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STUDY OF THE SYNTHESIS PARAMETERS OF AN UREA-FORMALDEHYDE RESIN AND THEIR IMPACT ON PARTICLEBOARD PROPERTIES

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Abstract:
This paper presents the results for the optimisation of different synthesis variables. An industrial UF resin was synthesised using the alkaline-acid process (alkaline methylolation, acidic condensation and neutralization and finally the last urea addition) at different values of pH, temperature and final viscosity and characterised according to different analysis methods. The particleboards were also produced and characterised according to the standard tests. For this study, a statistical analysis using JMP software was performed, and the main conclusion is that small changes in the synthesis of resins variables do not affect the final performance of particleboards.

Key words: *urea-formaldehyde resin; particleboards; synthesis parameters; JMP Statistical Software.*

INTRODUCTION

In the last decades, the industry of wood products is going through a great evolution thanks to companies like Sonae Arauco, which focus has been on developing more and better wood-based products. In 2015, Portugal produced 1 million and three hundred thousand m^3 and exported 278 million euros of wood-based panels (FAO 2015). Among these products, the best known are the commercially available particleboard (PB), medium density fibreboard (MDF), oriented strand board (OSB) and plywood (PW). For all these types of panels the use of a synthetic adhesive is required. Among the wide range of adhesives/resins employed in the wood industry, the most important are the amino resins which include urea-formaldehyde (UF) resins, melamine-formaldehyde (MF) resins and melamine-urea-formaldehyde (MUF) resins.

Amino resins are thermosetting polymers and they are normally used in the production of wood-based panels, linings and high and low pressure laminates. There are essentially three types of these resins: urea-formaldehyde, melamine-formaldehyde and melamine-urea-formaldehyde. UF resins are commonly used in the manufacture of wood products, especially particleboard and medium density fibreboard, due to their high reactivity, low cost and excellent adhesion to wood (Dunky 2001). The major disadvantages are the low moisture resistance, and formaldehyde emission during the production and lifetime of the panels. Although the free formaldehyde levels of these resins have been declining over the past decades, the re-classification of formaldehyde by International Agency for Research on Cancer (IARC) as "carcinogenic to humans" in 2004, and the consequent emergence of more restrictive legislation, forced resin producers to develop a new generation of resins that lead to a decrease in formaldehyde emissions to the levels of natural wood (Carvalho *et al.* 2012).

The industrial production of UF uses the alkaline-acid process. This process is performed in three steps: alkaline methylolation, followed by an acidic condensation and neutralization and finally the last urea addition (Pizzi 2003). There is also an alternative process, the strongly acidic process in which the condensation step is carried out under strongly acidic conditions and occurs simultaneously with the methylolation step. This process leads to panels with low formaldehyde emissions without modifying any physical or mechanical properties, but it requires strict control of reagents supply and a high capacity cooling system (Ferra *et al.* 2011).

The most important factors that influence the resins properties are the formaldehyde/urea (F/U) molar ratio, the temperature and reaction time, and pH during the condensation step. Many studies have been carried out and different kinetic models proposed (Carvalho *et al.* 2006). However, the reversibility and the occurrence of intramolecular reactions leads to the formation of a great variety of chemical structures as methylene bridges, methylene ether, methylols, and even cyclic amide derivative groups, which makes the prediction of the properties of these resins a complex task (Costa *et al.* 2013).

The impact of the formulation of these resins in the performance of wood products was the subject of several studies, some of which used statistical tools as methodology to optimize the resins synthesis parameters in order to produce panels with maximum internal resistance and minimum formaldehyde emissions (Ferra *et al.* 2010; Guo *et al.* 2013). Some strategies to reduce formaldehyde emissions have been done directly in the resins: reducing the molar ratio Formaldehyde/Urea, doping with melamine and the addition of formaldehyde scavengers (Costa *et al.* 2013; Paiva *et al.* 2012). However, the strategies cause a loss of reactivity and cure rate, since formaldehyde is required for curing the resin. Thus, the suitability of the characteristics of UF and MUF resins for wood-based panels manufacturing is important to reduce formaldehyde emissions without changing physical and mechanical properties and without losing productivity. So, an optimisation of both resins synthesis and the production of wood-based panels (namely the pressing operation) becomes a crucial task.

OBJECTIVE

The main objective of the present research was to optimise different variables related to resins synthesis, trying to better understand their impact on wood-based panels properties, in particular particleboards. In an initial approach, an industrial UF resin was synthesised at different values of pH, temperature, and final viscosity. The resins were characterised using empirical quality control methods and advanced physicochemical characterisation techniques. The panels produced were characterised using standard tests. The results were then analysed using the JMP Statistical Software. With this study it will be possible to better understand the main variables of the process and how to change them.

MATERIAL, METHOD, EQUIPMENT

Formaldehyde (55 wt.% solution), urea, melamine, ammonium sulphate, sodium hydroxide (50 wt.% solution) and acetic acid (25 wt.% solution) were provided by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal). Wood particles and paraffin for the production of particleboards were supplied by Sonae Arauco (Oliveira do Hospital – Portugal).

Resins production and characterisation

The resins were synthesised in a laboratory reactor. The synthesis was carried out in 2.5 L round bottom reactor, equipped with mechanical stirring and thermometer. A heating mantle heated the reactor and the temperature was controlled with a thermometer. The pH and viscosity measurements were performed offline on samples taken from the reaction mixture (and re-added after). All resins were produced according to the alkaline-acid process. These resins were divided in three series. Resins in the first series (resin A, B, C, D, E, F and G) were produced under different pH. The resins in second series (resin H, I, J and K) were produced under different temperature. Finally, the resins in third series (resins L, M and N) were produced with a different stop viscosity, between 250 and 600mPa.s.

Common characterisation methods involved the determination of physical and chemical properties that are related to the resin performance, such as viscosity, solid content, gel time and pH. However, advanced methods, such as chromatography and spectroscopy techniques have been carried out, in order to provide more specific and detailed information of the structure and subsequent performance of the resins.

The resin pH was measured using a combined glass electrode. pH values for UF resins are usually between 7.5 and 9.0. The viscosity (mPa.s) value gives a rough indication of the degree of polymerization of the resin. Viscosity was measured using a Brookfield and/or Ford cup viscometer (ASTM 1200) at a constant temperature of 25ºC. The resin density ($kg.m^{-3}$) is usually determined based on the weight/volume ratio and it can be measured using a hydrometer. The solid content (%) is determined by evaporation of volatiles in two grams of resin up to weight constant. Generally, this corresponds to three hours at 120ºC. Gel time (s) is the time needed for the resin gelification under similar conditions of the hot-pressing process (at 100ºC), after addition of a latent hardener. For this measurement, 100g of a sample (diluted to 50% solid content) was weighed in a beaker with 3mL of a 30 % latent hardener. In a test tube 0.250mL of the previous solution was added and it was immersed in boiling water. A rod was used for stirring the solution until resin gelification. HPLC is a chromatographic technique that allows separation of a mixture of different molecular weight compounds. This method is very effective in identifying low molecular weights (Ferra *et al.* 2010; Kumlin and Simonson 1978; Ludlam *et al.* 1986). The use of this technique in the analysis of UF resins allows the separation and identification of unreacted urea (% U), monomethylolurea (% MMU) and dimethylolurea (% DMU). A HPLC JASCO system equipped with a refractive index detector, JASCO IR-2031 Plus was used. The high-pressure pump used was a JASCO PU-2080 Plus pump. The column used was an YMC Polyamine II, conditioned at 30 ºC using an external oven JASCO PU-2067 Plus. The flow rate was 1.5 $mL.min^{-1}$ and acetonitrile/water (ACN/H_2O) was used as the mobile phase. The samples were prepared by dissolving 75 to 80mg of resin in 1mL of DMF, and after stirring for 1 minute, the mixture was diluted in 2mL of 90% of ACN and 10% H_2O. When the mobile phase was added, flocculation occurred. The sample was then left to rest (10 minutes), filtered and then injected. The calibration was performed using urea and dimethylurea standards.

Particleboards production and characterisation

Wood particles were blended with resins, paraffin and catalyst in a laboratory glue bender. Surface and core layers were blended separately. The amount of resin in both surface and core layers was 7 wt.% (solid resin per dry wood particles).The catalyst amount in the core layer was 3 wt.% (dry catalyst per solid resin). Three layers particleboards were hand formed in a square aluminium deformable container with 220 x 220 x 80 cubic millimetres. Surface and core layer differ in particle size distribution and moisture content. The upper surface layer had a mass of 20%, the core layer 62% and the bottom surface layer 18%. The pressing schedule of a continuous press is transposed to a batch cycle in a computer controlled laboratory press equipped with a linear variable displacement transducer (LVDT), a pressure transducer and thermocouples. For all series, eight boards were produced using four different pressing times (120, 150, 180, 210s).

The boards were tested according to the European standards for density (D) (EN 323), internal bond (IB) (EN 319), moisture content (MC) (EN 322) and thickness swelling (TS) (EN 317).

Statistical analysis

Trying to better understand the resins synthesis process and their impact on wood-based panels properties, different variables related to resins synthesis were studied (Table 1). For confidentiality reasons the process variables temperature and pH are encoded. In a first approach, an industrial UF resin was synthesized at different values of pH, temperature, and final viscosity. These parameters were analysed because they are crucial to the synthesis process. The values for this study were defined according to the medium value of the intervals of the variables. For UF synthesis, the process interval for pH of the first methylolation is between 8.0-10.0. As regards to the pH of condensation, the interval is 5.5-6.5. Finally, the pH of the second methylolation values are between 7.0-9.0. Thus, for UF synthesis, the process interval for

pH of the first methylolation is $pH1_{MI}$-$pH3_{MI}$, the pH of condensation interval is $pH1_C$-$pH3_C$ and the pH of the second methylolation values are between $pH1_{MII}$-$pH3_{MII}$.

Also for temperature, three different values were analysed. For methylolation temperature, the values corresponding to $T1_M$, $T2_M$ and $T3_M$ ºC were studied; and for condensation temperature: $T1_C$, $T2_C$ and $T3_C$ ºC. The viscosity was the last parameter studied, and the goal of this study was to have resins with different final viscosities: 100, 150, 200 and 250mPa.s.

The results were analysed using JMP Statistical Software after the characterisation of resins and particleboards. The main goal of the statistical analysis is to improve the internal bond and decrease the thickness swelling of particleboards.

Table 1

Factors and levels for statistical analysis

Factors	Units	Levels			
Methylolation I pH	-	$pH1_{MI}$	$pH2_{MI}$	$pH3_{MI}$	-
Condensation pH	-	$pH1_C$	$pH2_C$	$pH3_C$	-
Methylolation II pH	-	$pH1_{MII}$	$pH2_{MII}$	$pH3_{MII}$	-
Methylolation Temperature	ºC	$T1_M$	$T2_M$	$T3_M$	-
Condensation Temperature	ºC	$T1_C$	$T2_C$	$T3_C$	-
Final Viscosity	mPa.s	100	150	200	250
Pressing time	s	120	150	180	210

The parameters analysed in JMP can be divided in:

- Panel quality measurement (IB, TS);
- Resin properties (solids content (%), % U, % DMU, % MMU);
- Resins quality measurement (final viscosity, final pH, viscosity, pH, gel time, stability);
- Reaction parameters (pH methylolation/condensation, T methylolation/condensation, stop viscosity).

RESULTS AND DISCUSSION

In Table 2, the results for the resins characterisation for all produced resins are presented. An industrial resin is also presented for comparison. Related to viscosity and pH, all resins have the desirable value. The gel time is between 57-84 s and the solids content is between the defined values. All the resins had a normal stability (30 days). Comparing these resins (lab resins) with an industrial one (Ind) it is possible to notice that their characteristics are really similar.

Table 2

Characterisation of resins

Resin	Final viscosity (mPa.s)	Final pH	Viscosity (mPa.s)	pH	Gel time (s)	Solids content (%)
A	140	9.07	150	8.61	77	64.42
B	250	8.97	210	8.38	64	64.72
C	150	9.06	155	8.60	64	63.45
D	205	8.99	195	8.66	72	64.12
E	225	8.92	245	8.85	84	65.47
F	170	8.99	185	8.53	77	64.64
G	155	9.48	145	8.84	71	64.56
H	120	9.70	145	8.98	62	64.24
I	200	9.01	170	8.43	78	68.07
J	180	9.49	165	8.69	63	65.27
K	130	9.03	110	8.46	70	64.83
L	240	9.09	260	8.53	76	66.75
M	170	9.21	170	8.37	58	64.32
N	110	9.03	115	8.35	62	64.12
Ind	-	-	180	8.13	57	63.03

The first JMP analysis permitted to establish a relationship between panel quality and resin properties (Fig. 1). From the values presented in Table 3, it can be concluded that the % DMU significantly influences the IB, not being significantly influenced by other variables. This means that the IB is significantly affected by the % DMU but other variables hardly have any effect. The % MMU and % DMU significantly influence TS value. As the goal is to maximize the IB, this property was chosen as a control measure. Therefore, according to these results, it is desirable to have the highest % DMU, since the IB increases as the % DMU increases. These results can be explained with a widespread theory that a good UF resin should incorporate low molecular weight species that are important for penetration into wood, and higher molecular weight species that contribute to the cohesion of the particles. Thus, polymers with higher molecular weight should lead to an increase in the internal bond of the panels.

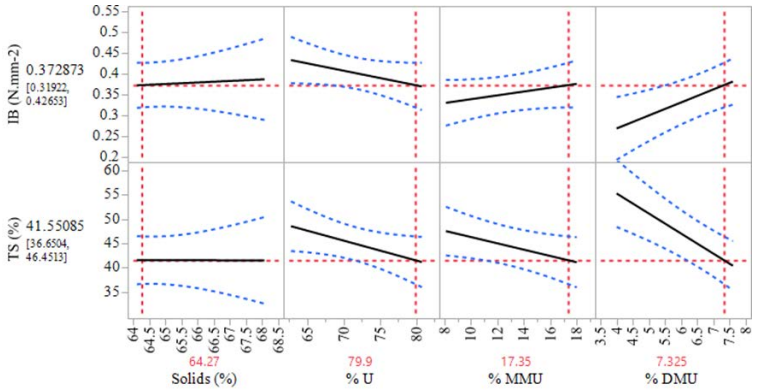

Fig. 1.
Effect of resin properties on panel quality (internal bond and thickness swelling).

Table 3

Parameters estimated and significance level (*5%, **1%, ***0%) for panel quality measurement as a function of resin properties

Factors	IB (N.mm^{-2})	TS (%)
Solid content (%)	0.7544	0.9932
% U	0.1350	0.0580
% MMU	0.1984	0.0495*
% DMU	0.0046**	<0.0001***

The gel time is significantly affected by solids content and % U. By analysing the results, it is possible to conclude that a higher solids content corresponds to a less reactive resin. Regarding the solids content, it would make more sense for the gel time to decrease with increasing solids content. This is because that by decreasing the solids content, the concentration of the reactants decreases. Therefore, there is more water entering in the system which acts as a retardant to the curing of the resin. Thus, the cure rate decreases, decreasing the gel time.

The final viscosity and the next day viscosity are influenced by solids content and % U. The higher the solids the higher the viscosity, and the higher the % U the lower the viscosity. For the same amount of solids, the viscosity increases with an increase in the proportion of the condensate structures. As well, the proportion of molecules with high molecular weights increases with increasing the degree of condensation.

Stability as related to viscosity will depend significantly on solids content and % U. Stability decreases with the increase in solids content and increases with % U. With this analysis, it seems there is a relationship between the lower molecular weight particles and the stability of the resin.

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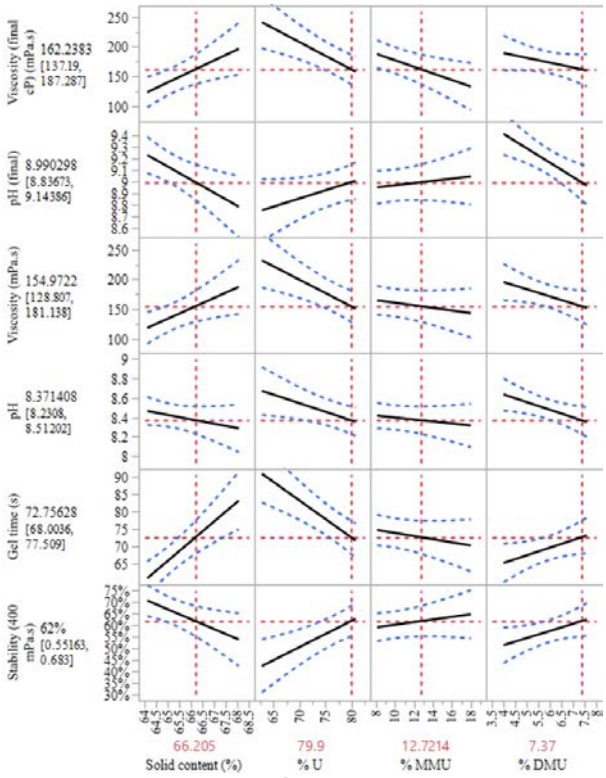

Fig. 2.
Resins quality measurement as a function of resin properties.

Table 4

Parameters estimated and significance level (*5%, **1%, ***0%) for resins quality measurement in function of resins properties

Factors	Final viscosity (mPa.s)	Final pH	Viscosity (mPa.s)	pH	Gel time (s)	Stability
Solid content (%)	0.0071**	0.0073**	0.0144*	0.2304	<0.0001***	0.0170*
% U	0.0009***	0.0843	0.0018**	0.0209*	<0.0001***	0.0018**
% MMU	0.0080**	0.4392	0.3068	0.3702	0.241	0.2862
% DMU	0.1818	0.0014**	0.0592	0.0241*	0.0580	0.0542

From the previous analysis and relating the IB to the % DMU, it was concluded that a higher % DMU in the resin yielded an increase of the IB in the final panel. Thus, analysing the reaction parameters with the properties of the resins and maximizing the value of % DMU, the "optimal solution" can be obtained for this set of results and for the resins under study. Through the statistical analysis performed, it asserted that the % DMU is significantly influenced by the stopping viscosity. This factor may be related to the fact that the stop viscosity is related to the condensation step and that a more condensed polymer will have a larger number of species with higher molecular weight. The solids content and % MMU are influenced by several factors and will not be considered in this analysis. The % U is influenced by T methylolation. This value increases with increasing T methylolation.

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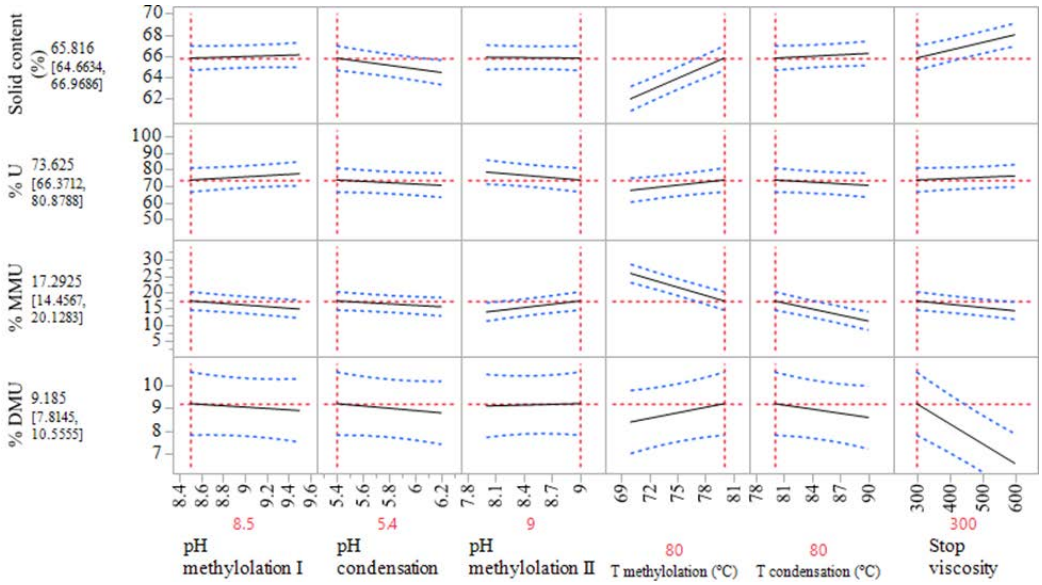

Fig. 3.
Reaction parameters as a function of resin properties.

Table 5

Parameters estimated and significance level (*5%, **1%, ***0%) for reaction parameters in function of resins properties

Factors	Solids content (%)	% U	% MMU	% DMU
pH methylolation I	0.5129	0.1909	0.0302*	0.5819
pH condensation	0.0047**	0.2695	0.1145	0.4634
pH methylolation II	0.8612	0.1002	0.0038**	0.8542
T methylolation	<0.0001***	0.0354*	<0.0001***	0.1458
T condensation	0.3385	0.2695	<0.0001***	0.2731
Stop viscosity	<0.0001***	0.3351	0.0038**	<0.0001***

After this study, the “optimal” resin was synthesised in laboratory using the correspondent factors levels, namely temperatures and pH for the methylolation and condensation and also stop viscosity that gave the best resin. The results obtained have demonstrated that the internal bond strength obtained was similar compared to the others resins previously synthesised and here presented. So, a small change in the synthesis parameters do not interfere on the final properties of particleboards.

CONCLUSIONS

The results obtained within the present research allowed: to understand the synthesis process for an UF resin and the manufacture of particleboards; the characterization methodology for resins and wood-based panels; and the identification of crucial factors for the synthesis. It also allowed to conclude that the % DMU is statistically significant for the internal bond. However, small changes in the synthesis parameters do not have a significant effect on the final properties of particleboards. These results were important for the company because it proves that small fluctuations, inherent to industrial synthetic process will not have a significant impact on the performance of the resin and consequently on particleboards properties. Furthermore, these results have also identified synthetic parameters that are worthy of fine tuning to yield better adhesive properties if required.

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