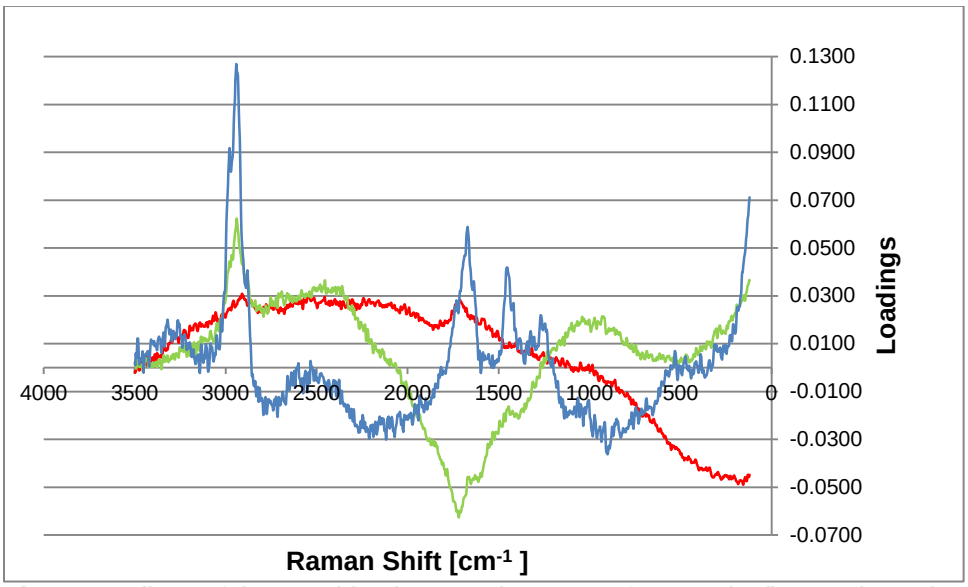

Fig. 3. Loadings of the wood-leather panel's spectra for PC1 (red), PC2 (green) and PC3 (blue)

Figure 3 shows the loadings of the PCs after the PCA. As the loading of PC 3 resembles the Raman spectrum of leather, the relevant separation between wood and leather takes place on PC3. By applying K-means clustering analysis with Euclidian distance measuring, three clusters can be distinguished, whereby Cluster 2 represents the wet blue, 3 represents wood, and 1 is a mixture of wood and lignin. This is shown in Fig. 4.

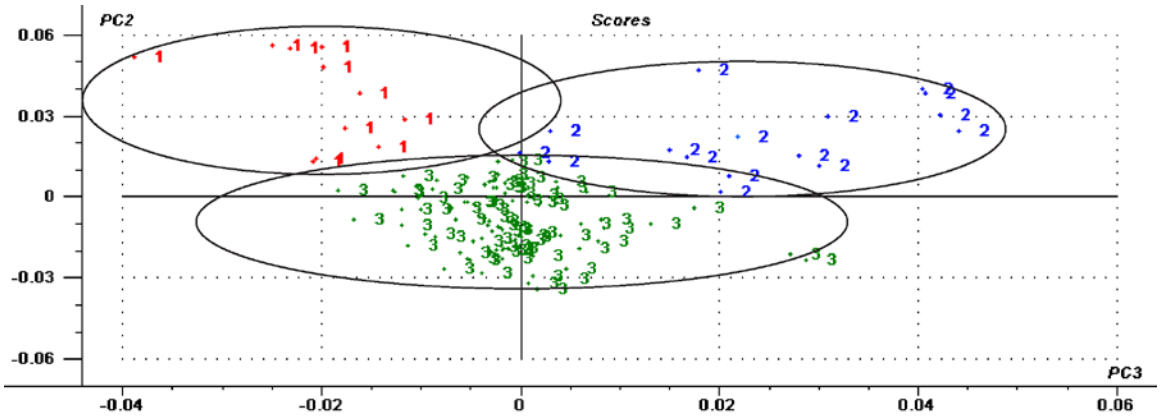

Fig. 4. Principal Components analysis of the wood-leather panel PCs leather (blue/2), wood (green/3), and mixed (red/1)

When visualizing this clustering within the Raman map, the leather regions become clearly visible as blue regions in Fig. 5B. By unifying Cluster 1 and Cluster 3, it is possible to reduce the complexity of the system and describe leather and non-leather regions as visible in Figure 5C, where black shows leather and white shows non-leather regions. When comparing the visible image (Fig. 5A) with the simplified cluster image (Fig. 5C), one can reliably discriminate most of the leather regions of the sample.

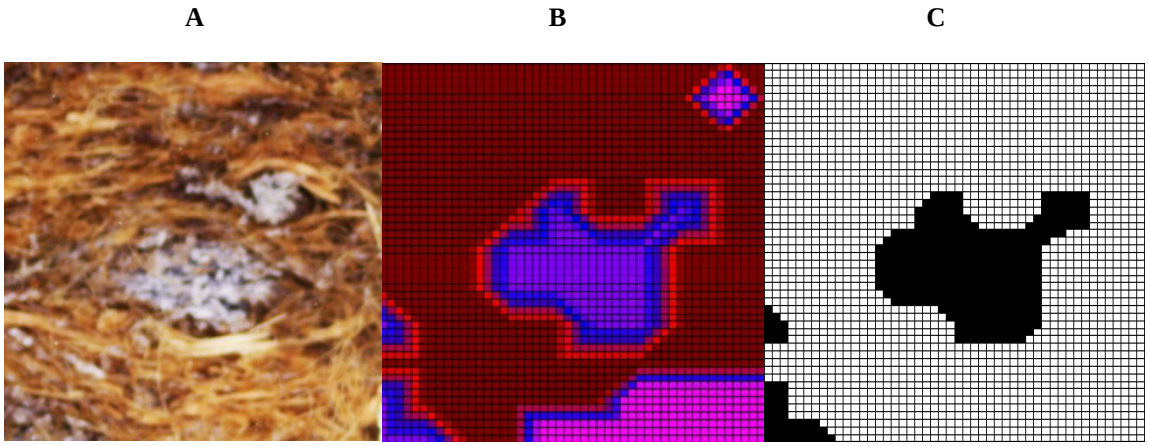

Fig. 5. Visible Image of the Sample (A), Result of Classification by chemometric methods (B), and simplified Classification by chemometric methods (C)

CONCLUSIONS

1. As shown, it is possible to reliably describe the heterogeneity of wood-leather panels using Raman spectroscopy. Distinguishing leather and non-leather areas is the most suitable way of discriminating, as the leather Raman spectrum offers the most distinctive Raman fingerprint. For a further connection between information gathered on heterogeneity and micro-mechanical models, a better knowledge on the interaction of wet blue and wood with lignin is necessary. The presented approach used a resolution of 1 mm, but theoretically a resolution of 0.1 mm would be possible. A dataset of this kind could enhance the understanding of the lignin interaction greatly.
2. In order to gain better knowledge for multi-scale mechanical modeling, additional imaging approaches are necessary, although the findings of this paper can be very helpful to analyze images gained with other imaging techniques. A possible approach could be the combination of the surface mapping with information of the substructure, generated by X-Ray computed tomography. With this approach the specific X-Ray absorption could be compared to the chemometric information of the Raman mapping. Bearing the general field of online spectroscopy in mind, the information obtained in this paper shows a possible approach for the distribution analysis in the wood-based panels industry. And as mentioned in the Introduction, the mixture of different materials is gaining importance. Therefore further approaches to determine the distribution are necessary in order to provide an even product quality.
3. Compared to other spectroscopic methods, such as NIR or FT-IR spectroscopy, Raman spectroscopy is less sensitive to the moisture content of the sample (Smith and Dent 2005). Another important point is, due to the laser excitation of the sample, the small probed spot can be as small as 0.1 mm. This gives precise information on the conditions on that exact spot with a comparatively low effort.
4. Principal Components Analysis was shown to be a proper tool for identifying and isolating different constituents of a composite material. Regarding the single

constituents spectra, a cluster analysis would be sufficient to cluster the obtained spectra, but as the complexity of the spectra increases and the sharp definition by the peak at 2942 cm^{-1} disappears in the sample spectra, a more sophisticated approach is necessary. Reviewing literature (Backhaus et al. 2008; Bortz 1999; Kessler 2007), there seem to be no easier approaches to cluster spectral data of this kind. Another possible approach called Simca (Soft independent modeling of class analogies) is mentioned by Kessler, but this method is intended for supervised classification with a training data-set, which was not available in this approach.

5. By using Raman spectroscopy as in the present approach, it is possible to distinguish wood and lignin as single constituents, but in the panel, there is no spectral information indicating lignin. As the presented wood-leather material is a mixture of three different constituents, a better knowledge on chemical changes is crucial for further improvements of the material. Possible chemical changes during hot pressing should be investigated in order to gain a better understanding of the chemistry of panel making. Thus, further investigations of panels produced under different conditions may provide valuable information on this topic by using analytical methods as either Raman spectroscopy or gas chromatography and mass spectrometry (GC-MS). The GC-MS could be useful to detect specific products of degradation at certain temperatures. This information could consequently be used and panels produced below that temperature show lower degradation.

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