Accepted Manuscript

Statistical evaluation of the effect of urea-formaldehyde resins synthesis parameters on particleboard properties

C. Gonçalves, J. Pereira, N.T. Paiva, J.M. Ferra, J. Martins, F. Magalhães, A. Barros-Timmons, L. Carvalho

PII: S0142-9418(17)31806-8

DOI: 10.1016/j.polymertesting.2018.04.007

Reference: POTE 5412

To appear in: Polymer Testing

- Received Date: 11 December 2017
- Revised Date: 29 March 2018

Accepted Date: 9 April 2018

Please cite this article as: C. Gonçalves, J. Pereira, N.T. Paiva, J.M. Ferra, J. Martins, F. Magalhães, A. Barros-Timmons, L. Carvalho, Statistical evaluation of the effect of urea-formaldehyde resins synthesis parameters on particleboard properties, *Polymer Testing* (2018), doi: 10.1016/j.polymertesting.2018.04.007.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Statistical evaluation of the effect of urea-formaldehyde resins synthesis parameters on particleboard properties

C. Gonçalves^{a,c}, J. Pereira^{a,b}, N. T. Paiva^c, J. M. Ferra^c, J. Martins^{a,d}, F. Magalhães^a, A. Barros-Timmons^e, L. Carvalho^{a,d,*}

^aLEPABE - Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n 4200-465, Porto, Portugal ^bARCP - Associação Rede de Competência em Polímeros, Rua Dr. Júlio de Matos 828/882, Porto, Portugal ^cEuroResinas – Indústrias Químicas SA, 7520-195, Sines, Portugal

^dDEMad - Departamento da Engenharia de Madeiras, Campus Politécnico de Repeses 3504-510, Viseu, Portugal ^eCICECO - Aveiro Institute of Materials and Departamento de Química, Universidade de Aveiro, 3810-193, Aveiro, Portugal

*Corresponding author: LEPABE – Faculdade de Engenharia, Universidade do Porto, Porto, Portugal E-mail address: lhora@fe.up.pt (L. Carvalho).

Abstract

This work discusses the optimisation of different synthesis parameters for a low emitting ureaformaldehyde (UF) resin. Industrially, this resin was synthesised using the alkaline-acid process (alkaline methylolation and acidic condensation) at different values of pH, temperature and final viscosity and characterised according to different analytical methods. Particleboards were produced using different pressing times and characterised according to the standard tests. A statistical analysis (ANOVA) was performed, and the main conclusion is that small changes on the synthesis of resins parameters do not affect the performance of particleboards.

Key words: urea-formaldehyde resin, particleboard, process optimisation, JMP software, ANOVA

1. Introduction

In 2016, Portugal produced 1,400,000 m³ and exported 240 million euros (850 million m³) of wood-based panels [1,2]. Among these, 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. These include urea-formaldehyde (UF) resins, melamine-formaldehyde (MF) resins and melamine-urea-formaldehyde (MUF) resins. Their widespread use is due mainly to low cost and good performance. These resins are thermosetting polymers normally used in the production of wood-based panels, linings and high and low pressure laminates. UF resins are commonly used in the manufacture of wood [3]. 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 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 [4]. Several strategies have been explored for reducing the formaldehyde release including the addition of formaldehyde scavengers directly to the resin or wood particles, the treatment of final wood panels with scavengers or impermeable coatings and the improvement of improved resin formulations [5–9].

The industrial production of UF follows the alkaline-acid process which is performed in three steps: alkaline methylolation, followed by an acidic condensation, neutralization and finally the last addition of urea [10]. There is also an alternative process, called strongly acidic process, in which the condensation and methylolation steps are carried out under at very low pH. This process leads to panels with low formaldehyde emissions without modifying physical and mechanical properties, but it requires strict control of reagents supply and a high capacity cooling system [11].

The most important parameters that influence the properties of the resins are the molar ratio of formaldehyde/urea (F/U), temperature, reaction time and pH during the condensation step. However, the reversibility and the occurrence of intramolecular reactions leads to the formation of a great variety of chemical structures such 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 [12]. 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 to optimize the resins synthesis parameters in order to produce panels with maximum internal strength and minimum formaldehyde emissions [5,6,9,13–18]. Several authors have described the synthesis process and studied different parameters for the properties of the resins. Six different categories of UF resins were manufactured by Sheikh et al., using different ratios of formaldehyde to urea, acid-catalyst, reaction time and reaction temperature. The optimum UF resin was obtained using F/U = 1.5, NaOH as base and formic acid as acid catalyst [9]. Ferra et al. (2010) described the optimisation of an alkaline-acid process, focusing mainly on the condensation step. Three parameters (number of urea additions, time span between urea additions, and pH of condensation reaction) were optimised. The optimum operating conditions that produced the minimum formaldehyde emission were: 4 for the number of urea additions in the condensation step; 13 s the value for time span between urea additions in the condensation step and 6.1 for the pH of the condensation step. They concluded that pH and time interval between consecutive urea additions in the condensation step have a strong influence on the analysed properties [5]. Park et al. (2013) investigated UF resins with different formaldehyde/urea (F/U) mole ratios, trying to understand the hydrolytic degradation of cured UF resins responsible for formaldehyde emission. The results showed that as the F/U mole ratio decreased from 1.6 to 1.0, the average distance between domains in cured UF resins decreased while the crystallite size increased. The presence of these crystallites in cured UF resins of low F/U mole ratio was found to be correlated to improved hydrolytic stability of the cured resins [19]. The competitive condensations of the methylolureas at alkaline condition were studied using different temperatures and F/U molar ratios. The

methylene ether bridges were exclusively formed under conditions of 80 and 90 °C with F/U = 2. At 80 °C with F/U = 1, the linear methylene bridge began to compete with ether bridges. At 90 °C with F/U = 1, the methylene bridges were found to be much more competitive. For the purpose of minimizing ether bridges, the initial F/U molar ratio of 2.0 (or higher) may not be a good choice [20]. Park and his co-workers (2017) studied the crystallinity in liquid UF resins using two different F/U molar ratios (1.60 and 1.10) as a function of hardener level and curing times at room temperature. The results showed that the liquid UF resin with a low F/U mole ratio had a higher degree of crystallinity than the one prepared using a high F/U mole ratio. The results of this work showed the importance of controlling the subtle interplay between crosslinking and formulation for the production and control of the size, quantity and morphology of crystals in UF resins [21].

The main objective of the present research was to optimise different parameters related to resins synthesis, trying to better understand their impact on wood-based panels properties, in particular on particleboards. In an initial approach, an industrial UF resin was synthesised at different values of pH, temperature and final viscosity. The particleboards were pressed using four different pressing times. The resins properties were measured using straightforward quality control methods and advanced physicochemical characterisation techniques. An ANOVA analysis was also done. The purpose of this study is to identify the main synthesis process parameters and how changes in these can influence the particleboards properties.

2. Experimental

2.1 Materials

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). A commercial resin (called Ind) was also provided by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal). Wood particles and paraffin (industrial paraffin E515), for the production of particleboards, were supplied by Sonae Arauco (Oliveira do Hospital – Portugal).

2.2 Resins production and characterisation

The synthesis of the resins 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 [11]. 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 stopping viscosity, between 300 and 600 mPa's.

Table 1 presents the parameters that were varied for the different resin synthesis. Resin C is a standard resin, produced in laboratory following the same formulation as the commercial (Ind), so all the values related to other resins are compared to this resin.

		-			-									
Parameter / Resin	А	В	С	D	E	F	G	Н	Ι	J	K	L	М	Ν
Methylolation I pH	-7.5 %	+7.5 %	рН _{МІ}											
Condensation pH	рН _С			-7.5 %	+7.5 %	рН _С					0	Y		
Methylolation II pH	рН _{МП}					-7.5 %	+ 7.5 %	рН _{МП}				1		
Methylolation Tmax	T _M							-7.5 %	+7.5 %	Тм				
Condensation Tmax	T _c									-7.5 %	+7.5 %	Tc		
Stopping viscosity	500							C	0			600	400	300

Table 1. Summary of different resins and parameters of process synthesis.

Common characterisation methods involved the determination of physical and chemical properties that are related to the resin performance, such as viscosity, solids content, gel time and pH. However, advanced methods, such as chromatography techniques (Gel Permeation Chromatography/Size Exclusion Chromatography - GPC/SEC and High-Performance Liquid Chromatography - HPLC) were also carried out in order to provide a 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 9.5. The viscosity (mPa·s) value gave a rough indication of the degree of polymerization of the resin. Viscosity was measured using a Brookfield viscometer at a constant temperature of 25 °C. The resin density $(kg \cdot m^{-3})$ is usually determined based on the weight/volume ratio and it can be measured using a hydrometer. The solids content (%) was determined by drying two grams of resin to constant weight. Generally, this corresponds to three hours at 120 °C. Gel time (s) is the time needed for the resin gelification, after addition of a latent hardener. For this measurement, 100 g of a sample (diluted to 50% solids content before weighing) was weighed in a beaker with 3 mL of a 30% latent hardener. In a test tube 0.250 mL of the previous solution was added and it was immersed in boiling water. A glass rod was used for stirring the solution until resin gelification. GPC/SEC was used as a support technique for the characterisation of the polymer, essentially of the polymer structure and hydrodynamic volume [22,23]. The mechanical and bonding properties of the adhesive are strongly dependent on its hydrodynamic volume [3]. A GPC/SEC equipped with a Knauer RI detector 2300 and a Knauer injector with a 20 µL was used. The column used was Gram-Pore size 30A and particle size 10 µm, conditioned at 60 °C using an external oven. The flow rate was 1 mL·min⁻¹ and dimethylformamide (DMF) was used as the mobile phase. Samples for analysis were prepared by dissolving a small amount of resin (100 mg) in

dimethylsulfoxide (DMSO), followed by vigorous stirring during 1 minute. Subsequently, the sample was left to rest (10 minutes), filtered through a 0.45 µm nylon filter and then the sample was injected. The calibration was done with polystyrene standards (162 – 66000 Da). 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 [24–26]. 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 °C using an external oven JASCO PU-2067 Plus. The flow rate was 1.5 mL·min⁻¹ and acetonitrile/water (ACN/H₂O) was used as the mobile phase. The samples were prepared by dissolving 75 to 80 mg of resin in 1 mL of DMF, and after stirring for 1 minute, the mixture was diluted in 2 mL of 90% of ACN and 10% H₂O. 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 dimethylolurea standards.

2.3 Particleboards production and characterisation

The standard mix of wood particles included 30% maritime pine, 15% eucalypt, 25% pine sawdust and 30% recycled wood. Wood particles were blended with resins, paraffin (1 wt.%) 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 210 x 210 x 80 cubic millimetres. The surface and core layers differ in particle size distribution, determined by analytical sieve shaker (size of particles in surface layer between 0.5 mm and 1.0 mm; size of particles in core layer between 1.4 mm and 4.0 mm) and moisture content (surface and core layer 2-3% before gluing). The upper surface layer had a mass of 20%, the core layer 62% and the bottom surface layer 18% (the difference between layers is explained by the tendency of small particles to fall between the larger particles). The mat was pressed at 190 °C to produce a board with a target density between 650-670 kg m⁻³ and thickness of 16 mm. The pressing schedule of a continuous press was 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 (2 x 4 pressing times) were produced using four different pressing times (120, 150, 180, 210 s).

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

2.4 Experimental design and Statistical analysis

As mentioned before, different parameters related to resins synthesis were studied (Table 2). In a first approach, a commercial UF resin was synthesised, at laboratory, at different values of pH, temperature,

and final viscosity. The process interval for pH of the first methylolation is between 8.0-10.0, the pH of condensation is between 5.5-6.5, and the pH of the second methylolation between 7.0-9.0. The methylolation temperature is between 60-80 °C and the condensation temperature between 70-90 °C. The pH and temperature values were varied +/- 7.5% in relation to the reference values commonly used in the synthesis. In addition, different values of stopping viscosities (which are the reference for terminating the condensation step) were tested: 300, 400, 500 and 600 mPa's. The commercial resin (Ind), synthesised at the company, was also analysed for comparison.

Table 2.	Parameters	and leve	els for si	tatistical	analysis.	

. .

Parameter	Unit	Level			
Methylolation I pH		-7.5%	рН _{MI}	+7.5%	
Condensation pH		-7.5%	pH _C	+7.5%	
Methylolation II pH		-7.5%	рН _{МІІ}	+7.5%	
Methylolation temperature	°C	-7.5%	T _M	+7.5%	
Condensation temperature	°C	-7.5%	T _C	+7.5%	
Stopping viscosity	mPa∙s	300	400	500	600
Pressing time	S	120	150	180	210
Methylolation temperature Condensation temperature Stopping viscosity Pressing time	°C °C mPa⋅s s	-7.5% -7.5% 300 120	$\frac{T_{M}}{T_{C}}$ $\frac{T_{C}}{400}$ 150	+7.5% +7.5% 500 180	600 210

The results were analysed using JMP Statistical Software after the characterisation of resins and particleboards. An analysis of variance (ANOVA) was performed to evaluate the significance level of the effects of the different parameters (p-value and significance level (*5%, **1%, ***0.1%)). The formaldehyde content or emission could also be a parameter, however in this study was not considered as an optimisation parameter. Nevertheless, it is intended to include formaldehyde emission in a future study.

The analysis of results was performed in two large groups: resins synthesis and wood-based panels preparation. Regarding the synthesis, the following parameters and responses were studied: pH and final viscosity, pH and viscosity one day later, solids content, gel time, stability, percentage of unreacted urea (% U), unreacted dimethylolurea (% DMU) and unreacted monomethylolurea (% MMU) (note that the GPC results were not here used for statistical analysis). In the case of the panels preparation, for each pressing time (120, 150, 180 and 210 s) the following properties were measured: internal bond (IB), density (D), thickness swelling (TS) and moisture content (MC).

To simplify the explanation of the study, five subgroups were defined:

• Reaction parameters (methylolation/condensation pH, methylolation/condensation T, stopping viscosity);

- Resin quality measurement (viscosity and final pH, viscosity and pH day after, gel time, stability);
- Resin properties (solids content, % U, % MMU, % DMU);
- Panel quality measurement (IB and TS);
- Press parameter (time).

The goals of statistical analysis were defined in terms of maximizing the IB of the panels and minimizing TS, with the aim of finding optimal synthesis parameters and consequently obtain an optimal resin.

3. Results and discussion

3.1 Characteristics of the UF resins produced

Table 3 summarises the general properties measured for all the UF resins produced in this work, namely: final viscosity and pH, gel time and solids content. It is important to note that final pH and viscosity are related to the synthesis parameters. According to the values in Table 1 the viscosity and pH fulfilled the specifications for commercial resins. The gel time has values between 58-84 s and the solids content present values in the range expected. The commercial resin (Ind) and the laboratory productions are similar.

Resin	Final viscosity (±10 mPa's)	Final pH (25 °C) (±0.20)	Gel time $(\pm 3 s)$	Solids content
		-		(±0.4%)
А	140	9.07	77	64.4
В	250	8.97	64	64.7
С	150	9.06	64	63.4
D	205	8.99	72	64.1
Е	225	8.92	84	65.5
F	170	8.99	77	64.6
G	155	9.48	71	64.6
Н	120	9.70	62	64.2
Ι	200	9.01	78	68.1
J	180	9.49	63	65.3
Κ	130	9.03	70	64.8
L	240	9.09	76	66.7
М	170	9.21	58	64.3
Ν	110	9.03	62	64.1
Ind	180	8.13	57	63.0

Table 1. Characteristics of UF resins produced in the lab and a commercial resin (Ind).

All resins were analysed by GPC/SEC a day after synthesis, to evaluate the fraction of insoluble molecular aggregates. Figure 1 shows a typical chromatogram for a UF resins synthesised in this work. The peak with higher retention volume corresponds to free urea, methylolureas and oligomers. The leftmost portion of the chromatogram corresponds to polymer with high molecular weight. The analysis of unreacted urea and methylolureas was performed using HPLC and the results were rather similar except for the resin prepared at commercial level (Ind). This difference between the laboratory and industrial results (Figure 2) can be explained by the mix of resins that sometimes happen inside the reactor at industrial level; and also, the sample preparation for HPLC (described above) at industrial level and at laboratory level can be different, causing a different result from HPLC analysis. For all parameters studied, the value of U, MMU and DMU are between the intervals presented in Table 4. The final

percentage of urea and methylolureas are related to the amount of urea added in the final and the free formaldehyde present in the final condensation step [25].

Resin	U (%)	MMU (%)	DMU (%)
All (average)	70±10	12±5	6±2
Ind	53	31	4

Table 2. Values of unreacted urea and methylolureas for the produced resins and commercial resin (Ind).

3.2 Particleboards properties

According to the standards specifications, the minimum value for type P2 board (NP EN 312) for IB strength is $0.35 \text{ N} \cdot \text{mm}^{-2}$. As it is possible to observe, just two resins are out of the limit for panels pressed for 180 s. Therefore, all particleboards properties were also measured and the results obtained are presented in Table 5 for pressing times of 180 s. For density, the values are between 630-690 kg m⁻³ and moisture content between 4.5-6.5%. The values for thickness swelling are high, however it is not a specification for type P2 boards.

Table 3. Experimental results for panel characterisation at a pressing time of 180 s.

Resin	IB $(N^{-}mm^{-2})$	$D(kg^{-}m^{-3})$	TS (%)	MC (%)
А	0.42 ± 0.02	676±1	62.6±4.4	5.3±0.0
В	0.36±0.01	675±9	62.2±1.8	6.6±0.0
С	0.40±0.03	645±6	49.1±0.6	4.9±0.1
D	0.42±0.03	635±4	41.7±4.3	4.9±0.1
Е	0.42±0.05	657±1	43.1±0.1	5.0±0.0
F	0.39±0.02	635±1	43.4±0.4	4.6±0.1
G	0.43±0.04	676±1	48.5±2.4	4.5±0.0
Н	0.41±0.04	650±2	46.4±4.1	5.5±0.1
Ι	0.34±0.01	686±12	54.3±0.2	5.9±0.2
J	0.23±0.04	673±13	55.6±0.6	5.9±0.0
K	0.38±0.07	670±2	48.5±2.9	5.5±0.4
L	0.24±0.01	643±0	64.1±0.4	5.3±0.1
Μ	0.37±0.04	661±3	45.3±2.7	5.6±0.1
Ν	0.38±0.01	669±8	52.3±2.9	5.5±0.4
Ind	0.37±0.01	681±8	44.1±5.3	5.9±0.4

3.3 Statistical analysis

The statistical analysis starts with the study between the results obtained for the particleboards. According to ANOVA results, the internal bond is significantly affected by pressing time (p-value < 0.0001^{***}). Thickness swelling also varies with pressing time, however there are other factors that affect this parameter (p-value = 0.0085^{**}). IB increases with increasing press time, as expected [27–30]. An increase in the pressing time causes an increase of heat transferred into the mattress, either by conduction from the press plates or by convection due to moisture evaporation, which will promote polymerization of the resin in the inner layers of the panels, allowing for an increase in IB. However, a significant increase in pressing time can lead to over-curing, which may lead to a decrease in IB. This over-curing can lead to

significant differences in stiffness along the plate resulting in more brittle and hence more susceptible to breakage of bonds. This causes an increase in thickness swelling with pressing time.

A relationship between panel quality and resin properties is presented in Figure 3. It can be concluded that the % DMU significantly influences IB (p-value = 0.0046**), which is not affected by other parameters. The % MMU and % DMU significantly influence TS (p-value = 0.0495* and < 0.0001***, respectively). As the goal is to maximize IB, the % DMU was chosen as a control measurement. Therefore, according to these results, it is desirable to have the highest % DMU, since IB increases as % DMU increases. Indeed, it has been suggested in the literature that an UF resin should incorporate low molecular weight species, to allow penetration into wood, and higher molecular weight species that contribute for cohesive adhesion of the particles. Thus, polymers with higher molecular weight should lead to an increase in the internal bond of the panels [25,31].

Figure 4 shows the influence of resin properties on resins quality measurement. It is possible to observe that the gel time is significantly affected by solids content (p-value $< 0.0001^{***}$) and % U (p-value $< 0.0001^{***}$). By analysing the results, it is possible to conclude that higher solids content corresponds to a less reactive resin [27,32,33].

The final viscosity and the next day viscosity are influenced by solids content (p-value = 0.0071^{**} and 0.0144^{**}) and % U (p-value = 0.0009^{***} and 0.0018^{**}). 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. In the same way, the proportion of molecules with high molecular weights increases with increasing degree of condensation. The stability, being related to viscosity, depends significantly on solids content (p-value = 0.0170^{*}) and % U (p-value = 0.0018^{**}). Indeed, the stability decreases with the increase in solids content and increases with % U [25]. With this analysis, it seems that there is a relationship between the lower molecular weight species and the stability of the resin. The final pH and the next day pH are influenced by different factors. The final pH is significantly influenced by solids content and % DMU (p-value = 0.0073^{**} and 0.0014^{**}). The next day pH is significantly influenced by % U and % DMU (p-value = 0.0209^{*} and 0.0241^{*}). The next day pH decreases with the increase of % U and % DMU.

From the previous analysis and relating the IB to the % DMU, it is 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 is asserted that the % DMU is significantly influenced by the stopping viscosity (p-value < 0.0001^{***}). This factor may be related to the fact that the stopping 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 synthesis factors (solid content for pH condensation p-value = 0.0047^{**} , T methylolation p-value < 0.0001^{***} , Stopping viscosity p-value < 0.0001^{***} ; % MMU for

pH methylolation I p-value = 0.0302^* , pH methylolation II p-value = 0.0038^{**} , T methylolation p-value $< 0.0001^{***}$, T condensation p-value $< 0.0001^{***}$ and stopping viscosity p-value = 0.0038^{**}) and will not be considered in this analysis. The % U is influenced by T methylolation (p-value = 0.0354^*), increasing as this temperature increases. Figure 5 presents, the influence of synthesis parameters on resin properties.

After the statistical analysis, the optimal resin was synthesised in laboratory using the synthesis parameters that gave the best result – maximizing IB and minimizing TS (Table 6).

Resin	pН	pH	pH	Т	Т	Stopping
	methylolation I	condensation	methylolation	methylolation	condens	viscosity
			II		ation	
Optimal	-7.5%	-7.5%	+7.5%	+7.5%	-7.5%	300

 Table 6. Optimal resin obtained from the statistical analysis.

Table 7 shows the properties of the optimal resin. The results obtained for the characterisation of this resin are similar to those presented in Table 3 (Resins A to N), being the final viscosity the most different value obtained. With regard to GPC/SEC, the chromatogram is similar to that shown in Figure 1, with high molecular weights associated with retention volumes between 8 and 12 mL and higher retention volume corresponds to free urea, methylolureas and oligomers. HPLC values are within the range of values presented in Table 4 (unreacted U 71%, unreacted MMU 13% and unreacted DMU 8%). The similarity between the results can also be observed for the panel characterisation (Table 5 compared with Table 8), regarding IB and TS values. Therefore, it can be concluded that in the ranges considered in this study the synthesis parameters do not affect the final properties of the particleboards.

Table 7	Characteristics	of the	ontimal	rosin	nroduced	in tl	he lah
Tuble 7.	Churacteristics	0j ine	optimut	resin	produced	111 11	ie iub.

Resin	Final	Final pH	Gel time (±3	Solids	U (%)	MMU (%)	DMU (%)
	viscosity	(25 °C)	s)	content			
	(±10 mPa s)	±0.20		(±0.4%)			
Optimal	100	9.08	68	64.6	71	13	8

Table 8. Experimental results for panel characterisation at a pressing time of 180 s.

Resin	$IB (N^{-}mm^{-2})$	$D(kg^{-}m^{-3})$	TS (%)	MC (%)
Optimal	0.38±0.02	668±16	49.7±1.2	5.4±0.1

4. Conclusions

This work allowed to study the effect of synthesis parameters on particleboards properties using a statistical analysis approach. The main goal was to improve internal bond and decrease the thickness swelling of particleboards. The results obtained from the ANOVA analysis indicate that:

- The gel time is significantly affected by solids content and % U;
- The final viscosity and the next day viscosity are influenced by solids content and % U;
- % DMU is significantly influenced by the stopping viscosity;

- % DMU is statistically significant for the internal bond.

However, the results obtained for the optimal resin enabled to conclude that when small changes (such as those presented in this article) are applied in the synthesis parameters, there is no significant effect on the final properties of particleboards. This shows that this type of formulation is robust, so that small deviations in the synthesis, inherent to an industrial process, will not have a significant impact on the performance of the resin and consequently on particleboards properties.

Acknowledgements

The author thanks ENGIQ – Doctoral Programme in Refining, Petrochemical and Chemical Engineering (PDERPQ); FCT and EuroResinas – Indústrias Químicas for the PhD grant PD/BDE/174352/2016. This work was financially supported by: Project POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT -Fundação para a Ciência e a Tecnologia; the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement and 2GAR project under PT2020.

References

- [1] Instituto Nacional de Estatística, Instituto Nacional de Estatística, (2017). https://www.ine.pt/xportal/xmain?xpgid=ine_main&xpid=INE.
- [2] Food and Agriculture Organization of the United Nations, Forestry Production and Trade, (2017). http://www.fao.org/faostat/en/#home.
- [3] M. Dunky, The Chemistry of Adhesives, in: COST Action E13 Wood Adhes. Glued Prod., 2001.
- [4] L. H. Carvalho, F.D. Magalhães, J. Ferra, Fomaldehyde Emissions from Wood-based Panels -Testing Methods and Industrial Perspectives, in: Formaldehyde Chem. Appl. Role Polym., Nova Science Publishers, 2012.
- [5] J. Ferra, P.C. Mena, J. Martins, A. Mendes, M.R.N. Costa, F.D. Magalhães, L.H. Carvalho, Optimization of the synthesis of urea-formaldehyde resins using response surface methodology, J. Adhes. Sci. Technol. 24 (2010) 1455–1472. doi:10.1163/016942410X501043.
- [6] N. Costa, J. Pereira, J. Ferra, P. Cruz, J. Martins, F.D. Magalhães, A. Mendes, L.H. Carvalho, Sodium metabisulphite as a scavenger of air pollutants for wood-based building materials, Int. Wood Prod. J. 4 (2013) 242–247. doi:10.1179/2042645313Y.0000000037.
- [7] N. Costa, J. Pereira, J. Ferra, P. Cruz, J. Martins, F.D. Magalhães, A. Mendes, L.H. Carvalho, Scavengers for achieving zero formaldehyde emission of wood-based panels, Wood Sci. Technol. 47 (2013) 1261–1272. doi:10.1007/s00226-013-0573-4.

- [8] N. Paiva, A. Henriques, P. Cruz, J. Ferra, L. Carvalho, F.D. Magalhães, Production of melamine fortified urea-formaldehyde resins with low formaldehyde emission, J. Appl. Polym. Sci. 124 (2012) 2311–2317. doi:10.1002/app.35282.
- [9] A. Sheikh, I. Khokhar, M. Anwar, M. Khan, A. H., Studies on Synthesis and Properties of Urea formaldehyde Adhesives, J. Chem. Soc. Pakistan. 30 (2008) 20–22.
- [10] A. Pizzi, Urea–Formaldehyde Adhesives, in: Handb. Adhes. Technol., 2003. doi:10.1201/9780203912225.ch31.
- [11] J. Ferra, A. Henriques, A. Mendes, M.R.N. Costa, L.H. Carvalho, F.D. Magalhães, Comparison of UF Synthesis by Alkaline-Acid and Strongly Acid Processes, J. Appl. Polym. Sci. (2011). doi:10.1002/app.
- [12] N. Costa, D. Martins, J. Pereira, J. Martins, J. Ferra, P. Cruz, A. Mendes, F.D. Magalhães, L.H. Carvalho, 13 C NMR study of presence of uron structures in amino adhesives and relation with wood-based panels performance, J. Appl. Polym. Sci. (2013). doi:10.1002/app.39688.
- [13] G. Myers, How mole ratio of UF resin affects formaldehyde emission and other properties: a literature critique, For. Prod. J. 34 (1984) 34–41.
- [14] R.M. Rammon, The Influence of Synthesis Parameters on the Structure of Urea-formaldehyde Resins, Washington State University, 1984.
- [15] A. Pizzi, L. Lipschitz, J. Valenzuela, Theory and practice of the preparation of low formaldehyde emission UF adhesives, Holzforschung. 48 (1994) 254–261.
- [16] B.Y. No, M.G. Kim, Syntheses and properties of low-level melamine-modified urea-melamineformaldehyde resins, J. Appl. Polym. Sci. 93 (2004) 2559–2569. doi:10.1002/app.20778.
- [17] M.G. Kim, H.U.I. Wan, B.Y. No, W.L. Nieh, Examination of Selected Synthesis and Room-Temperature Storage Parameters for Wood Adhesive-Type Urea – Formaldehyde Resins by 13 C-NMR Spectroscopy . IV, J. Appl. Polym. Sci. 75 (2001) 1155–1169. doi:10.1002/app.1950.
- [18] N. Paiva, J. Pereira, J. Ferra, P. Cruz, L.H. Carvalho, F.D. Magalhães, Study of influence of synthesis conditions on properties of melamine-urea formaldehyde resins, Int. Wood Prod. J. 3 (2012) 51–57. doi:10.1179/2042645312Y.0000000009.
- [19] B. Park, V. Causin, Crystallinity and domain size of cured urea-formaldehyde resin adhesives with different formaldehyde/urea mole ratios, Eur. Polym. J. 49 (2013) 532–537. doi:10.1016/j.eurpolymj.2012.10.029.
- [20] T. Li, X. Guo, J. Liang, H. Wang, X. Xie, G. Du, Competitive formation of the methylene and methylene ether bridges in the urea – formaldehyde reaction in alkaline solution : a combined experimental and theoretical study, Wood Sci. Technol. 49 (2015) 475–493. doi:10.1007/s00226-015-0711-2.
- [21] A. Nuryawan, A.P. Singh, M. Zanetti, B. Park, V. Causin, Insights into the development of crystallinity in liquid urea-formaldehyde resins, Int. J. Adhes. Adhes. 72 (2017) 62–69.

doi:10.1016/j.ijadhadh.2016.10.004.

- [22] H.G. Barth, B.E. Boyes, C. Jackson, Size Exclusion Chromatography and Related Separation Techniques, Anal. Chem. 70 (1998) 251–278. doi:10.1021/a1980015t.
- [23] B. Jeong, B. Park, Effect of Analytical Parameters of Gel Permeation Chromatography on Molecular Weight Measurements of Urea-Formaldehyde resins, J. Korean Wood Sci. Technol. 45 (2017) 471–781.
- [24] K. Kumlin, R. Simonson, Urea formaldehyde resins. 1. Separation of low molecular weight components in urea formaldehyde resins by means of liquid chromatography, Die Angew. Makromol. Chemie. 68 (1978) 175–184. doi:10.1002/apmc.1978.050680113.
- [25] J. Ferra, A. Mendes, M.R.N. Costa, F.D. Magalhães, L.H. Carvalho, Characterization of Urea-Formaldehyde Resins by GPC/SEC and HPLC Techniques: Effect of Ageing, J. Adhes. Sci. Technol. 24 (2010) 1535–1551. doi:Doi 10.1163/016942410x501070.
- [26] P.R. Ludlam, J.G. King, R.M. Anderson, Liquid chromatographic procedure for the separation and characterisation of simple urea-formaldehyde reaction products, Analyst. 111 (1986) 1265. doi:10.1039/an9861101265.
- [27] M. Dunky, Urea-formaldehyde (UF) adhesive resins for wood, Int. J. Adhes. Adhes. 18 (1998)
 95–107. doi:10.1016/S0143-7496(97)00054-7.
- [28] A.H. Iswanto, F. Febrianto, Y.S. Hadi, S. Ruhendi, The Effect of Pressing Temperature and Time on the Quality of Particle Board Made from Jatropha Fruit Hulls Treated in Acidic Condition, Makara J. Technol. 17 (2013) 145–151. doi:10.7454/mst.v17i3.2930.
- [29] M. Ghorbani, F. Bavaneghi, Effect of Press Cycle Time on Application Behavior of Board Made from Chemically Modified Particles, Drvna Industrija. 67 (2016) 25–31. doi:10.5552/drind.2016.1443.
- [30] Q. Wu, C. Piao, Thickness swelling and relation with internal bond, Compos. Manuf. Prod. 49 (1999) 50–55.
- [31] M. Zanetti, A. Pizzi, M. Beaujean, H. Pasch, K. Rode, P. Dalet, Acetals-induced strength increase of melamine-urea-formaldehyde (MUF) polycondensation adhesives. II. Solubility and colloidal state disruption., J. Appl. Polym. Sci. 86 (2002) 1855–1862. doi:10.1002/app.11105.
- [32] B. Park, Y.S. Kim, A.P. Singh, K.P. Lim, P.E.T. Al, Reactivity, Chemical Structure, and Molecular Mobility of Urea–Formaldehyde Adhesives Synthesized Under Different Conditions Using FTIR and Solid-State 13 C CP/MAS NMR Spectroscopy, J. Appl. Polym. Sci. 88 (2002) 2677–2687.
- [33] C. Xing, S.Y. Zhang, J. Deng, S. Wang, Urea Formaldehyde-Resin Gel Time As Affected by the pH Value, Solid Content, and Catalyst, J. Appl. Polym. Sci. 103 (2006) 2–5. doi:10.1002/app.

Figure captions

Figure 1. Adjusted RI (refractive index) for a typical UF resin.

Figure 2. Peak areas of urea (U), monomethylolurea (MMU) and dimethylolurea (DMU) for three

different parameters and commercial resin (Ind).

Figure 3. Effect of factor levels (resin properties) on panel quality (internal bond and thickness swelling).

Figure 4. Effect of factor levels (resin properties) on resins quality.

Figure 5. Effect of factor levels (synthesis parameters) on resin properties.



Figure 1. Adjusted RI (refractive index) for a typical UF resin.



Figure 2. Peak areas of urea (U), monomethylolurea (MMU) and dimethylolurea (DMU) for three different parameters and commercial resin (Ind).



Figure 3. Effect of factor levels (resin properties) on panel quality (internal bond and thickness swelling).



Figure 4. Effect of factor levels (resin properties) on resins quality.



Figure 5. Effect of factor levels (synthesis parameters) on resin properties.

Highlights: Gel time is significantly affected by solids content and % U; % DMU is significantly influenced by the stopping viscosity; % DMU is statistically significant for the internal bond; this type of formulation is robust