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PHENOL - WHEAT PROTEIN - FORMALDEHYDE ADHESIVES FOR WOOD - BASED PANELS

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Abstract:

Phenol-formaldehyde (PF) resins were prepared with a level of 10%, 20% and 30% substitution of the phenol in the resin by three types of wheat gluten protein hydrolysates having different characteristics, namely (i) an enzymatic hydrolysate, (ii) a lower molecular weight enzymatic hydrolysate, and (iii) a middle sized molecular weight acid hydrolysate. The mixed protein-phenolic oligomer species distribution formed in the preparation of these resins were identified by matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry.

Key words: *biobased resins; phenol formaldehyde resins; wheat gluten proteins; wood adhesives.*

INTRODUCTION

Exterior and marine grade particleboard and other panels of the same type for construction use phenol-formaldehyde (PF) binders for their durability, particularly in North America. Although the emission of formaldehyde from PF bonded panels is relatively low reduction of formaldehyde emission and at least a partial substitution of the oil-derived phenol with natural material are still a topic. Literature on both, the reduction of formaldehyde and in particular on the partial substitution of phenol itself with natural materials exists. Partial or total substitution of phenol with condensed tannins (Pizzi 1983), with hydrolysable tannins (Spina *et al.* 2012, 2013), with soy protein hydrolysates (Kaichang *et al.* 2007), or combinations of soy protein or flours with isocyanates (Amaral-Labat *et al.* 2008) have been tried, some with a fair degree of success. Some studies were even conducted on the feasibility to use gluten in wood-panels adhesives (Lei *et al.* 2009, 2010; Krug 2003; Krug *et al.* 2010). It must be kept in mind that just in Europe alone there are more than half a million tons/year of wheat gluten that is extracted from wheat to produce starch and starch derivatives. Main part (75%) of the extracted gluten is added to bakery products in order to fortify wheat flour and a significant amount is used for animal feed (~20%) but there is still a significant potential of use in industrial applications.

OBJECTIVE

This article is the about the feasibility of replacing and capture formaldehyde in wood adhesives by natural components like wheat gluten proteins.

METHOD

Three types of wheat protein hydrolysates having different characteristics have been tested (Fig. 1): (i) *Solpro 508* (enzymatic hydrolysates); (ii) *LMW Protein* (smaller enzymatic hydrolysates), and (iii) *Solpro 050* (middle sized acid hydrolysates).

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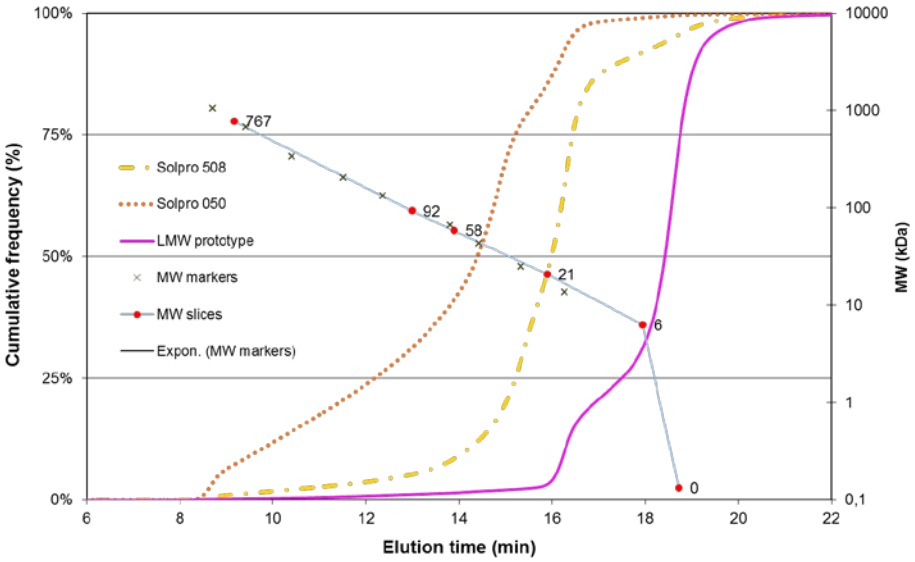


Fig. 1.
Title: Cumulative molecular weight distribution of wheat protein hydrolysates (LMW Protein, Solpro 508 Solpro 050) and calibration curve for the used column set.

All proteins have been provided by Tereos Syral (Marckolsheim, France). Hydrolysates have been prepared by proprietary process in mild process conditions. Wheat proteins are extracted from wheat flour by an aqueous extraction process yielding a concentration in proteins from approximately 10% protein in wheat flour to 75-80% protein in vital wheat gluten. Remaining components are mainly residual starch and lipids. Here wheat gluten has been used as substrate for the hydrolysates, the other proteins present ion wheat (albumins and globulins) are only present in traces.

Wheat protein hydrolysates are a yellow light powder. Solpro 508 and LMW protein have solubility (pH 6.2) of 65%; they have target values of crude protein of 80%, of crude ash of 1% and of crude fat of 6%. Solpro 050 has solubility (pH 6.2) of 65%; they have target values of crude protein of 82%, of crude ash of 4% and of crude fat of 8.5%.

Cumulative molecular weight distribution of wheat protein hydrolysates (LMW Protein, Solpro 508 Solpro 050) and calibration curve are shown in Fig. 1 (The molar mass distribution is shown like in a mirror). These data are obtained by a Size-Exclusion Chromatography (SEC) including size exclusion High Performance Liquid Chromatography (HPLC) analysis (Table 1).

Table 1

Standards used for the SEC-HPLC analysis of wheat protein hydrolysates

Standards	*MW (Da)*
Thyroglobulin	1,050,000
	670
	335
Bovine albumin	204
	132
	66
Ovalbumin	43
Chymotripsinogen A	25
Ribonuclease A	13,7
Blue Dextran = Vo	2,000,000
Asparagine = Vt	132

1.1. Synthesis of phenolic resins and particle boards

1.1.1. Phenol formaldehyde resin

The PF control resin (molar ratio F/P = 1.7) was synthetized as follows: 1 mole of phenol as a 80% phenol, 0.35 mole of sodium hydroxide as a 30% water solution, and 1.7 mole of formaldehyde as a 37% aqueous solution were used according to a preparation procedure already reported earlier (Zhao *et al.* 2000).

The mixture is slowly brought in about 30 minutes to reflux at 94°C under continuous stirring. Once this temperature is reached, the mixture is left to react for 30 minutes.

In a second step, 0.5 mole of formaldehyde is added. The reaction is continued until a viscosity of 500 to 800mPa.s at 25°C is reached. The pH of the resulting resin is approximately 11.

1.1.2. Phenol formaldehyde resin with wheat protein hydrolysates

Three degrees of mass substitution of 80% phenol by the three types of protein hydrolysates are tested: 10, 20, and 30% in mass, based on the same formulation and procedure outlined above. The same amounts of sodium hydroxide and of formaldehyde were added. This type of resin has an original molar ratio F/P = 1.7 (Pizzi *et al.* 2013).

A second type of resin containing proteins was synthesized with protein hydrolysates of low molecular weight (LMW protein), with substitutions rates of 10 and 20%. In this case no second addition of formaldehyde was performed. This type of resin had an original molar ratio F/P = 1.5 (also called type 2 resin).

These mentioned molar ratios only refer to phenol, but in reality amino acids present in amino groups in hydrolysates proteins are capable to react also with the formaldehyde and thus the real molar ratios are even lower.

As the resin was done under alkaline conditions two reactions predominate: (i) the reaction of phenolic ortho and para free sites with the methylol groups on the PF resin and with any free formaldehyde present, and (ii) the initial addition reaction of the formaldehyde both as such, as well as in the form of methylol groups on the PF resin with the amide groups of the protein and with the scarcer amino groups of some amino acids. As the initial addition (not condensation) of formaldehyde with amides in alkaline environment in presence of a PF resin is competitive with the phenol-formaldehyde reaction itself (Pizzi 1994 & Pizzi *et al.* 1993). This leads to the formation of methylene bridges between different sites, namely, phenol top phenol, and phenol to amide group of the protein.

1.1.3. Preparation of particleboards

Triplicate, one layer laboratory particleboards of dimensions 350x300x14mm with target density of 700kg/m^3 were prepared. The panel was sanded in order to have a final thickness of 13mm. The pressing cycle was of 7.5 minutes (first step at 28kg/cm^2 during 3min; second step at 12kg/cm^2 and 2min and last step at 5.8kg/cm^2 and 2.5min). The long press time used is standard in this laboratory as the press cannot give a temperature higher that 180°C against a present factory working temperature of 220°-230°C. Under these conditions we are able to compare different adhesives performance in relation to what would be expected on a factory line. The NF EN 312 standard does not specify length of pressing time, but only IB strength, thus one can compare results to the standard whatever the press time used. Wood chips moisture content before adhesive application was 2.5%. The resin solids content on dry wood was 10%. For each formulation two different types of boards were made: one with the resin alone and another with 7% triacetin on dry weight of resin as an accelerator of PF resin curing (Zhao *et al.* 1999, 2000; Pizzi *et al.* 1994, 1997).

1.2. Test on adhesive resins

1.2.1. pH, viscosity and solid content

The pH was 11 at 20°C.

The end of the condensation reaction was fixed by the viscosity of resin, determined by Brookfield viscometer measurement at 25°C, with a speed of 50rpm.

The solids content of the resins was determined according to the European Norm NF EN ISO 3251 (AFNOR 2008), by drying in an oven at 103°C, until that the mass of residue is stable, generally it takes 1 day.

1.2.2. MALDI-TOF analysis

MALDI-TOF-MS: The spectra were recorded on a AXIMA Performance MALDI instrument (Shimadzu, Manchester, UK). The irradiation source was a pulsed nitrogen laser with a wavelength of 337nm. The length of one laser pulse was 3ns. The measurements were carried out using the following conditions: polarity-

positive, flight path-linear, mass-high (20kV acceleration voltage), 100-150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200-800ns.

MALDI-TOF Sample Preparation: The samples were dissolved in acetone (4mg/mL). The sample solutions were mixed with an acetone solution (10mg/mL acetone) of the matrix. As the matrix 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation NaCl was added to the matrix. The solutions of the sample and the matrix were mixed in equal amounts and 0.5 to 1µL of the resulting solution were placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer.

1.2.3. Thermo Mechanical Analysis (TMA)

TMA (Mettler Toledo TMA 40, Switzerland) was used to perform the analyses. The samples for this test were composed of two pieces of beech veneer (0.5x5x21mm) with an amount of 30mg resin evenly spread on this area (15mg on each piece), they are immediately placed in contact and tested. All resins were tested with and without triacetin.

For TMA, a three-point bending force of 0.1 to 0.5N applied and relaxed with a period of 6s/6s causes periodical deflection of the sample and enables calculation of the modulus of elasticity (MOE) of the joint sample as function of the increasing temperature (ramp 10°C/min).

The maximum of the elasticity modulus is achieved for the maximum of the polymerization temperature; indeed at this temperature all chains are fixed. At this time, the polymerization is over and if the temperature is still increasing, the degradation of the resin begins and there are no further reactions.

1.3. Tests of the prepared lab particleboards

Density profiles of the particleboards samples were determined by X-rays densitometry (Grecon DAX 5000, Germany).

The difference between the density of the panel at its surface and at its core is expressed by using a ratio: (Density at the core of the panel) / (Density at the surface of the panel).

The panels were tested according to NF B51-262 (AFNOR 1972) for two hours boiling water swelling. This test consists in immersing the samples (50x50mm) during two hours in boiling water. After they are placed in an oven at 103°C and dried during 24 hours.

The internal bond strength was measured according to NF EN 319, (AFNOR 1993) with an Instron 4467 (UK) universal testing machine at a rate of 2mm/min.

The tests for subsequent formaldehyde emission are performed according to NF EN 717-3 (Flask method). A calibration curve is made using spectrophotometric analysis of dilution series of formaldehyde solution (whose concentration was determined using an iodometric titration).

Approximately 20 grams of a panel are inserted into the jar, in which there is 50mL distilled water, and then the jar is placed for 180 minutes in an oven at 40°C. The solution obtained is then reacted with a solution of ammonium acetate and a solution of acetylacetone and is then placed in a water bath at 40°C during 15 minutes.

After one hour rest away from light, solutions can be measured using the spectrophotometer. The detected value of absorbance provides the formaldehyde concentration (mg/mL) using the calibration curve and then we can calculate the formaldehyde emission of the panel (mg/100g dry panel). The time between cutting and the test does not exceed 72 hours as specified in the standard.

RESULTS & DISCUSSION

2.1. Test on adhesive resins

2.1.1. pH, viscosity, and solid content

Generally, the viscosities are between 500 and 800mPa.s (Table 2).

The target was to have a viscosity at 25°C, between 500 to 800mPa.s, so all resins don't have exactly the same reaction time, and we cannot do a link between viscosities and types of protein.

The pH values are in the range of 10.3 to 11.7 and are all lower than for the PF control and this even if the amount of NaOH was the same for every prepared resin. It is due to the pH of protein which is around 6 (Table 2).

The high viscosity of solutions of the hydrolysates of gluten proteins at concentrations of 50% where possible or otherwise of 25% in water (Table 3) indicate that (i) the viscosity obtained for PF-protein cocondensates shown in Table 2 are indeed possible, and (ii) that is rather likely that higher molecular weight fractions of the proteins exist in the hydrolysates higher than what determinable by MALDI-TOF spectrometry.

Table2 2

pH, viscosity, and solid content of all PF resins tested

Resins	*pH*	*Viscosity (mPa.s)*	*Solid content (%)*
PF	12.3	695	46.9
PF-10% LMW	10.3	642	45.2
PF-20% LMW	11.2	715	49.5
PF-30% LMW	11.3	850	48.4
PF-10% LMW (Type 2)	11.4	950	49.1
PF-20% LMW (Type 2)	11.1	462	50.6
PF-10% Solpro 508	11.3	850	45.6
PF-20% Solpro 508	11.7	895	45.8
PF-30% Solpro 508	11.4	875	48.0
PF-10% Solpro 050	11.4	550	47.8
PF-20% Solpro 050	11.5	795	48.4

Table 3

Viscosity of all wheat protein hydrolysates tested

Proteins	*Viscosity (mPa.s)*
LMW protein (50% in water)	20,100
Solpro 508 (50% in water)	38,330
Solpro 050 (25% in water)	62,580

Moreover the SEC-HPLC curves in Fig. 1 show that very high molecular weight fractions are present in the hydrolysates. As traces of carbohydrates are not detected in the MALDI-TOF analysis it must be considered that this higher molecular weight fractions are due to protein material too.

The solids are near 50%, as stipulated in the experimental procedure adopted (Zhao *et al.* 2000) (Table 2). As the liquid 80% phenol was replaced by solid hydrolysates protein, the higher the substitution of phenol with the protein hydrolysate, the higher the solid contents are, except in the case of the resin with LMW protein with an original molar ratio F/P =1.7). At low replacement rate the solid contents are partly still lower than the PF control, as in the case for the LMW and the Solpro 508. Maybe in the other cases, some reaction takes place during the determination of the solid content and yield to the formation of water which then also is evaporated so solids contents are higher.

2.1.2. MALDI-TOF analysis

Three formulations were tested: PF- (10% and 20%) Solpro 050 and PF-20% LMW (type 2).

According to the literature (Finney *et al.* 1982 & Belderok *et al.* 2000) gluten is the main component in wheat protein and the main amino acids in gluten are at 31.9%: Glutamine (MW 146.2), at 14.1%: Proline (MW 115.1), at 7.2%: Leucine (MW 131.2), at 5.7%: Serine (MW 105.1) and at 5.4%: Glycine (MW 75,1) (Rombouts *et al.* 2009).

As we are dealing with gluten protein hydrolysates, thus with heavily modified materials, it was necessary to control their composition relative to gluten itself as shown in the literature. For this reason MALDI-TOF mass spectrometry was used to determine the composition of the materials we used.

In reality there is a variation of composition between the gluten hydrolysates we have used and the relative amino acids distribution in gluten itself. Thus, while in our materials the amino acids Glutamine, Proline, Leucine, Serine and Glycine predominate in gluten itself (Rombouts *et al.* 2009) the distribution is rather Glutamine, Leucine, Phenylalanine, Tyrosine, and Alanine.

As control PF resins were synthesized by basic catalysis as polycondensation of phenol and formaldehyde. Phenol units are linked in order to form a polymer via methylene bridges. Each ortho or para position of phenolic rings may react with formaldehyde (Schrod *et al*. 2003). It is not possible to determine from MALDI-TOF analysis the predominance of ortho-ortho, ortho-para or para-para linkages. In reality classical phenol-formaldehyde reaction theory indicates that while the reactivity of the para sites is slightly

higher than the ortho one, the presence of two ortho sites and only one para site give distribution that are often not very different (Megson 1958).

Reactions between phenol and formaldehyde give -CH_2; -CH_2^+, or -CH_2OH attached to phenol.

The focus in the paper here is on the reactions of the amino acids present in the protein hydrolysates with formaldehyde or with already formed PF groups during the resin preparation. Fig. 2 shows as one example the MALDI-TOF spectrum of the PF resin modified with 20% LMW and without second addition of formaldehyde (type 2 reaction).

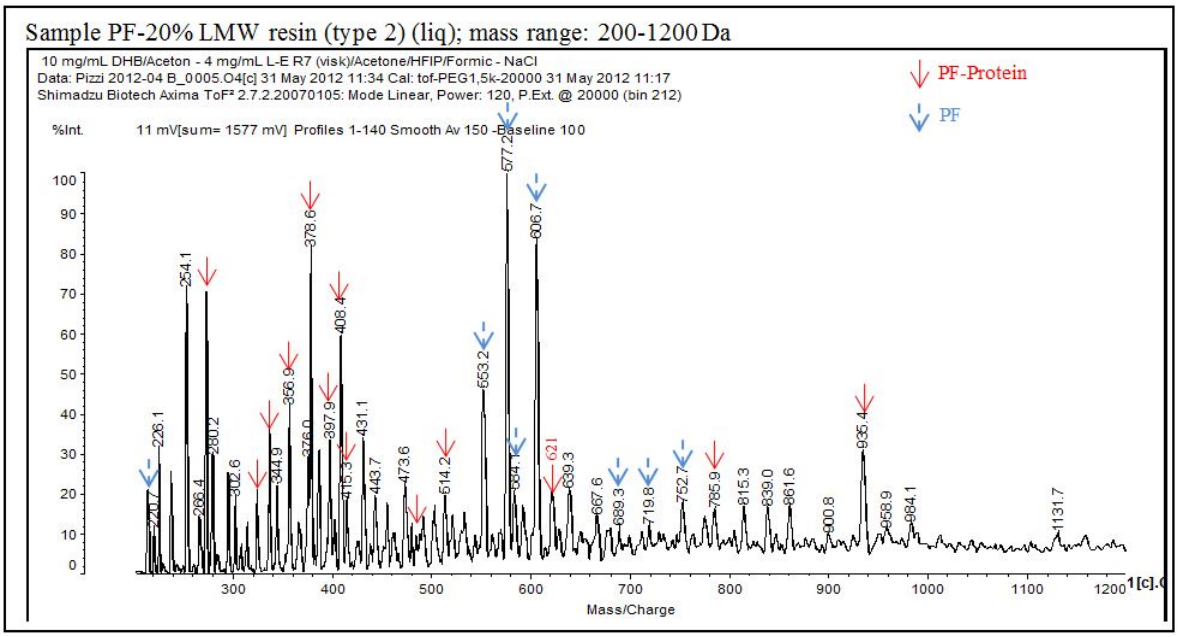


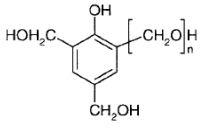
Fig. 2.
MALDI-TOF spectrum of the liquid resin PF-20% LMW (type 2) for a range from 200 to 1200 Da.

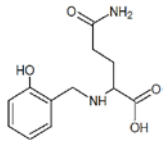
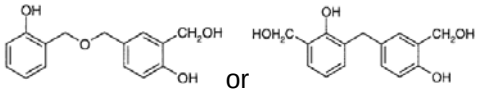
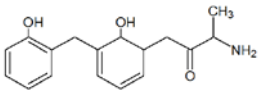
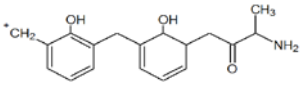
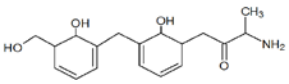
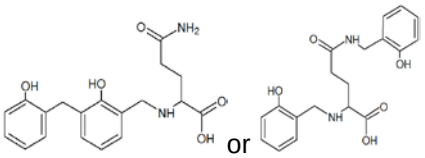
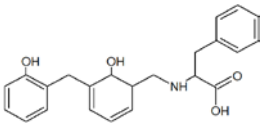
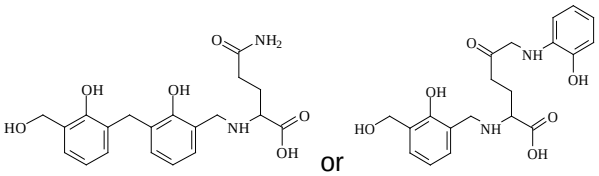
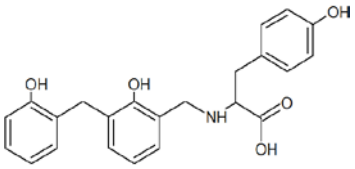
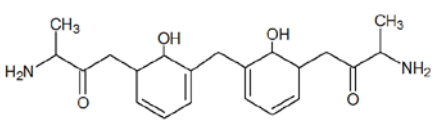
Peaks representing the reactions which involve various PF resin groups and protein hydrolysates are marked with arrows in solid lines. Peaks only resulting from the reaction between phenol and formaldehyde are indicated by dotted arrows. We can assume that there are reaction between PF resin groups and the amino acids of the protein, because as it was found previously, PF resin spectrum give peaks until 800Da and here it is quite the same range but with a number of peaks more important (Lagel *et al.* 2014).

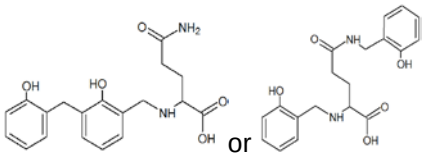
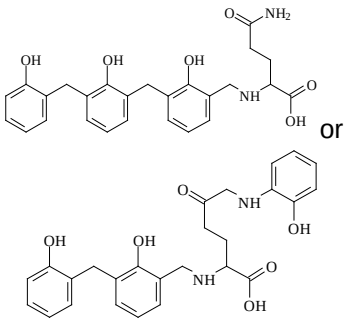
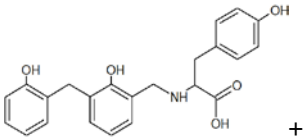
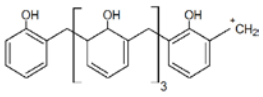
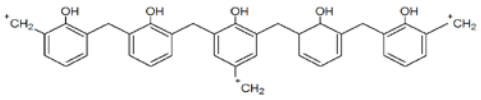
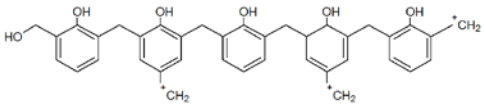
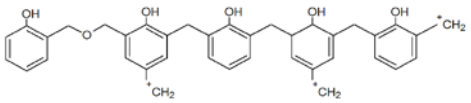
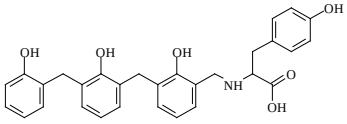
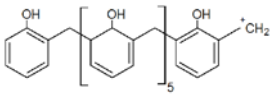
Table 4 summarizes the molecules which can be assigned to the various molecular weights according the reactions between (i) phenol and formaldehyde as well as (ii) between the amino acids of the protein and PF resin groups. It was calculating by adding the molecular weight of amino acid with PF resin groups and the molecular weight of Na. The possibility that amino group of the amino acids reacts directly with formaldehyde is excluded in this study because the spectra always begin solely at 200Da.

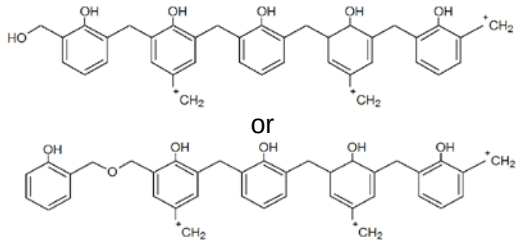
Table 4

Peaks corresponding (i) to PF resin groups with different molecular weight and (ii) to structures resulting from reactions between PF resin groups and key amino acids of gluten in PF-20% LMW resin (type 2, without second formaldehyde addition)

Molecular weight with Na^+ (Da)	*Theoretical molecular weight with Na^+ (Da)*	*Molecules*	*Amino acid*
238.4	237	 n=2	PF resin group

274.2	274		Glutamine
284.7	283	 or	PF resin group
324.5	324		Alanine
336.6	336		Alanine
356.9	356		Alanine
378.6	379	 or	Glutamine
397.9	398		Phenylalanine
408.4	408	 or	Glutamine
415.3	414		Tyrosine
425.6	425		Alanine

480.1	480	 or + -CH_2-alanine	Alanine and glutamine
485	485	 or	Glutamine
514.2	515	 + -CH_2-alanine	Alanine and tyrosine
553.2	553		PF resin group
577.2	577		PF resin group
606.7	606	 or 	PF resin group
621	621	 + -CH_2-alanine	Alanine and tyrosine
752.7	754		PF resin group

785.9	786	 or + Tyrosine attached to the -CH_2	Tyrosine
935.4	934	786 + Glutamine attached to -CH_2	Tyrosine and glutamine

The results in the Tables 4 and 5 shows, that glutamine is the amino acid most implicated in reactions with phenol and formaldehyde, leading to molecular weights of 379, 274, and 408Da in order of predominance. It could be explain be the fact that this amino acid is more reactive due to the presence of two amino groups, indeed the others amino acids contain only one amino group.

Because of the important number of peaks, this analysis is focused on the resin containing LMW protein hydrolysates (protein hydrolysates of smaller size relative to the others). So there is an important number of different created molecules and this even if molecular weights of the created molecules are quite the same (go until 1132Da) than protein hydrolysates Solpro 050 where the last molecule is at 1047Da in our range of analysis. So we cannot see an influence of the molecular weight of the hydrolysates on the speed of the reaction with phenol and formaldehyde. We can presume that if for the analysis of the resin with protein hydrolysates Solpro 050 we do not see a lot of peaks, it is because amino acids reacted with PF resin groups have rushed and it would be for this reason they do not appear in spectra. And so there are not so much different molecules that have been created during the reaction. Analyses of dry samples do not provide additional information.

Table 5 summarizes the main reactions between PF resin groups and key amino acids of gluten in the three formulations which were analyzed by MALDI-TOF.

Table 5

Peaks corresponding to the molecular weight of main reactions between phenol and formaldehyde as well as the amino acids alanine, glutamine, and tyrosine

		PF-20% LMW (type 2)		***PF-10% Solpro 050***		***PF-20% Solpro 050***	
Theoretical molecular weight with Na^+ (Da)	*Amino acid involved*	*Molecular weight with Na^+ (Da)*	*Peak intensity (%)*	*Molecular weight with Na^+ (Da)*	*Peak intensity (%)*	*Molecular weight with Na^+ (Da)*	*Peak intensity (%)*
274	Glutamine	274.2	71	273.1	4	272.3	1
324	Alanine	324.5	22	325.3	4	326.1	4
336	Alanine	336.6	36	/	/	336.2	2
356	Alanine	356.9	42	/	/	357.2	1
379	Glutamine	378.6	82	378.2	2	378.6	30
408	Glutamine	408.4	60	407.5	4	408.6	100
480	Alanine and glutamine	480.1	13	/	/	480.3	3
786	Tyrosine	785.9	17	/	/	786.0	4

The peaks intensities are given in relation to the most important peak of each spectrum for each tested resin. In PF-20% LMW (type 2) resin the peak at 379Da is the most intense one at 82%; in contrast in the PF-10% Solpro 050 resin this peak only shows a very low intensity of 4%, which is the lowest one. The highest peak is at 577 Da and corresponds to a PF resin group alone.

In the PF-20% Solpro 050 resin the most important peak (associated with 100% intensity) occurs at 408 Da involving glutamine. Also the peak with the second highest intensity at 379Da involved glutamine.

Evaluating all three spectra the most important reactions yield the peaks at 379 and 408 Da involving glutamine.

In MALDI-TOF experiences the methylene linkages between the phenols of the PF resin are stable (Schrod *et al.* 2003 & Pizzi *et al.* 2004), thus one does not experience decomposition or rearrangements on this part of the product. However, some instability may exist in the case of the methylene linkages between the PF resin and amino groups, and between amino groups (Despres *et al.* 2007) hence of the protein. In effect some rearrangements of the protein hydrolysates might occur, as indeed shown by the peaks at 274, 291, and 471Da (in order of predominance) (Fig. 3 & Table 6).

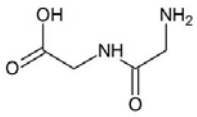
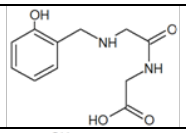
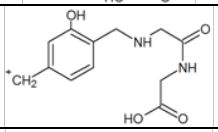
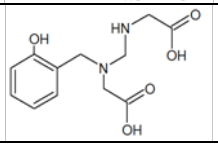
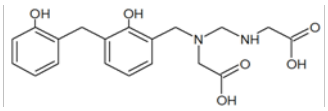
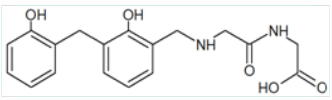
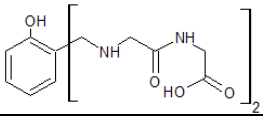
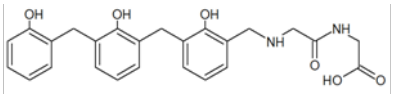


Fig. 3.
Title: Two glycines (MW 132).

Table 6

Reactions between glycines and PF resin groups as well as formaldehyde in PF-20% LMW (type 2) resin

Molecular weight with Na^+ (Da)	*Theoretical molecular weight with Na^+ (Da)*	*Molecules*
262	261	
274.2	274	
293.9	291	
308.5	309	
366.5	366	
402.6	404	
473.6	471	

2.1.3. Thermo Mechanical Analysis (TMA)

Concerning the resins containing 20% of LMW (Type 2) and 20% Solpro 050, the use of triacetin had a positive effect on the properties. A diminution of the maximum temperature of polymerization and also an augmentation of the maximum of elasticity modulus are notice (Table 7).

Table 7

Thermo mechanical analysis results tests

	Temperature (°C)		*Elasticity modulus (MPa)*	
Formulation	Without triacetin	With triacetin	Without triacetin	With triacetin
PF	165	151	3752	4267
PF-10% LMW	154	159	5029	5219
PF-20% LMW	153	156	6519	5891
PF-30% LMW	163	168	7183	8476
PF-10% LMW (Type 2)	164	157	5254	4899
PF-20% LMW (Type 2)	165	161	5809	9920
PF-10% Solpro 508	158	145	5364	3732
PF-20% Solpro 508	152	171	4981	5469
PF-30% Solpro 508	154	171	5637	6710
PF-10% Solpro 050	160	162	5779	10253
PF-20% Solpro 050	157	146	4823	7507

In comparison to PF resin, without triacetin, PF-hydrolysates proteins have lower maximum temperature of polymerization and have higher elasticity modulus. With triacetin, PF-hydrolysates proteins have higher maximum temperature of polymerization (except for PF-10% Solpro 508 & PF-20% Solpro 050) but they have higher elasticity modulus (except for PF-10% Solpro 508) in comparison to PF resin.

Looking at the elasticity modulus for the same substitution rate, the best performing protein hydrolysates are summarized in Table 8.

For a substitution rate of 10%, the best protein is Solpro 050, because the elasticity modulus is about twice with triacetin. And for substitution rates of 20 and 30%, the best protein is LMW, because with triacetin they have the highest elasticity modulus.

By correlating the results of thermo mechanical analysis and those of internal bond, the protein hydrolysates Solpro 050 gave satisfying internal bond and improved modulus of elasticity in the case of addition of triacetin. Indeed, it is the only one which for both substitution rates, the internal bond is improved.

2.1. Tests on particle boards

Despite of the panel's thickness after press and after sanding, there is a little variation in density between different samples. As the distribution of particles in the mold was made manually, it can lead to some difference in the final panel. Tests were done on samples having the densities the closest to the target density of 700kg/m^3.

2.1.1. Density profile

The surface density of the boards is greater than at its center as measured by X-rays density profiler (Table 8), which is explain by the fact that surfaces are directly in contact with heat source and the surface is like glossy. The higher the density ratio is, the closer the densities of the surfaces and the center of the panel are.

Generally, panels containing protein hydrolysates have density ratios that are higher than panels done with PF resin. The use of protein hydrolysates appears to allow for a better heat diffusion, this being the case with and without triacetin. The protein hydrolysates which gave panels of higher density ratios are those for which the hydrolysate had been prepared by enzymatic hydrolysis (LMW and Solpro 508). As regards the density profile ratio this is acceptable for laboratory panels for which the conditions are rather different than in a plant or a pilot plant.

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Table 8

Identification of best formulations

Formulation	Density ratio		Dry swelling after water immersion (%)		Elasticity modulus (MPa)		Before swelling				After swelling				Formaldehyde emission (mg/100g dry panel)	Total score for best substitutions	Total score for best hydrolysates
							Density (kg/m³)		Internal bond (N/mm²)		Density (kg/m³)		Internal bond (N/mm²)				
	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin			
PF	0.69	0.70	8.3	6.5	3752	4267	705	701	0.58	1.01	671	715	0.18	0.59	With triacetin	/	/
PF-10% LMW	0.73	0.73	19.3	7.0	5029	5219	680	711	0.26	0.94	663	708	0.01	0.27	4.32	3	4
PF-20% LMW	0.71	0.72	14.8	6.8	6519	5891	599	707	0.23	0.60	600	625	0.01	0.17	6.10	1	
PF-30% LMW	0.69	0.76	25.2	8.4	7183	8476	702	707	0.24	0.34	678	702	Break	0.19	4.90	2	
PF-10% LMW (Type 2)	0.71	0.73	18.3	4.5	5254	4899	594	598	0.28	0.60	589	594	Break	0.21	3.74	2	4
PF-20% LMW (Type 2)	0.73	0.78	Break	5.2	5809	9920	573	607	0.09	0.52	591	608	Break	0.22	4.52	2	
PF-10% Solpro 508	0.74	0.77	23.4	14.0	5364	3732	691	692	0.29	0.51	672	678	Break	0.03	6.01	1	1
PF-20% Solpro 508	0.73	0.73	25.8	14.9	4981	5469	679	689	0.31	0.46	652	655	Break	0.03	5.25	1	
PF-30% Solpro 508	0.72	0.72	31.3	15.0	5637	6710	682	676	0.18	0.56	664	607	0.04	0.06	4.62	0	
PF-10% Solpro 050	0.70	0.74	8.9	5.1	5779	10253	614	647	0.31	0.68	607	623	0.06	0.36	7.12	4	5
PF-20% Solpro 050	0.70	0.70	9.8	4.6	4823	7507	701	6942	0.68	0.86	697	689	0.17	0.50	2.11	3	

2.1.1. Swelling and internal bond tests

The standard NF EN 312 requires for a 13mm non construction purpose panel in P3 quality a maximum thickness swelling after 24h of 14%. However this value is given to a panel made of industry which has three layers, with the density substantially greater in the face layers than in the core layer.

The panels used in this project are monolayers. Thus, as the densities of the different layers are not the same, the values of swelling of industrial panels made with the same formulations should correspond to 60%-70% of the values found here. Contrary to what generally falsely believed the swelling of surfaces and core is rather different due to the difference in penetrability by a liquid in solids of higher density. In general, all panels containing proteins and triacetin comply the requirements of the standard. Moreover, panels without triacetin made with 20% LMW, 10 and 20% Solpro 050, get swelling ratio less than or around 14% (Table 8).

The choice was made to identify the best panels for the nearest 700kg/m3 density having significant internal bond. Panels of type P2, 13mm thick used in dry environments and non-construction purposes working, with higher internal bond than 0.35N/mm² are considered correct related to their internal bond (IB) strength (AFNOR 2010). None of the formulations containing proteins without triacetin yielded mechanically resistant panels, except in the case of protein hydrolysates Solpro 050 with a degree of substitution of 10% (Table 8).

All panels bonded with addition of triacetin to the adhesive have an internal bond (IB) strength higher than 0.35N/mm², except for the resin containing LMW protein hydrolysates using a degree of substitution of 30%. In this case the effect of the addition of triacetin is not sufficient to obtain a panel of sufficient mechanical resistance. The results obtained (Table 8) show that the panels containing protein hydrolysates have lower IB strength than those without proteins but they still meet the requirements of the standard.

Moreover, the panel bonded with a resin PF-10% Solpro 050 with triacetin has an internal bond comparable with those of the panel with 20% Solpro 050 without triacetin while it has a much lower density; this formulation is also worthwhile to note. For resins containing protein hydrolysates Solpro 508, the best formulation is 30% protein with triacetin. This yields a panel with better internal bond than others even if its density is slightly lower than 700kg/m3. Protein hydrolysates Solpro 050, gives the most suitable formulation, this being the one using a substitution rate of 20% with or without triacetin.

Comparing the results with those obtained for panels bonded with a PF resin (Table 8), one finds that the IB strength of the PF panels without and with triacetin are respectively 0.18 and 0.59N/mm². Thus, all the panels which have been subjected to swelling test and containing protein hydrolysates, (with or without triacetin) have lower IB strength than those of made with the pure PF resin. The only formulation which is closest to the results of panels made with PF resin is: PF-20% Solpro 050. Moreover, it is noteworthy that panels bonded with a resin PF-10% Solpro 050 with triacetin has a higher internal bond of those obtained for the panel containing 10% LMW with triacetin at a much lower density.

2.1.2. Formaldehyde emissions

Only the panels containing triacetin were tested. These panels gave IB strength values higher than the 0.35N/mm² required by the EN 312 (except for the formulation PF-30% LMW with triacetin, which gave internal bond of 0.34N/mm²).

According to the standard NF EN 312 (AFNOR 2010), the formaldehyde concentration should be less than 6.5mg/100g of dry board to be a panel of class E1. The tests done herewith were according to standard NF EN 717-3. Even if effectively standard NF EN 717-3 does not require a limit in panel's formaldehyde emissions.

Panels tested have a moisture content of about 5.9%.

By comparing panels bonded with PF-protein resins and panels with just PF resin, formulations PF-10% LMW (type 2) and PF-20% Solpro 050 are the only one which gave panels containing less formaldehyde. For LMW protein hydrolysates, whatever the P/F ratio, panels containing less formaldehyde are those with a substitution rate of 10%. Conversely, for protein hydrolysates Solpro 508 and 050, the panels presenting lower emission are those with the highest rates of substitutions (20% Solpro 050 and 30% for Solpro 508). As they have a bigger size, there is more sites and more place in order to fix the formaldehyde and do not let it release.

2.2. Comparison of different tests

In Table 8 are reported the best formulations for each tests.

Considering results of the tests lead with addition of triacetin, resins and panels which have the best properties for five out of six criteria are those which contain 10% Solpro 050. Resins with 10% LMW protein and 20% Solpro 050 with four out of six criteria being satisfied. Protein hydrolysates Solpro 050 are better for five out of six tests. Next comes the LMW protein hydrolysates that are interesting for four out of six tests,

and whatever the P/F ratio. In a nutshell, when using triacetin, protein hydrolysates Solpro 050 and LMW protein appear to have good properties as phenol-substitution additives for PF resins.

CONCLUSIONS

This study was conducted to compare the performances of phenolic resins containing wheat protein hydrolysates with conventional phenolic resins. The aim in the coming years is to develop the use of wheat proteins and more generally biomass in wood adhesives while retaining the properties of the standard panels.

The addition of triacetin to phenolic resins containing wheat proteins improves the performance of wood panels bonded with these resins. The most successful protein hydrolysates used appear to be the LMW and Solpro 050 protein hydrolysates.

It would be interesting to synthesize resins with higher a degree of substitution (30% or even higher), in using LMW protein and Solpro 050.

The results of this study on the addition of wheat protein hydrolysates in phenolic resins seem to be encouraging, and it's a further step toward the development of bio-based adhesives.

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