



Polyurethane Wood Adhesives from Microbrewery Spent Grains

Alex Mary¹, Pierre Blanchet¹, and Véronic Landry^{1,2}(✉)

¹ Department of Wood and Forest Sciences, NSERC Industrial Chair On Eco-Responsible Wood Construction (CIRCERB), QC G1V 0A6 Québec, Canada
alex.mary.1@ulaval.ca, veronic.landry@sbf.ulaval.ca

² Department of Wood and Forest Sciences, NSERC – Canlak Industrial Research Chair in Interior Wood-Products Finishes, Université Laval, Québec, QC G1V 0A6, Canada

Abstract. The building sector is responsible for nearly 40% of greenhouse gas emissions, which have a major impact on climate change. One of the strategies to alleviate this problem is to increase the use of wood in the construction of buildings. However, the adhesives used in the design of engineered wood products are synthetic adhesives that rely heavily on the use of materials of fossil origin and therefore non-renewable, such as formaldehyde. Common methods used to reduce formaldehyde emissions from wood panels are to use polyurethane adhesives, formaldehyde-free adhesives. In order to increase the biobased content, it is also common to add certain compounds such as proteins. Proteins are compounds present in appreciable quantities in plants, and can increase the adhesion strength of adhesives on different substrates, including wood. In this study, a protein concentrate was prepared from microbrewery spent grains. The nitrogen content, thermal behavior, molecular weight, and structure of these proteins were then evaluated to facilitate and understand their incorporation into a polyurethane adhesive system. The adhesives were formulated with different protein incorporation percentages: 5%, 10%, 15%, and 20% and compared to a petrochemical reference. This paper highlights the fact that the incorporation of proteins makes it possible to maintain, or even increase, the properties of the adhesives, particularly the mechanical strength. An increase in pot life was also observed.

Keywords: Wood · Engineered wood products · Building · Polyurethane adhesive · Microbrewery spent grains · Protein

1 Introduction

The building sector is responsible for nearly 40% of greenhouse gas emissions (UNEP, 2020). These emissions, which have an impact on climate change, could be significantly reduced by using existing strategies. One of the strategies to address this issue is to increase the use of wood in building construction. Wood is a renewable resource, sustainably harvested in Quebec, which allows for temporary carbon capture in buildings (Stevanovic and Perrin, 2009). However, the adhesives used in the design of wood structural elements (i.e. Cross Laminated Timber, GluLam, plywood, Laminated Veneer Lumber.

etc) are synthetic adhesives which, although interesting for wood structures, rely heavily on the use of fossil-based and therefore non-renewable materials, such as formaldehyde. Formaldehyde is classified by the World Health Organization as a human and animal carcinogen. Since 2021, regulations have been strengthened through the “Formaldehyde Emissions from Composite Wood Products Regulation”, a regulation under the Canadian Environmental Protection Act. It reflects the critical need for bio-based, formaldehyde-free adhesives for wood construction (Gui et al., 2016). The most compelling alternative to formaldehyde-emitting adhesives is polyurethane (PU) adhesives. PU adhesives can be used to bond many materials, are capable of forming hydrogen and covalent bonds with the wood substrate, and their small molecules allow the impregnation of porous substrates (Pizzi and Mittal 2005). They can be single-component, noted PUR 1K, or two-component, noted PUR 2K. PUR 1Ks are based on isocyanate-terminated polymers that can crosslink in the presence of moisture in the air, while the PUR 2Ks are composed of at least one prepolymer that contains an isocyanate, and a polyol. However, these adhesives are also petrochemical-based. Several studies have been conducted to increase the bio-based content of these adhesives, such as incorporating proteins into these adhesives. Proteins are biological macromolecules known to improve the adhesion of the adhesive to the wood substrate (Yang et al., 2006). Soy, cotton and milk proteins have been the most studied. Soy proteins increase the durability of adhesives but they also increase their viscosity and decrease their water resistance (Huang and Li, 2008; Lei et al., 2014; Thakur et al. 2017; Vnučec et al., 2017). Cotton proteins have proven to be a good alternative to soy proteins, as they increase the water resistance and tackiness of the adhesive (Cheng et al., 2013). Milk proteins-based adhesives, on the other hand, can create strong bonds with wood (Detlefsen, 1989). However, they are not able to withstand long-term exposure in humid environments without significant deterioration (Vick and Rowell, 1990). The proteins targeted for this study are derived from microbrewery spent grains, co-products from local resources. With the incorporation of proteins, the isocyanate will be able to react with the NH groups constituting the amino acids of the proteins, as well as with the OH groups of polyols. The proteins were extracted from the microbrewery grains and their nitrogen content, thermal behavior, molecular weight, and structure were evaluated to understand their incorporation into a polyurethane adhesive system. The incorporation of proteins was performed at different percentages and their impact on the adhesives properties has been studied.

2 Methodology

2.1 Materials

Microbrewery spent grains (MSG) are derived from grain crops and refer to microbrewery residues. These residues are generally thrown away or given as feed to livestock in limited quantities. The spent grains selected for this project come from the microbrewery Le Corsaire (Lévis, Canada), and have been used to produce a Pilsner made of 88% barley, 8% oats, and 4% wheat. Polymeric methylene diphenyl diisocyanate (pMDI) (mass equivalent amine = 32.5 Wt.%, viscosity = 129 mPa.s at 20 °C) and a polypropylene oxide-based triol (Multranol 8175) (acid value = 350–390 mg KOH/g

sample, molecular weight = 450 kDa, viscosity = 232–412 at 25 °C) were purchased from Covestro (Pittsburgh, USA). All chemicals were used as received.

2.2 Protein Extraction from MSG

MSG protein concentrate (MSGPC) was prepared by alkaline extraction of MSG (17% w/v) with 0.1 M NaOH at 60 °C (Celus et al., 2009). After 60 min of extraction, the solution was centrifuged at 5000 RPM for 10 min at 20 °C and the filtrate was collected. Samples were then washed with 2 mL of distilled water to be centrifuged again and the filtrate was collected. Proteins in the filtrate were precipitated by acidification to pH 4.0 using 2.0 M citric acid and then placed at 4 °C for 3 h. The obtained protein precipitate was then centrifuged at 8000 RPM for 10 min at 4 °C. The filtrate was disposed of, and the precipitate was washed with 2 mL of 0.1M NaOH before being centrifuged. The protein precipitate obtained after centrifugation was finally freeze-dried to recover the samples in powder form and remove traces of water.

2.3 Protein Characterization

Nitrogen content. To determine the protein content of the samples, it is necessary to know the percentage of nitrogen present in MSGPC. The analysis was performed using the “carbon, nitrogen, and sulfur (CNS) in Plant Tissue” method at a 1350 °C temperature on a TruMAC CNS (LECO Corporation, Midland, Canada). Once the nitrogen content has been obtained, the protein content can be determined using a conversion factor specific to each raw material, which is equal to 6.25 for microbrewery grains (AOAC International, 2000). The analyses were performed in triplicate.

Thermal Stability. The thermal stability of MSGPC was determined using thermogravimetric analysis (TGA). TGA was performed on a TGA/DSC 3 + (Mettler Toledo, Columbia, USA). MSGPC samples of 4–10 mg were placed onto the TGA sample pan. The samples were heated from 25 to 800 °C with a heating rate of 20 °C/min under nitrogen flow. The temperature at which protein begins to degrade was considered the starting temperature for the second stage of weight loss, the first being attributed to moisture loss (Ricci et al., 2018). The analyses were performed in triplicate.

Molecular Weight and Protein Identification. *Samples solubilization, gel migration and protein digestion.* Protein digestion and mass spectrometry analyses were performed by the Proteomics Platform of Quebec City CHU Research Center (Quebec, Qc, Canada).

Approximatively 4 mg of MSGPC was solubilized in 2 mL of 50 mM ammonium bicarbonate, 1% sodium deoxycholate. 14 µL of the sample was transferred and the volume was adjusted to 20 µL in 1X gel sample buffer and 1X reducing agent (Biorad 161–0788 and 161–0792 respectively). Samples were heated at 95 °C for 5 min and spun at 16 000 g for 20 s. Denatured proteins were then deposited on a 4–12% Bis-Tris acrylamide gel and migrated in the stacking portion at 200 V for 8 min (Biorad Precast Gel Criterion XT 4–12% 3450123) (Fig. 1) (Bilgraer, 2014).

Bands of interest were extracted from gels and placed in 96-well plates and then washed with water. Proteins were reduced with 10mM DTT and alkylated with 55 mM

iodoacetamide. Trypsin digestion was performed using 126 nM of modified porcine trypsin (Sequencing grade, Promega, Madison, WI) at 37 °C for 18h. Digestion products were extracted using 1% formic acid, 2% acetonitrile followed by 1% formic acid, 50% acetonitrile. The recovered extracts were pooled, vacuum centrifuge dried and then resuspended into 10 μ l of 2% acetonitrile, 0.05% trifluoroic acid and 5 μ l were analyzed by mass spectrometry.

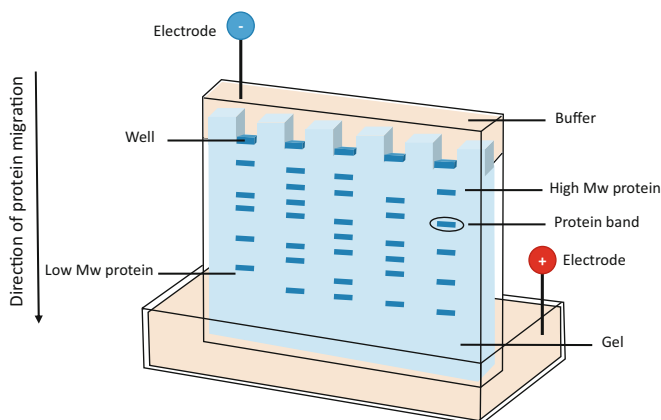


Fig. 1. Gel electrophoresis

Mass Spectrometry. Samples were analyzed by nano LC-MS/MS using a Dionex Ultimate 3000 nanoRSLC chromatography system (Thermo Fisher Scientific, San Jose, USA) connected to an Orbitrap Fusion mass spectrometer (Thermo Fisher Scientific, San Jose, USA). Peptides were trapped at 20 μ l/min in loading solvent (2% acetonitrile, 0.05% TFA) on a 5 mm x 300 μ m C18 pepmap cartridge pre-column (Thermo Fisher Scientific / Dionex Softron GmbH, Germering, Germany) for 5 min. Then, the pre-column was switched online with a Pepmap Acclaim column (Thermo Fisher Scientific, San Jose, USA) 50 cm x 75 μ m internal diameter separation column and the peptides were eluted with a linear gradient from 5–40% solvent B (A: 0.1% formic acid, B: 80% acetonitrile, 0.1% formic acid) in 30 min, at 300 nL/min. Mass spectra were acquired using a data dependent acquisition mode using Thermo XCalibur software version 4.3.73.11. Full scan mass spectra (350 to 1800m/z) were acquired in the orbitrap using an automatic gain control target of 4e5, a maximum injection time of 50 ms and a resolution of 120 000. Internal calibration using lock mass on the m/z 445.12003 siloxane ion was used. Each scan was followed by MS/MS fragmentation of the most intense ions for a total cycle time of 3 s (top speed mode). The selected ions were isolated using the quadrupole analyzer in a window of 1.6 m/z and fragmented by Higher energy Collision-induced Dissociation with 35% of collision energy. The resulting fragments were detected by the linear ion trap in rapid scan rate with an automatic gain control

target of $1e4$ and a maximum injection time of 50 ms. Dynamic exclusion of previously fragmented peptides was set for a period of 20 s and a tolerance of 10 ppm.

Database Searching. Mascot generic format peak list files were created using Proteome Discoverer 2.3 software (Thermo Fisher Scientific, San Jose, USA). Mascot generic format sample files were then analyzed using Mascot (Matrix Science, London, UK; version 2.5.1). Mascot was set up to search a contaminant database using the following database: *Hordeum vulgare* (UP000011116, 35907 entries), assuming the digestion enzyme trypsin and with a fragment ion mass tolerance of 0.60 Da and a parent ion tolerance of 10.0 ppm. Carbamidomethylation of cysteine was specified in Mascot as a fixed modification. Deamidation of asparagine and glutamine, oxidation of methionine were specified as variable modifications.

Criteria for Protein Identification. Scaffold (version Scaffold_5.1.2, Proteome Software Inc., Portland, OR) was used to validate MS/MS based peptide and protein identifications. Peptide identifications were accepted if they could be established at greater than 89.0% probability to achieve an FDR less than 1.0% by the Scaffold Local FDR algorithm. Protein identifications were accepted if they could be established at greater than 99.0% probability to achieve an FDR less than 1.0% and contained at least 2 identified peptides. Protein probabilities were assigned by the Protein Prophet algorithm (Nesvizhskii et al., 2003). Proteins that contained similar peptides and could not be differentiated based on MS/MS analysis alone were grouped to satisfy the principles of parsimony.

2.4 Preparation of Polyurethane Adhesives

Polyurethane adhesive formulations were prepared with a ratio of isocyanate to hydroxyl functions (NCO/OH) of 1.13, to ensure a complete reaction between the polyol and the isocyanate (Meier-Westhues, 2019). The incorporation of proteins was done by substitution of the hydroxyl groups of the polyol with the amine groups of the proteins. Proteins 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 done at 5%, 10%, 15%, and 20%. The petrochemical reference, formulated with the same chemicals as the protein-based adhesives, is represented by the formulation containing 0% protein.

2.5 Adhesives Characterization

Viscosity. Viscosity is an important physical parameter that affects the behavior of the adhesive. Proper viscosity gives the adhesive good flowability and facilitates handling to achieve high bond strength of the bonded product (Luo et al., 2016). Viscosity measurements were performed, at 25 °C, on systems consisting of the polyols and proteins using a ViscoLab 4100 (Cambridge Applied Systems Inc., Boston, USA).

Optical microscopy. The polyol/protein systems were observed using a VHX-7000 digital microscope (Keyence Co. Ltd., Osaka, Japan).

Pot Life. Pot life is the maximum period during which a multi-component adhesive can be used after mixing the components (International Organization for Standardization,

2018). The pot life was determined using French Standards NF EN ISO 10364:2018 method 3. Twenty grams of adhesive were prepared by mixing isocyanate, polyol and proteins as described in Sect. 2.4 and temperature monitoring was performed. In this method, pot life is considered to be the time elapsed from the start of mixing until the critical temperature is reached. The critical temperature was determined from the petrochemical reference and was set at 30 °C. The analyses were performed in triplicate.

Kinetics and Conversion. The polymerization kinetics of the adhesive systems prepared were studied by real-time Fourier transform infrared spectroscopy (RT-FTIR). The instrument used is the INVENIO® R (Bruker Optics Inc., Billerica, USA). The spectra were recorded in the range 450–4000 cm^{-1} for a duration of 215 min, corresponding to 400 measurements of 32 scans with a resolution of 4 cm^{-1} . Details of the expected FTIR bands are shown in Table 1 (Maji and Bhowmick, 2009). The analyses were performed in duplicate.

Table 1. Principal Peak Assignments in the FTIR Spectra of the isocyanate, polyol and cured PU

Observed peaks (cm^{-1})	Peaks assignments
3510 - 3100	-NH, -OH stretching vibrations
2970 - 2870	-CH stretching vibration
2260	-N = C = O stretching vibration
1730 - 1710	-C = O- stretching vibration of urethane
1620	-NH stretching vibration

Activation Energy and Reaction Heat. The differential scanning calorimetry analysis was performed on DSC 822e (Mettler Toledo, Columbia, USA). PU adhesives of 4–6 mg were placed onto the DSC sample pan and heated under nitrogen flow from 30 to 220 °C at different heating rates: 5 °C/min, 10 °C/min, and 20 °C/min. Those heating rates were used to obtain sufficient information to calculate the activation energy and the reaction heat of each adhesive according to the ASTM E698:2011 method (Lépine, 2013). The reaction heat represents the amount of energy released during the polymerization reaction, and the activation energy is the energy required to initiate the polymerization reaction (Lépine, 2013).

Block Shear. Wood cutting, bonding, and testing were conducted according to the ASTM D905:2008 test method. Black spruce (*Picea mariana*, Mill.) wood specimens were cut into rectangular panels of 32 × 65 × 20 mm^3 and 3.75g of adhesive, prepared according to Sect. 2.4., was applied to the wood within 24 h after cutting. The two pieces, one with adhesive and one without, were placed together for the adhesives to be cured at room temperature with a pressure of 150 psi exerted onto the contact area for 24 h. After that, the glued elements were cut according to the ASTM D905:2008 method. Wood specimens were conditioned at 20 °C with a relative humidity of 65% for seven days. Block-shear strength tests were performed on the Alliance RT/50 (Frank Bacon Machinery Sales Co., Warren, USA). The load was applied with continuous movement

of the moving head at a rate of 5 mm/min until failure. The analyses were performed on ten samples per adhesive.

3 Results and Discussion

3.1 Protein Characterization

Nitrogen content. Table 2 presents the protein content before and after the extraction described in Sect. 2.2. The protein content before extraction is higher than what can be found in the literature concerning barley, where it has been proven that it is between 10 and 15% (Yu et al., 2017). The increase in the protein content of the post-extraction samples, compared to the pre-extraction samples, suggests the viability of the extraction protocol used. In addition to obtaining a higher protein content, which should increase the water resistance of the adhesive according to Gui et al., extracted proteins under moderate alkaline conditions should enhance adhesive strengths compared with unextracted protein, as this extraction process makes polar and apolar groups of the proteins available (Gui et al., 2016; Hettiarachchy et al., 1995). The other components of barley grains are starch, cellulose and fat (Alijosius et al., 2016; Yu et al., 2017).

Table 2. Nitrogen and protein contents of microbrewery grains before and after extraction

Raw materials	Nitrogen content (%)	Protein content (%)
MG pre-extraction	3.7 ± 0.1	22.9 ± 0.6
MG post-extraction	9.6 ± 0.2	60.0 ± 2

TGA. TGA experiments were performed to study the thermal stability of MSGPC, which have been previously placed in an oven for 24 h at 50 °C (Fig. 2). The barley sample showed several peaks of mass loss following thermal events, including 71.50 °C and 315.33 °C. These losses were also observed by Borsato et al. (2019). The first mass loss (71.50 °C) is attributed to dehydration. The main phase of degradation, between 210 and 420 °C, presents a peak corresponding to the release of gases such as carbon monoxide, carbon dioxide, methane, and ethylene (Borsato et al., 2019). Since the adhesive system is formulated cold and samples degradation temperatures are higher than 300 °C, the proteins are not likely to degrade once incorporated.

Molecular Weight and Protein Identification. Protein separation on polyacrylamide gel electrophoresis allows the identification of a variety of proteins in MSGPC (Fig. 3). Liquid chromatography coupled with mass spectrometry ensured the identification and quantification of the various proteins present in raw materials. The most significant band present in the sample is the 40 kDa band associated with serpins, a superfamily of proteins commonly present in barley (Gettins, 2002). A second well-marked band is positioned around 23 kDa. This band has not been assigned, due to its low presence compared to the serpin protein, but can be assigned to a protein fragment. Having molecular weights

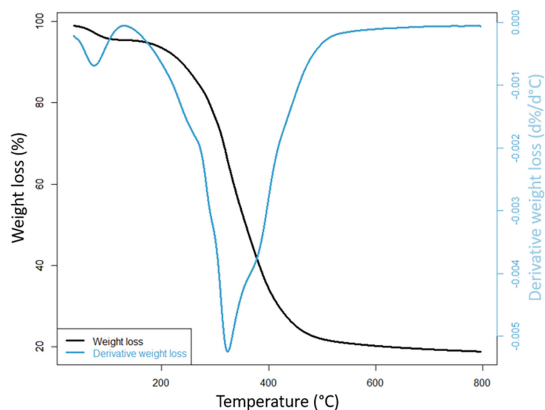


Fig. 2. TGA curves of MSGPC

around 40 kDa is not a barrier to adhesive formulation, as the literature has shown that protein-based adhesives up to 100 kDa can be obtained (Jenkins et al., 2013). In fact, having smaller proteins helps to promote protein incorporation into the adhesive and minimize the final viscosity of the system.

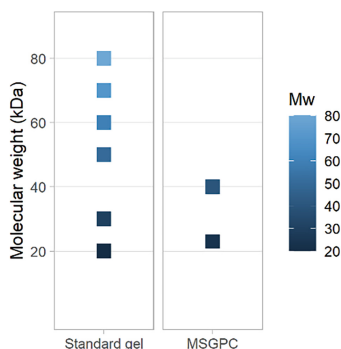


Fig. 3. Molecular weight of proteins contained in MSGPC

Viscosity. Viscosity measurements were performed at 25 °C on the systems consisting of polyols and proteins at different substitution rates (Fig. 4). The results show that protein incorporation causes an increase in viscosity. This increase is due to the protein molecules unfolding into the surrounding system once incorporated (Bacigalupe et al., 2015). These results are consistent with what can be found in the literature as it is well known that the addition of fillers to a polymer system leads to an increase in its viscosity (Markovičová, 2021; Schulze et al., 2003).

Optical Microscopy. The polyol/protein systems were observed using an optical microscope to better understand the behavior of the proteins once incorporated into the polyol (Fig. 5). Microscopic images were corrected with a contrast of 50%. The polyol is the

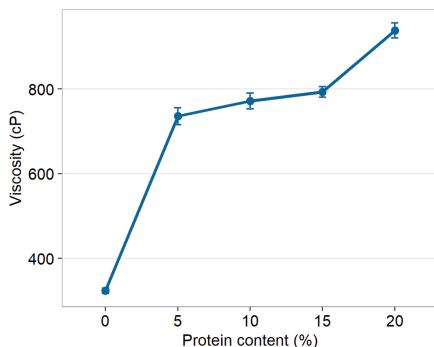


Fig. 4. Viscosity of polyol/protein systems at 25 °C

liquid matrix while the observable aggregates are the proteins. These analyses prove that when the percentage of proteins increases, protein clusters are formed and thus reduce the mobility of proteins in the polyol. At a protein incorporation of 20%, the protein clusters formed are prominent.

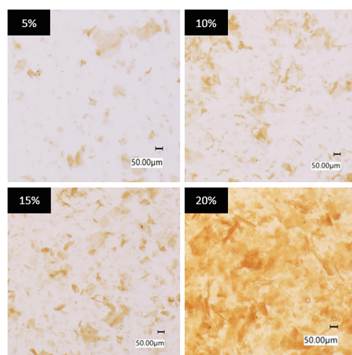


Fig. 5. Corrected microscope images of polyol/proteins systems at different protein content

Pot Life. Pot life, in this study, is considered to be the time from the start of mixing until the critical temperature, here 30 °C, is reached. The incorporation of proteins, regardless of the percentage, increases the pot life of the adhesive (Fig. 6). This increase means that the time before the adhesive significantly changes viscosity is lengthened, representing a definite advantage for the application of these adhesives. Since amine groups are more reactive than hydroxyl groups, it was expected that the pot life of protein-based adhesives would be shorter than the petrochemical reference. However, the opposite was found here. Several parameters must be taken into account to explain these results. First, part of the protein fraction is unreactive, making the probability of encounters between an isocyanate and the NH and OH groups lower. Second, the presence of cellulose and starch, which contain OH groups, may reduce the NCO/OH ratio set at 1.13 which could lead to a longer pot life. This increase in pot life could also be explained by an

incomplete polymerization of the adhesives. The following kinetic and conversion of adhesive analyses will investigate this hypothesis.

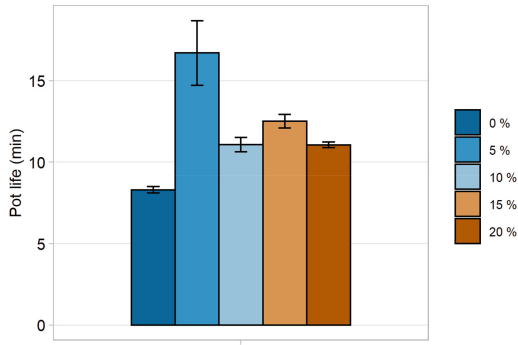


Fig. 6. Pot life of PU adhesives at different protein contents

Kinetic and Conversion of Adhesives. FTIR spectra of PU-MSGPC adhesives at different percentages of protein incorporation showed similarity in the absorption band. RT-FTIR spectra are shown in Fig. 7. A baseline correction was performed for all absorption peaks. The OH and NH stretching bands were recorded at 3335 cm^{-1} , the -CH stretching vibration band at 2920 cm^{-1} , the NCO stretching vibration band at 2260 cm^{-1} , the -C=O-Stretching vibration band of urethane at 1730 cm^{-1} , and the -NH stretching band at 1620 cm^{-1} .

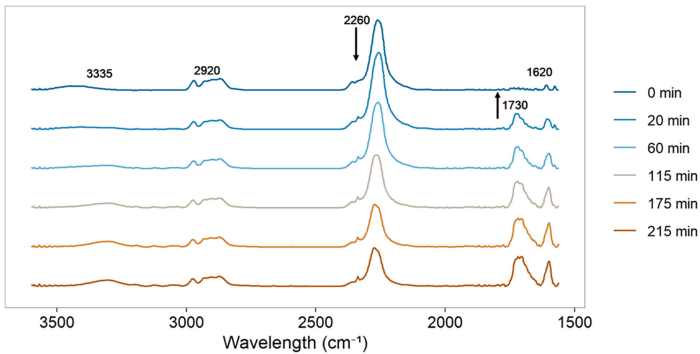


Fig. 7. FTIR spectra of PU adhesive with protein over time

The urethane formation can be monitored by the disappearance of the isocyanate's NCO vibration band at 2260 cm^{-1} and the appearance of the urethane's C=O vibration band at 1730 cm^{-1} . The isocyanate conversion (Fig. 8) can be used as the degree of curing reaction as follows (Eq. 1) assuming that there is an insignificant side reaction (Maji and Bhowmick, 2009).

$$\% \text{ NCO conversion} = 100 * \left(1 - \frac{A_{NCO_t}/A_{CO_t}}{A_{NCO_0}/A_{CO_0}} \right) \quad (1)$$

Isocyanate conversion

where, A_{NCO_0} is the 2260 cm^{-1} peak intensity at the initial time, A_{NCO_t} is the 2260 cm^{-1} peak intensity of absorbance at specified time during the curing, A_{CO_0} is the 1730 cm^{-1} peak intensity at the initial time, A_{CO_t} is the 1730 cm^{-1} peak intensity of absorbance at specified time during the curing. The curves representing the conversion rates being overlapped, it is possible to deduce that the incorporation of proteins has a few impacts on the conversion rate. Indeed, it is possible to see that the higher the protein level, the slower the reaction will start, which is consistent with the viscosity increase presented in Fig. 4.

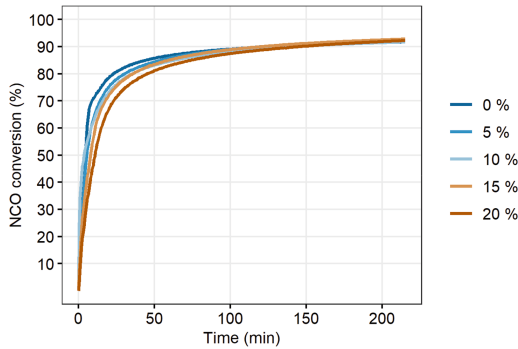


Fig. 8. Isocyanate band conversion rate versus time of PU adhesives at different protein contents

Activation Energy and Reaction Heat. Activation energy represents the energy required to initiate the polymerization reaction. The lower the energy, the easier it is for the resin to cure (Lépine, 2013). A 5% protein incorporation results (Fig. 9 left) in a decrease in activation energy, which can be explained by the fact that amine groups react faster with isocyanates than hydroxyl groups. The increase in activation energy at 10% and then a decrease at higher percentages can be explained by the increased viscosity of the adhesive. The heat of the reaction represents the amount of energy released during the polymerization reaction. Since the reaction is exothermic, high energy is characterized by greater chemical bond formation during the polymerization of the adhesive. The results obtained (Fig. 9 right) show that the incorporation of proteins has little effect on the formation of chemical bonds during polymerization.

Block Shear. This analysis covers the determination of comparative breaking point of adhesives used for bonding wood when tested in compression. The bar diagram obtained

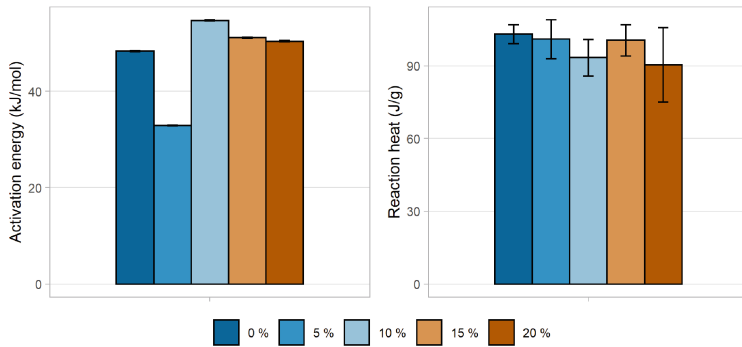


Fig. 9. Activation energy (left) and reaction heat (right) of PU adhesives at different protein contents

for comparing the maximum load at breaking point of the adhesives with an increasing percentage of protein is given in Fig. 10. The values obtained from the standard error analysis, which gives an indication of the sampling error, are also presented in Fig. 10. As it can be seen from the figure, the incorporation of protein appears to increase the maximum load at breaking point of the adhesive. This value increases with the percentage of protein. Parallels can be made with studies conducted on soy-based adhesives where increasing the percentage of protein in the adhesive was shown to increase the adhesion strength of the adhesive (Gui et al., 2016; Trinh, 2012).

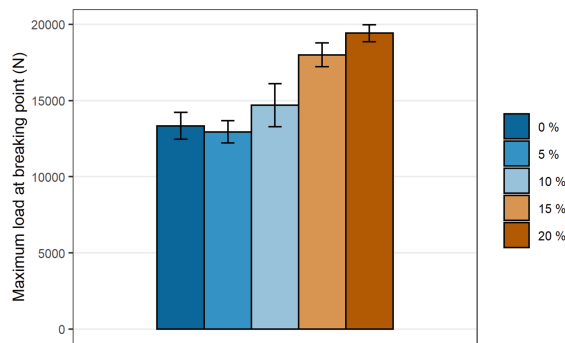


Fig. 10. Maximum shear force before the rupture of PU adhesives with different protein contents

4 Conclusion

Polyurethane adhesives are a commonly used alternative for reducing formaldehyde emissions from wood panels. Incorporating natural compounds, such as proteins, represents a step toward bio-based adhesives. The proteins selected for this study are from microbrewery spent grains and their structure as well as their chemical composition

has been taken into account before their incorporation into polyurethane adhesives. The protein-based adhesives exhibited a longer pot life as well as better mechanical resistance than the petrochemical adhesive. It was also shown that, although the polymerization of the adhesives takes longer to start as the percentage of protein increases, the adhesives form with a similar degree of conversion as the petrochemical reference. Although the technical feasibility of protein incorporation into polyurethane adhesives has been positively demonstrated, the number and accessibility of OH and NH groups in the molecules remain to be determined.

Acknowledgments. The authors are grateful to Marie Soula and Aurélien Hermann for their valuable assistance. Thanks to Patrick Leclerc for the CNS analysis, Victor Fourcassié and Sylvie Bourassa for their expertise on proteins, and thanks to Yves Bédard, Daniel Bourgault, Luc Germain, Benoit St-Pierre and Jean Ouellet for their help with the various analyses. The authors would also like to thank the Renewable materials research center and the NSERC industrial chair on eco-responsible wood construction (CIRCERB) and its industrial partners.

Funding. The authors are grateful to Natural Sciences and Engineering Research Council of Canada for the financial support through its IRC and CRD programs (IRCPJ 461745- 18 and RDCPJ 524504–18) as well as the industrial partners of the NSERC industrial chair on eco-responsible wood construction (CIRCERB). The authors are also grateful to the Ministère de l'Économie et de l'Innovation du Québec through the PSO-I-009 project.

Conflicts of Interest. There are no conflicts to declare.

References

- Alijosius, S., Kliseviciute, V., Sasyte, V.: The chemical composition of different barley varieties grown in Lithuania (2016). <https://www.researchgate.net/publication/311434685>
- AOAC International: AOAC Official Method 997.09:1997 Nitrogen in Beer, Wort, and Brewing Grains Protein (Total) by Calculation. Combustion Methode (2000)
- Bacigalupe, A., Poliszuk, A.K., Eisenberg, P., Escobar, M.M.: Rheological behavior and bonding performance of an alkaline soy protein suspension. *Int. J. Adhes. Adhes.* **62**, 1–6 (2015). <https://doi.org/10.1016/j.ijadhadh.2015.06.004>
- Bilgraer, R.: Decipher the histone code : epigenetics and placental toxicology (2014). <https://tel.archives-ouvertes.fr/tel-01195983>
- Borsato, V.M., Jorge, L.M.M., Mathias, A.L., Jorge, R.M.M.: Thermodynamic properties of barley hydration process and its thermostability. *Journal of Food Process Engineering* **42**(2) (2019). <https://doi.org/10.1111/jfpe.12964>
- Celus, I., Brijs, K., Delcour, J.A.: Fractionation and characterization of brewers' spent grain protein hydrolysates. *J. Agric. Food Chem.* **57**(12), 5563–5570 (2009). <https://doi.org/10.1021/jf900626j>
- Cheng, H.N., Dowd, M.K., He, Z.: Investigation of modified cottonseed protein adhesives for wood composites. *Ind. Crops Prod.* **46**, 399–403 (2013). <https://doi.org/10.1016/j.indcrop.2013.02.021>
- Detlefsen, W.D.: Adhesive from Renewable Ressources, Chapter 31 : Blood and Casein Adhesives for Bonding Wood (1989). <https://pubs.acs.org/sharingguidelines>

- Gettins, P.G.W.: Serpin Structure. Mechanism, and Function. (2002). <https://doi.org/10.1021/cr010170>
- Gui, C., Zhu, J., Zhang, Z., Liu, X.: Research progress on formaldehyde-free wood adhesive derived from soy flour. In: Adhesives - Applications and Properties, pp. 187–200 (2016). InTech. <https://doi.org/10.5772/65502>
- Hettiarachchy, A'N.S., Kalapathy, U., Myers, D.J.: Alkali-modified soy protein with improved adhesive and hydrophobic properties. In: JAOCS, Vol. 72 (1995)
- Huang, J., Li, K.: A new soy flour-based adhesive for making interior type II plywood. JAOCS, Journal of the American Oil Chemists' Society **85**(1), 63–70 (2008). <https://doi.org/10.1007/s11746-007-1162-1>
- International Organization for Standardization: ISO:10364 Structural adhesives - Determination of pot life (service life) of adhesives (2018)
- Jenkins, C.L., Meredith, H.J., Wilker, J.J.: Molecular weight effects upon the adhesive bonding of a mussel mimetic polymer. ACS Appl. Mater. Interfaces. **5**(11), 5091–5096 (2013). <https://doi.org/10.1021/am4009538>
- Lei, H., Du, G., Wu, Z., Xi, X., Dong, Z.: Cross-linked soy-based wood adhesives for plywood. Int. J. Adhes. Adhes. **50**, 199–203 (2014). <https://doi.org/10.1016/j.ijadhadh.2014.01.026>
- Lépine, E.: Synthèse d'adhésifs thermodurcissables à base de farine de soya et de furfural pour la fabrication de panneaux composites en bois (2013)
- Luo, J., Luo, J., Li, X., Gao, Q., Li, J.: Effects of polyisocyanate on properties and pot life of epoxy resin cross-linked soybean meal-based bioadhesive. In: Journal of Applied Polymer Science, Vol. 133, Issue 17. John Wiley and Sons Inc. (2016). <https://doi.org/10.1002/app.43362>
- Maji, P.K., Bhowmick, A.K.: Influence of number of functional groups of hyperbranched polyol on cure kinetics and physical properties of polyurethanes. J. Polym. Sci., Part A: Polym. Chem. **47**(3), 731–745 (2009). <https://doi.org/10.1002/pola.23185>
- Markovičová, L.: The Effect of Filler Content on the Viscosity of Polymer Composites **3**, 293–298 (2021). <https://doi.org/10.2478/cqpi-2021-0028>
- Meier-Westhues, U.: Polyurethanes: coatings, adhesives and sealants. European Coatings. (Vincentz Network). European Coatings Tech Files (2019)
- Nesvizhskii, A.I., Keller, A., Kolker, E., Aebersold, R.: A statistical model for identifying proteins by tandem mass spectrometry. Anal. Chem. **75**(17), 4646–4658 (2003). <https://doi.org/10.1021/ac0341261>
- Pizzi, A., Mittal, K.L.: Handbook of Adhesive Technology (2005)
- Ricci, L., et al.: On the thermal behavior of protein isolated from different legumes investigated by DSC and TGA. J. Sci. Food Agric. **98**(14), 5368–5377 (2018). <https://doi.org/10.1002/jsfa.9078>
- Schulze, K.A., Zaman, A.A., Söderholm, K.J.M.: Effect of filler fraction on strength, viscosity and porosity of experimental compomer materials. J. Dent. **31**(6), 373–382 (2003). [https://doi.org/10.1016/S0300-5712\(03\)00091-5](https://doi.org/10.1016/S0300-5712(03)00091-5)
- Stevanovic, T., Perrin, D.: Chapitre 1 “Chimie et analyse des produits naturels.” In : Chimie du bois, pp. 3–46. Presses polytechniques et universitaires romandes (2009)
- Thakur, V.K., Thakur, M.K., Kessler, M.R.: Handbook of composites form renewable materials - Volume 1 : Structure and Chemistry (2017)
- Trinh, E.H.: Formulation of green adhesives from mixtures of soy protein isolates and rosin ester resin (2012)
- UNEP : Rapport 2020 sur l'écart entre les besoins et les perspectives en matière de réduction des émissions (2020)
- Vick, C.B., Rowell, R.M.: Adhesive bonding of acetylated wood (1990)
- Vnučec, D., Kutnar, A., Goršek, A.: Soy-based adhesives for wood-bonding—a review. In: Journal of Adhesion Science and Technology, Vol. 31, Issue 8, pp. 910–931. Taylor and Francis Ltd. (2017). <https://doi.org/10.1080/01694243.2016.1237278>

- Yang, I., Kuo, M., Myers, D.J., Pu, A.: Comparison of protein-based adhesive resins for wood composites. *J. Wood Sci.* **52**(6), 503–508 (2006). <https://doi.org/10.1007/s10086-006-0804-5>
- Yu, W., et al.: Relationships between protein content, starch molecular structure and grain size in barley. *Carbohyd. Polym.* **155**, 271–279 (2017). <https://doi.org/10.1016/j.carbpol.2016.08.078>