

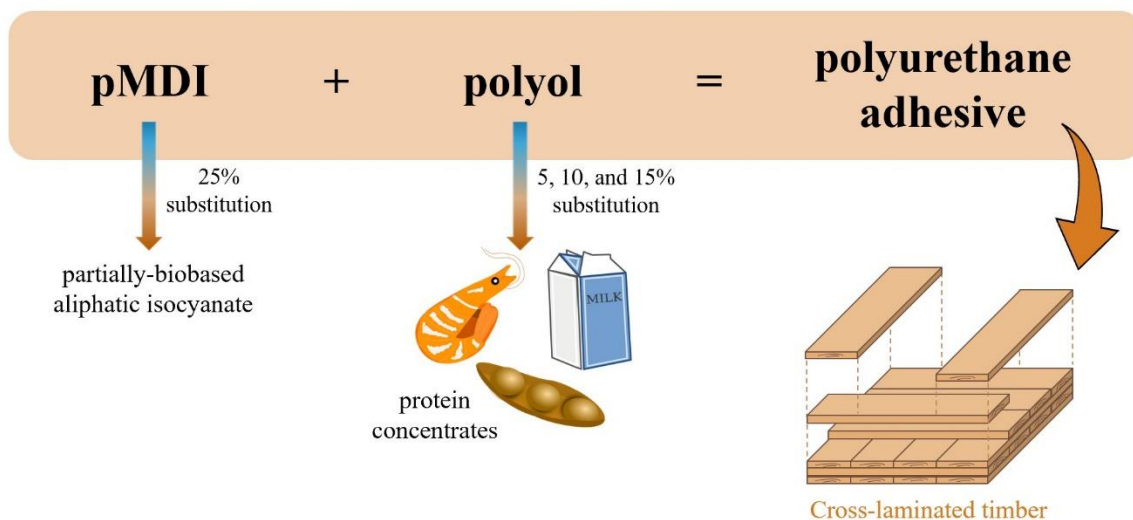
Industrial Byproducts as Adhesive Allies: Unraveling the Role of Proteins and Isocyanates in Polyurethane Wood Bonding

Alex Mary,^{a,b} Pierre Blanchet,^{a,b} Simon Pepin,^{a,b} Aurélien Hermann,^b Stéphane Charron,^c and Véronic Landry^{a,b,*}

*Corresponding author: veronic.landry@sbf.ulaval.ca

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GRAPHICAL ABSTRACT



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Wooden structures are becoming increasingly popular in the construction world. However, these structures often rely on synthetic adhesives, raising concerns about the environmental risks associated with their chemical composition. In response to these concerns, this study aims to explore sustainable alternatives, particularly focusing on polyurethane adhesives that incorporate proteins from industrial byproducts. The investigation involved three protein sources: soybean meal, shrimp shells, and skim milk, modified under mild alkaline conditions to obtain protein concentrates. These concentrates were then incorporated into the adhesives at varying protein contents: 5%, 10%, and 15%. Additionally, two isocyanate systems were examined, one being petrochemical-based and the other a partially bio-based blend. Chemical, thermal, optical, and mechanical characterizations were conducted to evaluate the adhesive performance. This study demonstrates that the adhesives' thermal properties remain unaffected by both the protein content and the isocyanate system. However, these factors influence the adhesive penetration into the wood substrate. Ultimately, the results suggest that higher protein content offers superior retention of mechanical strength in adhesives compared to the petrochemical reference when subjected to humid conditions. Overall, this research demonstrates the potential of proteins from industrial byproducts as sustainable adhesive allies, providing valuable insights into their interactions with different isocyanates.

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Keywords: Wood; Engineered wood products; Polyurethane adhesive; Isocyanate; Byproducts; Proteins

Contact information: a: NSERC - Industrial Chair on Eco-Responsible Wood Construction (CIRCERB), Université Laval, Québec, QC G1V 0A6, Canada; b: Department of Wood and Forest Sciences, Université Laval, Québec, QC G1V 0A6, Canada; c: Buildwise (ex-BBRI), 1342, Limelette, Belgium;

*Corresponding author: veronic.landry@sbf.ulaval.ca

INTRODUCTION

Wood structures are experiencing a surge in popularity due to their versatility and sustainability potential (Raydan *et al.* 2021). However, the conventional reliance on petroleum-based adhesives for structural wood products poses significant environmental challenges. These petroleum resources deplete finite reserves and contribute to harmful environmental impacts, exacerbating concerns over climate change and pollution. In response to these pressing environmental issues, the primary motivation of this research is to develop more sustainable and environmentally responsible adhesive solutions for wood bonding. In this context, biopolymers such as proteins, tannins, lignin, starch, and oils,

have emerged as promising candidates for sustainable adhesive formulations (Pizzi and Mittal 2005; Calle *et al.* 2016; Gui *et al.* 2016; Vnučec *et al.* 2017; Luo *et al.* 2020; Arias *et al.* 2022).

Proteins, which can be of plant or animal origin, have attracted increased interest in the potential improvement of industrial wood adhesives. They are abundant biomass resources with low toxicity and a reduced environmental footprint and can improve adhesive adhesion to wood (Yang *et al.* 2006; Raydan *et al.* 2021). Adhesives derived from plant-based proteins, including wheat gluten, soybean meal, and cottonseed, exhibited commendable adhesive strength but poor water resistance (Raydan *et al.* 2021). In contrast, animal-origin adhesives, such as those derived from blood, caseins (milk proteins), keratin, and collagen, demonstrated improved water resistance compared to their vegetable counterparts (Raydan *et al.* 2021). However, they come with drawbacks, such as a non-homogeneous composition with the formation of agglomerates that may affect the integrity of the glue line (Raydan *et al.* 2021).

Studies, including this one, are underway to develop protein-based adhesives that have properties comparable to their petrochemical counterparts while being more environmentally friendly. To do so, polyurethane adhesive was selected for this study as a reference adhesive for several reasons. It allows the assembly of a wide range of materials, can form hydrogen and covalent bonds with the wood substrate, does not require formaldehyde, and its small molecules allow the penetration of porous substrates (Pizzi and Mittal 2005). Furthermore, two-component polyurethane adhesives, consisting of a combination of isocyanate and polyol components, are flexible and are recommended for assemblies subject to high mechanical and thermal stress. Proteins were used to substitute the OH groups of the polyols with NH groups present in the proteins. This substitution leads to the formation of urea (C-N) bonds (Kumar and Pizzi 2019). As concerns regarding petroleum resource depletion and environmental protection continue to grow, using biological byproducts generated by industries offers a promising sustainable approach (Bai *et al.* 2020). Thus, three protein sources were used: soybean meal, shrimp shells, and skim milk powder, and incorporated for polyol replacement into the adhesives at varying protein contents. These three sources are industrial co-products. Soybean meal and shrimp shells are non-recyclable, while skim milk powder is in excess in Canada, due to higher demand for cream and butter, with nearly 19 tons of product exported in 2022 according to the Government of Canada. This incorporation follows on from and is described in a previous study (Mary *et al.* 2024). Additionally, the study examines two different isocyanate systems: one employing a petrochemical-based isocyanate and the other utilizing a partially bio-based blend comprising 75% petrochemical isocyanate and 25% partially bio-based isocyanate. This research aims to provide insights into the influence of proteins and isocyanates on adhesive performance through comprehensive chemical and mechanical characterization.

EXPERIMENTAL

Materials

The raw materials used as protein sources were non-recyclable or excess industrial byproducts from local resources. Soybean meal in pellet form was obtained from Sollio Agriculture (Lévis, Canada). Shrimp shell flour was provided by Les Pêcheries Marinard ltée (Gaspé, Canada). Skim milk powder was provided by Agropur (Longueuil, Canada).

Polymeric methylene diphenyl diisocyanate (Mondur MR-5) (NCO wt% = 32.5, viscosity = 129 mPa.s at 20 °C, typical functionality = 2.4) and a polypropylene oxide-based triol (Multranol 8175) (acid value = 350 to 390 mg KOH/g sample, molecular weight = 450 Da, viscosity = 232 to 412 mPa.s at 25 °C) were purchased from Covestro (Pittsburgh, PA, USA), provided by EMCO-Inortech (Terrebonne, Canada). Tolonate™ X FLO 100, an aliphatic isocyanate polymer (NCO wt% = 12.3 viscosity = 140 ± 80 mPa.s at 25 °C, functionality = 2) from Vencorex (Saint-Priest, France), was provided by EMCO-Inortech (Terrebonne, Canada). Mondur MR-5 is a petrochemical isocyanate, noted PI, and Tolonate™ X FLO 100, a partially bio-based and solvent-free isocyanate, noted as BI. All chemicals were used as received. The wood species used in this study was spruce wood (*Picea abies*, Karst) obtained from Buildwise (Limelette, Belgique).

Proteins Extraction

Protein concentrates were prepared for soybean meal and shrimp shells by alkaline extraction. The hydrolysis, washing, and centrifugation steps were detailed in a previous study (Mary *et al.* 2024). Based on precipitation and drying, a different protocol was used for skim milk powder (Husnaeni *et al.* 2019). The protein concentrates were then ground and passed through a 200 µm sieve. A previous study analyzed the properties of these protein concentrates, which are listed in Table 1. Protein concentrates derived from soybean meal, shrimp shells flour, and skim milk powder are designated B, S, and M, respectively.

Glycinin, β-conglycinin, and actin are globular proteins, while caseins behave like denatured globular proteins (Goff *et al.* 1996; Rangamani *et al.* 2014; Qu *et al.* 2019). These types of proteins adopt a spherical structure, resulting from the inward folding of the hydrophobic parts, while the hydrophilic parts are arranged around the outer surface, whereas fibrous proteins are made up of long polypeptide chains (Borasky 1963; He *et al.* 2020).

Table 1. Protein Content and Molecular Weight of Protein Concentrates Extracted from Soybean Meal, Shrimp Shells, and Skim Milk Powder (Mary *et al.* 2024)

Protein Concentrates	Protein Content (%)	Main Proteins	Molecular Weights (kDa)
B	66.8 ± 1.7	glycinin	40; 56
		β-conglycinin	72; 76
S	77.3 ± 0.2	actin	27; 50
M	82.3 ± 0.2	Caseins αs1, αs2, β, κ	28; 30; 38; 41

Preparation of Polyurethane Adhesives

Polyurethane adhesive formulations were prepared with an estimated isocyanate to hydroxyl functions (NCO/OH) ratio of 1.13 to ensure a complete reaction between the polyol and the isocyanate (Meier-Westhues 2019). The incorporation of proteins was completed by substituting the hydroxyl groups of the polyol with the amine groups of the proteins, resulting in the formation of urea bonds (Kumar and Pizzi 2019). Protein concentrates were incorporated into the polyol and dispersed at 1000 rpm for 3 min with a Dispermat LC30 Dissolver (VMA-Getzmann, Reichshof, Germany) with a 45 mm flat turbine. The substitution was made at 5%, 10%, and 15% in terms of chemical function.

Polyol substitution was based on the polyol and protein concentrates' OH and NH contents. The reference, formulated with the same chemicals as the protein-based adhesives, is represented by the formulation containing 0% protein.

Polyurethane adhesives were prepared using either a petrochemical isocyanate or a combination of 75% petrochemical isocyanate and 25% partially bio-based isocyanate. The extent of isocyanate substitution was determined based on the NCO content of the two isocyanates. In this study, two distinct types of adhesive formulations were used: P for the polyurethane formulated with the petrochemical isocyanate and PB for the polyurethane formulated with the combination of two isocyanates.

When the petrochemical isocyanate was used, the adhesives containing soybean meal, shrimp shells, and skim milk powder protein concentrates are labeled as P-B, P-S, and P-M, respectively. In contrast, when a combination of isocyanates was employed, they are denoted as PB-B, PB-S, and PB-M. The compositions of these adhesives, considering different protein contents, are provided in Table 2. For example, for a 10 g mass of adhesive, the mass of protein concentrate in the formulation is between 0.20 g and 0.80 g, depending on the substitution rate and the protein concentrate.

Table 2. Adhesive Compositions Based on the Isocyanates, Polyol, and Protein Concentrates Used

Adhesives	Protein Concentrates	Source of NCO Function (%)		Source of Nucleophilic Function (%)	
		PI	BI	Polyol	Protein
P	-	100	-	100	-
P-B5	B	100	-	95	5
P-B10	B	100	-	90	10
P-B15	B	100	-	85	15
P-S5	S	100	-	95	5
P-S10	S	100	-	90	10
P-S15	S	100	-	85	15
P-M5	M	100	-	95	5
P-M10	M	100	-	90	10
P-M15	M	100	-	85	15
PB	-	75	25	100	-
PB-B5	B	75	25	95	5
PB-B10	B	75	25	90	10
PB-B15	B	75	25	85	15
PB-S5	S	75	25	95	5
PB-S10	S	75	25	90	10
PB-S15	S	75	25	85	15
PB-M5	M	75	25	95	5
PB-M10	M	75	25	90	10
PB-M15	M	75	25	85	15

Adhesives Characterization

Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed to determine the sensitivity of adhesives to temperature. The temperatures of the maximum degradation rates in the

adhesive were determined using a TGA 851e analyzer (Mettler Toledo, Greifensee, Switzerland). Approximately 5 mg of adhesive was placed in a 70 μ L reusable sapphire crucible and heated from 35 to 800 $^{\circ}$ C at a 10 $^{\circ}$ C/min heating rate under nitrogen flow. The analyses were conducted in triplicate.

Gel time

The gel time is the maximum duration during which the system remains adequately fluid to be used as a substrate (Desai *et al.* 2003). Gel time measurements were conducted using a Gel Time Meter 22A (Sunshine, Philadelphia, PA, USA). Each sample was poured into a test tube and placed in an oil bath at 100 $^{\circ}$ C. The samples were heated until gel formed, and the time to reach this state was recorded in seconds. These measurements were carried out in triplicate.

Time-dependent viscosity

Viscosity serves as a crucial physical property that influences adhesive behavior. Suitable viscosity provides the adhesive with optimal flow characteristics, simplifies handling to attain strong bonding in the final product, and enables penetration into the initial wood cells, which is crucial for establishing mechanical anchoring (Luo *et al.* 2016). Viscosity measurements were conducted at 25 $^{\circ}$ C using a Bohlin Visco88 viscometer (Malvern Instruments Limited, Worcestershire, United Kingdom), taking a viscosity measurement every 5 min. This viscometer adopts a concentric cylindrical design comprising a rotating inner cylinder and a stationary outer cylinder. The inner cylinder has a diameter of 25 mm, while the outer cylinder has a diameter of 27.55 mm. The analyses were performed at a rotational speed of 6.39 rads^{-1} . The torque developed on the inner cylinder by the sample is directly correlated with the sample's viscosity and should be in a range of 0.5 to 9.5 mN.m to ensure accurate measurement. Approximately 15 mL of the sample was introduced into the viscometer cylinder. The analyses were performed in triplicate.

Effective penetration

Analyzing adhesive penetration is vital for evaluating the adhesive's capability to infiltrate the wood surface and pores, thereby ensuring the formation of a robust and durable bond. Two-layer laminated wood panels were prepared for each adhesive and sectioned into 1 cm^3 cubes. Cross-sections measuring 40 μm in thickness were precision-cut using a HistoCore AUTOCUT automatic rotary microtome from Leica Biosystems (Buffalo Grove, USA). These sections were mounted on glass slides, immersed in deionized water, covered with glass coverslips, and sealed with nail varnish to prevent water evaporation. The penetration of adhesives into the wood was visually assessed using a VHX-7000 digital microscope at 700x magnification, manufactured by Keyence Co. Ltd. (Osaka, Japan). To facilitate dark field observation, full ring lighting was employed. As described in prior studies, quantitative analysis of adhesive penetration into the wood substrate was performed by measuring the effective penetration depth (EP) (Sernek *et al.* 1999; Bastani *et al.* 2016; Qin *et al.* 2016). The EP quantifies the total adhesive area within the interphase region, divided by the bond line width. It specifically excludes the cell walls and the unfilled lumen area. EP can be calculated using the following Eq. 1,

$$EP = \sum_{i=1}^n \frac{A_i}{X_0} \quad (1)$$

where EP is the effective penetration depth (μm), A_i the area of adhesive object i (μm^2), and X_0 the width of the maximum rectangle defining measurement area (μm). Three measurement zones were studied for each adhesive.

The measurement parameters outlined in Eq. 1 are visually depicted in Fig. 1. Subsequently, ImageJ software was employed to quantify and measure these parameters. The results were analyzed using a least significant difference (LSD) test.

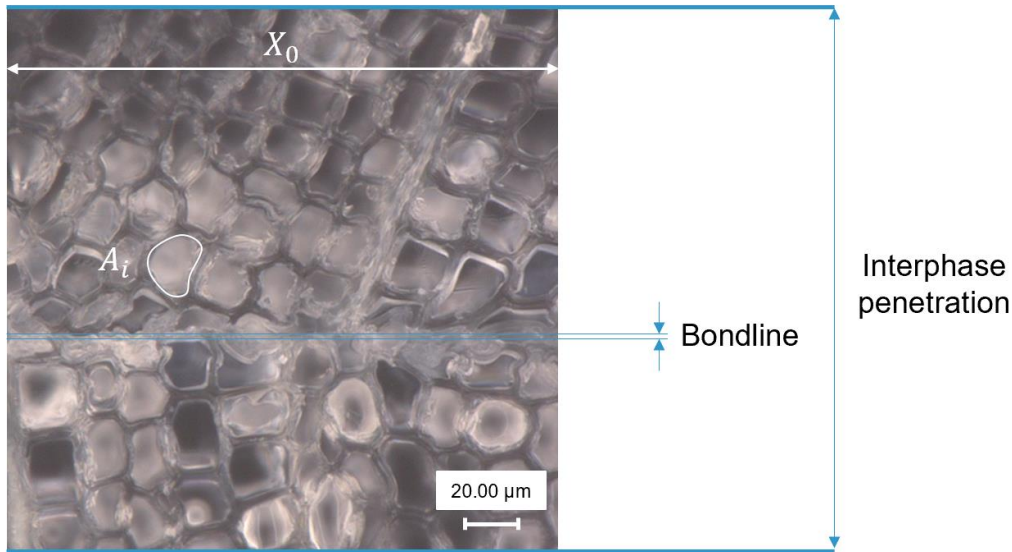


Fig. 1. Measurement parameters in an experimental image

Delamination

Delamination is a common failure mode in adhesive joints. It occurs when the glue bond is not adequate to resist moisture cycling, at the interface between the adhesive and the substrate, in this case, wood, or within the adhesive layer itself. The delamination tests were performed to evaluate cross-laminated wood panels' bond strength and delamination resistance under specified conditions. For this test, three-layer cross-laminated timber panels were produced using spruce wood (*Picea abies* Karst). The dimensions of one layer were $11 \times 11 \times 2 \text{ cm}^3$. A mass of 2.34 g of adhesive was deposited per layer. The panels were then pressed under a force of 10 kN at $20 \text{ }^\circ\text{C}$ for 2 h. A total of six panels were made per adhesive. The panels were conditioned at $22 \text{ }^\circ\text{C}$ with a relative humidity of 50% for seven days before being cut and subjected to analyses according to Annex A of the NBN EN 16351 (2021) standard. Finally, the percentage of delamination for each specimen was calculated using the following Eq. 2,

$$\text{Delamination (\%)} = \frac{l_{\text{tot,delam}}}{l_{\text{tot,bonding joint}}} * 100 \quad (2)$$

where $l_{\text{tot,delam}}$ is the total length of delamination, expressed in mm, and $l_{\text{tot,bonding joint}}$ is the sum of the lengths of all bonding joints in a delamination, expressed in mm. Delamination for each adhesive composition is expressed as the average of the delamination results per specimen. The results were analyzed using an LSD test.

Shear strength

Mechanical analyses were carried out to determine the shear strength of the adhesives used to bond the wood.

Two-layer glued laminated timber panels were produced. The dimensions of one layer were 11 x 11 x 2 cm³. A mass of 2.34 g of adhesive was deposited per layer. The panels were pressed under 10 kN of force at 20 °C for 2 h. A total of two panels were made per adhesive using spruce wood (*Picea abies*, Karst). Wood specimens were conditioned at room temperature with a relative humidity of 50% for seven days. Subsequently, the panels were cut into specimens with dimensions of 5 x 5 x 4 cm³ for conducting shear strength tests according to Annex D of the NBN EN 14080 (2013) standard.

Before carrying out the shear tests, the specimens were divided into two groups: the first group was subjected to treatment A1 of standard NBN EN 302-1 (2013), *i.e.*, seven days at 20 °C at 65% relative humidity, and the second group to treatment A2 of standard NBN EN 302-1 (2013), *i.e.*, seven days at 20 °C at 65% relative humidity followed by four days of immersion in water at 15 °C. The tests were carried out for the specimens subjected to treatment A2 in the wet state. The load was reported in Newtons (N).

The test results are presented as the arithmetic average of the load of the valid tests, defined as those that exhibit a linear portion of the load-displacement curve. The results were analyzed using an LSD test.

Confocal Raman spectroscopy

Raman analyses were conducted to elucidate the adhesive-wood interaction and enhance comprehension of shear strength results. The analyses were conducted on the same cross-sections used for optical microscopy, using a Senterra II Raman microscope (Bruker Optics Inc., Billerica, USA) equipped with a motorized table (Märzhäuser Wetzlar, Wetzlar, Germany) and an x100 immersion oil objective featuring a numerical aperture of 1.3 (Olympus). The spectra were acquired with a 532 nm laser at 2.5 mW, employing a 250 ms integration time and 8 or 24 co-additions per spectrum. Chemical mapping was performed by scanning an area of 40 x 30 μm with 25 x 25 points.

Table 3. Assignment of Selected Vibrational Bands of Polyol, Proteins, Isocyanate, Urethane, Urea Bonds, and Wood Components

Wavenumber (cm ⁻¹)	Component	Assignment
3510 to 3100	Polyol, Proteins	-NH, -OH stretching vibrations
2970 to 2870	Proteins	-CH ₂ stretching vibration
2897	Wood	-C-H stretching vibration (cellulose)
2260	Isocyanate	-N=C=O stretching vibration
1730 to 1710	Urethane	-C=O stretching vibration
1658	Proteins	-C=O stretching vibration (amide I)
1650	Urea	-C-N stretching vibration
1650	Wood	-C=O stretching (lignin)
1550	Urethane	-C-N stretching vibration
1550	Urea	-N-H bending (amide II)
1516	Proteins	-N-H stretching vibration (amide II)
1462	Wood	-H-C-H and H-O-C bending (lignin, cellulose)
1239	Proteins	-C-N and -N-H stretching vibration (amide III)

The main characteristic vibrational bands attributed to the various components are displayed in Table 3 (Ukishima *et al.* 1995; Oliveira Vieira da Cunha *et al.* 2004; Roohpour *et al.* 2009; Ghobashy and Abdeen 2016; Ling *et al.* 2018; Zeng *et al.* 2023; Cadieux-Lynch *et al.* 2024).

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Thermogravimetric analyses were performed to determine the thermal resistance of the various adhesives. Figure 2a illustrates the TG curves (thermogravimetric analyses), and Fig. 2b the DTG (derivative thermogravimetric) curves of polyurethane adhesives based on protein concentrates with varying isocyanate compositions. The weight loss of these adhesives can be categorized into two distinct stages. The maximum decomposition temperatures for each stage are presented in Table 4. In the first decomposition phase, observed at approximately 340 °C, the urethane and urea bonds undergo intensified decomposition (Awad *et al.* 2010; Jiang *et al.* 2017; Członka *et al.* 2020; Luo *et al.* 2020; Jiang *et al.* 2021). This decomposition phase at 340 °C also corresponds to the decomposition of protein concentrates, which involves the cleavage of the amino acid chains during thermal degradation and is consistent with a previous study (Mary *et al.* 2024). The second decomposition phase occurs above 450 °C and corresponds to the degradation of the isocyanate hard segments (Jiang *et al.* 2021).

Notably, the maximum degradation temperatures of the different adhesives remain unaffected by the protein source, isocyanate type, or urea formation, indicating no substantial influence on this parameter.

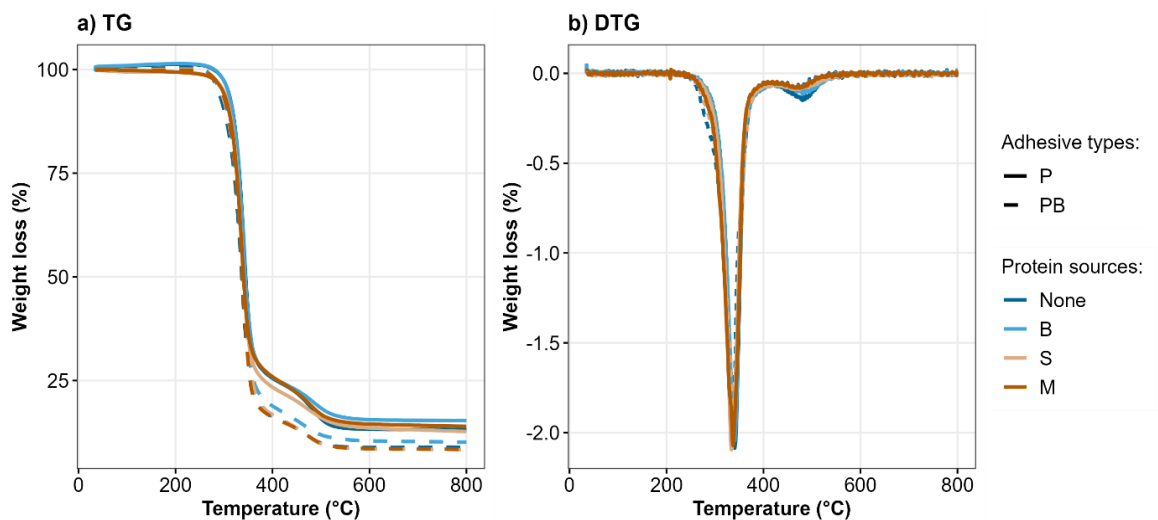


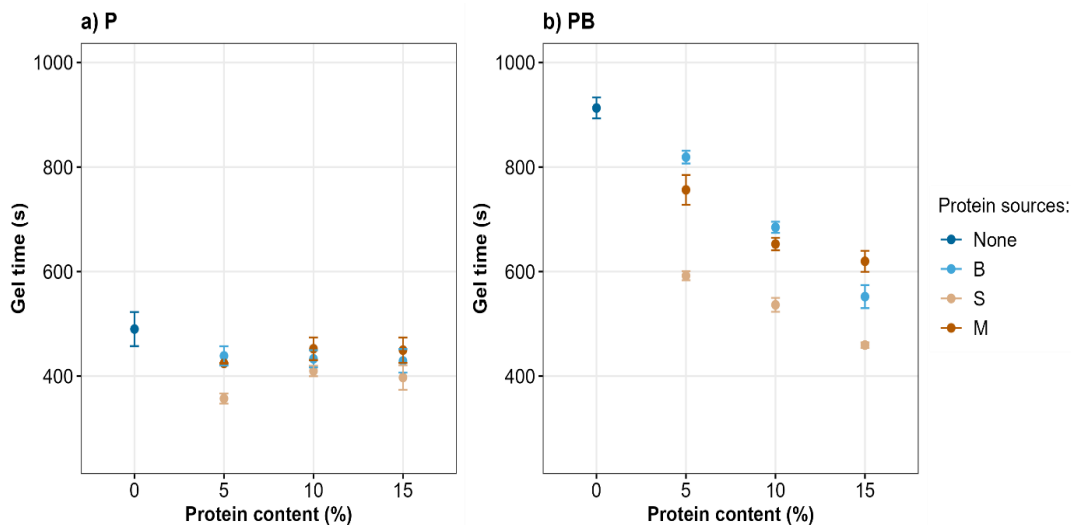
Fig. 2. TG thermal curves and DTG thermal curves of polyurethane adhesives according to protein sources, protein contents, and isocyanates

Table 4. Maximum Decomposition Temperatures of Polyurethane Adhesives According to Protein Sources, Protein Concentrates Contents, and Isocyanates

Adhesives	1st Step (°C)	2nd Step (°C)	Adhesives	1st Step (°C)	2nd Step (°C)
P	341 ± 0	487 ± 13	PB	344 ± 4	471 ± 2
P-B5	340 ± 1	480 ± 0	PB-B5	343 ± 5	466 ± 5
P-B10	340 ± 1	479 ± 2	PB-B10	340 ± 1	469 ± 1
P-B15	340 ± 1	478 ± 5	PB-B15	339 ± 1	462 ± 4
P-S5	339 ± 1	489 ± 17	PB-S5	342 ± 3	474 ± 4
P-S10	337 ± 1	481 ± 2	PB-S10	337 ± 1	460 ± 2
P-S15	338 ± 1	472 ± 1	PB-S15	335 ± 1	453 ± 12
P-M5	343 ± 2	481 ± 1	PB-M5	340 ± 2	472 ± 6
P-M10	341 ± 1	479 ± 6	PB-M10	342 ± 3	470 ± 2
P-M15	343 ± 1	479 ± 0	PB-M15	340 ± 2	471 ± 2

Gel Time

The gel time of the different PU adhesive formulations is reported in Fig. 3. Observations show that PB adhesives exhibited longer gel times than P-adhesives. Similar results have been presented in the literature (Malik and Kaur 2018). Indeed, aromatic isocyanates are more reactive than aliphatic isocyanates, due to the negative charge shift towards the direction of the aromatic ring structure (Bengtström *et al.* 2016). Consequently, the interaction between aliphatic isocyanates and polyol occurs at a slower pace, elucidating the longer gel time observed in PB adhesives compared to their P counterparts (Malik and Kaur 2018).

**Fig. 3.** Gel time of polyurethane adhesives according to protein sources, protein contents, and isocyanates

Moreover, replacing polyol with protein concentrates leads to a reduction in gel time compared to the references. NH_2 , being more nucleophilic than OH due to its easy donation of a lone electron pair and the larger size of the nitrogen atom compared to oxygen, is closer in energy to the transition state, lowering the activation energy and thus accelerating the polymerization reaction (Afagh and Yudin 2010). This reduction is particularly pronounced for PB adhesives.

Given the low molecular weight of M, which ensures a better dispersion into the adhesive matrix, a shorter gel time was expected for P-M and PB-M adhesives compared to those based on other protein concentrates. However, the observed results may be attributed to differences in the protocols for obtaining the various concentrates. While soybean meal and shrimp shells are precipitated at pH 4 after hydrolysis, skim milk is precipitated with acetic acid to pH 3. Literature suggests that a low pH has an impact on nucleophilic groups, which may decelerate urea and urethane formation, resulting in a longer gel time (Maillard *et al.* 2021). This could explain why the gel times of M-containing adhesives are not shorter than those of the other adhesives in this study (Maillard *et al.* 2021).

While a prolonged gel time can provide an advantage during the assembly of structural components by allowing sufficient time for application before adhesive curing, it is essential to maintain this duration within reasonable limits to ensure efficient panel manufacturing from an industrial standpoint.

Time-dependent Viscosity

Viscosity measurements were conducted for the various adhesive systems at 25 °C, as illustrated in Fig. 4. These analyses were performed immediately upon mixing the adhesive components.

Notably, the findings indicate a distinct increase in the initial viscosity associated with the inclusion of proteins, regardless of the adhesive type. These results align with established literature, consistently highlighting those introducing fillers, into a polymer system results in heightened viscosity (Schulze *et al.* 2003; Markovičová, 2021). The greater protein content in M reduces the quantity required to add to the adhesive to achieve the desired protein concentration, thereby reducing viscosity over time. The low molecular weight of its proteins also helps explain these viscosity results. A greater difference was expected between adhesives containing B and adhesives containing S and M due to the presence of β -Conglycinin proteins in B, whose molecular weights are higher than those of S and M (Table 1).

Notable differences emerged between the two adhesive types. The PB adhesives exhibited a longer period to reach maximum viscosity, leading to lower viscosity values for PB adhesives measured at a specific time t compared to P adhesives. It is worth mentioning that BI is designed for ultra-low viscosity applications, which may also explain the difference between PB and P adhesives. In addition, these results are consistent with the gel time findings presented in Fig. 3, which illustrate that PB adhesives exhibit a lengthier gel time, resulting in lower viscosity values for PB adhesives at a given time t compared to P adhesives.

The reduced viscosity of PB adhesives is advantageous, enabling the potential increase in polyol substitution rates with protein concentrates while maintaining viscosity at levels conducive to proper application on wood. This advantage is more challenging to exploit with P adhesives, where higher substitution rates would elevate viscosity to a degree incompatible with effective application in wood bonding processes and industrial practices.

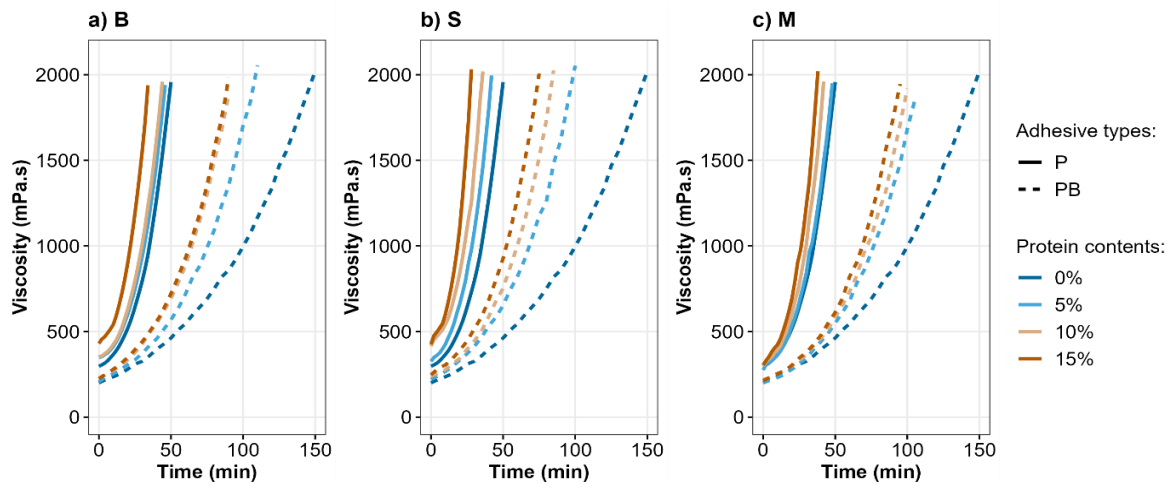


Fig. 4. Viscosity analysis of polyurethane adhesives according to protein sources, protein contents, and isocyanates

Effective Penetration

Detailed analyses were made to explore the effect of integrating proteins into adhesives on the effective penetration depth of these adhesives into wood lumens, as depicted in Fig. 5.

During the penetration process, three primary factors must be considered: the adhesive's properties, the characteristics of the wood, and the parameters governing the processing (Kamke and Lee 2007). Because the parameters for wood and gluing/pressing process were kept uniform across all adhesives, these factors were not considered when comparing different adhesives. However, the attributes of the adhesive, such as its viscosity and gel time, can influence the extent to which various adhesives penetrate the wood substrate (Kamke and Lee 2007).

It was observed that PB adhesives exhibited greater penetration in the lumens than P adhesives. This aligns with the gel time results (Fig. 3) because PB adhesives, with their longer gel times, have more time available before curing for penetrating compared to P adhesives.

Table 5 shows that PB adhesives with 15% protein content penetrate significantly better into the lumens than the other adhesives in this study. Regarding viscosity, as illustrated in Fig. 4, both B and S result in increased viscosity for both P and PB adhesives. This increase in viscosity contributes to enhanced adhesive penetration into the lumens as protein content increases (Vnučec *et al.* 2015, 2016). Indeed, low-viscosity adhesives have been demonstrated to flow into the lower part of samples during the pressing process, through the radial bands of parenchyma, reducing the effective penetration into the lumens (Vnučec *et al.* 2015, 2016). However, the rise in viscosity with increasing protein content is relatively less substantial for P adhesives, resulting in a reduction in lumen penetration compared to PB adhesives.

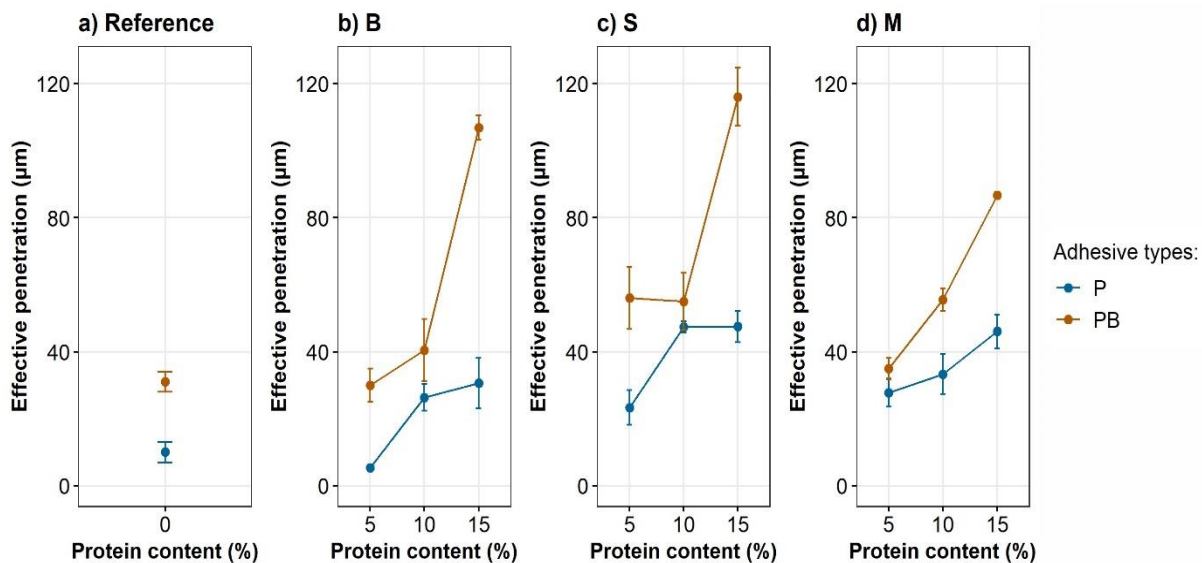


Fig. 5. Effective penetration of polyurethane adhesives in wood according to protein sources, protein contents, and isocyanates

Table 5. LSD test for Effective Penetration of Polyurethane Adhesives in Wood According to Protein Sources, Protein Contents, and Isocyanates

Adhesives	LSD Groups	Adhesives	LSD Groups
P	gh	PB	efg
P-B5	h	PB-B5	efg
P-B10	efgh	PB-B10	cdef
P-B15	efg	PB-B15	ab
P-S5	fgh	PB-S5	c
P-S10	cde	PB-S10	cd
P-S15	cde	PB-S15	a
P-M5	efg	PB-M5	cdef
P-M10	def	PB-M10	c
P-M15	cde	PB-M15	b

Different letters indicate significant differences at $P \leq 0.05$

Delamination

The effect of isocyanate substitution and the impact of protein content on adhesive performance was investigated for the three different protein sources (Fig. 6).

For P-B and P-S adhesives, increasing protein content helped to reduce delamination, as shown in Fig. 7 and Table 6. The observed results can be explained by the ability of proteins to interact with the isocyanate. Indeed, isocyanates can interact with nucleophilic functional groups, such as hydroxyl and amino groups, present in proteins. The extent of these interactions is directly related to the concentration of proteins in the system, with higher protein content leading to more opportunities for isocyanates to react with the amino groups (Mekonnen *et al.* 2014). Through these interactions, crosslinked networks are formed, which can improve the adhesive’s bond strength and water resistance of the adhesives (Zeng *et al.* 2021). In contrast, increasing protein content has no significant

impact on P-M adhesives. It has been demonstrated that M protein concentrate has a lower molecular weight than B and S protein concentrates (Table 1). This lower molecular weight leads to less viscous adhesives that penetrate less into the lumens of the wood, which can impact delamination results.

When isocyanates are substituted, adhesives show slightly higher delamination. This may be attributed to the greater crosslinking of P adhesives compared to PB adhesives, due to the greater functionality of PI compared to BI (Kumar and Pizzi 2019).

However, it is noteworthy that the obtained results for P-S and PB-S adhesives align with the findings from the study on adhesive penetration in wood. The superior mechanical anchorage of these adhesives can increase their resistance to delamination. Specifically, increased protein content correlates with enhanced penetration and reduced delamination.

Nevertheless, it is important to note that even the petrochemical reference is not sufficiently resistant to delamination to be used in construction. This is underscored by ASTM D2559 (2018), which stipulates that delamination in any bond line should not exceed 1% for softwoods and 1.6% for hardwoods (ASTM D2559 2018).

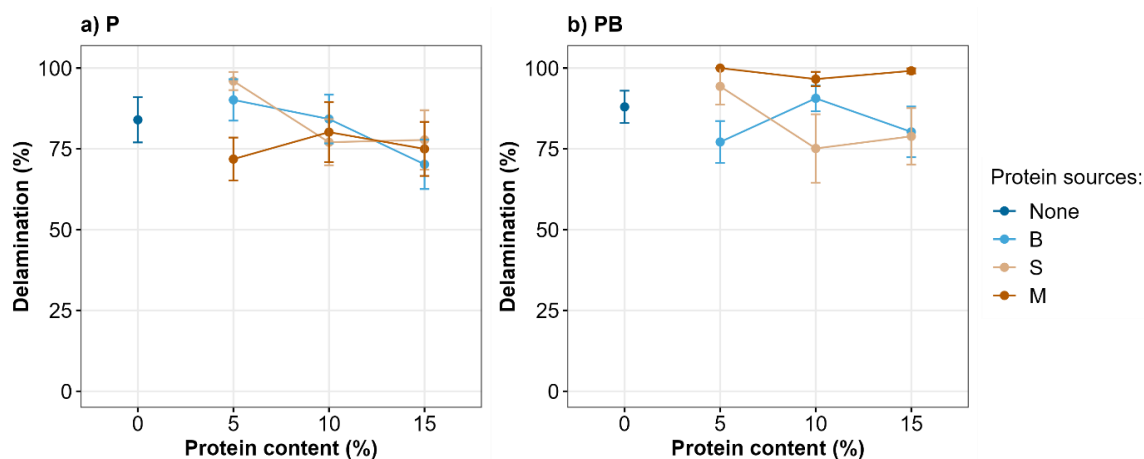


Fig. 6. Delamination results of polyurethane adhesives in wood according to protein sources, protein contents, and isocyanates

Table 6. LSD test for Delamination of Polyurethane Adhesives in Wood According to Protein Sources, Protein Contents, and Isocyanates

Adhesives	LSD Groups	Adhesives	LSD Groups
P	abcdef	PB	abcdef
P-B5	abcde	PB-B5	cdef
P-B10	abcdef	PB-B10	abcde
P-B15	f	PB-B15	abcdef
P-S5	abc	PB-S5	abcd
P-S10	cdef	PB-S10	def
P-S15	bcdef	PB-S15	bcdef
P-M5	ef	PB-M5	a
P-M10	abcdef	PB-M10	abc
P-M15	def	PB-M15	ab

Different letters indicate significant differences at $P \leq 0.05$

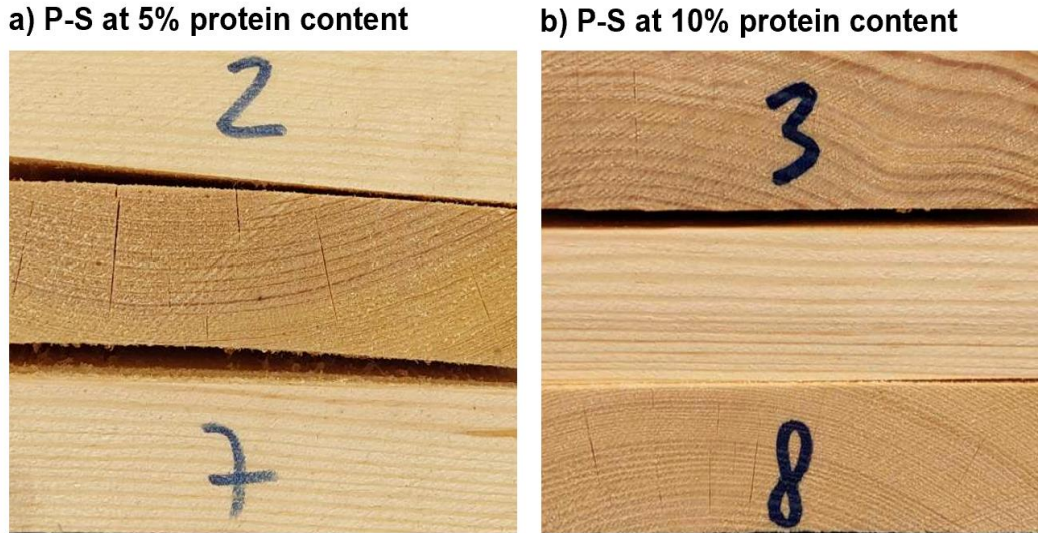


Fig. 7. Observed delamination on a wood panel bonded with a) P-S5 adhesive and b) P-S10 adhesive

Shear Strength

Mechanical analyses were performed on P and PB adhesives to assess their mechanical behavior after treatments A1 and A2 (Fig. 8). Table 7 shows that a portion of failures occurred within the adhesive joint in this treatment, and Fig. 9 illustrates the distinction between a 100% failure in the wood and a 100% failure in the adhesive joint.

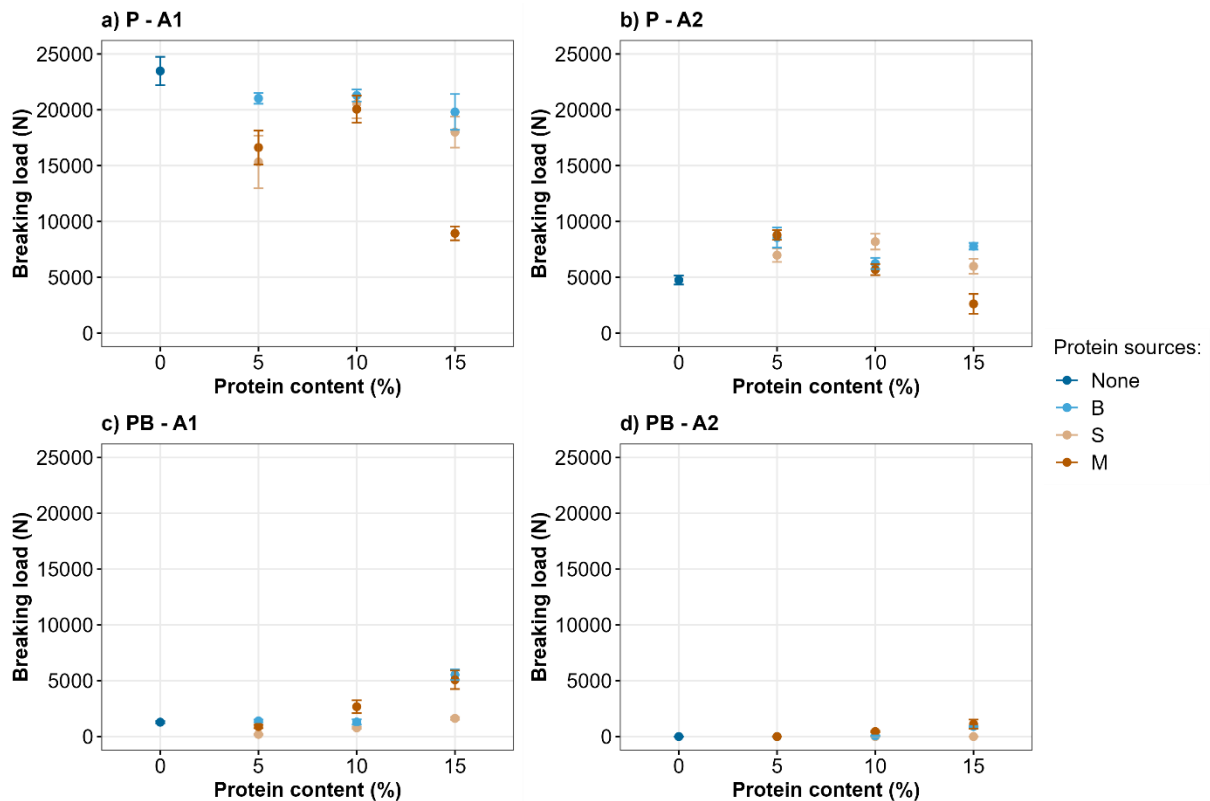


Fig. 8. Maximum breaking load before the rupture of polyurethane adhesives in wood according to protein sources, protein contents, and isocyanates after A1 and A2 treatments

Table 7. Fracture Percentage in Wood of P Adhesives Based on Protein Content and Isocyanate Type After A1 and A2 Treatments

A1 Treatment		A2 Treatment	
Adhesives	Fracture (%)	Adhesives	Fracture (%)
P	68 ± 6	P	0 ± 0
P-B5	63 ± 7	P-B5	4 ± 5
P-B10	100 ± 0	P-B10	9 ± 4
P-B15	96 ± 2	P-B15	8 ± 1
P-S5	31 ± 9	P-S5	0 ± 0
P-S10	65 ± 8	P-S10	10 ± 4
P-S15	68 ± 8	P-S15	0 ± 0
P-M5	8 ± 1	P-M5	9 ± 4
P-M10	29 ± 8	P-M10	0 ± 0
P-M15	13 ± 3	P-M15	0 ± 0

Table 8. LSD Test for Maximum Breaking Load Before the Rupture of Polyurethane Adhesives in Wood According to Protein Sources, Protein Contents, and Isocyanates After A1 and A2 Treatments

A1 Treatment		A2 Treatment	
Adhesives	LSD Groups	Adhesives	LSD Groups
P	a	P	defghi
P-B5	ab	P-B5	de
P-B10	ab	P-B10	defg
P-B15	abc	P-B15	de
P-S5	c	P-S5	def
P-S10	ab	P-S10	de
P-S15	abc	P-S15	defgh
P-M5	bc	P-M5	de
P-M10	abc	P-M10	defgh
P-M15	d	P-M15	efghi
PB	ghi	PB	i
PB-B5	fghi	PB-B5	i
PB-B10	ghi	PB-B10	hi
PB-B15	defghi	PB-B15	ghi
PB-S5	hi	PB-S5	i
PB-S10	ghi	PB-S10	i
PB-S15	fghi	PB-S15	i
PB-M5	ghi	PB-M5	i
PB-M10	efghi	PB-M10	hi
PB-M15	defghi	PB-M15	ghi

Different letters indicate significant differences at $P \leq 0.05$

The statistical analyses, as delineated in Table 8, indicate a noteworthy superiority of P adhesives from treatment A1 over those from treatment A2, except for P-M15. For P adhesives after treatment A1, the addition of proteins decreased mechanical performance compared to the reference adhesive; however, the LSD multiple comparison test proves that this difference was not significant for most P adhesives. When P adhesives were exposed to moisture in treatment A2, the mechanical performance of the adhesives deteriorated. However, the decline in performance was more pronounced for the petrochemical reference adhesive, which exhibited an 80% reduction in maximum breaking load before failure between treatments A1 and A2, meaning that the petrochemical reference is more sensitive to water immersion of the A2 process than protein-based P-adhesives. This can be explained by the fact that urea bonds, present in protein-based polyurethane adhesives, are more stable than urethane bonds (C-O) (Liu *et al.* 2019).



Fig. 9. Wood samples with 100% wood fracture (top) and 100% adhesive fracture (bottom)

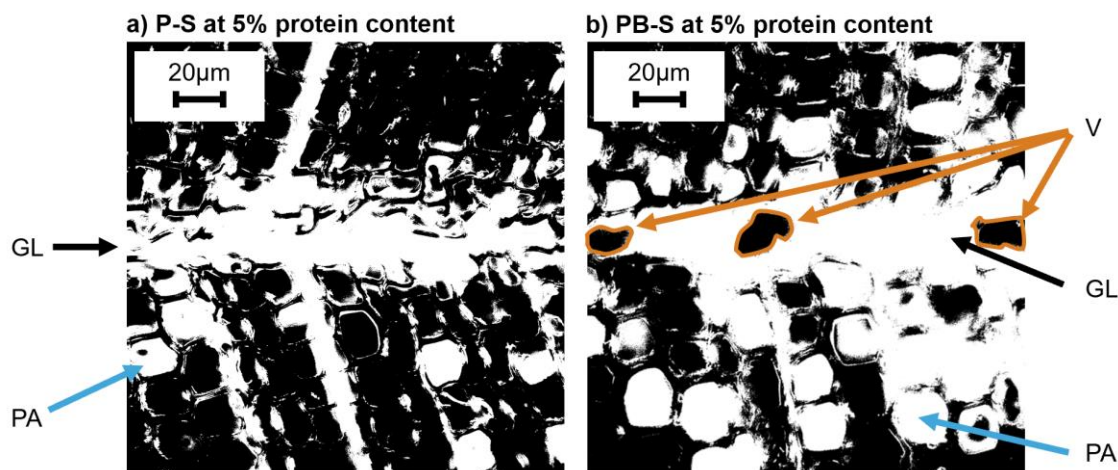


Fig. 10. Optical micrographs of wood samples bonded with a) P-S at 5% protein concentrate content and b) P-S at 5% protein concentrate content. The glue line is marked with GL, the penetrated adhesive is marked with PA, and voids in the glue line are marked with V.

Upon the partial substitution of PI with BI, there was a considerable decrease in the mechanical performance of the adhesives following treatment A1. Although Fig. 5 demonstrates that PB adhesives exhibited greater effective penetration compared to P adhesives, it is essential to emphasize that effective penetration, while important, does not singularly dictate these outcomes. Indeed, PI, having higher functionality than BI contributes to a greater crosslinking density in the adhesive (Kumar and Pizzi 2019). In addition, the presence of aromatic rings contributes to the adhesive's resistance. Indeed, polyurethanes formulated from aromatic isocyanates have been shown to have better mechanical performances than those formulated from aliphatic isocyanates (Touchet and Cosgriff-Hernandez 2016). This factor may account for the superior performance of P adhesives in comparison to PB. Another comprehensive understanding of the mechanical strength of PB adhesives can also be acquired by investigating the condition of the adhesive glue line. As depicted in (Fig. 10), through microscopic analysis, voids were detected within the glue line of PB adhesives, a characteristic absent in the glue line of P adhesives. These observations can be rationalized by the excessive penetration of PB adhesives into wood lumens, creating voids that weaken the glue line and can affect the adhesive's mechanical strength. The voids could initiate the rupture mechanism.

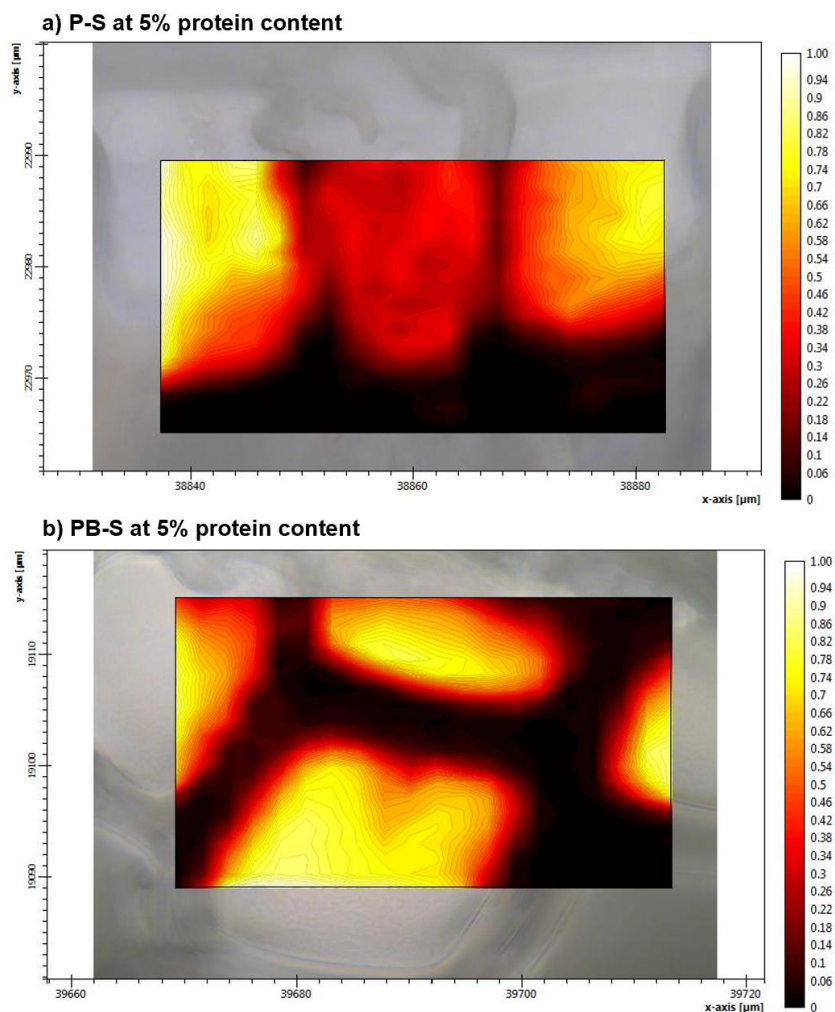


Fig. 11. Raman image of wood cell wall of a) P-S at 5% protein concentrate content and b) P-B-S at 5% protein concentrate content

Moreover, in the context of PB adhesives, mechanical anchoring, as indicated by effective penetration, holds greater significance, while chemical anchoring is less present, as demonstrated in Raman spectroscopy images (Fig. 11). Raman analyses, performed by following the -C-N bond stretching vibration of urethane and the -N-H bending bond of urea at 1550 cm^{-1} , confirmed the presence of adhesive within the lumen, as depicted in Figs. 11a and 11b. These specific bands were chosen for the study due to their spectral position, which avoids interference with bands characteristic of wood compounds (Table 3).

Additionally, in the case of P adhesives, the adhesive exhibited reactivity with the wood cell walls, as illustrated by the presence of urethane and urea bonds beyond the lumens in Fig. 11a. The enhanced chemical anchoring of P adhesives to wood cell walls, facilitated by their reactivity, can be attributed to the greater functionality of PI. Additionally, the smaller size of P adhesive molecules promotes chemical reactions with wood cell walls. In contrast, the longer chains of PB adhesives and their lower reactivity, stemming from their isocyanate blend, may contribute to a reduced chemical interaction compared to P adhesives. This distinction might elucidate the observed variance in mechanical performance between these two adhesive types.

Nonetheless, in the case of PB adhesives, even if all failures occurred entirely within the adhesive joint and chemical anchoring was less present than in P adhesives, the breaking load before failure exhibited an increasing trend with an increase in protein content when the adhesives underwent both treatments A1 and A2, which is consistent with the effective penetration of these adhesives shown in Fig. 5. However, these results remained lower than those of P adhesives due to the discontinuity of the adhesive line. In addition, a reduction in the breaking load before failure was also noted between treatments A1 and A2, which is consistent with the observations in P adhesives.

CONCLUSIONS

1. This study aimed to explore sustainable alternatives to petroleum-based adhesives, with a particular focus on polyurethane adhesives incorporating proteins sourced from industrial byproducts. The investigation delved into the influence of proteins and isocyanates on adhesive performance. To minimize environmental impact, local raw materials derived from non-recyclable or excess industrial waste, such as soybean meal, shrimp shells, and skim milk powder, were selected.
2. The thermal properties of the adhesives remained unaffected by the protein content and isocyanate system variations, ensuring stability and reliability in these formulations.
3. The addition of proteins increased the viscosity and the effective penetration of the adhesives but it either decreased or maintained the gel time compared to the petrochemical reference. An equilibrium must be found in formulating P and PB adhesives to harness the optimal properties of each adhesive.
4. The mechanical characterization of the adhesives underwater exposure revealed a positive correlation between increased protein content and the retention of mechanical strength in adhesives compared to the reference adhesives without protein. However, partial substitution of isocyanate resulted in mechanical strength losses of up to 98%.

5. While the incorporation of proteins reduces the delamination, particularly for B and S protein concentrates, further studies are still needed to reduce the delamination performance of different adhesives.
6. Further work needs to be done to optimize the pressing conditions to reach the optimal performances of the structural bond lines.
7. The partially biobased isocyanate used in this study is an aliphatic isocyanate, and this type of isocyanate produces adhesives with inferior performances. Therefore, it is necessary to explore the development of biobased aromatic isocyanates.

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Author Contributions

Conceptualization, A.M., P.B., and V.L.; methodology, A.M., P.B., S.P., S.C., and V.L.; software, A.M.; validation, A.M.; formal analyses, A.M.; investigation, A.M.; writing—original draft preparation, A.M.; writing—review and editing, A.M., P.B., S.P., A.H., S.C., and V.L.; supervision, P.B., and V.L.; project administration, P.B., and V.L.; funding acquisition, A.M. and P.B. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare that there are no conflicts of interest. The funders had no role in the design of the study; the collection, analysis, or interpretation of data; the writing of the manuscript; or the decision to publish the results.

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