Natural Additive for Reducing Formaldehyde Emissions in Urea-Formaldehyde Resins

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ABSTRACT: This work studies the use of soy protein as a natural formaldehyde scavenger in wood particleboard production. The protein is incorporated in two forms: a) as a powder, during the blending process of wood particles with urea-formaldehyde binder resin, and b) as an aqueous solution, added at different times during resin synthesis. Analysis of variance (ANOVA) was used to evaluate the significance level of two effects (amount of added soy and time of addition) on internal bond strength, thickness swelling, and formaldehyde content of the resulting panels. The results showed that soy protein can contribute to decrease the formaldehyde content of particleboard panels. Addition in powder form or in solution during the resin condensation step leads to the highest formaldehyde reduction, without significantly affecting the physical properties of the panels.

KEYWORDS: Wood adhesives, soy protein, wood-based panels, formaldehyde emission

1 INTRODUCTION

Wood has followed mankind throughout its evolution. The development of science has led to the emergence of wood-based products whose main raw material is wood waste/residues and a binder system usually called resin or adhesive. One of the most important classes of wood-based panels is particleboard, which is mainly produced with urea-formaldehyde (UF) resins.

UF resins represent 80% of the total production of amino resins due to their various advantages such as good performance, low cost and high reactivity. However, these resins and their products emit formaldehyde, both due to the presence of non-reacted formaldehyde and due to the hydrolytic degradation of the polymer [1, 2].

In 2004, this problem became even more pertinent due to the reclassification of formaldehyde by the International Agency of Research on Cancer (IARC) as a carcinogenic to humans, Group 1 [3]. As a consequence, various authorities and institutions have been concerned about formaldehyde as a serious indoor pollutant, and new regulations have emerged enforcing increasingly lower exposure limits. The issue of formaldehyde emissions has thereby reached the area of national and international commerce. This way, methods such as lowering the molar ratio of formaldehyde to urea (F/U) of the resins, one of the most used industrially, have become insufficient to meet the market and legislation requirements [4]. Thus, new efforts have been made to deal with this challenge. The use of formaldehyde scavengers both in the synthesis of resins and in the production of wood-based panels has been one of the most studied methods [5].

In the past 10 years, the concept of bioadhesives has emerged, which, in a very simplified way, is based in the incorporation of biomolecules in the synthesis of resins [6–9] or in the production of the particleboards or, in a more radical approach, in the synthesis of a bio-based resin, as, for instance, soy or casein, among others [10].

The main goal is to evaluate the potential of soy or, more specifically, soy protein, as a formaldehyde scavenger when incorporated either directly in the production of wood panels or in the synthesis of the urea-formaldehyde resins used in panel production.

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2 MATERIALS AND METHODS

2.1 Soy Protein Solution

The soy protein solution was prepared at 13.5 wt% concentration, following a procedure described by Qu *et al.* [9]. The protein was dissolved/dispersed in water at 70 °C under agitation, adding afterwards 3 ml of 50 wt% sodium hydroxide solution and keeping it for 1 h.

2.2 Resin Preparation

The resins were synthesized according to the so-called alkaline-acidic process, which consists of three steps: methylolation under alkaline conditions, followed by condensation reaction under acidic conditions and then final urea addition. The soy protein aqueous solution was added in each of the three steps. Percentages of 5%, 10% and 15% of soy protein incorporation were studied, based on the total quantity of dry resin.

2.3 Resin Properties Determination

Viscosity, pH and solids content were determined at the end of each synthesis. Viscosity was measured with a Brookfield viscometer at 25 °C. The resin pH was measured using a combined glass electrode. The solid content was determined by evaporation of volatiles in 2 g of resin for 3 h at 120 °C.

2.4 Production of Particleboard Panels

The production process of the particleboards is divided into three steps: blending of wood particles with the adhesive system, mat forming and pressing. The panels are composed of three layers: two face and one core layer. In a first approach, particleboard panels were produced using a commercial resin, supplied by Euroresinas – Indústrias Químicas S.A., and 5%, 10% and 15% of soy protein powder were added during the blending process of the resin with the core layer's wood particles. Three-layer particleboards were hand-formed in an aluminium container with 220 × 220 × 80 mm and boards were then pressed at 190 °C during 150 s in a laboratory-scale hot press controlled by computer. In a second approach, panels were produced using lab-synthesized resins with incorporated soy protein. These were subjected to the same pressing conditions and the resin was used in the core and face layers.

2.5 Board Testing

After pressing, boards were tested according to European standards. The internal bond strength was determined according to NP EN 319 (tensile strength perpendicular to the plane of the board) and formaldehyde content was determined according to NP EN 120 (perforator method).

2.6 Design of Experiments

Table 1 summarizes the factors and levels considered. In the first trial, soy protein in powder form was added to core layer particles (wt%, based on dry wood mass) during the blending operation. In the second trial, hydrolyzed soy protein solution (13,5 wt%) was added during UF synthesis (wt%, based on resin mass) in each of the different stages of reaction (methylolation, condensation, final urea). In the third trial, different concentrations (wt%) of the hydrolyzed soy protein solution were added in the condensation stage at 15 wt%, based on resin mass.

Due to the large number of parameters to be studied, a statistical experimental design tool (JMP) was used.

In order to evaluate the significance level of the effects of the different factors on the internal bond strength, thickness swelling and formaldehyde content, an analysis of variance (ANOVA) was performed. In order to analyze the results of the three trials, the

Table 1 Factors and levels studied.

Factors	Levels				
Quantity of soy protein in powder form added to core layer particles (wt%, based on dry wood mass) during the blending operation	0	5	10	15	
Quantity of hydrolyzed soy protein solution (13,5 wt%) added during UF synthesis (wt%, based in resin mass)	0	5	10	15	
Concentration (%wt) of the hydrolyzed soy protein solution added in the condensation stage at 15 wt%, based in resin mass	25	30			
Stage of addition	Standard	Blending	Methylolation	Condensation	Final urea

quantity of soy protein was adjusted to the same basis (wt% of solid soy protein based on dry wood mass). Then the effect of four factors on three particleboard properties were considered: stage of addition in the production process, quantity of soy protein, density and moisture content.

3 RESULTS AND DISCUSSION

The ability of soy protein to perform as a formaldehyde scavenger was assessed using two approaches: addition of soy protein powder in the production process of the panels, and addition of soy protein aqueous solution in the synthesis of the UF resin to be used as panel binder. The major results of the first approach, where soy protein powder was mixed with the core layer particles, are seen in Figures 1 and 2. An increase in the percentage of added soy protein leads to a slight decrease in the formaldehyde content of the particleboard (Figure 1), without significant change in its properties, namely in terms of internal bond strength (Figure 2).

In the second approach, the hydrolyzed soy protein was added as an aqueous solution during UF resin synthesis. A standard UF resin (control) and 3 resins with added soy protein were synthesized. The soy protein solution was added in different amounts and at different times during synthesis: methylolation, condensation or final step, as described in Table 2 (resins R0 to R9). The resins synthesized with soy protein presented a slower condensation in comparison with a standard resin. Resins R3, R6 and R9 have a lower final viscosity, as the addition of hydrolyzed soy protein in the final urea step leads to a dilution of the final resin, without actual covalent incorporation in the polymer structure. This is not the case of addition in the condensation stage, where the observed

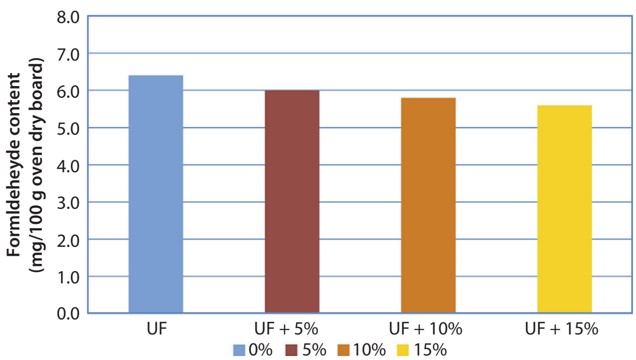

Figure 1 Formaldehyde content (mg/100 g oven dry board) of particleboards produced with soy protein powder in the core layer.

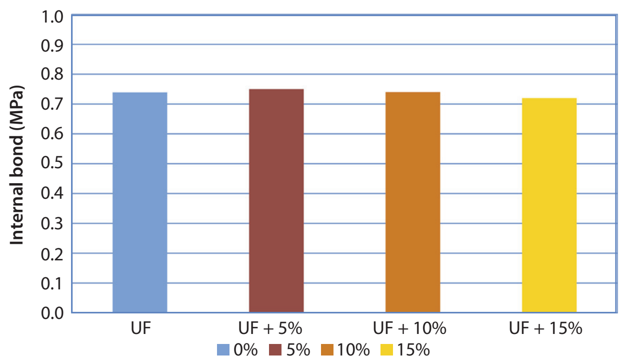

Figure 2 Internal bond of particleboards produced with soy protein powder in the core layer.

Table 2 Properties of resins with hydrolyzed soy protein solution added during synthesis.

Resin	Quantity of soy protein wt%	Addition stage	Theoretical solid content (%)	Viscosity (cP)	pH	Solid content (%)	Reactivity (s)
R0	0	–	63.0	180	8.20	62.7	54
R1	5	Methylolation	60.4	200	8.30	60.5	54
R2		Condensation	60.3	220	9.04	60.3	53
R3		Final urea	60.3	130	9.42	60.7	53
R4	10	Methylolation	57.9	160	9.23	57.1	57
R5		Condensation	57.9	150	8.68	57.4	57
R6		Final urea	57.8	110	9.67	56.8	55
R7	15	Methylolation	55.4	180	8.34	54.6	62
R8		Condensation	55.4	150	9.04	55.8	60
R9		Final urea	55.3	100	9.73	54.7	60
R10	25	Condensation	57.1	200	8.79	56.8	99
R11	30	Condensation	57.9	200	8.75	57.3	105

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increase of viscosity indicates grafting of soy protein into the growing polymer chains. However, further studies using complementary analytical techniques, such as NMR, should permit confirming if the soy protein is actually integrated in the final UF polymer.

As expected, solid content decreases as the quantity of soy protein addition increases, since more water is added, as the concentration of the solution of soy protein is maintained at 13.5 (wt%). An increase in the percentage of soy protein causes a slight decrease of reactivity (increase of gel time).

A larger reduction in the formaldehyde content is observed when the addition of soy protein is performed in the condensation step, when compared to addition in the methylolation and the final urea steps (Figure 3). Once again, the mechanical properties of the particleboard did not experience significant changes (Figure 4).

After the selection of the best stage for addition, the quantity of added soy protein was increased, without increasing the quantity of added water. Two different protein solutions were added, with concentrations of 25 (wt%) and 30 (wt%). The resulting resin properties are presented in Table 2 (resins R10 and R11).

A slower condensation step than for the standard resin was again observed. The final viscosity of both resins is similar. The reactivity for both resins is also lower than for the resins presented in Table 2.

An ANOVA was performed in order to evaluate the significance level of the effects observed for the different factors in terms of particleboard properties: internal bond, thickness swelling and formaldehyde emission. As these properties are generally affected by density and moisture content, these properties were also considered as factors. Table 3 presents the statistical significance level of the four factors. The stage of addition and the quantity of soy protein are significant for the three properties. Density and moisture content have statistical significance only in the case of thickness swelling.

Figure 5 presents the effects of the different factor levels on internal bond, thickness swelling and formaldehyde content. The addition of soy protein, in either powder form in the blending process or in solution during the resin condensation step, leads to the highest reduction in the formaldehyde content of particleboard panels. As expected from the results presented above, when increasing the net quantity of incorporated soy protein, either in powder or solution form, the formaldehyde emission decreases. However, the physico-mechanical properties tend to be slightly impaired. The internal bond decreases as the network formed by cured resin and wood particles might present different stiffness. The thickness swelling probably increases because the panel becomes more hydrophilic when soy protein is present, in conjunction with the higher board porosity induced by the springback that occurs after pressing, as a consequence of the lower bond stiffness.

4 CONCLUSIONS

The incorporation of a natural compound, soy protein, either in powder form in the blending process or in solution during resin synthesis, can contribute to a decrease in the formaldehyde content of particleboard panels.

Although further work has to be performed in order to evaluate the real changes on the polymer structure, it appears that soy protein can bind chemically with free formaldehyde, effectively acting as a formaldehyde scavenger, without sacrificing the physical properties of the resulting panels.

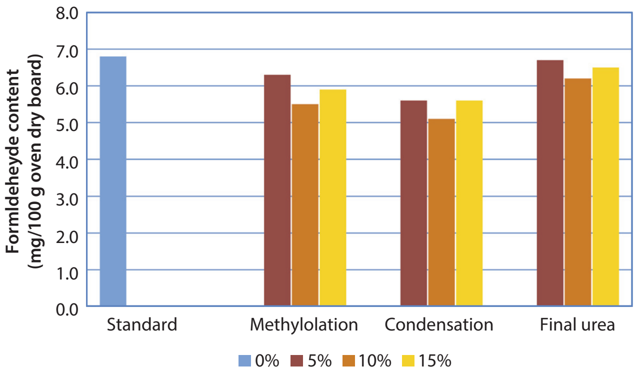

Figure 3 Formaldehyde content (mg/100 g oven dry board) of particleboards produced with soy protein solution in the two layers.

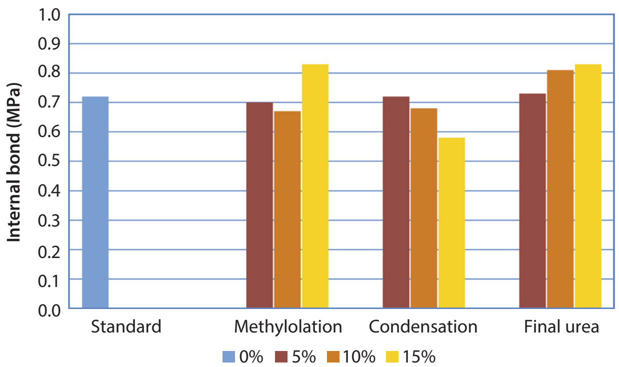

Figure 4 Internal bond strength of particleboards produced with soy protein solution in the two layers.

Table 3 ANOVA by factor for internal bonding strength, thickness swelling and formaldehyde content – mean (NS-not significant. *5%. **1%. ***0.1%. ****0.01%).

Factors	Degrees of freedom	Sum of squares	F ratio	p-value	Significance level
Internal bond (MPa)					
Stage of addition	4	0.044142	4.037386	0.004935	**
Quantity (wt%)	1	0.01874	6.856165	0.010563	*
Density (kg/m^3)	1	4.92E-06	0.001801	0.966254	NS
Moisture content (%)	1	0.002189	0.800711	0.373565	NS
Thickness swelling					
Stage of addition	4	104.0307	5.238027	0.000846	****
Quantity (wt%)	1	107.1968	21.58978	1.31×10^{-5}	****
Density (kg/m^3)	1	72.15388	14.53202	0.00027	***
Moisture content (%)	1	103.1191	20.76852	1.84×10^{-5}	****
Formaldehyde content (mg/100 g oven dry board)					
Stage of addition	4	9.721344	18.28761	1.05×10^{-10}	****
Quantity (wt%)	1	0.643565	4.842651	0.030648	*
Density (kg/m^3)	1	0.485503	3.653276	0.05954	NS
Moisture content (%)	1	0.245223	1.845234	0.178157	NS

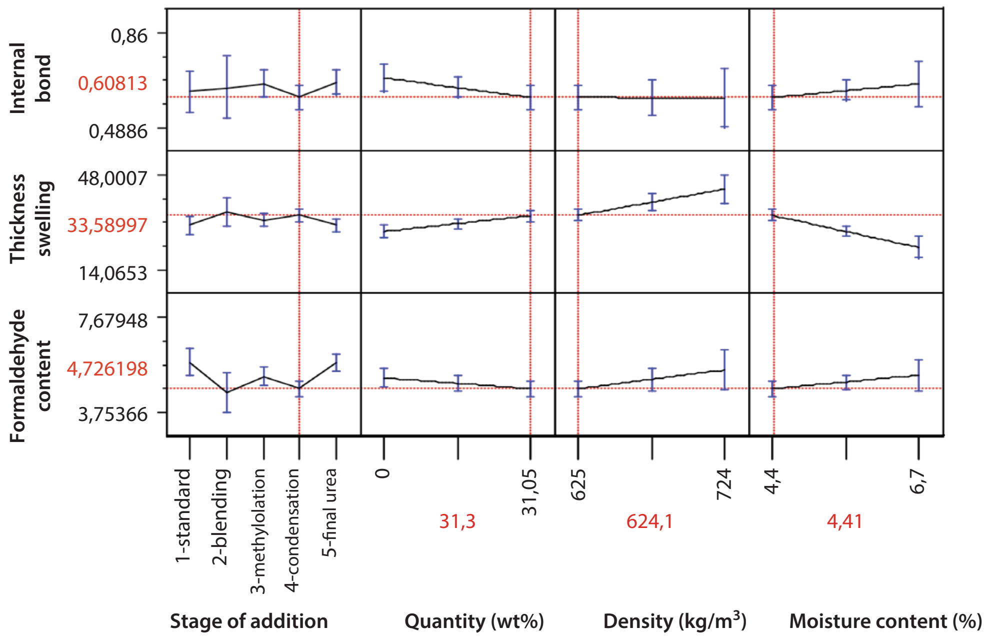

Figure 5 Effects of factor levels on internal bond, thickness swelling and formaldehyde content (mean).

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