<http://www.diva-portal.org>

Postprint

This is the accepted version of a paper published in *Journal of Adhesion Science and Technology*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the original published paper (version of record):

Trischler, J., Sandberg, D., Dorn, M. (2018)
Effect of temperature during vital gluten adhesive preparation and application on shear-bond strength.
Journal of Adhesion Science and Technology, 32(4): 448-455
<https://doi.org/10.1080/01694243.2017.1362807>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

This is an Accepted Manuscript of an article published by Taylor & Francis in *Journal of Adhesion Science and Technology* on 17/08/07, available online: <http://www.tandfonline.com/10.1080/01694243.2017.1362807>.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:lnu:diva-67324>

1   **Effect of temperature during vital gluten adhesive preparation and**
2   **application on shear-bond strength**

3   Johann Trischler ^{1*}, Dick Sandberg ¹, Michael Dorn ²

4   ¹ *Luleå University of Technology, Wood Science and Engineering, SE-931 87 Skellefteå, Sweden*

5   ² *Linnæus University, Department of Building Technology, SE-351 95 Växjö, Sweden*

6   **corresponding author: johann.trischler@ltu.se*

7

Effect of temperature during vital gluten adhesive preparation and application on shear-bond strength

If protein-based adhesives are to become a competitive bio-based alternative to synthetic adhesives, the preparation and application methods have to be considerable improved to reduce process time and thereby improve the economy of the adhesive system. The purpose of this study was to investigate the impact of the temperature during preparation and application on the shear-bond strength of an adhesive based on vital gluten for use in wood applications. Vital gluten was used in its natural form and mixed with water of different temperatures (preparation temperature 0°C or 20°C), and applied on beech veneer at different temperature (application temperature -10°C, 20°C, 60°C and 100°C). Tensile shear-bond strength samples were prepared and tested according to EN 205. The results showed that an increase in veneer temperature during application of the adhesive led to a decrease in the shear-bond strength, but that the preparation temperature of the adhesive had no influence on the strength.

Keywords: application temperature; bond line; preparation temperature; protein adhesive.

Introduction

Proteins or their derivatives have traditionally been used as a basis for adhesives for use in wood applications, but the development of synthetic adhesives has made it more difficult for protein-based adhesives to compete with synthetic adhesives from both an economic and a performance-related perspective [1]. In most cases, the formulations are sensitive to the source of the protein and require time-consuming adjustments leading to low production rates and therefore also high costs [2].

Recently, research has been focused on the use of vegetable proteins because they can be produced in sufficient volume for wood adhesive applications and are reasonable in cost. Although most of the research has been on proteins from soy beans, some work has also been done on other sources, such as canola (rapeseed), wheat

gluten, lupin flour, and zein [2, 3]. Of those, wheat gluten is the cheapest source of protein suitable for the development of wood adhesives [4].

Wheat gluten is derived from whole wheat kernels or flour by a separation of starch and gluten. Vital gluten is gluten isolated and produced at a mild temperature, especially with regard to the drying process, and it therefore still has its ability to form a molecular network with viscoelastic properties [5]. A group of polymeric gluten proteins is called glutenin, and consists of gliadins and glutenins [6]. These molecules are composed of subunits of high molecular weight (HMW) and low molecular weight (LMW), linked together with disulphide bonds [7].

To be used as a wood adhesive, proteins have to be denaturised to achieve an unfolding of the protein and blended with water. The folding and unfolding of proteins depend on local and non-local interactions among the monomers, i.e. the energies and the angles of the peptide bonds [8]. According to the literature, denaturation of proteins in aqueous solution can be achieved with different reagents: guanidine hydrochloride (GuHCl), urea, proteins which are random coils in their native states, salts (other than guanidine hydrochloride), thermal transitions (both reversible and irreversible denaturation), acid and alkaline pH, organic acids, alcohols and dioxane, and detergents.

There is a temperature of maximum “stability” of the protein where the rate of denaturation is a minimum and, with increasing distance from this optimum temperature, the rate of denaturation increases with the increasing temperature [9].

Although from a thermodynamic aspect the effect of an increase in temperature seems quite clear, this is not the case with a decrease in temperature. Earlier studies suggest that this is an effect of hydrophobic side chains which are exposed to solvent water during the unfolding of the protein and of the different solvation of the non-polar groups [9, 10]. Recent studies suggest that the hydrophilic effect is much more important than

the hydrophobic effect in cold denaturation, assuming that the hydrophilic interactions are the predominant forces for the folding of proteins and enabling protein solubility [11, 12]. The stability of proteins is probably a dual concept involving both thermodynamic stability and thermal resistance, and denaturation occurs as thermal denaturation at high temperatures and cold denaturation at low temperatures [13].

According to the literature, temperature has a strong impact on the properties of proteins, and this is important when proteins are used as a base for adhesives as it influences their solubility in aqueous solutions and the reactivity of the adhesive. The purpose of this study was therefore to investigate the influence on the tensile shear-bond strength of the temperature during the preparation and application of a vital gluten-based adhesive aimed for wood applications.

Materials and Methods

Beech (*Fagus sylvatica* L.) veneers with an initial moisture content (MC) of 6% and a thickness of 5 mm were conditioned at various temperatures and glued in pairs with a gluten-based adhesive prepared at different temperatures.

Amygluten powder from Tereos® (Fig. 1) was used as a base for the adhesive. This gluten was mixed with water in proportions of 1:3 by weight. The temperature of the solvent during preparation was either 0°C or 20°C, Table 1. The adhesive was applied within 5 min. after its preparation. The adhesive application was 200 mg/m².

[Figure 1 near here]

Before application of the adhesive, the veneers were conditioned for 20 min. at temperature of -10°C, 20°C, 60°C or 100°C. Adhesive was applied to one of the veneers, and an unglued veneer was then pressed on the top of it for 3 hours under a pressure of 2.0 MPa at a temperature of 60°C. The moderate setting temperature was

chosen to reduce temperature-related effects such as thermal denaturation of the protein, but at the same time to give a reasonably quick drying of the water.

For comparison, specimens were also glued with a PVAc adhesive (Casco Adhesive 3316). To compare the two adhesives, the PVAc adhesive was diluted to achieve equal dry basis spread amount at comparable tests. It was applied only on samples conditioned at 20°C.

The tensile shear-bond strength specimens were of 500 x 200 x 10 mm in size, prepared according to the standard EN 205 [14]. The bonded area was 20 x 10 mm², Fig. 2.

[Figure 2 near here]

Before testing, samples were conditioned according to the classifications D1 and D2 of the standard EN 204 [15]. Classification D1 requires one week conditioning at 20°C and 65% relative humidity (RH), and classification D2 requires one week at 20°C and 65% RH, followed by a water-bath at 20°C for 3 hours and a second conditioning one week at 20°C and 65% RH.

For each series, 10 specimens were tested (Table 1). The tensile shear tests were run at a speed of 9 mm/min., and the tensile shear-bond strength and the average amount of wood failure in quartiles of the total area of rupture were evaluated according to EN 205. The average amount of wood failure was determined using an optical microscope.

Results

The results of the tensile shear-bond test are presented in Table 1. Fig. 3 shows the median and the upper and lower quartiles of the strength values as a box-and-whiskers plot.

[Table 1 near here], [Figure 3 near here]

The statistical evaluation shows that there is no significant difference in bond strength between the different test series after conditioned according to the D1 classification (Nos. 1 to 8). Conditioning according to the D2 classification (Nos. 9 to 16) did, however affect the bond strength. The independent-samples t-test was used to closer examine the results, Table 2.

[Table 2 near here]

The statistical analysis shows that there is no significant difference between the D1 and the D2 conditioning. For the series Nos. 1 to 8 conditioned according to classification D1 neither the preparation nor the application temperature affect the shear-bond strength. After a dry-wet-dry conditioning cycle according to classification D2, however, the application temperature does significantly affect the shear-bond strength. Although, the preparation temperature has no significant influence.

The sample conditioned according to classification D1, with the vital gluten-based adhesive showed on average a bonding strength 18% lower than the PVAc adhesive but 21% higher than that required by the standard. In the case of the samples conditioned according to classification D2, the vital gluten-based adhesive showed on average values 40% lower than those given by the PVAc adhesive, at the minimum level required by the standard, see Fig. 3.

Discussion

In contrast to prior studies on wheat protein as an adhesive for wood products [6, 16, 17] where the wheat protein was pre-treated before application, vital gluten was used in this study in its natural form and set at a relatively low temperature to avoid changes in its chemical and physical structure not related to the shear-bond preparation and application temperature.

134 In general, changes in the chemical and physical structures of the protein during
135 preparation are desired, as they improve the bonding strength of the adhesive. In this
136 study, an attempt was made to achieve a denaturation of the protein simple by
137 controlling the temperature under preparation and application of the adhesive. A low
138 temperature should increase solubility and lead to an unfolding of the wheat protein
139 when solved in water. The mild curing conditions after application on wood assume that
140 the adhesive system can be interpreted as being a dispersion adhesive which is not
141 curing but is setting by evaporation of the solvent [18].

142 The results demonstrate that regulating the temperature during adhesive
143 preparation and application may be essential for the development of protein-based wood
144 adhesives. (1) The time-consuming and energy-extensive pre-treatment processes may
145 thus be reduced [16]. (2) The selection of the protein is important. Vital gluten, for
146 example, can lead to a viscoelastic network [5]. (3) The poor solubility of the wheat
147 protein can be overcome and can be an advantage after setting of the adhesive. (4)
148 Using lower temperature during adhesive preparation and application seems to have no
149 negative impact on the complex protein structure and functionality. The proteins were
150 eventually more unfolded which is important to achieve both strong intra-bonding
151 (within the protein complex) and inter-bonding (between the protein and the substrate).
152 The results showed that a mild temperature during application seemed to have a positive
153 impact on the water-resistance of the bond-line.

154 Within the different series tested according to classification D1 the variation in
155 the bonding strength was small, and the preparation and application temperatures had no
156 significantly influence on the bonding strength. There was however a large variation in
157 the extent of wood failure within this group. Specimens conditioned according to
158 classification D2 showed a decrease in bonding strength with increasing application

temperature and a smaller variation in the extent of wood failure. The adhesive blended at 20°C performed worse with increasing application temperature regardless of how the specimens were conditioned before the tensile shear test.

The Standard EN 205 requires a minimum shear-strength value for the bond strength for the D1 and D2 classifications of 10 MPa and 8 MPa, respectively. The vital gluten adhesive reached the D1 level for all combinations of adhesive preparation and veneer temperatures. The D2 level was only reached with veneer temperatures of -10°C and 20°C. These results suggest that a decrease in temperature effectuates an unfolding of the protein resulting in the exposure of reactive bonds [11].

In general, the results show a remarkably good bonding strength of vital gluten and the ability to reach the required standard even after water immersion, although the performance is lower than that of PVAc adhesive, Ref₁ and Ref₂. Nevertheless, the values of bonding strength are comparable to those presented in the literature, e.g. Nordqvist [17]. In the present study, however, vital gluten was used in its natural way or cold-dissolved and curing was avoided, whereas in the studies presented in the literature it was treated before application in different ways and curing was achieved by using higher temperatures [16, 17, 19]. Curing of the protein-based adhesive should lead to polymerisation and thus a greater water resistance of the bond line.

Cold-dissolution and application on a cool substrate seem to give the protein the ability to unfold and develop bonds (inter-bonding) and this performance is much better at higher humidity. At the same time, vital gluten seems not to lose its ability to build a viscoelastic network (intra-bonding) which seems responsible for the good performance regarding the bonding strength in general. These assumptions are strengthened by the fact that a higher temperature during application lead to a strong decrease in bonding strength after water immersion, which indicates that a larger amount of hydrophilic

groups are accessible to water so that the protein applied at a higher temperature was not able to develop proper inter- or intra-bonds.

Conclusions

In this study, the impact of preparation and application temperature on the shear-bond strength of vital gluten blended with water and applied as a dispersion adhesive on beech veneer was studied. The adhesive was prepared at two different temperatures and applied on veneers at temperatures from -10°C to 100°C, and the specimens were thereafter conditioned according to the classifications D1 and D2 in the standard EN 205 before the tensile shear-bond strength was evaluated. The results show that the application temperature influences the bonding strength after a water immersion according to classification D2. Here, an increase in veneer temperature during application of the adhesive considerably decreased the shear-bond strength. The results not only demonstrate that wheat protein has a strong potential for use as a wood adhesive, but also that the use of plant proteins in the area of wood adhesives is still in an initial state.

Acknowledgement

We would like to thank Tereos® for providing the wheat protein Amygluten®. Support from the COST Action FP1407 “ModWoodLife” project (Understanding wood modification through an integrated scientific and environmental impact approach), is gratefully acknowledged.

References

1. Yang I, Kuo M, Myers D, Pu A. Comparison of protein-based adhesive resins for wood composites. *Journal of Wood Science*. 2006;52:503-8.
2. Frihart CR, Birkeland MJ. Soy properties and soy wood adhesives. In: Brentin RP, editor. *ACS Symposium series 1178: Soy-based chemicals and materials*. New York, NY: Oxford University Press; 2014. p. 167-92.
3. Krug D, Tobisch S. Einsatz von Proteinen als Bindemittel für Holzwerkstoffe. *European Journal of Wood and Wood Products*. 2010;68:289-301.

4. D'Amico S, Müller U, Berghofer E. Effect of hydrolysis and denaturation of wheat gluten on adhesive bond strength of wood joints. *Journal of Applied Polymer Science*. 2013;129:2429-34.
5. Van Der Borcht A, Goesaert H, Veraverbeke WS, Delcour JA. Fractionation of wheat and wheat flour into starch and gluten: overview of the main processes and the factors involved. *Journal of Cereal Science*. 2005;41:221-37.
6. Nordqvist P, Nordgren N, Khabbaz F, Malmström E. Plant proteins as wood adhesives: Bonding performance at the macro- and nanoscale. *Industrial Crops and Products*. 2013;44:246-52.
7. Horvat D, Kurtanjek Ž, Drezner G, Šimić G, Magdić D. Effect of HMM glutenin subunits on wheat quality attributes. *Food Technology and Biotechnology*. 2009;47:253-9.
8. Dill KA, Bromberg S, Yue K, Fiebig KM, Yee DP, Thomas PD, Chan HS. Principles of protein folding - a perspective from simple exact models. *Protein Science: A Publication Of The Protein Society*. 1995;4:561-602.
9. Tanford C. Protein denaturation. In: C.B. Anfinsen MLAJTE, Frederic MR, editors. *Advances in protein chemistry*. Volume 23. San Diego, CA: Academic Press; 1968. p. 121-282.
10. Privalov PL. Cold denaturation of protein. *Critical Reviews in Biochemistry and Molecular Biology*. 1990;25:281-306.
11. Ben-Naim A. Theory of cold denaturation of proteins. *Advances in Biological Chemistry*. 2013;3:29-39.
12. Ben-Naim A. The rise and fall of the hydrophobic effect in protein folding and protein-protein association, and molecular recognition. *Open Journal of Biophysics*. 2011;1:1-7.
13. Sanfelice D, Temussi PA. Cold denaturation as a tool to measure protein stability. *Biophysical Chemistry*. 2016;208:4-8.
14. CEN. EN 205:2003 Adhesives - Wood adhesives for non-structural applications - Determination of tensile shear strength of lap joints. Brussels, Belgium: CEN, 2003.
15. CEN. EN 204:2001 Classification of thermoplastic wood adhesives for non-structural applications. Brussels, Belgium: CEN, 2001.
16. Khosravi S, Khabbaz F, Nordqvist P, Johansson M. Protein-based adhesives for particleboards. *Industrial Crops and Products*. 2010;32:275-83.
17. Nordqvist P. Exploring the wood adhesive performance of wheat gluten. Stockholm, Sweden: 2012.
18. Frihart CR. Wood adhesion and adhesives. In: Rowell RM, editor. *Handbook of wood chemistry and wood composites*. Second Edition. Boca Raton, FL: Taylor & Francis; 2013. p. 255-319.
19. Metzger MT. Naturnahe Bindemittel aus nachwachsenden Rohstoffen auf Proteinbasis zur Herstellung von Holzwerkstoffen. München, Germany: Technische Universität München; 2007.

Table 1. Tensile shear-bond strength results for specimens glued with vital gluten adhesive (Nos. 1 to 16) or PVAc adhesive (Ref₁ and Ref₂) at different preparation and application temperatures, conditioned according to EN 204, and the mean shear-bond strength (standard deviation) and wood failure of specimens tested according to EN 205.

Series No.	Number of specimens	Temperature of the adhesive [°C]	Temperature of the veneer [°C]	Type of conditioning	Shear-bond strength [N/mm ²]	Wood failure [%]
1	10	0	-10	D1	12.5 (1.4)	50
2	10	20	-10	D1	12.4 (1.1)	75
3	10	0	20	D1	11.1 (1.4)	75
4	10	20	20	D1	12.4 (1.3)	0
5	10	0	60	D1	12.1 (1.5)	25
6	10	20	60	D1	11.5 (1.1)	0
7	10	0	100	D1	12.8 (0.9)	25
8	10	20	100	D1	12.2 (1.7)	25
Ref ₁	10	20	20	D1	14.8 (1.2)	50
9	10	0	-10	D2	8.2 (1.8)	25
10	10	20	-10	D2	10.2 (2.1)	25
11	10	0	20	D2	9.5 (2.1)	25
12	10	20	20	D2	9.0 (1.9)	0
13	10	0	60	D2	8.3 (2.5)	0
14	10	20	60	D2	5.8 (2.1)	0
15	10	0	100	D2	6.9 (2.2)	25
16	10	20	100	D2	5.7 (2.0)	25
Ref ₂	10	20	20	D2	13.3 (2.0)	50

Table 2. Statistical analysis of the significance of the effect on the tensile shear-bond strength of the type of conditioning (D1 and D2), the preparation temperature (0°C and 20°C) and the application temperature (>40°C and <40°C).

Tested series No.	Independent variable	Sample size	Means	Standard deviations
1 – 8 (class. D1)	Preparation temperature	4/4	12.11/12.11	0.72/0.40
	Application temperature	4/4	8.25/7.66	1.06/2.26
9 – 16 (class. D2)	Preparation temperature	4/4	12.08/12.14	0.65/0.51
	Application temperature	4/4	9.22/6.69	0.84/1.22

265

266 Figure 1. Wheat protein (vital gluten) in its natural form as a white-greyish powder.

267

$l_1 = 150 \pm 5$ mm total length of specimen

$b = 20.0 \pm 0.2$ mm width of specimen

$l_2 = 10.0 \pm 0.2$ mm length of overlap
(length of tested bond line)

$s = 5.0 \pm 0.1$ mm thickness of the veneer

268

269 Figure 2. Specimen for tensile shear-bond strength test according to the standard EN

270 205 [14].

271

272

273 Figure 3. Box-and-whiskers plot showing the means (red lines) and the upper and lower
 274 quartiles (vertical dashed lines) of the shear-bond strength of specimens glued with vital
 275 gluten adhesive (Nos. 1 to 16) or PVAc adhesive (Ref₁ and Ref₂). Horizontal green
 276 dashed lines show the values of the D1 and D2 classifications required by standard.