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WHEAT PROTEIN AS ADHESIVE FOR WOOD PRODUCTS FOR INTERIOR USE

Johann TRISCHLER
Linnæus University, Forestry and Wood Technology,
SE-351 95 VÄXJÖ, Sweden
E-mail: johann.trischler@lnu.se

Dick SANDBERG
Luleå University of Technology, Wood Science and Engineering,
SE-931 87 SKELLEFTEÅ, Sweden
E-mail: dick.sandberg@ltu.se

Abstract

Protein is one of the most researched and widely used natural adhesives. Before the break through of synthetic adhesives in the wood industry, proteins were commonly used in furniture production. Today, proteins in the form of industrial by-products e.g. soy protein, blood and wheat protein are on the market, and these proteins can in general be used as a base for wood-products adhesives. Proteins are in general denatured by a change in pH, heat or organic solvents before they can be used as adhesives. In this study, a cold-dissolution of wheat protein (gluten) was tested with regard to its usability for the production of particleboards and laminated veneer products. The bonding was evaluated by testing the internal bond strength, thickness swelling, tensile strength and tensile shear strength. The results showed that the strength of the bond-line was in some cases as high as the strength of the wood material, but also that there were in some cases problems with the penetration of the adhesive into the wood and this lowered the bond-line strength considerably. The main conclusion is that cold-dissolved gluten adhesives are a good alternative to commercial synthetic adhesives for interior use, but that there are still challenges with the poor moisture resistance of the adhesive.

Key words: *cold-dissolution; laminated veneer products; mechanical strength; particleboard; vital gluten.*

INTRODUCTION

Animal- and vegetable-based proteins can be used as adhesives for wood products. Proteins from soy beans and blends consisting of animal proteins such as blood and casein were traditionally used in plywood production until the 1960s before the petrochemical adhesives were developed (Lambuth 1994; Frihart 2005; Lambuth 2006). Especially the lower price and better water resistance favoured synthetic adhesives like PF (phenol-formaldehyde) (Frihart 2005). In recent years, proteins from mussels-feet, gecko food pads and marine bacteria as well as mixtures of them are of high interest for research because of their proper water-resistance, and also because they are the most well-known proteins with the strongest adhesive forces (Müller et al. 2007; Wilker 2010). The animal-based adhesives include all kinds of gelatine derived from by-products of the meat and tanning industries (Anon 1955) such as collagen extracted from animal bones and hides, blood, fish skins and also casein from milk (Rowell 2012). Collagen is the basic constituent of animal and fish skin and can be associated with other proteins and reduced to gelatine by hydrolysis (Hull and Bangert 1952).

Proteins are polymers consisting of at least 20 amino-acid monomers with side groups carrying a variety of functional groups (Frihart 2010). The structure of the proteins as well as the order and presence of amino acids in the polypeptide chains determine the physical and chemical properties of the proteins (Rowell 2012). The different amino acids are characterized by at least one carboxyl group (-COOH, acid) and an amino group ($-NH_2$, alkaline) each, and this makes them ampholyte. This generally means that the pH-value can be neglected when handling proteins and makes it possible to combine them with a wide range of additives (Müller et al. 2007).

Gluten is a complex mixture of proteins containing monomers (gliadins) and disulphide-cross-linked polypeptides. Its hydrophobic nature makes it insoluble in water even when water-soluble proteins are trapped in the folded gluten matrix. In spite of its hydrophobic nature, gluten absorbs approximately twice its dry weight of water and forms a hydrated visco-elastic mass (Day et al. 2006). The lack of solubility is affected by the non-polar side chains of the amino acids which have both polar and non-polar side chains (Singh and MacRitchie 2001). The electrostatic and ionic interactions which may occur between the different charged amino acids are important for stabilising the structure and functions of proteins and are strongly influenced by the pH-value and environment (Kinsella 1982).

Further, insolubility is due not to an unfavourable enthalpic interaction but to a negative entropy change. For amorphous polymers such as gluten, solubility requires that the solute disperses molecularly with a decrease in free energy of the system. With increasing weight of the polymer, and glutenins are the largest protein molecules in nature, the solubility decreases as the frequency of charged groups decreases, leading to lower entropy of mixing, which means that the insolubility id due to a lack of ionisable groups and the high molecular weight (Singh and MacRitchie 2001).

Hydrophobic interactions are entropy driven leading to the repulsion of non-polar groups, which thermodynamically interact unfavourably with water (Kinsella 1982). When a molecule is dissolved in water, the surrounding water molecules re-orientate and form a more ordered hydrogen-bonding arrangement (Singh and MacRitchie 2001). This disordering of the water structure is connected with large entropy. In the vicinity of non-polar groups, water is forced into a more ordered hydrogen-bond cage-like arrangement having a negative entropy effect. A decrease in temperature also weakens the hydrophobic interactions because the water is more hydrogen-bonded and structured and it becomes more difficult for proteins to fold the non-polar groups into their hydrophobic interior. The weakened hydrophobic interactions allow the cold-dissociation of some proteins (Kinsella 1982).

Before proteins can be used as adhesives denaturation is necessary. Denaturation, which is achieved by heat, acid/alkali, organic solvents, detergents, or urea (Sun and Bian 1999; Huang and Sun 2000; Wang et al. 2005; Wang et al. 2008; Lei et al. 2010; Nordqvist et al. 2010; Van Herwijnen et al. 2010) is an unfolding process which exposes more polar groups for solubilisation and bonding via hydrogen bonds (Rowell 2012).

Denatured proteins can have different structures (Frihart 2010): a quaternary state – native structure; a tertiary state – individual polypeptides in native folded structure; a secondary state – long range expansion of the native folded structure; or a primary state – polymer chain after disruption of α-helices and β-sheets. For soy protein, the best adhesion is achieved between the tertiary and secondary state, when the tertiary structure is opened into short-range and then long-range expansion, leaving the secondary structure intact (Frihart 2010). Besides the formulation of the dispersion, the method of application also influences the bond strength (Khosravi et al. 2011). When wheat gluten was used as matrix in natural fibre-reinforced composites, it was shown that the influence of the process temperature on the mechanical properties decreased with increasing fibre content (Kunanopparat et al. 2008).

Due to their low price, easy handling and opportunity for modification, proteins from wheat gluten and soy flour are favoured for use as wood adhesive (Liu and Li 2004; Wescott et al. 2006). Wheat protein, which consists mainly of alcohol-soluble gliadins and acid- or alkaline-soluble glutenins has a more hydrophobic character than soy protein which consists mainly of water-soluble albumins and salt-solution-soluble globulins (Nordqvist et al. 2010). Approved binding and water-resistance properties of wheat gluten and soy flour can be achieved by enzymatic treatment (Schmitz Jr. 2009; Nordqvist et al. 2012). The simplest way to increase the water resistance of a protein adhesive is by using admixtures with synthetic resins such as PF (phenol-formaldehyde) or MUF (melamine-urea-formaldehyde) (Wescott et al. 2006; Lin et al. 2012) which, according to literature, is also the only way protein adhesives can economically compete with the synthetic resins (Krug and Tobisch 2010).

OBJECTIVE

The purpose of this study was to investigate the bonding properties of a new adhesive formulation based on cold-dissolved wheat protein (vital gluten).

MATERIAL AND METHODS

Adhesive System

Vital gluten (Amygluten 110), obtained by physical extraction from wheat, was used. It is a fine, slightly yellowish powder with a protein content of 76.75%/ds and is insoluble in water. Three different adhesive systems based on the vital gluten were tested, Fig. 1:

No. 1: vital gluten in its original powder form,
No. 2: vital gluten in liquid form mixed with ice-water to achieve cold-dissolution, and
No. 3: vital gluten as a foam produced by beating the cold-solution.

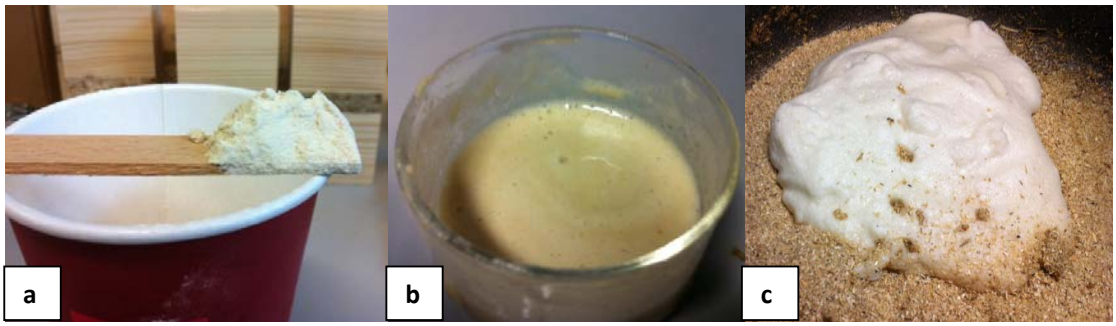

Fig. 1.
The tested adhesive systems based on vital gluten (Amygluten 110): a) in its natural form, b) in liquid form, and c) as foam

Test of the Bonding Properties

The bonding properties of the adhesive systems were tested according to:

- internal bond strength (CEN 1993b) and thickness swelling (CEN 1993a) of a particleboard,
- tensile strength of the bond-line between solid wood, and
- shear strength (CEN 2003a) of the bond-line between veneers.

Internal Bond Strength and Thickness Swelling

The adhesive systems 1 and 2 were successfully applied to particleboards but the adhesion system 3 led to problems in mixing particles with the gluten foam. The adhesion system 2 was tested on wood particles with a temperature of 20°C, and on cooled particles with a temperature of -10°C. The amount of vital gluten for all the boards was 10% based on the weight of wood particles with a moisture content of 5.8%. The wood particles were a mixture of Norway spruce (80%) and Scots pine (20%). The target density of the boards was 400 to 600kg/m^3 and was determined after pressing. The temperature of the press plates were 140 or 200°C. Pressing times were based on the change in temperature during pressing and the evaporation of water, and was between 8 and 21 seconds per millimetre thickness. After pressing, samples of 50x50mm in size were cut and conditioned at 20°C and 40% RH (relative humidity) for two weeks before testing with regard to internal bond strength (IB). Thickness swelling (vol%) in water at a temperature of 20°C was determined during a time of 1-72 hours.

Tensile Strength

To determine the tensile strength of the bond-line, wooden cubes of Norway spruce, Scots pine and black poplar were glued together. The adhesive systems 2 and 3 were successfully applied, but the moisture content of the wood was too low for successful gluing of the wood samples using adhesive system 1. The adhesive were mixed with food colouring (Dr. Oetker's gel food colour, sky blue) to give a contrast between adhesive and the wood surface after breakage. The wood surfaces were cooled to a temperature of -10°C before application of the adhesive. After application of the adhesive, the wooden parts were pressed together and cured at 20°C for 24 hours or for 4 hours at 60°C or at 100°C. Thereafter, samples of 50x50mm in size were prepared and the area around the bond-line was reduced to 25x25mm to increase the probability that rupture occurs in the bond-line. The tensile strength was determined after the cubes had been conditioned at 20°C and 40% RH for two weeks.

Tensile Shear Strength

To determine the tensile shear strength, six mm thick veneers of beech were glued together flatwise (overlapping) with parallel fibre orientations. As in the tensile strength test, the moisture content of the wood was too low to achieve proper adhesion with adhesive system 1. The adhesive systems 2 and 3 was partly mixed with food colouring (Dr. Oetker's gel food colour, sky blue) to give a contrast between the adhesive and the wood surface after breakage. The veneers were cooled to a surface temperature of -10°C before application of the adhesive. The overlapping area between the veneers was 20x20mm^2. The veneers were pressed together and cured at 20°C for 24 hours or for 4 hours at 100°C. Samples of 20x220mm in size were prepared and shaped to give a reduced width (10mm) around the bond-line. Hence, shear was tested on an area of 20x10mm^2. The samples were conditioned for two weeks at 20°C and 40% RH before testing.

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RESULTS AND DISCUSSION

Fig. 2 shows vital gluten cold-dissolved in water and its denaturation after raising the temperature of the solvent. The denaturation leads to agglutination of the dissolved gluten. In this state, gluten is not soluble in water. After separation from the water, the denatured gluten still shows good bonding between gluten molecules. The curing of the gluten-based adhesive used in this study was achieved by evaporation of the water.

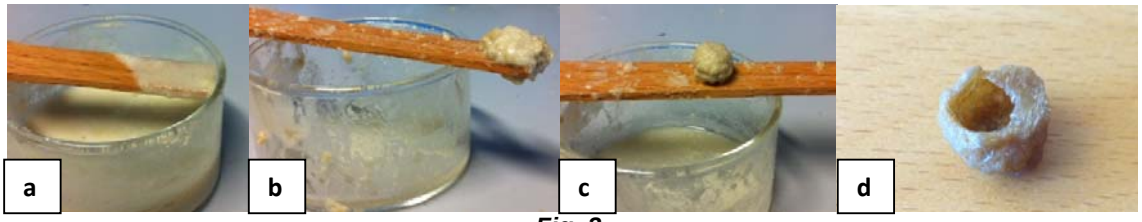

Fig. 2.

Vital gluten: a) dissolved in ice-water, b) jelly mass of denatured gluten after increasing the temperature of the water/solvent, c) visco-elasic ball formed from denatured gluten by compacting the jelly mass, d) cured gluten-ball after drying out, showing a hole after the loss of the large amounts of "bonded" water

The tests on particleboards showed that both the IB (internal bond strength) and the thickness swelling decreased when the gluten was denatured during the application process (Table 1). This means that cooling the particles before and during application of the adhesive is favourable for bonding. Comparing the values in Table 1 to the standards, IB for P2 = 0.40 MPa and thickness swelling for P4 = 16% (CEN 2003b), shows that sample 3 performed in the range of the standard.

Table 1

Results from the internal bond strength (IB) and thickness swelling (TS) tests of vital gluten applied as adhesive system 1 and 2 for particleboards. D – density of the boards

Sample No.	Adhesive No.	Temperature (°C)		D (kg/m^3)	IB (MPa)	TS (%)
		Particles	Pressing			
1	1	20	200	544	0.10	14.8
2	2	20	200	551	0.07	21.0
3	2	-10	140	540	0.38	13.0

The results of the long-term watering tests over three days, which were done in addition to the thickness swelling test according to the standard, showed that there is no additional thickness swelling over time, and that gluten restores the form stability when dried but without shrinking to the original thickness, Fig. 3.

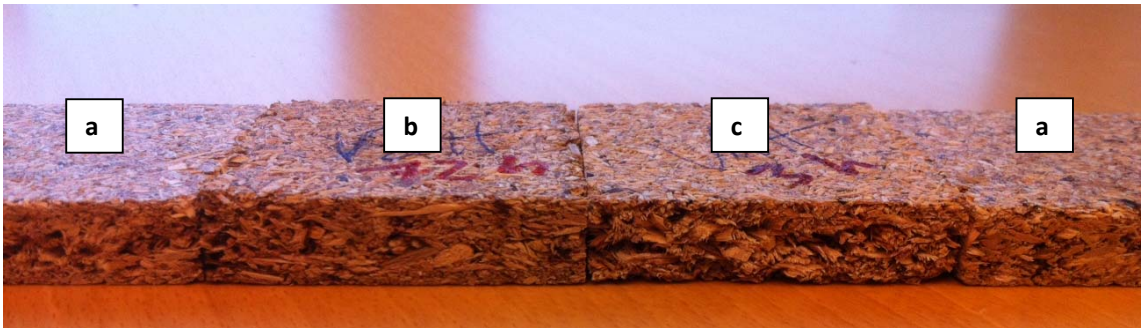

Fig. 3.

Particleboard samples glued with cold-dissolved vital gluten (Table 1, sample 3): a) after pressing, b) after long-term watering for 3 days, and c) after long-term watering for 3 hours. The thickness swelling of b) and c) was 13%vol

Table 2 shows the results of the tensile strength and tensile shear strength tests on solid wood and veneer respectively. The curing temperature seems to have no influence on the bond-line strength, nor does the adhesive system or the wood species (samples 2-4 and 5-7). The lower values of tensile strength for adhesives cured at a high temperature can be due to shrinkage of the wood

during the curing of the adhesive (samples 1 and 2-4). The tensile shear strength of samples cured at 100°C was higher than that of samples cured at 20°C (samples 5 and 6-7).

Table 2

Results of the strength test of vital gluten applied as adhesive systems No. 2 and 3 with different wood products and species, and cured at different temperatures. The surface temperature is the temperature at the wood surface at gluing. SW – solid wood, V - veneer

Sample No.	Type of test	Test material		Adhesive No.	Temperature (°C)		Strength (MPa)
					Surface	Pressing	
1	tensile strength	SW	Pine	2	-10	20	4.72
2	tensile strength	SW	Poplar	2	-10	60	2.27
3	tensile strength	SW	Spruce	2	-10	100	2.97
4	tensile strength	SW	Spruce	3	-10	100	2.61
5	tensile shear strength	V	Beech	2	-10	20	6.78
6	tensile shear strength	V	Beech	2	-10	100	7.63
7	tensile shear strength	V	Beech	3	-10	100	8.47

The solid wood tensile and the veneer tensile shear tests showed in general a combined adhesive-wood failure, Figs. 4 and 5. In Fig. 4, the coloured adhesive system revealed the failure of the bond-line in the surface of the earlywood. The wooden splinters on the bond-line surface and wood failure in Fig. 5 show that the mechanical strength of the bond-line in shear was similar to that of the wood. Nevertheless, the presence of bond-line failure in both tests shows that the adhesives do not penetrate into the wood to any great extent.

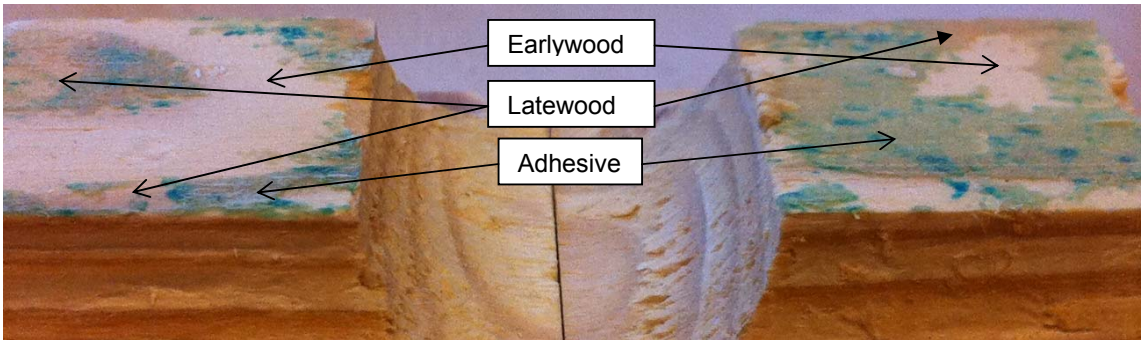

Fig. 4.

Rupture after solid wood tensile test of Scots pine glued with cold-dissolved, vital gluten (blue coloured) (Table 2, sample no. 1). The low penetration of the adhesive led to rupture of fibres of the earlywood

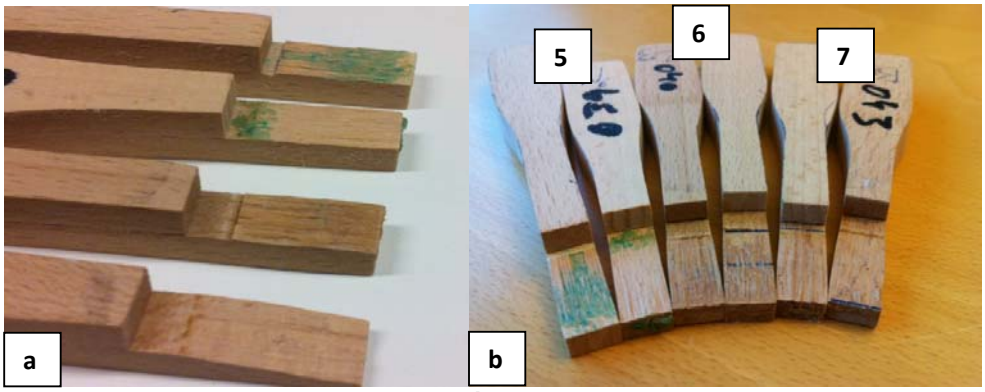

Fig. 5.

Beech samples glued with vital gluten (Table 2, samples 5-7) after tensile shearing tests. a) different types of failure, from wood failure only (bottom) to mostly adhesive failure (top) which illustrate that the strength of the bond-line is in the range of the wood strength, and b) specimens sorted according to curing temperature and type of adhesive system with comparable failure in the bond-line, from the left: 20°C, liquid (sample 5); 100°C, liquid (sample 6); 100°C, foam (sample 7)

The fact that it is possible to blend vital gluten with water without denaturation of the gluten is astonishing. In general, gluten has a hydrophobic character which in our tests it seems can be overcome by cold-dissolution. An explanation can be that cold-dissolution leads to a stronger change in the relation of enthalpy and entropy than when water at a higher temperature is used.

The behaviour of vital gluten during the denaturation means that gluten after denaturation shows strong bonds between the gluten molecules but a weak bond between gluten and wood. Cooling the particles and keeping the adhesive-particle blend cool until pressing gave an IB nearly four times higher than that when the particles were not cooled.

The adhesive systems 2 and 3 did not penetrate into the wood to any great extent. Further, rupture often occurred in the wood surface, especially of the earlywood. Therefore, vital gluten is favourable for particleboard-applications, but a better penetration of adhesive into the wood is necessary for veneer applications. The pressure can influence the veneer tensile shear strength indicated by the differences in strength between samples 6-7 and sample 5 (Table 2) as the samples cured at the higher temperature were fixed in the hydraulic press while the samples cured at 20°C were fixed by ferrules.

When using cold-dissolved vital gluten it is important to ensure that it does not change its behaviour towards water after curing. Although it has a hydrophobic character, gluten absorbs water which increases the visco-elasticity of gluten (even when cured at higher temperature) and this leads to a break in the bond-line as the gluten reverts to a jelly-like mass.

Further research has to be done to find the optimal application technique and temperature for different wood applications. Regulation of the viscosity of the adhesive might help to achieve a proper application process. For that purpose, as well as to increase the penetration into the wood, it is necessary to determine the exact process of cold-dissolution of vital gluten. It seems realistic that the method presented in this study is only the first step towards a bio-based adhesive system based on vital gluten.

CONCLUSIONS

This study presents the results of the first tests using cold-dissolved vital gluten as an adhesive for wood material. Vital gluten (Amygluten 110) was cold-dissolved in water to overcome its hydrophobic character. A strong gluten-to-wood bond was achieved with this adhesive when the wood was cooled to a temperature of -10°C before pressing, as shown by determining the internal bond strength of particleboard, the tensile strength of solid wood and the tensile shear strength of veneers.

The results give the following information: (1) vital gluten can be cold-dissolved in water; (2) the adhesive should be kept cool during application which means that the wooden components should also be cooled; (3) the curing of the adhesive is achieved by evaporation of the water; (4) the species seems to have no influence on the quality of the glue line; (5) there seem to be no influence of the curing temperature on the glue line. Further work is necessary, especially regarding the analysis of the process of dissolution, the penetration behaviour, the application process, and the deterioration of the bond-line over time.

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