Combined FTIR spectroscopy and rheology for investigating the influence of different wood extracts on adhesive curing

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INTRODUCTION

Adhesive bonding of wood plays a crucial role in the development of new advanced wood-based materials and composites. However, wood bonding is not a straightforward process as wood has inherently complex chemical and structural properties. In particular, wood extracts can accumulate at the surface and create a chemical boundary layer with different surface permeability, polarity, and wettability as well [1-3]. Therefore, the interactions between the wood and adhesives are supposed to determine the quality of wood-adhesive bonds. In this study, interactions between the adhesive and extractable wood constituents were investigated systematically.

A special focus was given to analyze Melamine Urea Formaldehyde (MUF) adhesive, which is one of the most widely used wood adhesives in Europe, in particular, as MUF adhesive is a water based system, how the water extractable constituents interact with the MUF adhesive was analyzed. The simultaneous examinations of the progress of chemical reactions and rheological properties of both MUF adhesive and MUF adhesive-extract mixtures were performed using a real-time FTIR spectroscopy and *in situ* rheology. The results confirm significant influences of the extracts on the curing process of MUF adhesive, in particular for the chestnut extract having a higher amount and acidity level (pH=3.8), and provide fundamental information on their chemical interaction.

MATERIALS and METHODS

Extraction

Seven wood species: spruce (*Picea abies*), pine (*Pinus sylvestris*), Douglas fir (*Pseudotsuga menziesii*), larch (*Larix decidua* Mill), beech (*Fagus sylvatica* L.), oak (*Quercus* spp.), and chestnut (*Castanea sativa)* were chosen for the extraction.

milling → water extraction at room temperature for 48 hours → MUF adhesive+extracts to be analyzed by Rheonaut

Figure 1. Demonstration of the extraction step.

Table 1. Extract addition and number of measurements

Sample code	Extract [%] addition to MUF	Number of measurements (n)
MUF-Ref	-	14
MUF-Sp	0.066	5
MUF-Pi	0.566	5
MUF-Do	0.120	5
MUF-La	0.629	5
MUF-Be	0.170	5
MUF-Oa	0.166	6
MUF-Ch	0.899	5

Reference (Ref), Spruce (Sp), Pine (Pi), Douglas fir (Do), Larch (La), Beech (Be), Oak (Oa), Chestnut (Ch)

In-situ Rheology and FTIR Spectroscopy

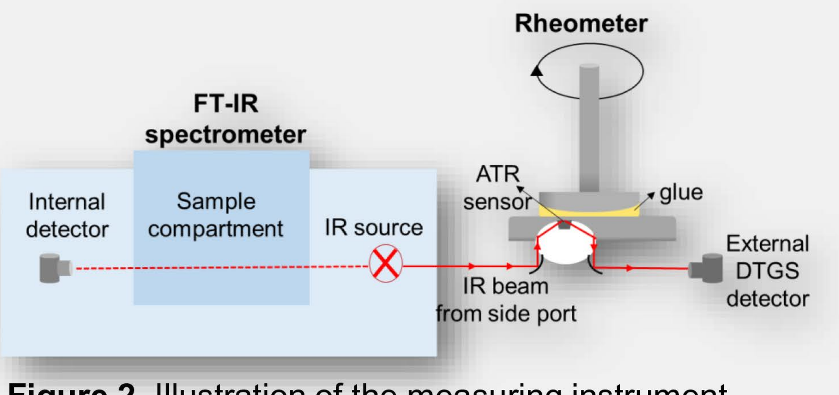

Figure 2. Illustration of the measuring instrument Rheonaut® (Resultec, Germany), a combination of FTIR spectroscopy with an ATR crystal and rheology

such an analytical technique allows for the understanding of **rheological** phenomena (e.g. curing of the adhesives) on the **molecular level** !

RESULTS

Extraction

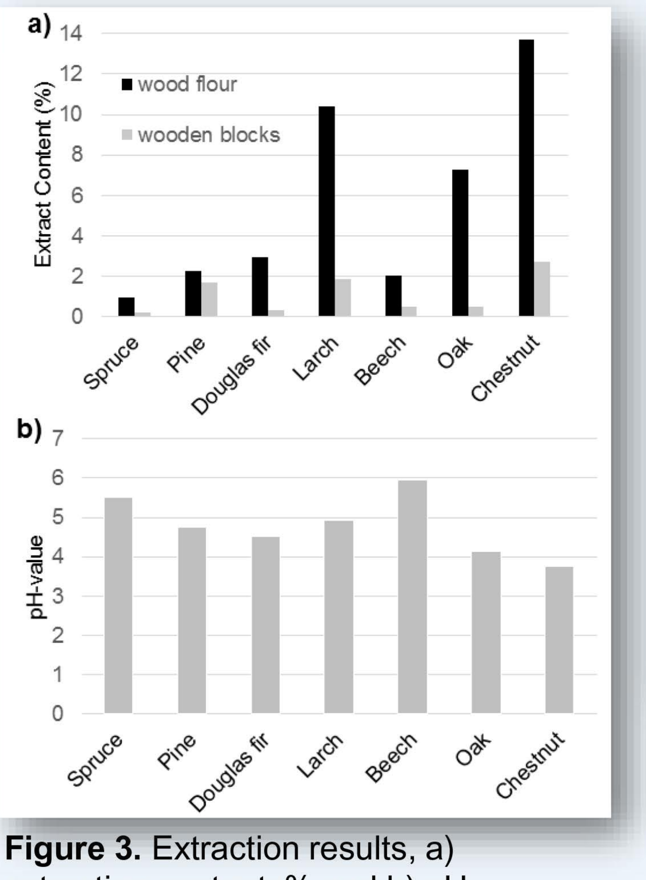

Figure 3. Extraction results, a) extraction contents% and b) pH values.

- Higher extract content was achieved by extraction of wood flour.
- Chestnut showed the highest extract content and the highest acidity (pH=3.8).
- Main compounds of the chestnut extract were gallic acid, ellagic acid, C5 and C6 sugars based on GC/MS results.

Rheological and Curing Properties

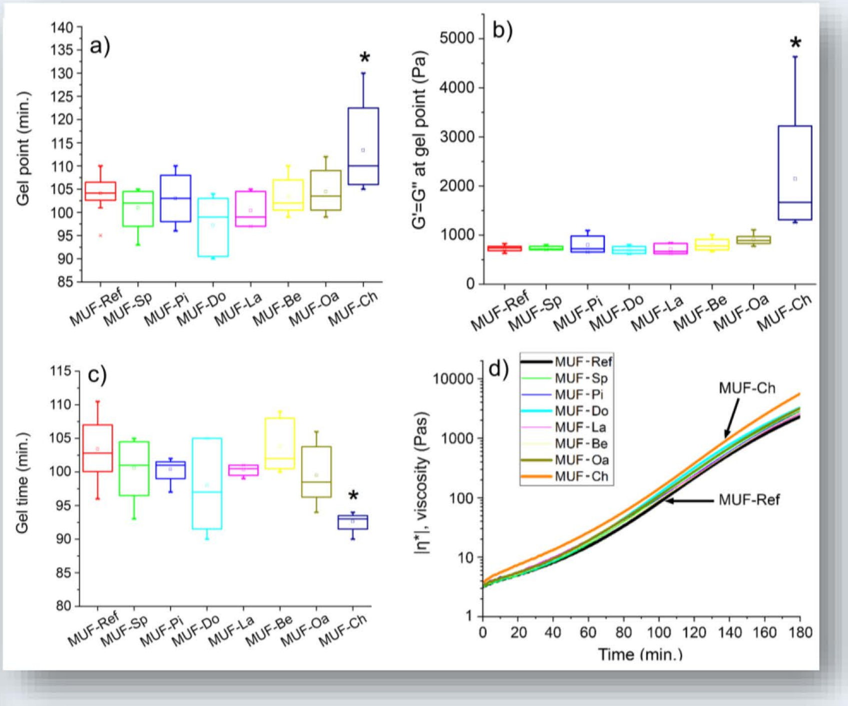

Figure 4. Rheology result, a) gel point, b) modulus at gel point, c) gel time (at η=100 Pas), and d) viscosity curves.

- Statistically significant changes in MUF curing in case of addition of the chestnut extract:

  → a delay in curing as a result of a higher gel point, higher modulus at gel point and an acceleration in viscosity rise (lower gel time).

- A positive correlation of the gel point with chestnut and gallic acid (as the main component of chestnut extract) addition (%) [4].

Curing Reactions by FT-IR Spectroscopy

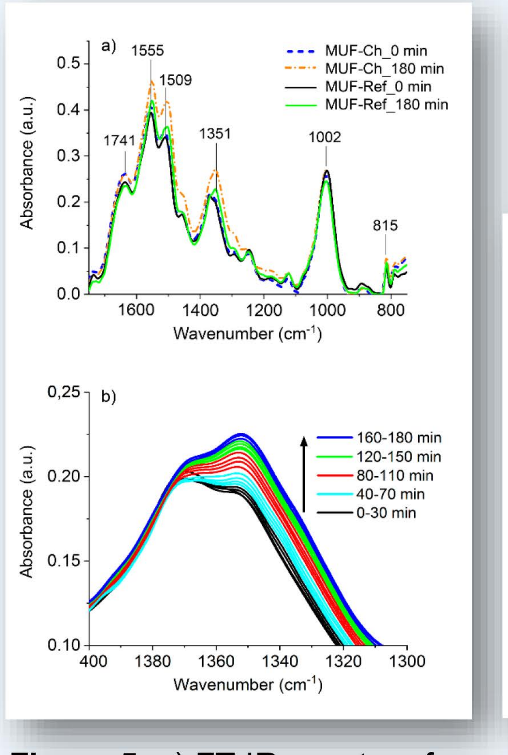

Figure 5. a) FT-IR spectra of MUF-Ref and MUF-Ch (0.9%) at t=0 min and t=180 min, b) formation of methylene bridges in MUF-Ref by time.

- Slight spectral differences between MUF-Ref and MUF-Ch have to be revealed by PCA:

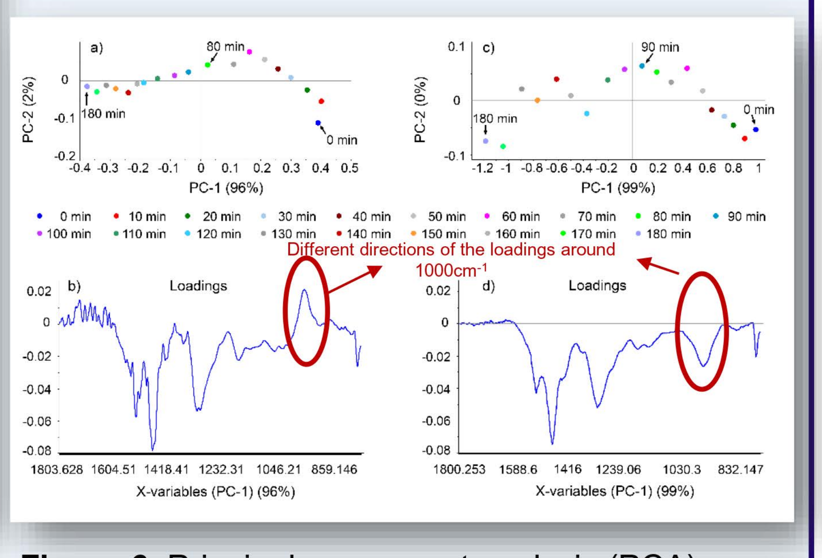

Figure 6. Principal component analysis (PCA) scores and loadings of FT-IR spectra a-b) MUF-Ref, c-d) MUF-Ch (1.68%, high content)

- Two specific spectral changes related to MUF curing [5-6] :

  → at 1351 cm^{-1} (C-H str.): an increase due to formation of methylene bridges by time.

  → at 1002 cm^{-1} (C-O str. of methylolurea): decreases by time as a result of the crosslinking reactions.

- PC1 divides the spectra into two groups, in MUF-Ref: as 0-80 min and 90-180 min and in MUF-Ch: as 0-90 min and 100-180 min. Therefore, the delay in curing reactions of MUF-Ch was already reflected in PCA results as well.
- When the loadings, which are responsible for the separation of the groups, compared:

  → most significant difference was found ~1002 cm^{-1}.

  → instead of a decrease, in MUF-Ch, this band increased by time which indicates less crosslinking of the resin after 180 min.

CONCLUSION

- The combination of rheology and FT-IR spectroscopy is a suitable method to investigate the interactions between wood extractives and adhesives.
- The curing behavior of MUF adhesive was influenced significantly by chestnut wood extract.
- Chestnut extract led to a delay in curing reactions and an acceleration in the viscosity rise.
- PCA loadings of the FT-IR spectra showed differences for the band around 1000 cm^{-1} which can be interpreted as a lower crosslinking of MUF-Ch resin.
- This study shows the influence of extracts on the curing properties of the adhesives and therefore the potential of the further investigations on this topic.

This study is supported by BMWi via AiF/iVTH (IGF 19314 N) which is acknowledged.

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Wood Research Munich (HFM)

References:

[1] Hse, Chung-Yun, and Mon-lin Kuo (1988), *Forest Prod. J 38 (1): 52-56*

[2] Bockel, S., Mayer, I., Konnerth, J., Harling, S., Niemz, P., Swaboda, C., ... & Pichelin, F. (2019). *Int. J Adhes Adhes, 91*, 43-53.

[3] Roffael, E. (2016) *App. Microbiol. and biot.*, *100*(4), 1589-1596.

[4] Ozparpucu M, Wolfrum T, Windeisen-Holzhauser E, Knorz M, Richter K (2020), Eur. J of Wood Wood Prod. 78:85-91

[5] Merline DJ, Vukusic S, Abdala A (2013), Polym J 45(4):413

[6] Kandelbauer A, Despres A, Pizzi A, Taudes I (2007), . J Appl Polym Sci 106(4):2192–2197