

Crosslinking of Shellac with Citric and Phosphoric Acids for Improved Wood Adhesive Performance

Maks Brus

University of Ljubljana

Klemen Kotnik

University of Ljubljana

Luka Kramarič

University of Ljubljana

Milan Šernek

`milan.sernek@bf.uni-lj.si`

University of Ljubljana

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Abstract

Shellac is a renewable and biodegradable polyester resin produced by the *Kerria lacca* insect, with good adhesion properties. Although its dry adhesive strength is high, it remains below the requirements of modern European standards for thermoplastic adhesives for bonding wood. To improve the dry and wet bond strength of shellac, this study employed crosslinking with citric acid (CA), a green crosslinking agent, and phosphoric acid (H_3PO_4) as catalyst. To verify the reaction between shellac and CA, FTIR, ethanol solubility testing, and DSC were used. The effect of crosslinking on bond strength was determined using an Automated Bonding Evaluation System (ABES) combined with Design of Experiments (DOE) methodology, and validated with standardised performance testing (EN 204 and EN 205). The results confirmed the esterification reaction between shellac and CA, with increase in the ester peaks in FTIR spectra, decreased ethanol solubility, and a broad exothermal peak around 140–160°C in DSC, corresponding to polycondensation. The addition of H_3PO_4 lowered the activation energy of the reaction, demonstrating that H_3PO_4 can catalyse CA esterification. Bond strength increased with temperature and reached a maximum at 175°C; furthermore, increasing CA concentration improved bond strength. Adhesive formulations of shellac and shellac-CA achieved bond strengths above 10 MPa, classifying them as suitable for non-structural applications in dry conditions (D1). The moisture resistance of shellac-CA bonded specimens improved compared with neat shellac bonded specimens. This study shows that the shellac curing process can be accelerated, and its bonding performance and water resistance improved, using a green, sustainable crosslinking strategy with CA.

1 Introduction

Shellac is a natural thermoplastic polyester resin produced by the *Kerria lacca* insect. It is one of the oldest polyesters used by humans to produce dyes, varnishes and adhesives (Gardner 1941; Farag 2010; Derry 2012). Chemically, it is a mixture of terpenic resin, about 70% of which is polyester and 30% single esters; the other components are wax, coloured substances and other impurities in varying degrees (Wadia et al. 1969; Maiti and Rahman 1986). The chemical structure is not fully understood; however the most widely accepted model was proposed by Limmatvapirat et al. (2007), consisting of an aleuritic acid backbone connected by ester links to terpenic acids (Fig. 1). This combination of hydrophilic and hydrophobic groups gives shellac its amphiphilic properties (Sharma et al. 1983).

Due to its properties shellac has been considered as an adhesive for binding various materials, such as metals (Coyle 1971), photographic paper (Cannon 2012), pottery (Koob 1984), glass (Davison 1984), wood (Gupta et al. 1983), and even insects (Deans 2018; Toppa et al. 2021). Bonding wood presents a unique challenge, as the substrate is susceptible to dimensional changes caused by heat and moisture, leading to the buildup of stress in the adhesive bond. The adhesive must therefore be elastic enough to adapt to these dimensional changes but also retain high strength to meet rigorous standard requirements. Previous studies have found that while shellac can achieve high shear strengths bonding wood (9.8 MPa) in dry conditions, moisture resistance remains a key consideration (Brus et al. 2026a).

To improve the water resistance of shellac, heat treatment has proved a simple and effective solution (Ahuja et al. 2024; Brus et al. 2026a). Chemical modifications have also been attempted to enhance alcohol, and alkali resistance (Licchelli et al. 2013), reduce brittleness and ageing, and improve strength (Luangtana-anan et al. 2007; Bar and Bianco-Peled 2020), as well as by mixing with chitosan and tannic acid for water resistance (Vrabič-Brodnjak 2023). Since shellac contains many free hydroxyl groups, it can esterify with polycarboxylic acids (Gardner 1941; Maiti and Rahman 1986). One such natural polycarboxylic acid is citric acid (CA), which has been widely studied due to its natural origin and low cost compared to synthetic alternatives (Widsten et al. 2014). It has been shown that CA can react with shellac to prepare biocomposites (Rohaeti 2015; Nurhayati et al. 2020), as well as for the modification of shellac with CA for enteric coatings in pharmaceuticals (Pearnchob et al. 2004; Yuan et al. 2021).

CA is a trifunctional carboxylic acid with one hydroxyl group. All three acid groups and the hydroxyl group can participate in esterification reactions to form a crosslinked polyester network (Chen et al. 2025). The reaction most likely proceeds via the formation of a reactive CA anhydride intermediate at temperatures between 120°C and 180°C, which then reacts with hydroxyl groups to form an ester bond (Noordover et al. 2007). Although the formation of the anhydride is difficult to prove due to its high reactivity and the possibility of self-catalysed reactions of CA occurring at temperatures as low as 80°C, it remains the most likely reaction pathway at high temperatures (Yang and Wang 1996; Yang et al. 1997; Shen et al. 2015; Chen et al. 2025). Shellac can esterify with CA to form one, two, or three ester bonds, with the latter two facilitating network formation (Fig. 2). CA can also react with the wood substrate by reacting with the hydroxyl groups of cellulose and hemicellulose (Šefc et al. 2009; Feng et al. 2014; Mubarak et al. 2020; Ando et al. 2024), serving as a chemical bond between shellac and wood and potentially increasing adhesion.

Although CA crosslinking reactions are typically catalysed using sodium hypophosphite (SHP) $\text{Na}_2\text{H}_2\text{PO}_2$ (Šefc et al. 2009; Feng et al. 2014; Shen et al. 2015; Liang et al. 2022; Chen et al. 2025), sodium hypophosphate ($\text{Na}_2\text{H}_2\text{PO}_4$) has been used as a cheaper and similarly effective alternative (Šefc et al. 2009). Self-catalysed reactions of CA are also possible, with typical reaction temperatures of around 120–180°C; higher temperatures result in shorter reaction times (Kolah et al. 2007; Noordover et al. 2007; Widsten et al. 2014; Csiszár et al. 2023). Phosphoric acid (H_3PO_4) has also been used as a catalyst for aspartic acid, facilitating dehydration in the condensation reaction (Wang et al. 2003). Since the formation of CA anhydride is a dehydration process, we hypothesise that H_3PO_4 could be used as a catalyst for CA crosslinking.

Previous literature has not focused on the crosslinking reaction between shellac and CA or its effects on bonding performance. Similarly, there is a lack of literature on H_3PO_4 -catalysed reactions of CA. Therefore, to better understand the underlying chemical reaction, the objective of this paper is first to study the crosslinking of shellac with CA, with and without H_3PO_4 as a catalyst, using FTIR to monitor chemical changes, ethanol solubility to determine the degree of crosslinking, DSC, and the Borchardt and Daniels method (Borchardt and Daniels 1956; ASTM International 2023) to study reaction kinetics.

Secondly, to understand bonding performance, Automated Bonding Evaluation System (ABES) will be used to determine the effects of process parameters on shear strength using design of experiment (DOE) methodology, as well as bond strength development modelling to determine the optimal pressing conditions, which will be validated using standard shear strength determination according to EN 205:2016. This combined approach will provide a deeper understanding of CA-based esterification of shellac and its effects on the bonding performance of wood, incorporating natural ingredients to produce new high-performance materials.

2 Materials and Methods

2.1 Materials

Platinum (SH2) shellac was used to prepare shellac mixtures. Shellac flakes were obtained from Samson Kamnik d.o.o. (batch October 2025), Slovenia. Ethanol 96% (Irij d.o.o., Kropa, Slovenia) was used as solvent to prepare the shellac sample mixtures. Citric acid monohydrate (Carlo Erba Reagents SAS, France) and phosphoric acid (H_3PO_4 , 85%) (Sigma Aldrich GmbH, Germany) were used to prepare different adhesive mixtures.

All bonded experimental specimens were made from European beech (*Fagus sylvatica* L.). Beech veneers with a thickness of 0.46 ± 0.05 mm were used for ABES testing (Adhesive Evaluation Systems Inc., Oregon, USA). Beech lamellae with final dimensions of 600 mm $\times$ 130 mm $\times$ 4.7 mm were used to prepare samples for EN 205:2016 testing. All wood samples were conditioned at a temperature of $20 \pm 2^\circ\text{C}$ and a relative humidity of $65 \pm 5\%$. The moisture content of the beech wood was $9 \pm 0.4\%$, and the density was 662 ± 4.8 kg/m³. All wood was provided by the Department of Wood Science and Technology, Biotechnical Faculty, University of Ljubljana, Slovenia.

2.2 Preparation of adhesives

2.2.1 Shellac solution

Shellac flakes were taken from the container and dissolved in ethanol to prepare a 60% (w/w) solution. The mixture was heated at 60°C in a double boiler and stirred until the shellac flakes were completely dissolved. Samples were labelled as SH2.

2.2.2 Shellac solution with citric acid

Monohydrate CA was first ground with a pestle and mortar to a fine powder, then added gravimetrically to the shellac ethanol solution based on the weight of shellac. The mixture was homogenised by stirring. Samples were labelled as CA_x, where CA denotes citric acid and x the concentration of CA per dry shellac.

2.2.3 Shellac solution with citric and phosphoric acid

An appropriate amount of phosphoric acid was added to shellac - CA mixtures with continuous stirring to prevent local spikes in acidity. Samples were labelled as CAxPy, where CA denotes citric acid and P denotes phosphoric acid (H_3PO_4), x and y represent their respective concentrations (% w/w). The different adhesive mixtures are presented in Table 1.

Table 1
Prepared adhesive mixtures with weight percentages of components. /sh indicates weight percentage per dry shellac, /ca indicates weight percentage per CA monohydrate. *Characterised for crosslinking.

Mixture designation	sh (%)	eth (%)	ca/sh (%)	p/sh (%)	p/ca (%)
SH2*	60	40	0	0	0
CA2.5	60	40	2.67	0	0
CA2.5P	60	40	2.67	1.67	62.5
CA10	60	40	10	0	0
CA10P	60	40	10	1.67	16.67
CA10P6.7	60	40	10	6.67	66.67
CA20*	60	40	20	0	0
CA20P	60	40	20	1.67	8.33
CA20P13.3*	60	40	20	13.33	66.67

2.3 Crosslinking of adhesive mixtures

To study the crosslinking of different mixtures (Table 1), adhesive mixtures were pipetted onto a sheet of aluminium foil to form drops of comparable size and baked in a laboratory oven at three different temperatures (125, 150 and 175) °C for five different time intervals (5, 10, 15, 30 and 60) minutes. The cured adhesives were then cooled and stored in an exicator prior to analysis of post-cure properties.

2.4 Chemical characterisation

To determine the effect of curing temperature and time on the formation of new bonds, ATR-FTIR was employed on cured adhesive mixtures. Measurements were conducted using a PerkinElmer Spectrum 2 with a UATR attachment (PerkinElmer Inc., Shelton, CT, USA). The scanning range was 400–4000 cm^{-1} , with a step of 4 cm^{-1} and averaging over 16 scans. The spectra were ATR-corrected, baseline-corrected and normalised prior to analysis. Second-derivative spectra were calculated using a Savitzky–Golay algorithm to identify overlapping carbonyl-related bands in the 1750–1650 cm^{-1} region. Maximal intensities were then determined in narrow spectral intervals centred on the positions of the derivative minima. Based on the identified component positions, characteristic band intensities and intensity ratios were determined and used to monitor changes in carbonyl environments as a function of curing temperature and time.

2.5 Determination of insoluble fraction of cured adhesive

To further determine the crosslinking of different adhesive mixtures as a function of temperature and time, the solubility of cured adhesives was studied. Solid samples were weighed and submerged in ethanol for 24 hours. After ethanol extraction, the insoluble fraction was filtered using Grade 391 fine filter paper (Sartorius AG, Göttingen, Germany) and dried in a fume cupboard at room temperature with constant ventilation for a minimum of 72 hours, or until a constant mass was reached. The test was repeated in triplicate.

2.5 Thermal characterisation

The thermal properties were studied using DSC with a Mettler Toledo HP DSC 1 (Mettler Toledo International Inc., Greifensee, Switzerland). Measurements were performed on cured samples to determine changes in glass transition temperature (T_g) and curing enthalpy. The heating range was 20–200°C, at a heating rate of 10°C/min in nitrogen atmosphere of 50 mL/min, at normal pressure. Results were evaluated in STARe® software (Mettler Toledo International Inc., Greifensee, Switzerland) using the Borchardt and Daniels method (Borchardt and Daniels 1956; ASTM International 2023), which can be used to estimate some important parameters in the curing process such as reaction order (n), activation energy (E_a), and degree of conversion (α), following Eq. (1).

$$\frac{d\alpha}{dt} = kT(1 - \alpha)^n \text{ Eq. 1}$$

2.6 Shear strength development with ABES

The bond strength of all adhesive mixtures was evaluated using ABES. This device combines a small hot press and a tensile-testing machine, enabling the determination of adhesive bond strength immediately after the specified pressing time and temperature in the hot press (Fašalek et al. 2025).

Beech veneers, 0.46 ± 0.05 mm thick, were cut using a sample preparation machine by AES (Adhesive Evaluation Systems). Approximately 150 g/m^2 of adhesive was applied to the bonded area, which measured $5 \text{ mm} \times 20 \text{ mm}$ (100 mm^2). After the selected pressing time had elapsed the bonded test piece was cooled with compressed air for 5 seconds. The bonded test piece was then subjected to tensile shear stress until rupture and applied maximum force was recorded (F). The exact surface area of the bond (A) was measured using digital callipers (Mitutoyo CD-15DC). For each combination of temperature and time, five measurements were taken. The shear strength (τ) was calculated using Eq. (2).

$$\tau = F/A \text{ Eq. 2}$$

2.6.1 Screening with ABES

To determine the optimal adhesive formulation and pressing parameters, screening was conducted on all adhesive mixtures presented in Table 1 at pressing temperatures of 125, 150, and 175°C, and pressing

times of 300 and 600 seconds, with five replicates per condition resulting in 270 measurements in total.

2.6.2 Bond shear strength development with ABES

Adhesive mixtures SH2, CA20 and CA20P13.3 (Table 1) were selected for modelling bond shear strength development. SH2 was used as the reference, unmodified shellac; CA20 was the adhesive mixture with the highest bond strength after screening; and CA20P13.3 was chosen for its high reactivity even at low temperatures. SH2 and CA20 were pressed at 175°C, while CA20P13.3 was pressed at 125°C. Pressing times ranged from 15 s to 1800 s, with five replicates per time interval.

2.7 Bond quality validation

To verify the bond quality European standard EN 205:2016 was followed for sample preparation and testing, and EN 204:2016 for classification (European Committee for Standardization (CEN) 2016a, b). The beech lamellae were planed to 4.7 mm with a thickness planer prior to bonding to ensure an active wood surface. Approximately 200 g/m² of the selected shellac adhesive was spread onto one of the lamellae using a spatula. The second lamella was placed on top to ensure adhesive transfer. Lamellas were pressed at a specific pressure of 1.2 MPa in a laboratory hot press. Pressing was carried out at 175°C for 15 minutes for SH2 and CA20, and at 125°C for 15 minutes for CA20P13.3 adhesive. These parameters were selected based on the results of bond shear strength development on ABES. At the end of the pressing period, the bonded lamellas were conditioned in a standard climate (20°C and 65% RH) for 7 days and then cut into test pieces. For dry shear strength (D1) the samples were tested after conditioning (Treatment 1). To test moisture resistance (D2), samples were additionally submerged in water (20 ± 5°C) and then reconditioned for 7 days in a standard climate before testing (Treatment 2). Shear strength was evaluated using a universal testing machine (Zwick Z100, Zwick Roell, Ulm, Germany) in accordance with EN 205:2016 for durability classes D1 and D2. The maximum applied force was recorded, and the percentage of wood failure (WF) of the adhesive bond was visually assessed (graded as 0%, 25%, 50%, 75% and 100% wood failure). 20 samples were tested for each durability class, unless specified. If a sample failed during water submersion a shear strength of 0 MPa was recorded.

2.8 Modelling and statistical analysis

2.8.1 General visualisation and analysis

The visualisation was prepared using the R programming language in R Studio (2026.04.0 Build 526) with the libraries ggplot2, ggh4x, patchwork, and ggrepel, as well as supporting libraries for data wrangling (dplyr, purrr, tidyverse, readr, stringr). To perform ANOVA and the post hoc Duncan's multiple range test (DMRT), the following libraries were used: lme4, lmerTest, emmeans, and multcompView.

2.8.2 Design of experiments modelling of ABES screening data

To evaluate the effects of temperature, pressing time, CA content, and H₃PO₄ (denoted as P in the model parameters for brevity) content on the shear strength of the prepared adhesives, design of experiments

(DOE) modelling of screening data was performed using MODDE 13 software (Sartorius AG, Göttingen, Germany). The model included four predictor variables: time (s) – 2 levels, temperature (°C) – 3 levels, CA (%sh) – 3 levels, and H₃PO₄ (%ca) – 3 levels, and one response variable: strength (MPa). An expanded mixed full factorial design was used, based on mixtures from Table 1 and pressing parameters from section 2.6.1. An excerpt from the worksheet is presented in Table 2, with full model information available in S 1 and S 2. Mean values from five measurements were used for the strength response variable. Fitting was performed using multiple linear regression (MLR), with coefficients exported unscaled and uncentred (S Table 2). Shear strength can then be expressed as the sum of the products of predictors and coefficients:

$$\tau = \sum_{i=1}^n k_i \bullet x_i \text{ Eq. 3}$$

which is in this specific case:

$$\tau = k_1 \bullet time + k_2 \bullet temp + k_3 \bullet CA + k_4 \bullet P \text{ Eq. 4}$$

This enables the calculation of shear strength based on process parameters (pressing time and temperature), and adhesive mixture composition (CA and H₃PO₄ content). The optimal setpoint was calculated using the software’s built in Optimizer function, with all factors set to free and the response variable (shear strength) set to Desired maximise. The function iteratively calculates the shear strength based on the model coefficients and outputs the values of the factors.

Table 2
Worksheet example from MODDE 13 software. Time, temperature, CA and H₃PO₄ (marked as P) content were the predictors, while strength was the response. Full sheet available in S Table 1.

Exp No	Exp Name	Run Order	Incl/Excl	Time (s)	Temp (°C)	CA (%)	P (%ca)	Strength (MPa)
42	N42	42	Incl	600	125	10	15.5	3.69
36	N36	19	Incl	600	175	20	62	6.50
7	N7	22	Incl	300	125	10	0	3.40
52	N52	52	Incl	600	175	20	7.75	7.22
2	N2	35	Incl	600	125	2.5	0	2.08

2.8.3 Nonlinear least squares fitting of ABES bond strength development data

Several nonlinear models (exponential, Gompertz, Avrami, logistic) were fitted to ABES data from 2.6.2 using R programming language and R Studio. The function nlSLM() from the package minpack.lm, was used to fit the models. The model fit was compared using Akaike information criterion (AIC) and Root mean square deviation (RMSE). A pseudo-R2 statistic was used to describe the goodness of fit. We selected the Avrami model, as it provided the lowest AIC and RMSE values:

$$\tau(t) = \beta \bullet (1 - \exp(-kt^n)) \text{ Eq. 5}$$

where β is the asymptotic value of shear strength, k describes the rate of bond development, and n is the Avrami exponent describing the shape of the growth curve. Values of $n \approx 1$ correspond to first-order growth kinetics (exponential model), conversely larger values of n indicate increasingly sigmoidal behaviour.

All raw data generated in this study are openly available in the Zenodo repository (Brus et al. 2026b).

3 Results and Discussion

3.1 FTIR

The FTIR spectra of pure shellac (SH2) and mixtures with citric acid (CA20) and citric/phosphoric acid (CA20P13.3) show distinct changes in the hydroxyl, carbonyl, and fingerprint regions, reflecting the chemical processes occurring during curing (Fig. 3a and S 3). A broad band corresponding to hydroxyl groups is present in the 3600–3100 cm^{-1} region. In pure shellac, its intensity decreases with increasing time and temperature, which is consistent with the consumption of hydroxyl groups during self-esterification reactions (Ahuja et al. 2024; Brus et al. 2026a). Similar behaviour is observed in CA-based systems, where esterification between hydroxyl and carboxyl groups represents the main cross-linking mechanism. In systems containing both citric and phosphoric acids, the interpretation is less straightforward, as the intensity of this band is also influenced by bound water and the reorganisation of hydrogen bonds during curing (Noordover et al. 2007; Chen et al. 2025).

The C–H stretching bands at approximately 2928 and 2856 cm^{-1} remain essentially unchanged throughout curing. Because these bands are largely unaffected by the curing reactions, they were used as internal reference bands for normalisation, in agreement with previous studies (Ahuja et al. 2024; Brus et al. 2026a).

The most pronounced changes were observed in the carbonyl region between 1750 and 1680 cm^{-1} , identified as one of the key regions for monitoring shellac curing and cross-linking (Striova et al. 2015; Ahuja et al. 2024; Brus et al. 2026a). Second-derivative analysis (S 4) resolved three recurring spectral components centred at approximately 1735, 1712, and 1686 cm^{-1} , representing stretching vibrations for carbonyl group of esters, carbonyl group of acids, and conjugated or hydrogen bonded carbonyl group, respectively. In pure shellac, the 1712 cm^{-1} component remained dominant throughout curing, while the relative contribution of the 1735 cm^{-1} component increased only moderately with increasing curing time and temperature. Accordingly, the intensity ratio I_{1735}/I_{1712} increased from approximately 0.67 to 0.87 (Fig. 3b). In contrast, the addition of CA resulted in a progressive increase of the ester component, leading to substantially higher I_{1735}/I_{1712} ratios. An even stronger effect was observed for CA20P13.3, where the ratio exceeded 1.0 at 125 and 150°C after prolonged curing. These results, shown in Fig. 3, indicate an increasing contribution of the 1735 cm^{-1} ester carbonyl component relative to the 1712 cm^{-1} band and provide quantitative evidence for progressive esterification and network formation during

curing. The increasing intensity of the 1735 cm^{-1} component is consistent with the formation of ester carbonyl groups through reactions between shellac hydroxyl groups and citric acid carboxyl groups (Noordover et al. 2007). This also supports the self-esterification reaction that occurs in shellac and has been previously reported as aging (Frag 2010; Bar and Bianco-Peled 2021).

In addition, the position of the 1712 cm^{-1} component gradually shifted to higher wavenumbers with increasing curing time and temperature (S 5). The shift was relatively small for pure shellac but reached approximately 20 cm^{-1} in the phosphoric acid-containing system, indicating a substantial change in the chemical environment of the carbonyl groups.

An absorption band in the region $1780\text{--}1800\text{ cm}^{-1}$ became increasingly visible in CA20, and particularly in CA20P13.3, at higher curing temperatures (S 3). The literature indicates that citric acid can form cyclic anhydride intermediates at temperatures close to its melting point (Yang et al., 1997; Yang and Wang, 1996), representing an important step in esterification and subsequent cross-linking. This band could therefore be attributed to the formation of anhydride structures or reactive citric acid intermediates. Its higher intensity in the phosphoric-acid-containing system suggests that phosphoric acid accelerates dehydration and esterification reactions (Y. Wang et al., 2003), although FTIR alone does not provide unambiguous evidence for the incorporation of phosphate groups into the cured network (Noordover et al. 2007; Berube et al. 2018).

Significant changes are also observed in the fingerprint region ($1500\text{--}500\text{ cm}^{-1}$). Compared with pure shellac, the modified systems show progressive broadening and overlap of characteristic absorption bands, particularly between 1200 and 1000 cm^{-1} . These changes are consistent with the formation of ester and C–O–C linkages, together with increasing structural heterogeneity of the polymer network. The effect is most pronounced for CA20P13.3, indicating the greatest extent of chemical transformation. With increasing curing time and temperature, the spectra gradually lose their well-defined peaks and become broader, reflecting the development of a more heterogeneous, cross-linked structure.

Overall, the FTIR results show that shellac curing involves the progressive consumption of hydroxyl groups, accompanied by substantial changes in the carbonyl region. The addition of citric acid promotes the formation of ester structures, while the presence of phosphoric acid further enhances these processes, particularly at higher temperatures. The appearance of an additional band at approximately $1780\text{--}1800\text{ cm}^{-1}$ further supports the hypothesis that citric acid anhydride intermediates are formed, which play an important role in the esterification mechanism and the development of a cross-linked structure.

3.2 Solubility and crosslinking

We evaluated the ethanol solubility of cured adhesive samples to monitor curing as a function of time and temperature (Fig. 4a). Significant differences among treatment groups were determined using ANOVA, followed by DMRT, with differences indicated by letter annotations. Solubility decreased with curing time, reflecting progressive crosslinking of the shellac adhesives. Reference shellac (SH2) cured

at 125°C showed full solubility for curing times up to 30 minutes, with the first significant drop in solubility observed at 60 minutes. Adding CA to shellac greatly reduced solubility to around 70% even after only 5 minutes of curing at 125°C, with longer curing times yielding a relatively stable solubility of around 30%. Addition of H_3PO_4 to the mixture reduced solubility further to 40% under the mildest curing conditions, and increasing the curing time led to a stable decrease in solubility to around 18%, indicating that phosphoric acid facilitated the formation of a more stable structure.

At higher curing temperatures, solubility dropped further. At 150°C shellac starts to self-esterify, forming an insoluble structure due to temperature-induced crosslinking, as previously reported (Ahuja et al. 2024; Brus et al. 2026a). After 30 minutes of curing, solubility of shellac decreased to around 40%, and after 60 minutes it reached a minimum of 15%. By including CA, the initial solubility after 5 minutes of curing was around 35% and steadily declined to around 6%. Adding H_3PO_4 produced similar results up to 30 minutes of curing, after which the presence of H_3PO_4 resulted in a less stable and more soluble polymer with around 20% solubility. Similarly, at 175°C, shellac rapidly polymerised and reached its lowest solubility after 30 minutes; further increases in curing time did not cause a significant additional decrease. Adding CA again reduced solubility further: it started at around 30% and rapidly dropped to 6% after just 15 minutes, and to 1% after 30 minutes of curing. With H_3PO_4 , the initial solubility was at its lowest at just under 20%, but it did not change significantly with increasing curing time, remaining at around 15–20%.

These results show that adding phosphoric acid at higher curing temperatures had a positive effect only at short curing times, while longer curing leads to a less stable polymer than when CA is used alone. The physical appearance of the cured adhesives showed that H_3PO_4 addition caused a marked darkening of the material (Fig. 4b). Combined with the poorer ethanol resistance, this darkening may indicate polymer degradation. At elevated temperatures, long curing times and the low pH resulting from phosphoric acid addition could cleave polymer chains. Another possibility at these temperatures is that H_3PO_4 reacted with OH groups of either shellac or CA to form phosphate ester bonds (Wang et al. 2023), lowering the overall crosslinking density because phosphoric acid cannot link multiple chains effectively due to steric hindrance. We conclude that the esterification reaction of shellac and CA at high curing temperatures (> 150°C) yields a more highly crosslinked polymer than when H_3PO_4 is used as a catalyst, although the addition of H_3PO_4 allows shorter curing times.

3.3 DSC

The curing kinetics of shellac crosslinked with CA, and CA catalysed with H_3PO_4 , were studied using the Borchardt and Daniels method (Fig. 5). Difficulties in measuring the heat flow due to solvent evaporation from the vacuum-dried samples led us to use samples cured at 175°C for 5 minutes, as these showed the highest curing enthalpy. We acknowledge that cured samples exhibit a declining trend in curing enthalpy compared with uncured samples (S 6a); however, relative comparisons are still possible. The curing peak of CA esterification was broad and of low intensity (< 20 J/g), with a peak temperature (T_p) between 130°C and 160°C depending on the curing conditions (S 6b). The activation energy E_a

determined by DSC was 75.6 kJ/mol, which is close to that of the self-catalysed model reaction between CA and ethanol proposed by Kolah et al. (2007). On adding H_3PO_4 , T_p did not change significantly; the uncured sample had a T_p of around 150°C. The activation energy was significantly lower at 59.8 kJ/mol, demonstrating that phosphoric acid acts as a catalyst for CA esterification, similar to its effect on aspartic acid (Wang et al. 2003). The observed decrease in activation energy is in line with previous studies using SHP as a catalyst (Shen et al. 2015; Liang et al. 2022).

The glass transition temperature (T_g) was difficult to measure by DSC on cured samples. We were unable to determine the T_g of samples cured at 125°C due to the lack of inflection point. In general, the T_g increased with curing time, and higher temperatures led to higher T_g values (S 6c). This trend is most obvious for CA20 samples, where the T_g raised from around 46°C to just over 60°C when cured at 175°C for 5 and 60 minutes, respectively. A similar effect was observed for SH2 samples. Previous studies reported larger T_g changes for solid shellac cured under the same conditions (Brus et al. 2026a). Clearly, there seems to be a decrease in the measured T_g when shellac is cured in ethanol solution rather than in bulk. A similar effect was found for epoxy adhesives containing acetone as a solvent, where the presence of solvent reduced the conversion rate, resulting in improper curing and a decreased T_g (Rodrigues et al. 2021). In bulk shellac the reactive groups are locally concentrated due to hydrogen bonding between OH and COOH groups, which can then readily react upon heating. In solution, however, the hydrogen bonds within shellac are broken and the reactive groups are further apart, leading to fewer opportunities for interaction and a lower crosslink density. Another possibility is the presence of residual solvent in the cured sample, which acts as a plasticiser by increasing the free volume and disrupting intermolecular interactions and hydrogen bonding. The presence of ethanol could also cause a shift in the condensation reaction due to inefficient water removal, lowering the crosslinking density.

3.4 DOE of ABES

After confirming the esterification reaction between shellac and CA, we performed experiments to test the adhesive performance of the shellac mixtures for bonding wood. To determine the optimal process parameters and adhesive mixture formulation we used ABES measurements in combination with DOE screening. We built a MLR model with factors of pressing time and temperature, CA and H_3PO_4 content in the adhesive mixture, while the response variable was shear strength determined with ABES. The model explained the data well (adjusted $R^2 = 0.87$) and had good predictive ability ($Q^2 = 0.84$), with high reproducibility (0.987) and model validity higher than the pure error (0.40) (Sartorius Stedim Data Analytics AB 2017).

All considered factors had a positive effect on shear strength (Fig. 6). The most significant process parameter was pressing temperature, followed by the adhesive mixture factors of CA content and H_3PO_4 content, pressing time had the least effect. This shows that pressing temperature has a significant effect on the adhesive bond strength development, suggesting that the reactions between the adhesive components favour higher temperatures. These findings are supported by our reaction analysis and by

literature, as the crosslinking reactions of CA require higher temperatures to facilitate the formation of reactive anhydride intermediates which then react with OH- rich polymers (Kolah et al. 2007; Noordover et al. 2007; Chen et al. 2025). CA increased bond strength, as it acts as a crosslinker for shellac; therefore, by increasing the CA content, the number of reactive molecules increases, allowing the formation of a denser polymer network and resulting in higher bond strength. The positive effect of H_3PO_4 can be related to the lower activation energy required for the reaction as measured by DSC, with H_3PO_4 acting as a catalyst and promoting dehydration and anhydride formation (Wang et al. 2003).

The interaction component of temperature and phosphoric acid was however negative, meaning that with increasing temperatures the effect of H_3PO_4 content begins to reduce shear strength. Similarly, with increasing CA content, the addition of H_3PO_4 can reduce shear strength. There was a similar observation with solubility, as the curing temperature increased, the adhesive mixture containing H_3PO_4 increased in solubility, while the mixture with only CA became insoluble (Fig. 4a). While CA always had a positive effect on shear strength, the addition of H_3PO_4 was only beneficial when pressing temperature was low or CA content was low. The reasons could be as described in section 3.2 regarding the possible degradation of shellac adhesive. Additionally, as the bond strength depends on the cohesive strength of the adhesive and substrate (wood), as well as the adhesion between the two, it is possible that the addition of H_3PO_4 caused a degradation of the wood substrate due to low pH. We observed darkening of the wood substrate when H_3PO_4 was present, potentially indicating wood degradation lowering the overall bond strength. Similar was found when bonding wood with liquified wood, which has low pH due to H_2SO_4 content (Žigon et al. 2022).

To visualise the optimal parameters, we used response contour plotting (Fig. 7). The optimal setpoint was calculated via the software and is also presented in the plot in the top right of all subplots, and was 175°C, 600 s, 20% CA and 0% H_3PO_4 . Maximum shear strengths can only be achieved using the highest CA content of 20% and a high temperature. As pressing temperature has a high impact on the energy consumption when manufacturing wood-based composites (Li et al. 2007), response contour plots can be used to determine strategies to reduce pressing temperature (Fig. 7). In this case by increasing the pressing time or by increasing the H_3PO_4 content the pressing temperature can be reduced. To achieve at least 6 MPa in ABES, we can use the formulation of CA20P13.3 at 125°C, effectively reducing the pressing temperature by 50°C, while retaining decent bond strength.

3.5 Bond strength development

Using screening, we determined that the optimal parameters and mixture for maximum shear strength were 20% CA at 175°C. To reduce the pressing temperature, we analysed the response contour plot and found that by adding H_3PO_4 to the adhesive mixture, we could reduce the pressing temperature to 125°C. To study the bond strength development of these two mixtures and the reference unmodified shellac at their respective pressing temperatures, we performed ABES at 12 time intervals for each adhesive. We determined that the Avrami model best fit the data, as it provided the lowest AIC and RMSE values (S

Table 3). Overall shear strength increased with increasing pressing time (Fig. 8). The shellac reference (SH2) displayed much greater variability when pressing times were short. In most cases we observed that vapour build-up inside the bondline caused the bond to open, either fully or partially, when the press was opened, due to insufficient bond development, leading to reduced shear strength. At longer pressing times this phenomenon was not observed. The reference reached maximum shear strength after 1800 s, while both modified adhesives reached their maximum after just 600 s. This is supported by the k -parameter, which is 0.0143, 0.0083, and 0.0014 for CA20, CA20P13.3 and SH2, respectively. The k -parameter in the Avrami model represents the curing rate, showing that the CA20 adhesive had the highest curing rate and SH2 the lowest. The β -parameter is the asymptotic value of shear strength and can be used to predict ultimate shear strength in ABES testing. The reference shellac adhesive and CA-modified adhesive had similar β values, 8.02 MPa and 7.26 MPa, while CA20P13.3 had a significantly lower predicted ultimate strength, 5.85 MPa. This is in line with our DOE results, as the predicted bond strength for CA20 was 7.7 MPa and ~ 6 MPa for CA20P13.3. This shows that DOE and ABES bond strength development modelling produce similar bond strength predictions. We found that the modified shellac adhesives had higher reactivity than the reference, while the maximum predicted bond strength was slightly lower when samples were pressed at the same temperature.

3.6 Model validation by industrial standard

To validate the models, we conducted EN 205:2016 test for shear strength and classification according to EN 204:2016. The results of the shear strength test for the three different shellac adhesive mixtures (SH2, CA20 and CA20P13.3) are shown in Fig. 9. The pressing parameters were taken from ABES bond strength development – SH2 and CA20 were pressed at 175°C and 15 minutes, CA20P13.3 was pressed at 125°C and 15 minutes.

Both unmodified shellac (SH2) and citric acid crosslinked shellac (CA20) achieved a mean dry bond strength above 10 MPa, classifying them as suitable for non-structural use in dry applications (D1). The CA20P13.3 mixture had the lowest shear strength among the three adhesive mixtures ($p < 0.001$), likely due to inadequate curing conditions - low temperature, or too short time, which is in line with modelling. Almost all test specimens bonded with CA20P13.3 mixture fell apart after water submersion according to Treatment 2. CA20 mixture showed the most promising results after water submersion, with half of the prepared specimens reaching the D2 classification requirement of 8 MPa, while the other half did not. The samples with high shear strength showed a high WF rate (~ 100%), while the others had a WF rate of 0%. We attribute this variation to the variability in the properties of wood, as the two groups were prepared from two separate wood lamella, and the gluing procedure was the same. As wood is exposed to water it expands, and releases stress induced during the high temperature pressing, weakening the bond. Macroscopic anatomical features, such as growth ring width, orientation, grain angle could affect the amount of stress that is released when wood is submerged in water.

The highest dry strength was achieved by the shellac adhesive mixtures with citric acid (CA20), but it was not significantly different to unmodified shellac ($p > 0.05$). We have shown that CA can react with

shellac to form new ester bonds, effectively crosslinking and contributing to the improvement of shear strength. The increased bond strength could also be due to the reaction of CA with the hydroxyl groups of cellulose in wood (Šefc et al. 2009; Feng et al. 2014; Mubarok et al. 2020; Ando et al. 2024), improving the adhesion between shellac and wood substrate, which is supported by the higher WF rates, compared to reference shellac.

The unmodified shellac (SH2) achieved slightly higher bond strength than was previously reported (Brus et al. 2026a), which highlights the need for more in depth study of this material and its specific curing conditions. Perhaps a longer post curing period after pressing is required to evolve residual solvent and improve bond strength and reduce variability of results. Studies on the ageing performance of adhesive bonds of shellac should also be performed, as crosslinking of shellac occurs naturally with time (Koob 1979; Coelho et al. 2012).

These results show that shellac adhesives modified with 20% CA can pass the requirements of EN 204:2016 for thermoplastic adhesives in dry conditions (D1). We found that wood variability was the main issue in water exposure (D2), as two different lamellae samples prepared in the same way exhibited different shear strengths – one passing and one failing the requirements.

4 Conclusions

We demonstrated that a reaction occurs between shellac and CA, with an exothermic peak corresponding to condensation between 90°C and 190°C. The reaction is an esterification between the hydroxyl groups of shellac and the carbonyl groups of CA, leading to a relative increase in the absorbance ratio I_{1735}/I_{1712} , which confirms the consumption of COOH groups and the formation of ester groups. Dissolution in ethanol showed a greater decrease in solubility for cured samples containing CA than for neat shellac. We confirmed that H_3PO_4 can act as a catalyst for the esterification of shellac with CA, as the activation energy for the reaction decreased from 75.6 to 59.8 kJ/mol. We also observed a larger increase in the I_{1735}/I_{1712} ratio compared with CA alone, with values even exceeding 1.0. Ethanol solubility showed that the addition of H_3PO_4 led to higher reactivity at lower temperatures but resulted in a less stable structure when curing conditions were severe. Using design of experiments modelling combined with the ABES method, we identified temperature as the main parameter influencing the adhesive bond strength of bonded wood specimens, followed by citric acid content, H_3PO_4 content and time. By additionally modelling adhesive bond strength development with ABES, we determined the optimal pressing parameters, which were validated with EN 205:2016 testing, and classified the mixtures of shellac and shellac with 20% citric acid as suitable for non-structural use in dry conditions (D1 class). The water resistance of shellac–citric acid adhesives was improved compared with neat shellac and, under specific conditions, could reach D2 classification. Further research should be conducted on the rheology and penetration of shellac-based adhesives to better understand their adhesion properties.

Declarations

Competing Interests:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contribution

M.Š. and M.B. conceptualised the research. M.B., K.K. and L.K. conducted the research, analysed the results and wrote the main manuscript text. M.B. prepared the figures and tables. M.Š. supervised the research and secured the funding. All authors reviewed the manuscript.

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Data Availability

All research data supporting the findings of this study are publicly available in the Zenodo repository at <https://doi.org/10.5281/zenodo.21642082>.

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Figures

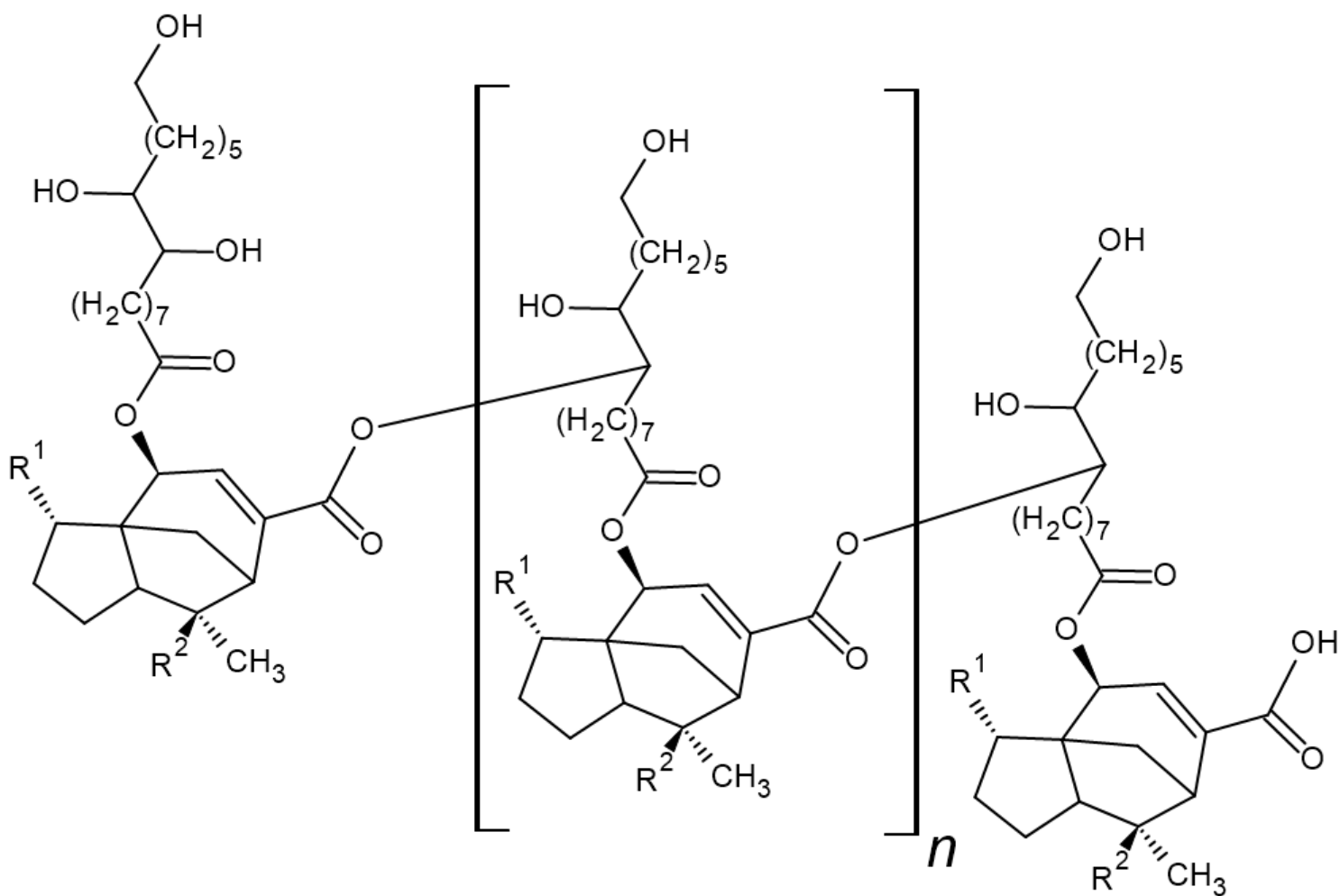


Figure 1

Shellac chemical structure adapted from Limmatvapirat et al. (2007)

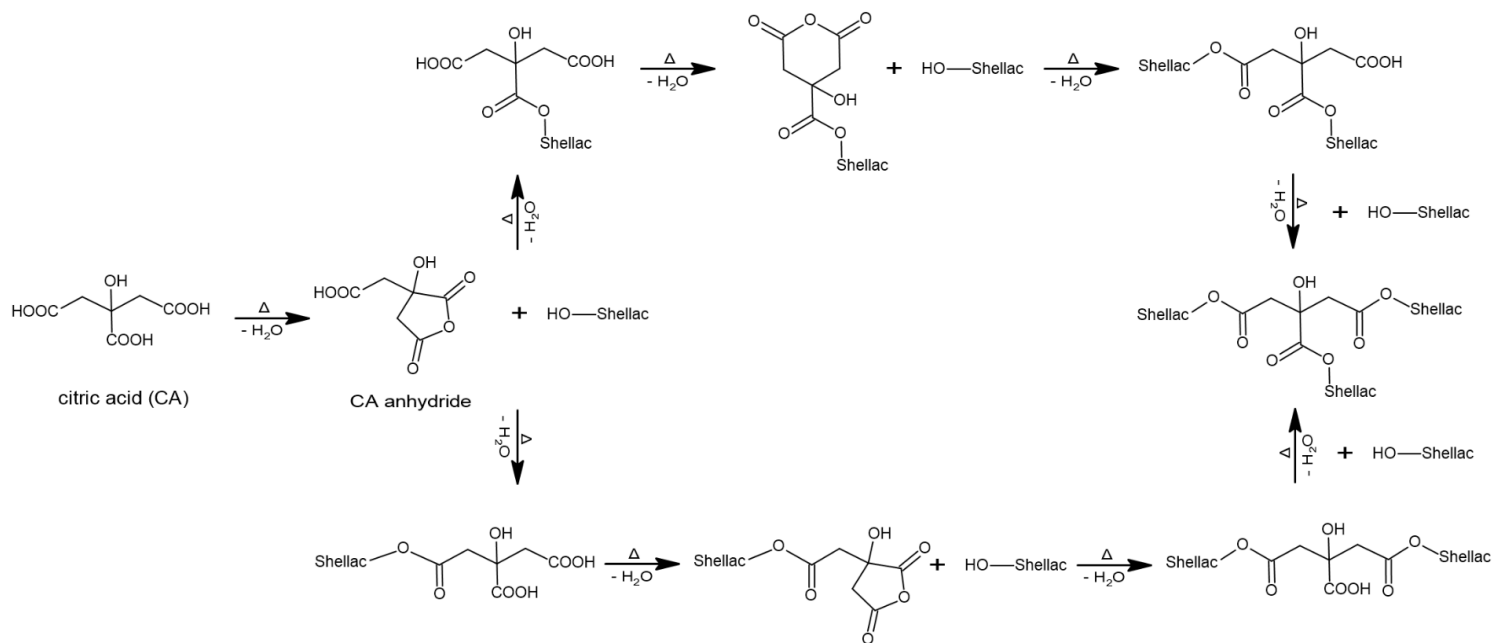


Figure 2

Reaction scheme of citric acid with shellac with possible products and reaction pathways presented.

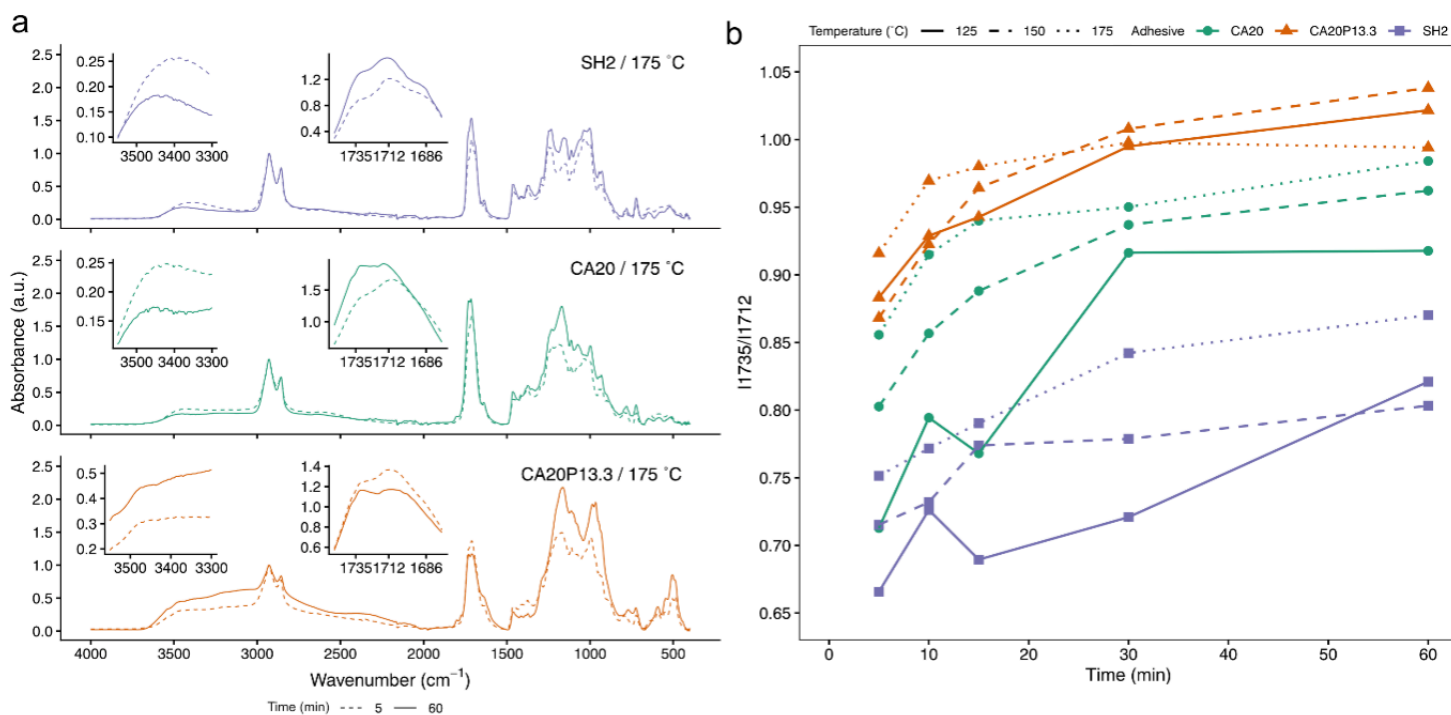


Figure 3

Changes in chemical structure of shellac adhesives due to curing at 175 °C (a). Evolution of the carbonyl band intensity ratio (I_{1735}/I_{1712}) during curing (b).

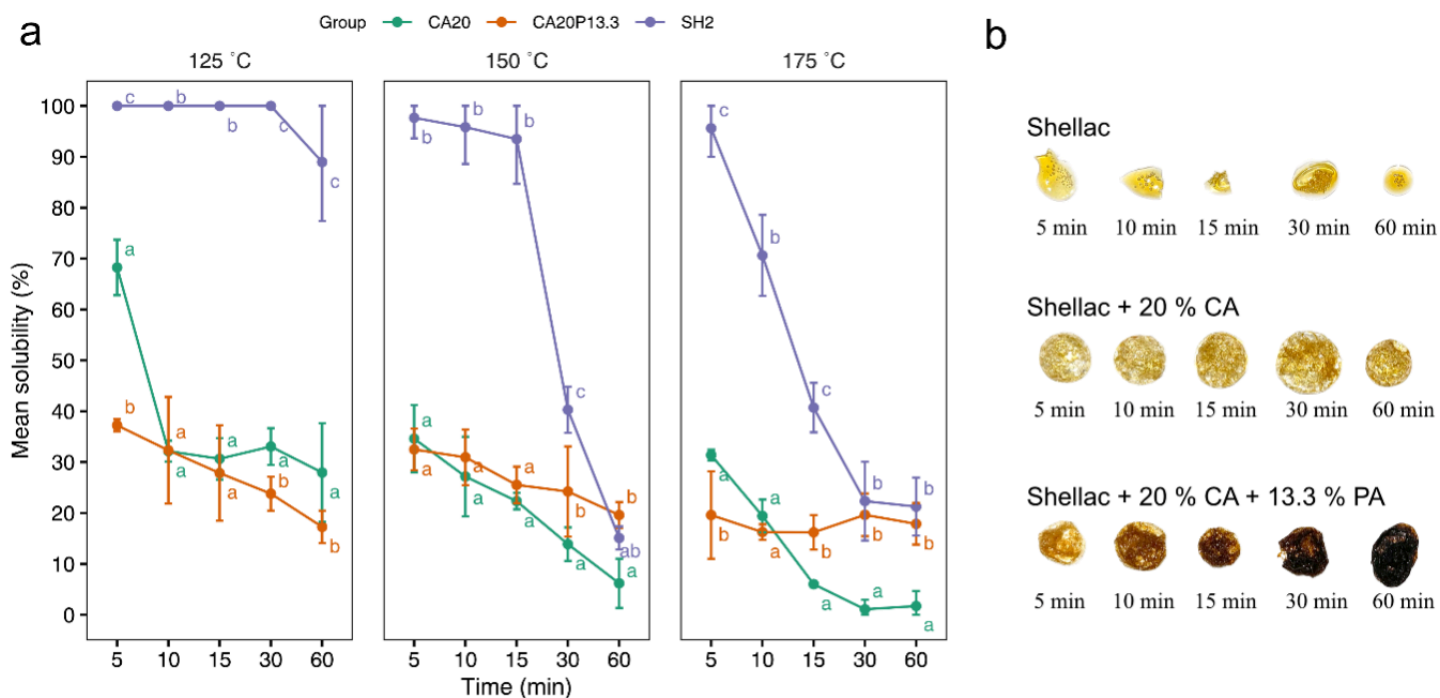


Figure 4

Solubility decrease of cured samples points to the formation of a crosslinked network of shellac adhesives (a). Photographs of cured shellac adhesives after different curing times at 175 °C (b). Mixtures containing phosphoric acid show clear darkening.

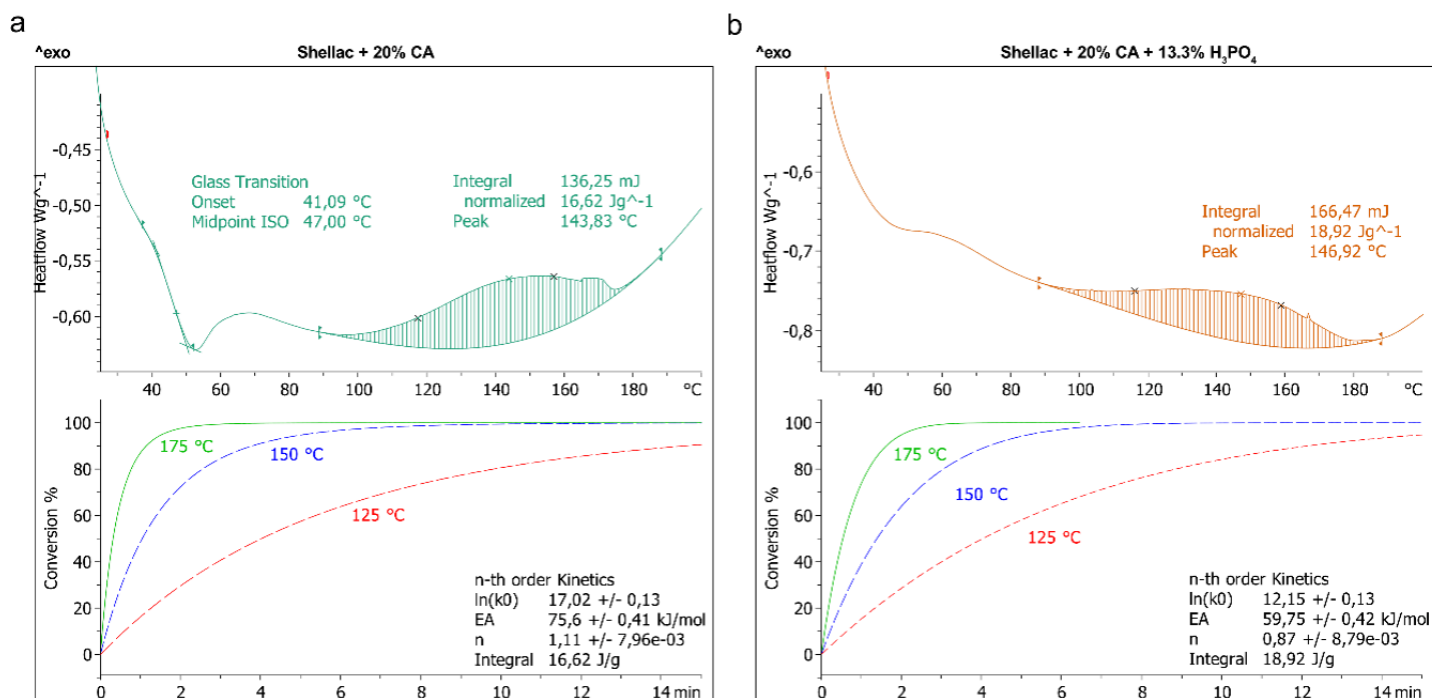


Figure 5

Phosphoric acid reduces activation energy of shellac – CA crosslinking. DSC thermograms, kinetic parameters according to Borchardt and Daniels method, and simulated conversion curves for uncatalysed reaction (a), and catalysed reaction (b).

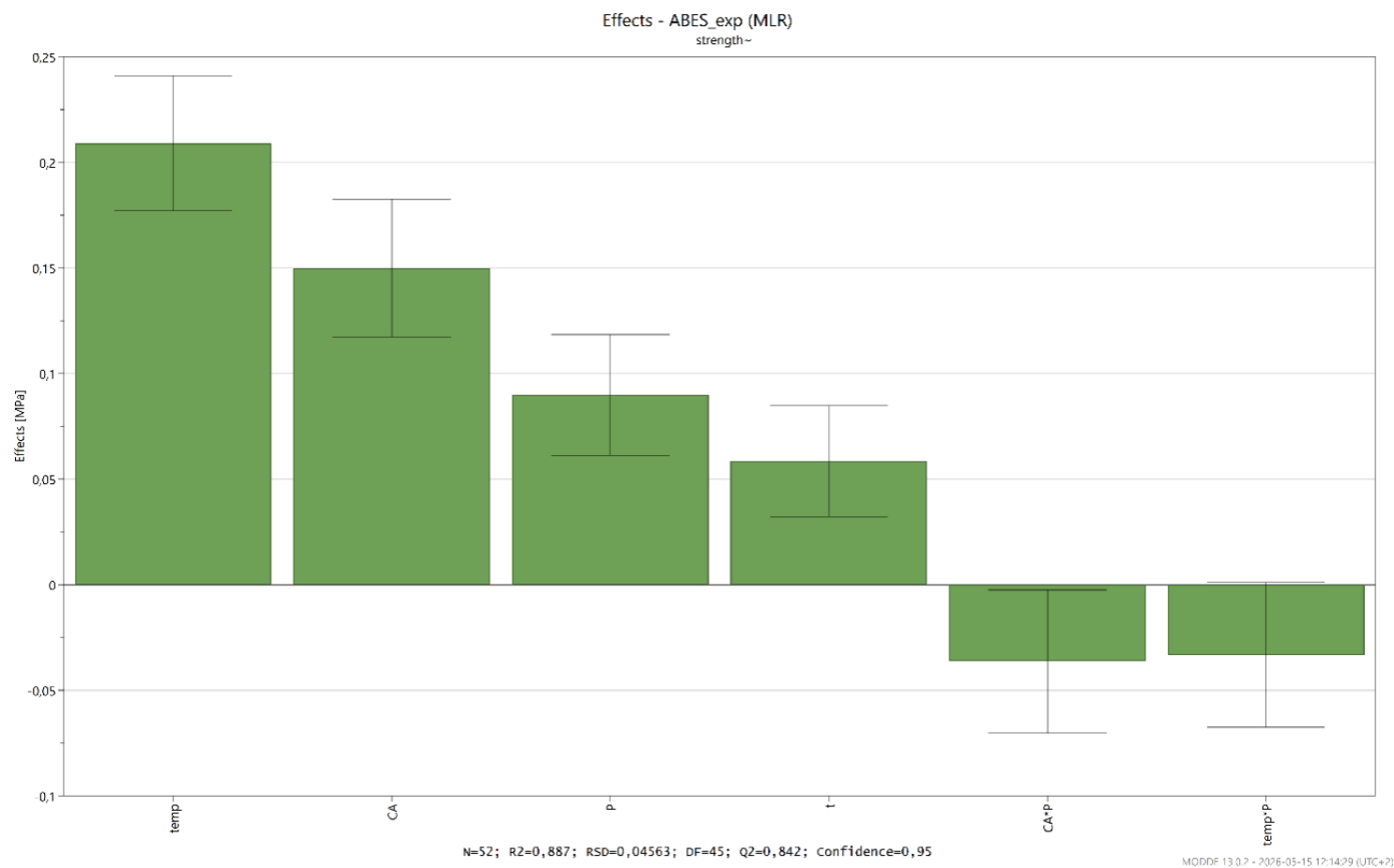


Figure 6

Effects of model parameters on shear strength show clear temperature dependence of reaction.

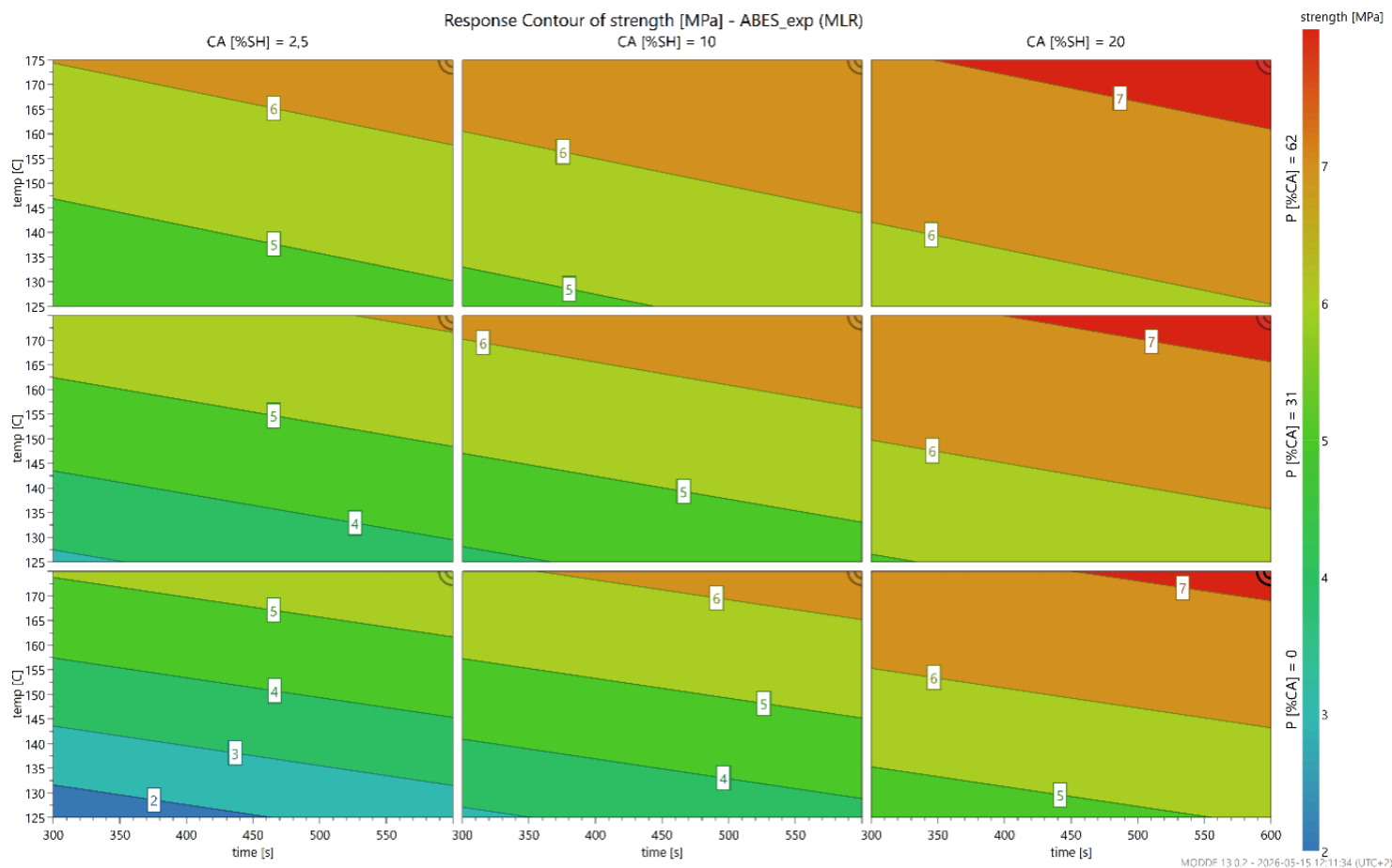


Figure 7

Response contour plot of shear strength of MLR model with optimal setpoint shown in top right of all subplots. Highest shear strengths are expected at higher temperatures and CA content.

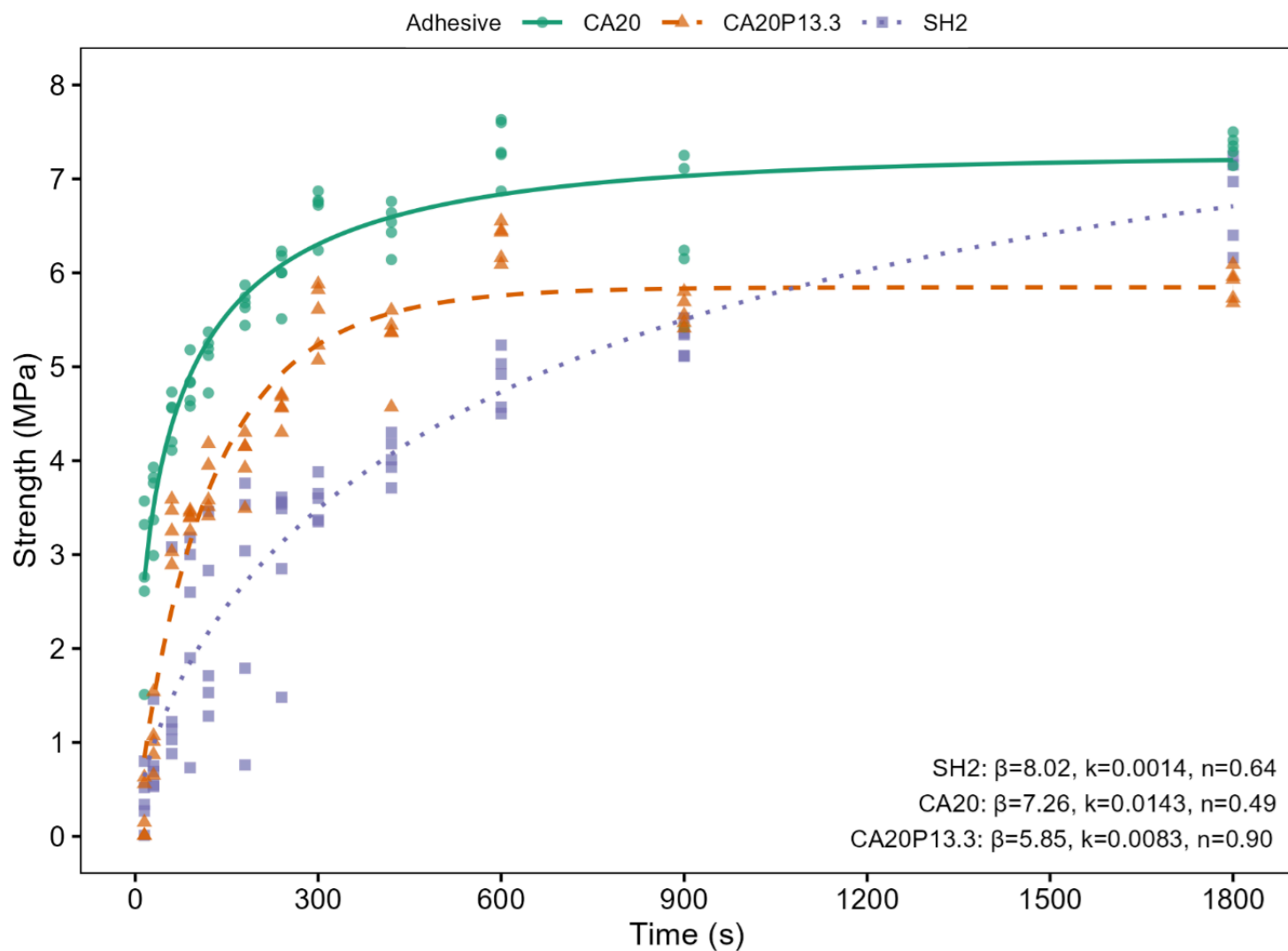


Figure 8

Bond strength development of shellac adhesives shows that CA20 cures fastest. Avrami model parameters are shown in bottom right of plot for each adhesive.

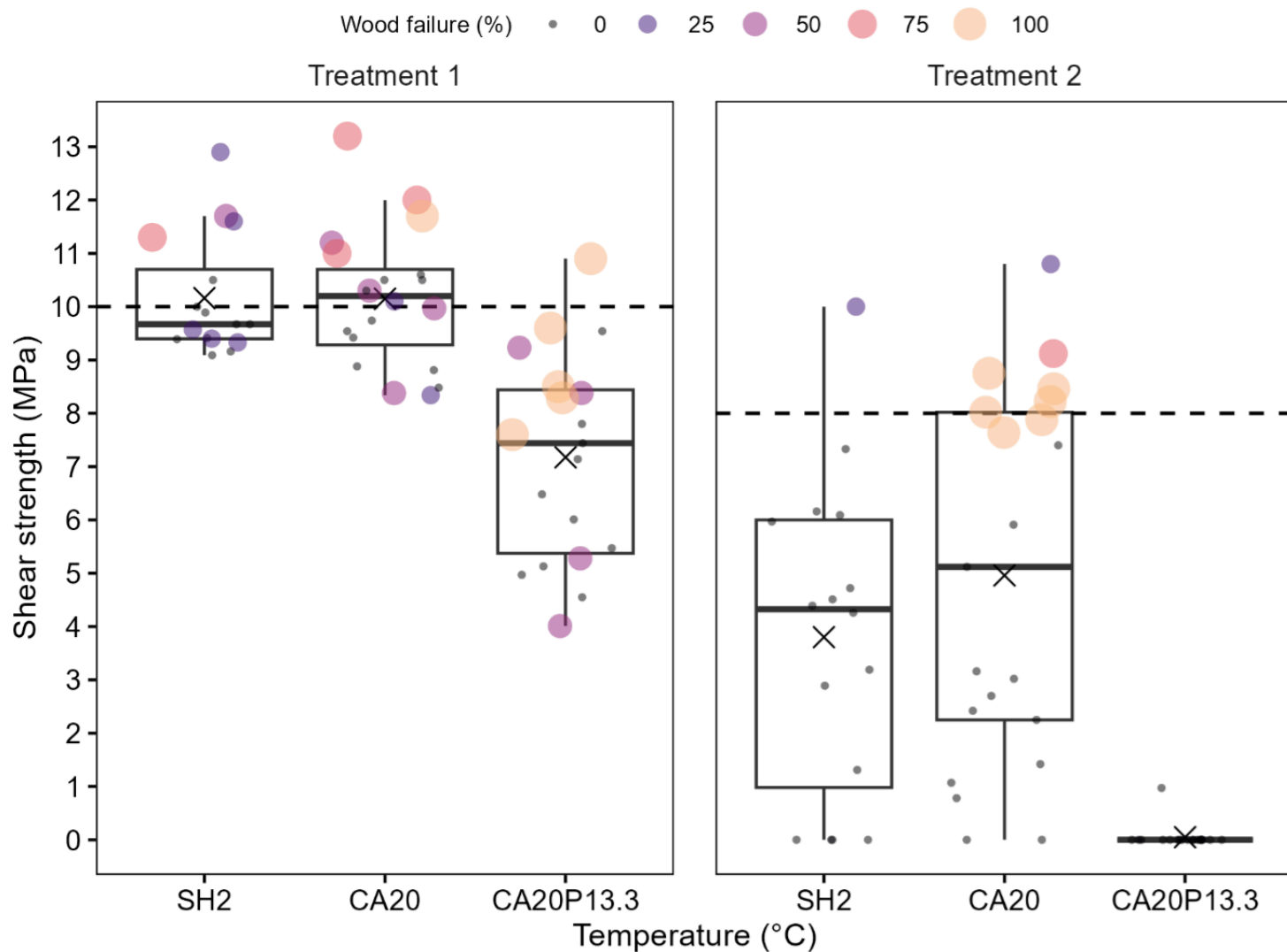


Figure 9

Shear test results for three different shellac adhesive mixtures with requirements (dashed line) according to EN 205:2016.

Supplementary Files

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