ORIGINAL

A new analytical approach to investigate the influence of wood extracts on the curing properties of phenol-resorcinol–formaldehyde (PRF) adhesives

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Abstract

In this study, the interactions between a phenol–formaldehyde resorcinol (PRF) adhesive and water-extractable wood constituents were investigated using combined *in-situ* FTIR spectroscopy and rheology analysis for a simultaneous examination of the progress of chemical reactions and coherent changes in rheological properties during adhesive curing. Complementary evolved gas analysis and pyrolysis gas chromatography/mass spectroscopy (Py-GC/MS) were performed to detect differences in the final crosslinking and chemical composition of the cured adhesive, respectively. The rheological and chemical analysis results correlated with the tensile shear strength of wood-PRF assemblies. The results showed that adhesive curing was significantly affected by the presence of acidic wood extractives. In particular, the acidic extractives of chestnut wood led to a delay in the resin curing and less final crosslinking of the cured adhesive. This was most likely caused by a reduction in the catalytic effect of the base-catalyzed curing of the adhesive rather than by direct chemical reactions between the extracts and adhesive. These findings can be useful for adapting the resin formulation to the chemistry of acidic wood species.

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Introduction

Wood bonding is considered to be a challenging process as wood has a complex hierarchical structure and is highly variable in terms of species-specific chemical and structural properties. The actual reason behind this is the potential physical (e.g. the alterations in surface phenomena: pH, wetting behaviour etc.) or chemical interactions (e.g. chemical interference of the adhesive curing by the wood chemistry) between the chemical wood constituents, in particular the wood extractives, and the adhesives. These interactions between the wood extractives and the adhesives are known to be influential on the wood bonding performance (Roffael 2016; Özparpucu et al. 2020).

Phenol–formaldehyde (PF) adhesive is one of the most widely used wood adhesives, which in addition to wood composite bonding is also accredited for engineered wood products. PF-wood bondings outperform aminoplastic resins in humid environments (delamination, thickness swelling) but show slower curing time, dark colour of the bond line, and more importantly, difficulties in the bonding of various acidic wood species (e.g. oak, chestnut, birch etc.) (Dunky and Niemz 2013). In the literature, there are a considerable amount of attempts to investigate the wood-PF adhesive interactions (Tohmura 1998; Proszyk and Zakrzewski 1992; Wang 1992). However, how wood interacts with PF adhesive and how these interactions influence the adhesive bonding is still under debate, as the studies mostly gave some conflicting results. Some studies showed an increase in the activation energy of phenolic adhesive, and therefore, prolonged curing when mixed with wood powder (He and Riedl 2004; Mizumachi 1975). Wang (1992) reported inhibitory effects of white oak extractives on phenolic adhesive curing. Similarly, acidic wood extractives decelerated the bonding of alkaline PF resin in one of the studies (Roffael 2016). Prolonged curing times for the phenolic adhesives were also reported when gluing oak and Kapur (Hse and Kuo 1988).

Deviating from this, other studies reported lower activation energy of PF curing in the presence of wood (Pizzi et al. 1994; Proszyk and Zakrzewski 1992; Tohmura 1998; He and Yan 2005). For example, Tohmura (1998) reported an acceleration of the curing reactions of PF adhesive due to the presence of Merbau wood extractives containing a high amount of flavonoids. No correlation could be found between the gel time of a PF resin and the pH and buffer capacity of the wood species (Lee et al. 2007). In a recent study, it was found that various acidic compounds (e.g. acetic acid, gallic acid, linoleic acid etc.) accelerated phenol resorcinol formaldehyde (PRF) adhesive curing as well (Bockel et al. 2019).

The heterogeneity of the findings can be most likely attributed to the different experimental approaches and different wood species used. The differences in the starting pH value of the studied adhesives might also be responsible for the different outputs (He and Yan 2005). Furthermore, remarkably, in most of the studies, a large amount of wood powder and/or extracts ($> 10\%$) was mixed into the PF adhesive (Bockel et al. 2019; He and Riedl 2004; He and Yan 2005). While such approaches allow for minimizing the high variabilities due to the complex nature of wood, in parallel, they might complicate the evaluation because of the overlapping chemical

and physical interactions. All of the above-mentioned points show the complexity of the research topic.

Recently, the interactions of wood extractives from various wood species with the adhesive properties of melamine-urea formaldehyde (MUF) and also emulsion polymer isocyanate (EPI) have been studied, and the influence of the extractives on the adhesive curing properties could be successfully revealed using systematical, advanced analytical techniques. The *in-situ* rheology and FTIR investigations enabled the simultaneous characterization of the curing behaviour and the chemical reactions when even a small amount ($<1\%$) of extracts was mixed to the adhesives (Özparpucu et al. 2020, 2022). Such an experimental design is believed to better represent the actual wood extract conditions on the bonding surface and also minimize the overlapping of the chemical and physical effects. Therefore, in this current study, using a similar approach, the interactions of the wood extractives from seven different European softwood and hardwood species and PRF adhesive were investigated. Understanding the interactions not only allows for advancing the bonding performance of currently commercial PRF adhesives but can also provide insights for the modification of phenoplast adhesives to achieve environmentally friendly, high-quality wood-adhesive bonds.

Materials and methods

In-situ rheology-FTIR measurements

The wood water extracts were obtained from seven different 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)* by water solution at room temperature for 48 h (Özparpucu et al. 2020).

The extraction results were used to determine the amount of extract addition to the PRF adhesive for the analysis. Briefly, an approximate amount of wood extracts% was calculated on one wood bonding surface in proportion to the total surface area, as explained in Özparpucu et al. (2020) and then, for the measurements, the corresponding extract% amounts for each species were mixed into approx. 1 g of PRF adhesive (resin: Aerodux 185, hardener: HRP 150, with resin to hardener ratio of 5, Dynea AS, Norway) on a Sartorius (1712MP8, Germany) scale with a precision of ± 0.01 mg (Table 1). The components were mixed manually using a micro spatula and a constant mixing time of 40 s was used. After mixing the components, the rheology measurements were performed immediately.

It should be noted that as the PRF is a water-based system, the focus in this study was on the water extracts. Moreover, the qualitative GC/MS analysis results of the extracts are provided in Table S1, and the identified compounds were in line with the literature (Fengel and Wegener 2003). Some additional *in-situ* rheology-FTIR measurements were also performed with some standard compounds, such as gallic acid representing an acidic compound in the extract chemistry.

Table 1 Sample codes, extract additions (%), and number of measurements

Sample codes	Extract addition [%] to PRF	No. of measurements (n)
PRF-Ref	–	5
PRF-Sp	0.072 ± 0.0017	3
PRF-Pi	0.560 ± 0.0048	3
PRF-Do	0.126 ± 0.029	3
PRF-La	0.645 ± 0.012	3
PRF-Be	0.172 ± 0.0028	3
PRF-Oa	0.170 ± 0.0016	3
PRF-Ch	0.901 ± 0.0072	3

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

The rheology measurements were performed by an oscillation mode using a plate-plate system for 180 min and a 0.5 mm measurement gap (Haake Mars 40, Thermo Fisher Scientific). The diameter of the upper plate was 25 mm, the temperature of the lower plate was kept at both 25 °C and 40 °C to see the influence of the temperature on the PRF curing. The oscillation parameters were set to 0.1% strain at a frequency of 1.0 Hz ($\omega = 6.3$ rad/s), which was performed in the linear viscoelastic region (LVR) to avoid the influence of high deformation on the curing properties (Künniger et al. 2019; Bockel et al. 2019).

The *in-situ* FTIR absorbance measurements (Meyer et al. 2012) were performed in the spectral range of 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1} (iS 50 FTIR (Nicolet), Thermo Fisher Scientific), where the infrared beam was reflected by attenuated total reflection (ATR) on the lower plate of the rheometer. Per minute, one data spectrum was recorded. Baseline corrected spectra were evaluated further using Unscrambler software (Camo Analytics).

Evolved gas analysis

The EGA measurements were performed with a double shot pyrolyzer Py-2020iD (Frontier Laboratories) connected to a 5975C Series GC/MSD system (Agilent Technologies). 100 µg of PRF-Ref and selected PRF and acidic extract mixtures were put into a stainless steel cup (Eco cup, Frontier Laboratories) and then, inserted into the pyrolysis furnace. Two measurements were taken on each sample ($n = 2$). The samples were heated continuously from 50 to 600 °C at a heating rate of 10 °C/min. The GC oven and the inlet were held isothermally at 300 °C. The evolved gases were transferred to the MS detector via a deactivated stainless steel EGA column (2.5 m × 0.15 mm). No chromatic separation was done. It should be noted, the same samples which were analysed by *in-situ* rheology and FTIR spectroscopy were used for the corresponding analysis. However, their EGA measurements were performed in the fully cured state (cured at room temperature in the glass tubes with the tube

lids closed to ensure similar humidity conditions) one month after the rheology measurements.

Pyrolysis gas chromatography/mass spectroscopy (Py-GC/MS)

The same samples measured by EGA were also selected for the Py-GC/MS analyses. Based on the thermal desorption isotherms taken by EGA, double shot analysis (DSA) was performed on the selected samples. DSA determines the volatile components of the adhesive systems sequentially in two stages: (i) thermal desorption (TD) and ii) pyrolysis (Py). Several analysis temperatures (both for TD and Py stages) were applied based on where the differences were observed in the EGA thermo profiles. After the TD stage, the resulting volatile compounds were trapped at the beginning of the GC column (30 m×0.25 mm×0.25 μm, VF-17 ms, Agilent Technologies) and analysed via GC/MS (5975C Series GC/MSD system, Agilent Technologies), and the residual sample was pyrolyzed further at the selected temperature for 0.2 min. The emerging pyrolysis products were also analysed with GC/MS. For both thermal desorption and pyrolysis steps, the GC oven was set to 50 °C with a holding time of 1 min and then heated to 300 °C at a heating rate of 10 °C/min. Finally, it was kept at 300 °C for 4 min. The mass spectrometer was operated in EI mode (70 eV, scanning m/z 40–700 Da). The MS transfer line temperature was 250 °C. The MS ion source temperature was fixed at 230 °C and the MS quadrupole temperature at 150 °C.

Tensile shear tests

As the *in-situ* rheology-FTIR and thermal analysis results showed a significant influence of the chestnut extract on the PRF curing, the chestnut wood was selected for the tensile shear tests based on the wood quality specifications of the DIN EN 302–1:2013 standard. The selected chestnut wood was from the same source that had previously been used for the extraction (see Chapter In-situ Rheology-FTIR measurements). The sawn wood boards were stored for several months in the climate room at 20 °C and 65% RH to reach an equilibrium wood moisture content of $12\% \pm 1\%$. The boards were further processed into wood panels with dimensions of $0.3 \times 0.15 \times 0.01$ m^3 (L×W×T).

To analyse the influence of the extracts on the PRF-wood bonding performance, half of the chestnut panels were extracted by distilled water at room temperature, whereas the other half represented the reference material without any treatment. For more details of the extraction setup, the readers are referred to Özparpucu et al. (2022) and Wilhelm (2020). After the extraction process, the wood panels were dried at 30 °C and reconditioned in a climate room (at 20 °C and 65% RH). All panels were planed to a thickness of 5 mm by removing approx. 2.5 mm of material from both surface sides to obtain a fresh bonding surface. The bonding process was performed in the climate room at 20 °C and 65% RH. In total, 450 g/m^2 of mixed adhesive (with resin to hardener ratio of 5:1) was applied on one side of the wood panel with a spatula, and then, two panels were assembled. The closed waiting time

was 60 min, and the press time was 240 min under 1 N/mm^2 applied pressure. After pressing, the bonded wood assemblies were stored for 7 days in the climate room and cut into lap-shear specimens of the dimensions required for tensile shear test experiments according to the standard (Özparpucu et al. 2022). The shear tests were performed by both A1 (testing in dry state, at 20 °C and 65% RH) and A4 (testing in wet state, after 6 h boiling in the water at 100 °C, and additionally 2 h resting in cold water at 20 °C) treated samples using a universal test machine (TesT GmbH). The tensile shear strength and wood failure percentage (WFP%: visually evaluated) were compared between the reference and extracted samples.

Results and discussion

### In-situ rheology-FTIR spectroscopy

Measurements at 25 °C

The rheological properties were evaluated based on the gel point (the cross over point of storage modulus (G`) and loss modulus (G''), indicating the transition from liquid-like to the solid-like state by curing) and gel time (the time point where the complex viscosity: |η*| reached 100 Pas). Moreover, the modulus (G') of the samples at the end of the measurements (at $t = 180$ min) was also compared.

Statistical analysis revealed significant differences in the curing behaviour of PRF resin with the chestnut extract addition, whereas the other extract types did not change the rheological properties significantly. While PRF-Ref had a gel point of 95 min, the gel point of PRF-Ch showed a delay of approximately 7 min (Fig. 1a, b). However, no significant difference could be found in the modulus at the gel point (G'=G'') between the samples.

The gel time of PRF-Ref was found to be 94 min, and the averaged gel time showed a tendency of a slight decrease with the addition of most of the extracts (except chestnut). However, this decrease was found to be statistically insignificant (Fig. 1c).

The influence of the chestnut extract on the modulus was even much more pronounced, as it showed a 70% decrease in PRF-Ch compared to PRF-Ref and PRF with other extracts (Fig. 1d).

The curing reactions of resole type phenolic resin consist of two steps; in the first stage, phenol derivatives (phenol, resorcinol, etc.) react with the basic catalyst (e.g. NaOH) to form phenoxy anion. This phenoxy anion represents an electron-rich system which is activated, in particular, in ortho and para positions (by resonance). The preferential electrophilic attack of the carbonyl group of formaldehyde on the phenoxy anion results in "phenol-hydroxymethyl" structures. The reaction continues between formaldehyde and hydroxymethyl-phenol which then forms a mixture of phenol-mono-methylol and phenol-poly-methylol. Consequently, polycondensation reactions between phenol and hydroxymethyl-phenol, and also between hydroxymethyl-phenols form an ether (–CH$_2$OCH$_2$–) and
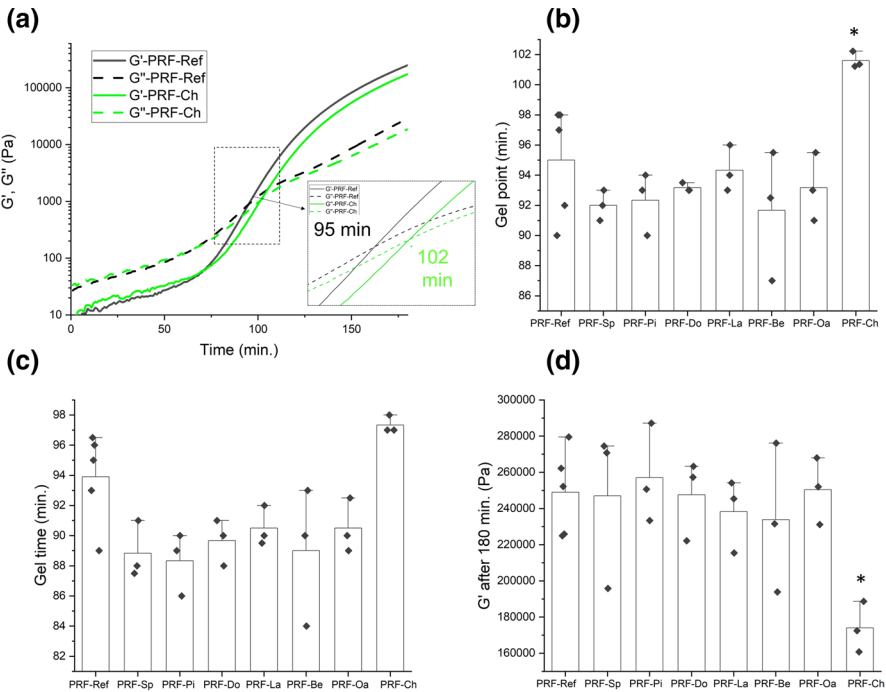
Fig. 1 Rheology results measured at 25 °C, **a** the averaged modulus (G') curves of PRF-Ref and PRF-Ch, **b** gel point, **c** gel time and **d** G' modulus at the end of the measurements ($t = 180$ min.); the bars indicate the individual measurements and standard errors, *shows statistically significant differences, ANOVA, at 95% confidence level

methylene chain (–CH$_2$–) between two methylol groups (Xu et al. 2019; Liu et al. 2017; Pizzi 2003), and thus, the crosslinked resin is formed.

The interpretation of the spectral changes due to the curing reactions is usually challenging due to similar functional groups of the prepolymers and also extractives. However, when the spectra in the initial state ($t = 0$ min) and the spectra at the end of the measurements ($t = 180$ min) are compared, some minor spectral changes caused by the curing reactions could be followed in the spectral range of 1800–700 cm^{-1} (Fig. 2).

In PRF-Ref, a decrease in the absorbance of the bands at 1595 cm^{-1}, 1500 cm^{-1}, 1167 cm^{-1} and 1150 cm^{-1} was found. These bands are known as characteristic bands of phenol and show the incorporation of the phenols into the curing reactions (1595 cm^{-1} and 1500 cm^{-1}: C=C aromatic ring, 1167 cm^{-1}: CH aromatic, in-plane, and 1150 cm^{-1}: C–O stretching), and similar spectral changes were also shown in the literature (Poljansek and Krajnc 2005). Besides, vibrations of methylene and methyl groups can be found in the spectral range of 1500–1350 cm^{-1} (Alpert et al. 2012). There, an increase in the absorbance of the bands at 1473 cm^{-1} (assigned to C-H aliphatic and –CH$_2$– deformation) and 1441 cm^{-1} (C=C plus –CH$_2$–) was observed (Poljansek and Krajnc 2005).
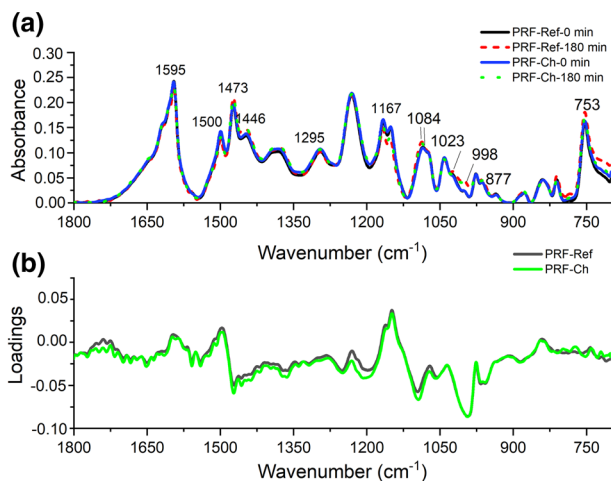
Fig. 2 Comparison of the **a** FTIR spectra of PRF-Ref and PRF-Ch (cured at 25 °C) at the beginning ($t=0$ min) and the end of the measurements ($t=180$ min.) in between 1800 and 750 cm-1 and **b** loadings (PC1)

This indicates crosslinking reactions through the formation of methylene bridges between phenol-resorcinols (Poljansek and Krajnc 2005; Scopelitis and Pizzi 1993; Myers et al. 1991; Liu et al. 2017; Dumitrescu et al. 2014).

The slight absorbance decrease at 1295 cm^{-1} (assigned to C–O stretching of phenols C–OH and C–O) can be attributed to the weakening of C–O bonds of phenols as a result of curing reactions (Bobrowski and Grabowska 2015; Hong et al. 2018). Moreover, C-O vibrations of –CH$_2$OH group can be seen at 1086 cm^{-1}; the increase in the absorbance of this band is highly related to the formation of ether bridges between methylol groups during condensation reactions (Poljansek and Krajnc 2005; Bobrowski and Grabowska 2015; Xu et al. 2019). Furthermore, the band at 1023 cm^{-1} also showed an increase. This band is assigned to 1,2- and 1,4-substituted aromatic rings and also C–O stretching of methylol groups, and the intensity of this band is expected to increase by curing and relates to the strength of the cured adhesive (Scopelitis and Pizzi 1993).

Furthermore, all these changes explained above were also seen in the spectra PRF-Ch; however, the relative changes were slightly less pronounced in PRF-Ch compared to PRF-Ref (Table SI 2). Noteworthy, the FTIR absorbance is proportional to the molar concentration of the materials and therefore relative changes in absorbance give semiquantitative information on the formation of the reaction products. Therefore, the slightly less pronounced spectral changes in PRF-Ch are in agreement with the rheology results (i.e. delayed curing by chestnut extract addition to PRF resin mix).

To further analyse the spectral differences between the PRF-Ref and PRF-Ch in more detail, a principal component analysis (PCA) was applied to the FTIR spectra. Prominent spectral changes were identified after 70 min in both PRF-Ref and PRF-Ch, as the spectra of the samples were divided into two groups (0–70 min and

80–180 min) by PC1, which explained the variability of 79–85% (Fig. SI 1). However, when comparing the loadings (loading 1), which are responsible for the separation of the spectra (i.e. indicating changes in chemical curing reactions), very similar trends could be found between the samples. Therefore, it can be concluded that curing reactions in PRF-Ch were to a large extent similar to the reactions in PRF-Ref.

Measurements at 40 °C

The measurements at 25 °C revealed the influence of the chestnut extract on the rheological properties during curing, but the spectral changes were minor even within PRF-Ref due to the lower curing degree at ambient temperatures. Moreover, no direct chemical interactions between the extracts and the adhesive could be detected. For this reason, additional *in-situ* rheology FTIR analyses were performed at a higher temperature of 40 °C (during 1 h) to achieve a higher degree of adhesive polymerization and a more detailed comparison between the samples.

The increase in the measurement temperature to 40 °C clearly catalyzed the polymerization of the PRF adhesive as the averaged gel point and the gel time of PRF-Ref significantly decreased to 15.80 min and 17.20 min, respectively (at 25 °C, gel point: 95 min, gel time: 94 min) (Fig. 3a, Fig. SI 2). When comparing the PRF-extract mixtures with the reference, the addition of the chestnut extract slightly increased the gel point and gel time without any statistical significance (Fig. 3a, Fig. SI 2). More importantly, despite a minor change in the gel point of PRF-adhesive in the presence of the chestnut extract, a significant decrease (approx. 70%) in the modulus was observed at the end of the measurements ($t = 60$ min.) (Fig. 3b), which was comparable to the results obtained at 25 °C.

At 40 °C reaction temperature, the spectral differences became much more pronounced between the initial (at $t = 0$ min) and final spectra (at $t = 60$ min) of the PRF-adhesive (Fig. SI 3a). However, based on PCA results, the differences between the PRF-Ref and PRF + extract mixtures were not clear enough as the variability within the reference samples was at the same level as the variability between the
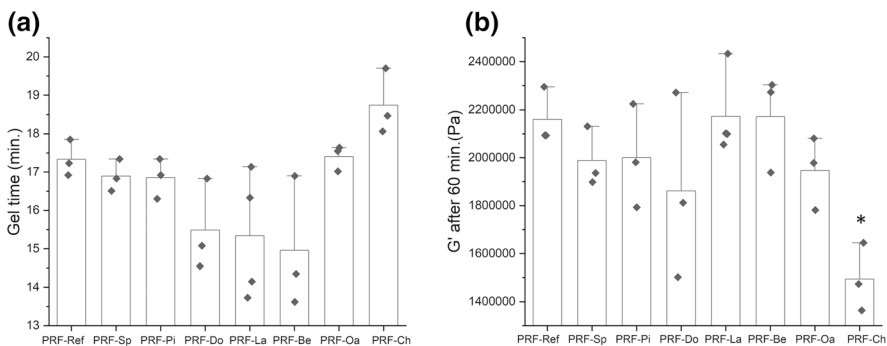

Fig. 3 Rheology results measured at 40 °C **a** gel time and **b** G' modulus at the end of the measurements ($t = 60$ min); the bars indicate the individual measurements and standard errors, *shows statistically significant differences, ANOVA, at 95% confidence level

reference and other samples (Fig. SI 3b). Therefore, some further experiments were designed next using higher amounts of specific organic compound additions to PRF-adhesive mix that represent the natural components of the wood extracts.

Gallic acid (Ga) has been reported as the main component of the chestnut extract (water extraction at room temperature) besides some sugar molecules, and when mixing Ga with some other adhesives types (e.g. MUF and EPI), it produced consistent results with the chestnut extract and corresponding adhesive mixtures (Özparpucu et al. 2020, 2022).

Therefore, different amounts of Ga (0.25–4%) were mixed into PRF and analysed at 40 °C. The Ga addition below 1% did not pronouncedly change the gel point and the gel time (Fig. SI 4). Ga additions above 1% resulted in a significantly higher gel point and gel time. For example, the addition of 2% resulted in a gel point of 22 min, whereas the gel point of PRF-Ref was around 16 min. In the case of 4% of Ga addition, the PRF resin did not even get cured within the whole measurement time of 60 min. The gel time of PRF with 4% Ga was significantly higher (47 min.) compared to the gel time of PRF-Ref (17 min). Moreover, the Ga addition (%) amount showed a clear relationship with the modulus (G' at $t=60$ min) at the end of the measurements. There, a non-linear negative correlation was found between these two variables (Fig. 4a). These results confirmed the current results with chestnut extract, as it led to a significantly lower stiffness of the PRF-adhesive when measured at both 25 °C and 40 °C.

To identify the chemical changes in PRF curing with the addition of Ga, the FTIR spectra of PRF-Ref and PRF-Ga (with a high content: 2%) were compared. The visual differences between the spectra were minor, which was in line with the study by Bockel et al. (2019), (Fig. SI 5a) and therefore, a PCA was applied in a stepwise manner to further reveal the differences between the samples. In the first step, PCA was applied only within the individual groups, and it was found that the curing reactions led to pronounced spectral changes after 30 min for both PRF-Ref and PRF-Ga (2%) (not shown); this point could be considered as the point where significant spectral changes started to occur due to the curing reactions. Then, in
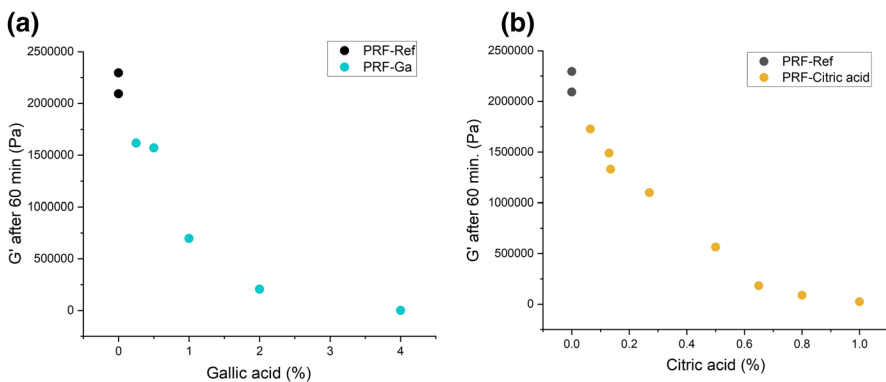
Fig. 4 Influence of acidic compounds on the modulus (G' at $t=60$ min.) of PRF adhesive: **a** gallic acid (pKa*: 3.94) and **b** citric acid (pKa*: 3.05),*based on ChemAxon database

the second step, PCA was applied to compare the spectra of PRF-Ref and PRF-Ga (2%) between each other after the point where the spectral changes became most remarkable in these samples (30–60 min) (Fig. SI 5b-c). PC1, which explained 97% of the variability, separated the spectra of PRF-Ref and PRF-Ga, and loading 1 indicated the spectral differences between the samples. (Fig. SI 5b-c). In particular, the decrease at 1600 and 1500 cm^{-1} (C=C str., phenols) and formation of methylene bridges (1500–1350 cm^{-1}) were more pronounced in PRF-Ref as an indication of a more promoted curing reaction. Besides, the formation of the ether bonds (1100–1000 cm^{-1}), which are another indication of the polymerization reactions, was also more pronounced in PRF-Ref. In the literature, an increase in the absorbance ratio of the bands "1022 cm^{-1}" (1,2 and 1,4 substituted aromatic rings and C–O str. of methylol groups) to "973 cm^{-1}" (C–O str. of resorcinol) has been shown by curing (Scopelitis and Pizzi 1993). The excess of free resorcinol (at 973 cm^{-1}) is related to a lower polymerization. Gallic acid addition to PRF resin led to a lower absorbance ratio (~50%, based on second derivatized spectra to eliminate the background effect) of the bands (1022 cm^{-1}/973 cm^{-1}) and thus, a lower final crosslinking of the resin. Moreover, the band at 810 cm^{-1} slightly shifted to lower wavenumbers in PRF-Ga. This band is assigned to –CH_2– deformation of the ortho position on the aromatic ring (Hong et al. 2018), and this band gave a considerable contribution to loading 1 (Fig. SI 5b). Therefore, there can be some additional supramolecular changes (e.g. position, length of methylene bridges, etc.) in PRF-Ga adhesive besides the changes in the crosslinking degree compared to PRF-Ref.

However, it is difficult to conclude whether these changes occurred due to a direct interaction of Ga with PRF adhesive or the presence of Ga influenced the curing reactions by altering the catalyzation efficiency of the basic catalyst (i.e. by pH changes) in the adhesive formulation.

It is well known that natural polyphenolic compounds (e.g. tannins) can be partially substituted by phenols in the phenol–formaldehyde (PF) type of adhesives. However, it was reported that the condensed tannins are usually more favourable for this substitution rather than that of the hydrolyzable tannins (i.e. phenols, sugar esters, gallic acid and digallic acid) mixture due to their higher reactivity to the formaldehyde (Pizzi 1982). Considering this fact and spectral analysis results (i.e. similar PC loadings between PRF-Ref and PRF-Ga/Ch), it seems that the influence of Ga is most likely due to a reduction in the catalyzation efficiency of the basic catalyst in the adhesive formulation, because, as previously mentioned, phenolic resoles react with formaldehyde under a basic catalyst. Most likely, a high amount of Ga addition to PRF resin might have lowered the catalyzation efficiency of the reactions which then led to a negative influence on the curing reactions (i.e. delay in curing reactions and less crosslinking).

Moreover, similar observations in PRF curing with citric acid (as a non-phenolic organic acid) addition supported this statement (Fig. 4b). Furthermore, the study by He and Riedl (2004) also showed that the activation energy of PF curing increases due to a decrease in pH value when acidic compounds were mixed into the adhesive, and their study revealed secondary force interactions between the wood molecules and PF adhesive instead of a direct chemical reaction between two components (He and Riedl 2004). In the current study, to further analyse the possible changes in the

chemical composition of the cured PRF adhesive, EGA and Py-GC/MS experiments were performed (in the fully cured state, one month after the rheology measurements), and the results will be discussed in the following chapter.

Evolved gas analysis (EGA) results

EGA analyses the evolved gases in terms of mass and constituents of the samples which were exposed to the heating, and such outputs could be qualitatively correlated with the polymerization and crosslinking degree of the adhesives (Özparpucu et al. 2022). The EGA thermoprofile of PRF-Ref showed three main peaks at around 200 °C, 230 °C and 340 °C (Fig. 5). The comparison of the EGA profiles of the PRF-Ref and PRF-with acidic compounds confirmed the rheology results. In particular, the PRF adhesive with the chestnut (PRF-Ch), Ga (PRF-Ga) and also citric acid (PRF-Ca) produced much higher gas abundances at lower temperatures (100–200 °C) compared to PRF-Ref most likely indicating a lower crosslinking degree of the cured adhesive which is in line with the *in-situ* FTIR and rheology results. It should be noted that the substances (Ch extract, Ga and Ca) themselves might also have an influence on the higher gas abundances evolved. The EGA thermoprofiles of PRF samples with all acidic compounds followed similar trends between each other (Fig. 5). Next, using the pyrolysis-GC/MS, the chemical composition of the evolved gases from the cured adhesive was investigated.

Pyrolysis (Py) gas chromatography/mass spectroscopy (GC/MS) results

For sequentially determining the volatile components of the cured PRF-adhesive, a double shot analysis (DSA) was performed in two stages (i.e. i: thermal desorption (TD) and ii: pyrolysis (Py) stages). The measurements were performed on the
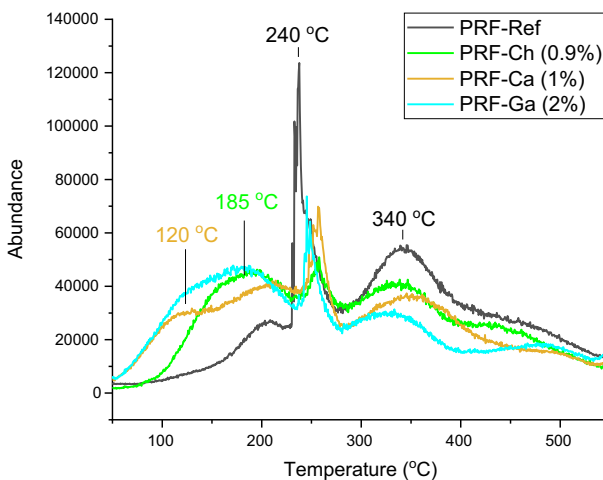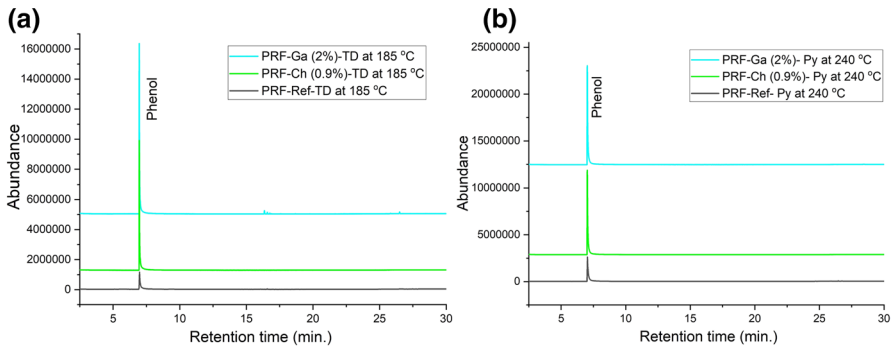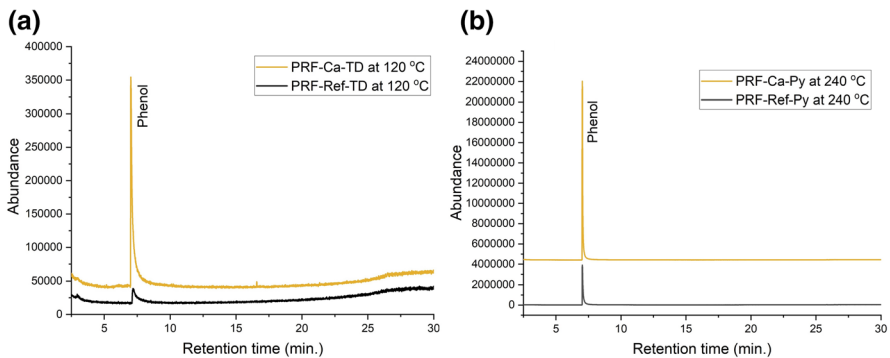

**Fig. 5** EGA thermoprofiles of the PRF adhesive samples cured at 40 °C

Fig. 6 DSA results of the PRF-Ref and PRF-Ch (0.9%) and PRF-Ga (2%) cured at 40 °C, **a** thermal desorption (TD) at 185 °C and **b** pyrolysis (Py) at 240 °C. Note: the graphs were plotted stacked in the Y-axis for better visualization

Fig. 7 DSA results of the PRF-Ref and PRF-Ca (1%) cured at 40 °C, **a** thermal desorption (TD) at 120 °C and **b** pyrolysis (Py) at 240 °C. Note: the graphs were plotted stacked in the Y-axis for better visualization

selected samples (PRF-Ref and PRF-Ch (0.9%), PRF-Ga (2%) and PRF-Ca (1%)) using different TD and Py temperatures where the EGA thermoprofiles showed clear differences (see Fig. 5). Regardless of the analysis temperature and sample type, the single major peak (at 7.05 min) was found to be as "phenol" in all samples (Figs. 6, 7, 8). When using a pyrolysis temperature of 340 °C, besides the major phenol peak at 7.05 min, some other minor compounds (i.e. at 10.28 min: cyclopentanol; at 12.53 min: resorcinol; and methylresorcinol; at 13.31 min) were found (Fig. 8b).

Although the volatile compounds were similar between the samples, the abundance of the main phenol peak (at 7.05 min., Mw: 94 g/mol) differed significantly. In particular, the addition of the acidic extracts to PRF adhesive increased the gas formation extremely (for quantitative comparison, see Table SI 3). These results confirmed the previous results that the addition of the acidic extracts to the PRF adhesive led to more pronounced changes in the

(a)

(b)
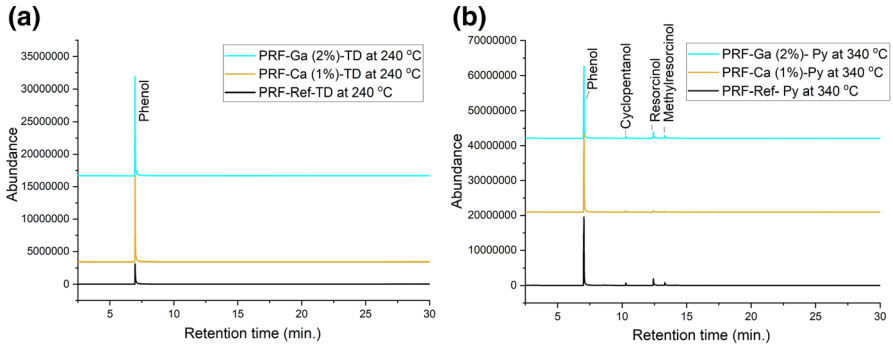
Fig. 8 DSA results of the PRF-Ref, PRF-Ga (2%) and PRF-Ca (1%) cured at 40 °C, **a** thermal desorption (TD) at 240 °C and **b** pyrolysis (Py) at 340 °C. Note: the graphs were plotted stacked in the Y-axis for better visualization

cross-linking degree (i.e. less crosslinking by acidic extracts, higher gas abundances most likely relate to a lower polymerization) of the cured adhesive rather than the compositional changes.

Tensile shear tests

Based on the previous results, the chestnut extract was found to have a major impact on the curing properties of the PRF adhesive. Therefore, the influence of the extracts on the mechanical performance of PRF-bonded wood was also investigated by tensile shear tests. The tests were performed on the reference (not extracted) and water extracted chestnut wood using two different A1 and A4 treatments. The extraction analysis confirmed the removal of 1.97% of extracts from the wood surface, which was a reasonable amount for the studied chestnut wood (Özparpucu et al. 2020, 2022).

In line with the *in-situ* FTIR-rheology but also the thermal analysis results, the reference wood consisting of wood extracts showed a lower mechanical performance. In particular, by extraction, a statistically significant improvement in the tensile shear strength was found for both treatments (14% and 28%, for A1 and A4, respectively) (Fig. 9a). Similarly, in the literature, a significant reduction in the tensile shear strength was reported when beech wood was bonded with PRF-adhesive and Ga mixture (Bockel et al. 2019). However, the current study enabled to reveal the direct negative influence of the acidic extracts on the mechanical properties by testing the real wood bonding surface. Finally, as another indication of a better bonding performance, the averaged wood fracture (%) values were higher for the extracted wood for both A1 and A4 treatments. However, statistical tests could not reveal any significance (Fig. 9b). It should be noted that the differences in the adhesive penetration were not significant either (Table SI4).

(a)

(b)
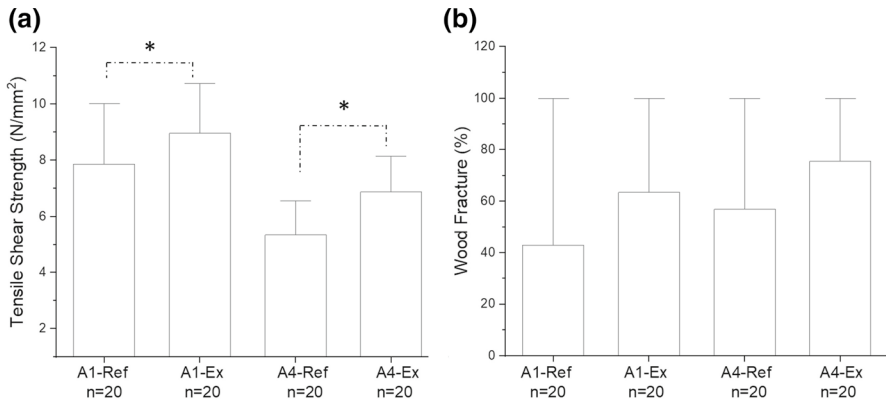
Fig. 9 Tensile shear test results on PRF-glued reference (not extracted) and water extracted (Ex) chestnut wood tested after A1 and A4 treatments, **a** shear strength, and **b** wood failure percentage (Wilhelm 2020) (*indicates statistical difference, ANOVA, Tukey test at 95% confidence level)

Conclusion

Phenol resorcinol formaldehyde (PRF) adhesive has been one of the most widely used adhesives for the production of various wood composites such as plywood, oriented strand board (OSB) glulam and laminated veneer lumber (LVL). In this study, the interactions between the PRF adhesive and water-soluble wood extracts from several European wood species were investigated using systematic, analytical techniques. For this studied system with species-specific adjustments of the amounts of extract addition to the PRF adhesive, acidic extracts were found to influence the PRF curing properties. In particular, it has been revealed that even the addition of a minor amount of acidic chestnut extract (< 1%) to the PRF adhesive influenced the adhesive curing prominently by resulting in prolonged curing reactions and less final crosslinking of the adhesive. These results showed good agreement with the tensile lap shear test results of the chestnut-PRF specimen as a significantly higher strength (up to 28%) was observed after the water-extraction treatment on the chestnut wood samples. Yet, it was challenging to identify the exact underlying reasons behind these influences, because the analysis of the FTIR spectra and also thermal degradation products could not show any direct chemical reactions between the wood extracts and the adhesive. This can be due to the overlapping effects of similar functional groups in the chemistry of the wood extracts and adhesive system. It is noteworthy that these techniques have previously revealed pronounced changes in the chemical curing reactions of isocyanate-based adhesives in the presence of the wood extracts (Özparpucu et al. 2022). Considering these facts, in the current studied adhesive system, the alterations in the catalytic efficiency of the basic-catalyzed adhesive curing reactions due to the presence of the acidic extracts and compounds seem to be responsible for the negative alterations in the adhesive curing properties, as the PRF curing typically requires a basic catalyst. Nevertheless, this output confirms that PRF bonding of acidic wood surfaces can be critical, and for highly

durable wood adhesive bonds, some surface treatments on the acidic wood surfaces (e.g. extraction, or primer applications for adjusting the surface pH etc.) might be beneficial. Alternatively, the adhesive formulation can also be specified (e.g. a higher starting pH of the adhesive) for the wood species having a high acidic extract content. Furthermore, the presented methodological approach to analyse *in-situ* the chemical and rheological changes over the adhesive curing process can give useful information for the adaptation of resin formulations to specific wood species chemistry, or the development of novel wood adhesive types in general.

Declarations

Conflict of interest The authors declare no conflict of interest.

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