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Study of the synthesis parameters of a urea-formaldehyde resin synthesized according to alkaline-acid process

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ABSTRACT

This paper presents a study of two crucial synthesis parameters of the alkaline-acid process of UF resin synthesis: condensation formaldehyde/urea (F/U) molar ratio and U feed rate during the methylolation step. The differences in the polymeric structures and the performance of the ensuing resins on particleboards (PBs) properties were analyzed and compared with a standard resin. The molecular weight distribution of the resins was monitored by gel permeation chromatography/size exclusion chromatography (GPC/SEC) and the unreacted oligomers by high-performance liquid chromatography (HPLC). The PBs produced were analyzed following European standards for mechanical tests and formaldehyde emission. The data obtained were also submitted to a statistical analysis.

The results obtained showed that the use of low molar ratios yield higher internal bond strength (IB) values and lower formaldehyde emissions (F). In turn, the effect of urea feed rate during the methylolation step on IB values depends on the F/U_{II} molar ratio used: (i) a reduction for the higher final molar ratio used, and no effect for the lowest final molar ratio used. Moreover, the statistical analysis carried out showed that F/UII molar ratio has significance on almost all of the resins' characteristics.

The resin used as standard yielded the best results when the final F/U molar ratio was 1.10 and the resulting PBs presented values of internal bond (IB) of 0.51 N mm^{-2} and formaldehyde content (F) of 5.1 mg/100 g o.d.b., complying with the market requirements.

Additionally, the effect of resin ageing was also studied and the PBs prepared using the best resin upon fifteen days of its production presented similar IB values and even lower F content in relation to those obtained using fresh resin.

1. Introduction

Urea-formaldehyde (UF) resins are the most widely used adhesives in the manufacture of wood-based panels due to characteristics such as low cost, water dispersibility, fast curing, and high performance. Unfortunately, formaldehyde used in the synthesis process is released in different stages such as the preparation process and application of the resins [1–3]. In order to reduce the health risk of UF resins, many works have been done on the development of low F emission UF resins without the loss of the high performance feature for these resins [4–9]. These studies showed that the key to reduce F emissions was cutting down the F/U molar ratio, even though this affects negatively the degree of crosslinking, and thus the mechanical properties of final particleboards.

UF resins are formed of only two monomers; however, the reaction between them is complex due to their high reactivity, the various reaction schemes, and the possible different molar ratios between the two raw materials. The classical synthesis process can be divided into three steps These include: methylolation under alkaline conditions (first addition of urea), condensation under acidic conditions (second addition of urea), and neutralization and addition of the so-called final urea

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or last urea (third addition of urea, but according to previous studies the conventional two step procedure presents good results and was used in this work [10,12]. Basically, the first load of U is added under controlled temperature until attaining the desired F/U molar ratio. The pH is adjusted to moderate acid and the condensation step is activated. As the desired viscosity is reached, the pH is adjusted to slightly alkaline and the condensation reactions are ceased. The cooling step starts and the second (and last) load of U is added until the desired F/U molar ratio. The chemical linkages formed during the process are presented in Fig. 1.

Some studies have shown that synthesis parameters such as F/U molar ratio, U feed rate, pH, and reaction temperature have a great effect on the structure and properties of UF resins and consequently on PBs performance [9,13–18]. Meyers reviewed the influence of the F/U ratio on free F and panel properties [9]. Rammon studied the parameters of UF resins synthesis via an alkaline-acid process and found that increasing pH in the alkaline phase or a longer acid condensation time lead to less formation of ether linkages, related to the release of F [14]. Pizzi et al. reported that the increase of the number of additions of U during the synthesis of the resin increases the bond strength [19,20]. Kim et al. synthesized resins with F/U molar ratios during the first and second U loads in weak alkaline pH. The effect of different cooling rates at the end of manufacture and storage times was also studied. Kumar et al. studied a four stage condensation process consisting of the first stage in a high acidic environment followed by an alkaline condensation, an acidic condensation and neutralization. These steps and the duration between additions of U were crucial to control the molecular weights and oligomeric structures [21]. According to Paiva et al., small variations in some synthesis parameters (F/U molar ratio and condensation U feed rate) of MUF synthesis may result in significant differences in the final resin properties [17]. On the other hand, our previous work showed that some resins produced according to the classical synthesis procedure are robust and small deviations in the process parameters (pH and temperature) do not have significant impact on the performance of the resin and consequently on PB properties [22]. The results for this study can be justified for the small changes applied. The pH and temperature values were varied ±7.5% in relation to the reference values commonly used in the synthesis. However, the variation used has been chosen slightly over the limits of the industrial fluctuations in the process.

The aim of the present work was to study two synthesis parameters (condensation F/U molar ratio and U feed rate), in order to optimize the procedure of the alkaline-acid process (two step procedure). More specifically, the main purpose was to find the best condensation F/U molar ratio and U feed rate during the methylolation step to obtain PBs with good properties whilst keeping the same pH and temperatures. For this purpose, a standard resin (Resin 1) was used as reference. Additionally, the effect of resin ageing was also assessed. The resins were characterized and the mechanical properties of the PBs measured using standard quality control methods and mechanical characterization techniques; the results obtained were submitted to statistical analysis.

2. Materials and methods

2.1. Materials

Formaldehyde (55 wt% solution), urea, ammonium sulphate (30 wt % solution), sodium hydroxide (50 wt% solution), and acetic acid (25 wt % solution) were provided by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal). Wood particles (recycled mix) and paraffin (50 wt% dispersion) for the production of PBs were supplied by Sonae Arauco (Oliveira do Hospital – Portugal).

2.2. Methods

2.2.1. Resins production

The production of the resins was carried out in a 2.5 L round bottom reactor, equipped with mechanical stirring and thermometer. The reactor was heated with a mantle and the temperature was measured with a thermometer. The pH and viscosity measurements were performed offline on samples taken from the reaction mixture (and re-added after).

Basically, the resins produced in this work were synthesized essentially according to the traditional two step procedure [12]. The first load of U (U_I) was added under controlled temperature ($T > 80$ °C) until attaining the desired F/U molar ratio. The pH was adjusted to moderate acid (4.0–6.0) and the condensation step was activated ($T > 80$ °C). When the desired viscosity was reached (see comment below) the pH was adjusted to slightly alkaline and the condensation reactions ceased when the cooling step started and the second (and last) load of U (U_{II}) was added until the desired F/U molar ratio. The second quantity of urea was added between 55 and 65 °C. At this step the temperature starts to decrease. The urea was added over a period of 30 min.

The stop viscosity (viscosity when the reaction stopped) was the same for all versions. However, as different molar ratios were used, the final viscosities were different. The target viscosity was defined according to the industrial process used in the company which usually uses a stopping viscosity for each process between 300 and 400 mPa.

In this study, two synthesis parameters were studied: the condensation F/U molar ratio (Resin 1, Resin 2 and Resin 3) and U feed rate during the methylolation step (Resin 1, Resin 4, Resin 5 and Resin 6). All the resins produced and the corresponding synthesis parameters are summarized in Table 1. For the final F/U molar ratio (F/U_{II}), three values were studied: 1.10, 1.18, and 1.25 (final molar ratio will only define the application of the resin).

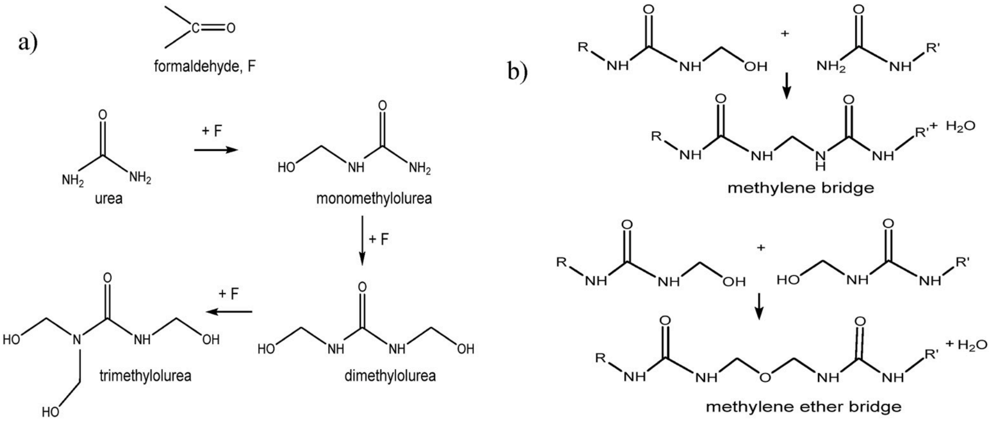


Fig. 1. a. Formation of methylolureas by the addition of F to U and b. Condensation step for a UF resin, where methylene and methylene ether bridges are formed.

Table 1
Synthesis parameters.

	Resin 1	Resin 2	Resin 3	Resin 4	Resin 5	Resin 6
$T_{methylolation}$ (°C)			80–100			
$T_{condensation}$ (°C)			80–100			
Condensation F/U molar ratio (F/U_I)	2.00–2.25	1.75–2.00	1.50–1.75		2.00–2.25	
U feed rate (min)		t		t – 10	t – 20	t – 30
Final viscosity (mPa·s)			150–300			
Final pH			7.5–9.5			
Final F/U Molar Ratio (F/U_{II})			1.10/1.18/1.25			

Table 2
Characterization of UF resins synthesized using different F/U molar ratios.

Resin	F/U_{II} Molar Ratio	Final Viscosity (±10 mPa s)	Final pH (25 °C) (±0.20)	Gel time (±3 s)	Density (±1 kg m^{-3})	Solids content (±0.4%)
Resin 1	1.10	170	7.97	64	1267	63.4
	1.18	170	8.03	50	1268	63.3
	1.25	200	8.16	54	1266	62.3
Resin 2	1.10	225	8.45	64	1269	63.0
	1.18	260	8.52	54	1268	62.4
	1.25	350	8.48	54	1268	62.3
Resin 3	1.10	290	8.37	66	1270	63.2
	1.18	350	8.45	55	1268	63.1
	1.25	375	8.30	53	1267	62.3

2.2.2. *Resins characterization*

The resins performance was evaluated using common characterization methods which included the determination of physical and chemical properties, such as viscosity, solid content, gel time and pH. Advanced methods, such as chromatography techniques (GPC/SEC and HPLC) were also used to obtain more specific and detailed information about the structure and subsequent performance of the resins.

2.2.2.1. Standard characterization. The resin pH was measured using a combined glass electrode. pH final values for UF resins are usually between 7.5 and 9.5, and measured at 25 °C. Viscosity was measured using a Brookfield viscometer at a temperature of 25 °C. 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 (%) was determined by evaporation of volatiles in 2 g of resin after 3 h at 120 °C. Gel time (s) is the time needed for the resin to harden after addition of a latent hardener (ammonium sulphate). For this measurement, 100 g of resin (diluted to 50% solid content) was weighed into a beaker with 3 mL of a 30% latent hardener solution; 0.250 mL of this mix was added into a test tube, which was immersed into boiling water. A rod was used for stirring the solution until resin gelation.

2.2.2.2. Gel permeation chromatography/size exclusion chromatography (GPC/SEC). A GPC/SEC equipped with a Knauer RI detector 2300 and a Knauer 20 μL injector was used. The column used was a Polarsil size 100A and particle size 5 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 for 1 min. Subsequently, the sample was left to rest (10 min), filtered through a 0.45 μm PTFE filter and then injected. The calibration was done with polystyrene standards (162–66000 Da). Even though the hydrodynamic volume of the linear polystyrene used as a standard is expected to be significantly distinct from that of the branched and loosely crosslinked structures present in the resins under study, for comparison purposes it is considered acceptable. The polystyrene standard molar masses were between 162 and 66000 Da.In the present study "low MW" was considered to be in the range between 162 and 12000 Da, whilst "high MW" was considered in the range between 12000 and 66000 Da.

2.2.2.3. High-performance liquid chromatography (HPLC). 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/H_2O) was used as the mobile phase. The samples were prepared by dissolving 75–80 mg of resin in 1 mL of DMF, and after stirring for 1 min, the mixture was diluted in 2 mL of 90% of ACN and 10% H_2O. When the mobile phase was added, flocculation occurred. The sample was then left to rest (10 min), filtered and then injected. The calibration was performed using U and DMU standards.

2.2.3. *PB production and characterization*

Wood particles (a standard mix including 30% maritime pine, 15% eucalypt, 25% pine sawdust and 30% recycled wood) were blended with resin, paraffin (1 wt%) and catalyst in a laboratory glue bender. Surface and core layers were blended separately (6 mg of resin solid/100 d dry wood). The hardener amount in the core layer was 3 wt % and in the surface layers was 1 wt % (dry hardener per solid resin). Three layers PBs were hand formed in a square aluminum deformable container having dimensions of 210 × 210 × 80 mm^3. Surface and core layers differed in particle size distribution and moisture content (MC). The upper surface layer had a mass of 20%, the core layer 62% and the bottom surface layer 18%. The press used was a laboratory batch press equipped with two plates and blocks with 16 mm of height for panels with a final thickness of 16 mm. The temperature was automatically controlled by the press and the position was fixed by the block thickness. The mat was pressed at 190 °C to produce a board with a target density between 650 and 670 kg m^{-3} and a thickness of 16 mm. For all resins, three boards were produced using a pressing time of 90 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). The formaldehyde content (F) of all samples was determined according to the perforator method (EN 12460–5).

2.2.4. *Statistical analysis*

In this work the computer software package JMP was used. A statistical analysis of variance (ANOVA) was performed to determine which synthesis parameters were statistically significant. For this analysis, the resin (final viscosity, final pH, gel time, density, and solids content) and PB (IB, TS, F) properties were analyzed and related to the synthesis parameters F/U_I molar ratio, F/U_{II} molar ratio, U feed rate during the methylolation step, and condensation time for all the six resins produced (Resin 1 to Resin 6).

3. Results and discussion

In this study, a set of resins was synthesized according to the alkaline-acid process, keeping all synthesis parameters constant except the two relevant parameters under investigation: F/U molar ratio at

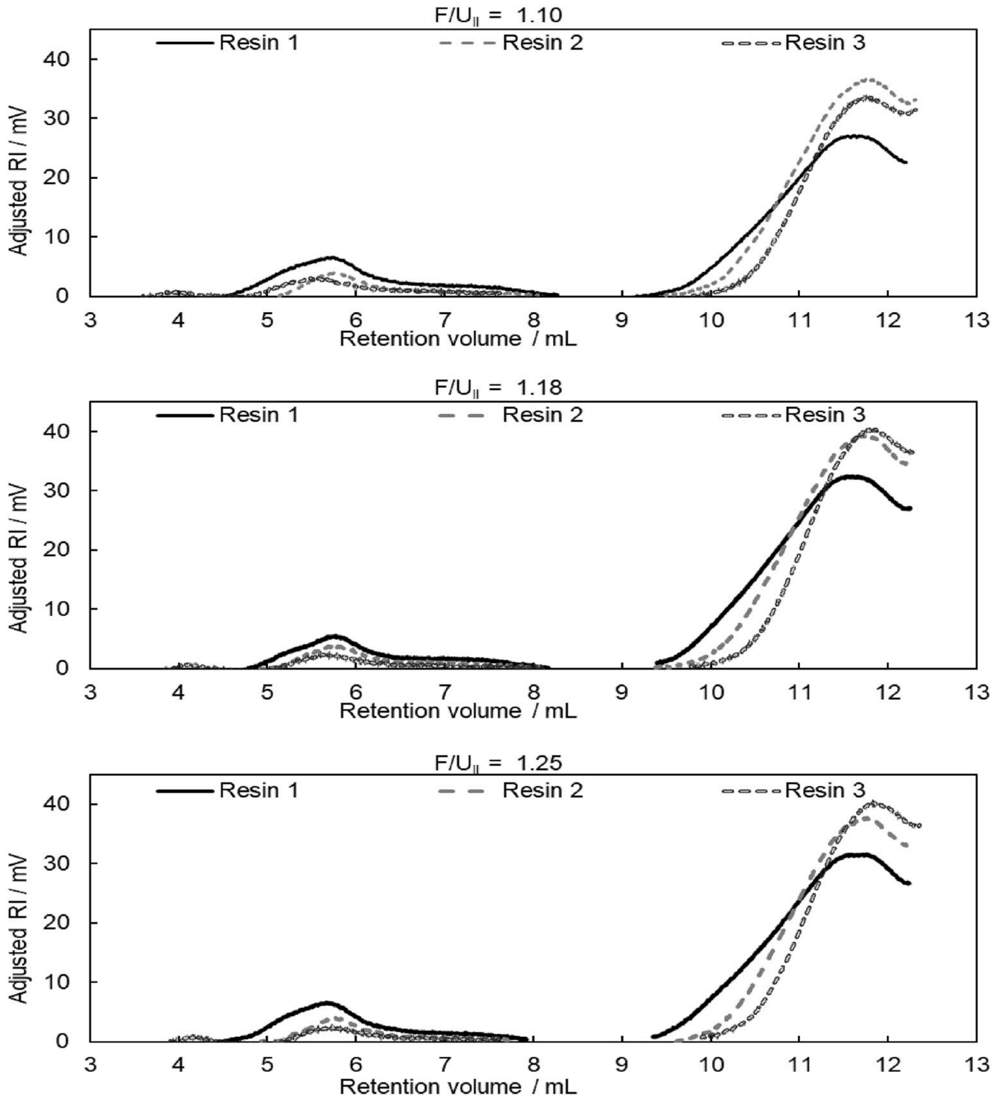


Fig. 2. GPC/SEC chromatograms of resins prepared using different F/U$_{II}$ molar ratio.

condensation step and U feed rate during the methylolation step. The amount of final U added after the condensation phase depends on the condensation molar ratio F/U$_I$ and the final F/U molar ratio F/U$_{II}$.

3.1. F/U$_I$ molar ratio

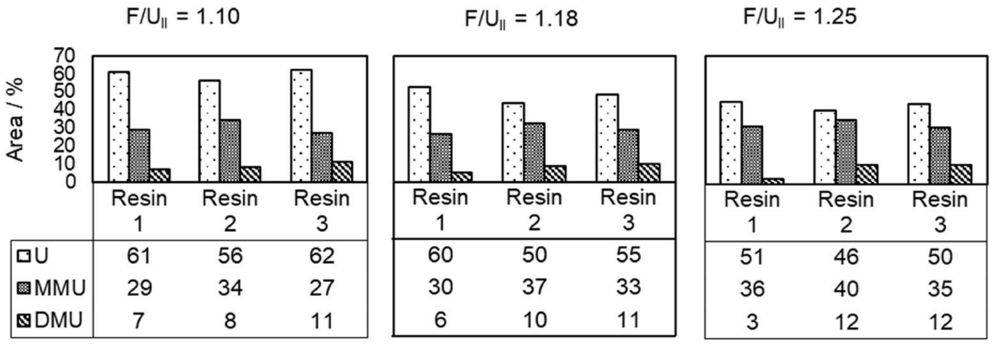
3.1.1. Standard characterization

Table 2 summarizes the results obtained from the standard characterization of the resins 24 h after synthesis. As observed, some of the characteristics depend on the F/U$_{II}$ molar ratio. The viscosity (mPa·s) gives a rough indication of the degree of polymerization of the resin, at the same final molar ratio and the same condensation molar ratio, which both determine the amount of urea to be added after the condensation step in order to achieve the targeted final molar ratio. For the same F/U$_{II}$ molar ratio, the viscosity is higher for resins prepared at a lower F/U$_I$ molar ratio. Additionally, the viscosity decreases with final molar ratio, because a higher amount of second urea is needed to adjust the lower final molar ratios. As the ratio of F and U is lower, the less the quantity of F is available for bonding with U hence, the condensation is slower and the polymer grows slowly yielding a lower viscosity for the same condensation time (viscosity Resin 1 < viscosity Resin 2 < viscosity Resin 3). The pH value is within the intended range (7.50 < pH < 9.00) for all resins. The density and solids content are also between the standard range of values (1265–1270 kg m^{-3} and 62.0–65.0%). In turn, the gel times directly depend on the F/U$_{II}$ used (64–66 s for F/U$_{II}$ = 1.10; 50–55 s for F/U$_{II}$ = 1.18; 53–54 s for F/U$_{II}$ = 1.25).

Table 3
Characterization of UF resins synthesized using different U feed rates.

Resin	F/U$_{II}$ Molar Ratio	Final Viscosity (±10 mPa s)	Final pH (25 °C) (±0.20)	Gel time (±3s)	Density (±1 kg m^{-3})	Solids content (±0.4%)
Resin 1	1.10	170	7.97	64	1267	63.4
	1.18	170	8.03	50	1268	63.3
	1.25	200	8.16	54	1266	62.3
Resin 4	1.10	190	8.01	59	1268	63.1
	1.18	205	8.06	58	1268	62.9
	1.25	210	8.10	56	1264	62.4
Resin 5	1.10	180	8.16	61	1267	63.9
	1.18	200	7.95	59	1266	62.9
	1.25	230	8.24	57	1265	62.5
Resin 6	1.10	150	8.06	61	1268	62.7
	1.18	170	8.02	58	1267	62.3
	1.25	170	7.96	52	1267	62.1

These results might be related to the fact that higher F/U$_{II}$ values are associated with a higher content of free formaldehyde and therefore a



	F/U$_{II}$ = 1.10			F/U$_{II}$ = 1.18			F/U$_{II}$ = 1.25		
	Resin 1	Resin 2	Resin 3	Resin 1	Resin 2	Resin 3	Resin 1	Resin 2	Resin 3
□U	61	56	62	60	50	55	51	46	50
▩MMU	29	34	27	30	37	33	36	40	35
▨DMU	7	8	11	6	10	11	3	12	12

Fig. 3. Peak areas of unreacted U, MMU and DMU for different F/U$_{II}$ molar ratios.

higher degree of crosslinking. These results are in agreement with those obtained by Jeremejeff who reported that the higher the F/U$_{II}$ value the higher the degree of branching of UF molecules, whilst studying the effect of different F/U molar ratios during the synthesis of UF resins in the liquid form [23].

3.1.2. *Gel permeation chromatography/size exclusion chromatography (GPC/SEC)*

In Fig. 2 it is possible to observe the molecular weight distribution (MWD) of the synthesized resins. GPC/SEC was used for the characterization of the resins, essentially of the polymer structure and hydrodynamic volume [24,25]. Even though the hydrodynamic volume of the

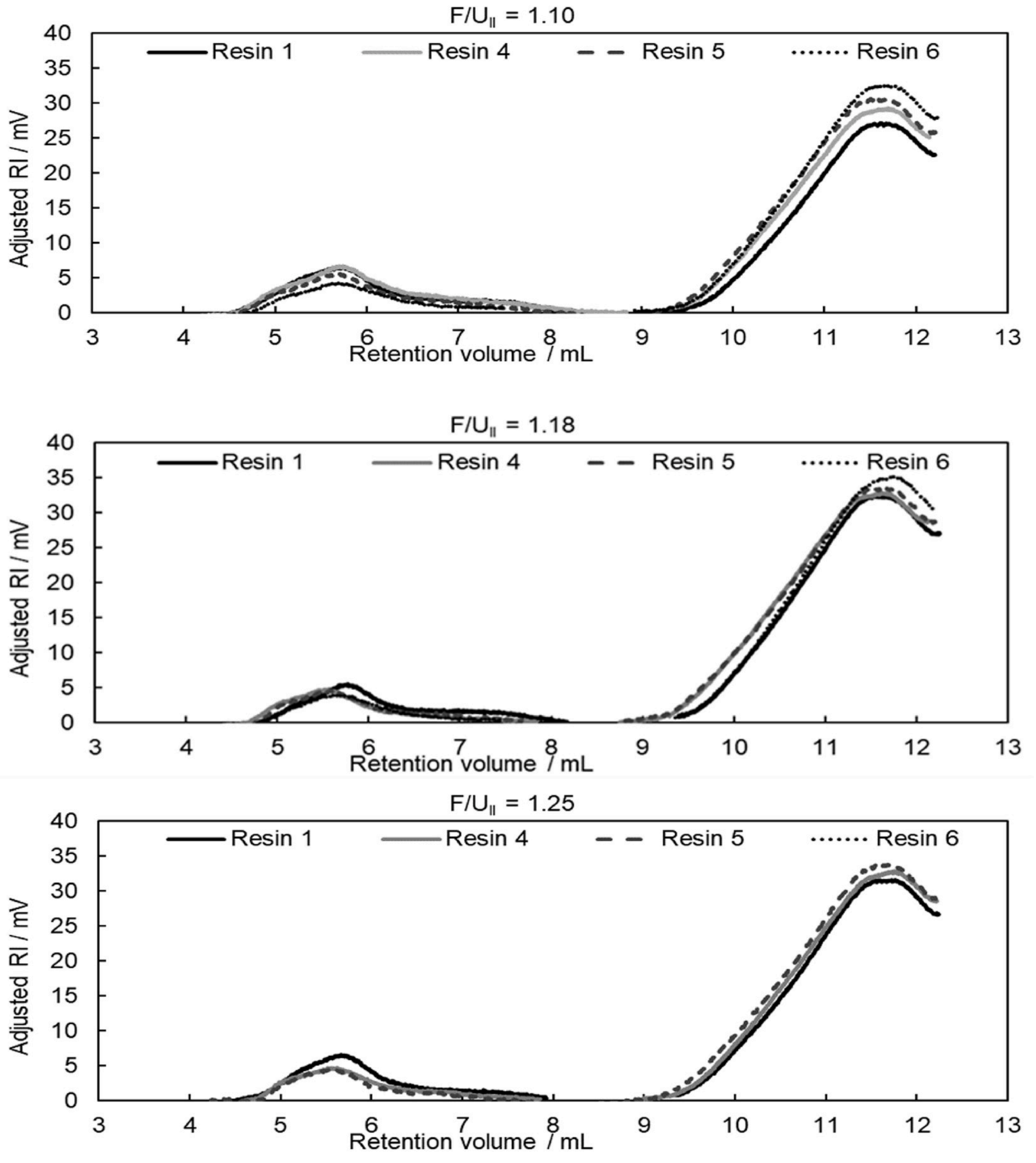
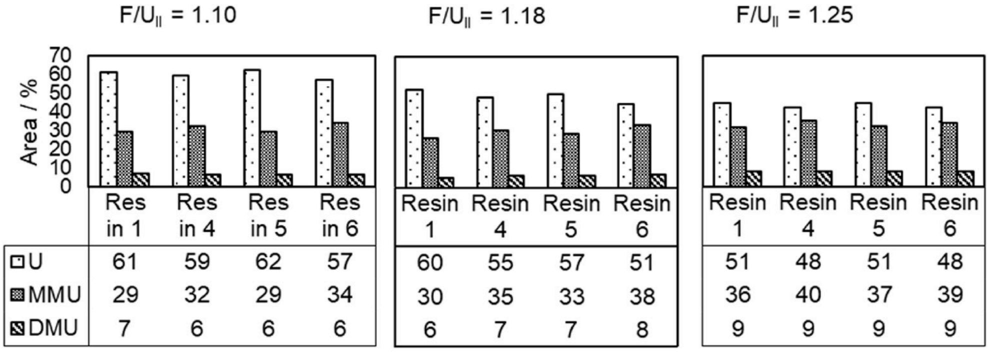


Fig. 4. GPC/SEC chromatograms of resins prepared using different U feed rates.



	F/U_{II} = 1.10				F/U_{II} = 1.18				F/U_{II} = 1.25			
	Resin 1	Resin 4	Resin 5	Resin 6	Resin 1	Resin 4	Resin 5	Resin 6	Resin 1	Resin 4	Resin 5	Resin 6
□U	61	59	62	57	60	55	57	51	51	48	51	48
▩MMU	29	32	29	34	30	35	33	38	36	40	37	39
▧DMU	7	6	6	6	6	7	7	8	9	9	9	9

Fig. 5. Peak areas of unreacted U, MMU and DMU for different U feed rates during the methylolation step.

linear polystyrene used as standards is expected to be significantly distinct from that of the branched and the already loosely crosslinked structures present in the resins under study, this approximation can be considered as acceptable for comparison purposes. Indeed, the presence of low and high molecular weight polymer chains is detected for all the resins. The same trend is observed when the different F/U_{II} molar ratios are compared. However, some differences can be detected when the different F/U_I molar ratios are considered. For example, in the region of higher molecular weights (MW), Resin 1 has the highest concentration signal (indicating a higher proportion of such higher molar masses, followed by Resin 2 and finally by Resin 3. Furthermore, it should be noted that in the case of Resin 3, prepared using the lowest F/U_I molar ratio in series (1.50–1.75), a small peak is detected around the retention volume of 4 mL. This is indicative of polymeric structures with MW even higher than Resin 1. This is thought to be associated with the fact that the higher amount of U added in the methylolation/condensation step may lead to the formation of higher molecular weight polymer and/or more linear chains resulting from reactions between oligomers intermediated by U molecules [17]. In turn, in the region of lower MW, the lowest concentration signal corresponds to Resin 3 followed by Resin 2 and then Resin 1 (MW Resin 3 < MW Resin 2 < MW Resin 1). Notice should however be made that due to the limitations mentioned in the experimental section regarding the calibration, the areas of these two regions should not be compared quantitatively.

3.1.3. *High-performance liquid chromatography (HPLC)*

HPLC is a chromatographic technique that allows the separation of a mixture of different molecular weight compounds. This method is very effective in identifying low molecular weights [26–28]. The use of this technique in the analysis of UF resins allows the separation and identification of unreacted U, monomethylolurea (MMU) and dimethylolurea (DMU). The amounts of urea and the two methylols consisting of the low MW fraction of the resins produced is shown in Fig. 3; increasing the F/U_{II} molar ratio, leads to a reduction of the amount of unreacted U. This result was expected because for $F/U_{II} = 1.25$ a smaller amount of U was added at the end.

Table 4
PBs properties at a pressing time of 90 s for F/U_I molar ratio.

Resin	F/U_{II} Molar Ratio	IB ($N·mm^{-2}$)	D ($kg·m^{-3}$)	TS (%)	MC (%)	F (mg/100 g o.d.b.)
Resin 1	1.10	0.51 ± 0.06	660 ± 8	32 ± 1	7.1 ± 0.6	5.1
	1.18	0.53 ± 0.07	653 ± 7	31 ± 1	7.0 ± 0.3	6.7
	1.25	0.69 ± 0.07	653 ± 7	26 ± 2	7.0 ± 0.1	8.8
Resin 2	1.10	0.44 ± 0.13	647 ± 25	30 ± 0	6.8 ± 0.1	4.5
	1.18	0.47 ± 0.04	659 ± 7	27 ± 3	6.6 ± 0.4	6.0
	1.25	0.49 ± 0.06	644 ± 18	27 ± 1	7.0 ± 0.2	6.0
Resin 3	1.10	0.41 ± 0.05	673 ± 12	31 ± 3	6.9 ± 0.1	4.0
	1.18	0.42 ± 0.01	665 ± 7	28 ± 1	6.9 ± 0.6	5.8
	1.25	0.54 ± 0.03	686 ± 10	29 ± 1	7.0 ± 0.2	7.8

3.2. *U feed rate*

3.2.1. *Standard characterization*

Table 3 summarizes the results obtained from the standard characterization of the resins prepared using different feed rates during the methylolation step as indicated in Table 1, after 24 h. As observed, some of the characteristics presented are again different depending on the F/U_{II} molar ratio. As seen for the F/U_I molar ratio analysis, for different F/U_{II} molar ratios, the viscosity is higher for resins when a higher F/U_{II} molar ratio is used. $F/U_{II} = 1.25$ is the highest molar ratio, as it takes the lowest amount of final U, so presents a higher final viscosity than other molar ratios (viscosity F/U_{II} 1.25 > viscosity F/U_{II} 1.18 > viscosity F/U_{II} 1.10) [17]. Despite these differences, all values for viscosity are between the target values which have been established for the lab cooks

Table 5
PBs properties at a pressing time of 90 s for U feed rate.

Resin	F/U_{II} Molar Ratio	IB ($N·mm^{-2}$)	D ($kg·m^{-3}$)	TS (%)	MC (%)	F (mg/100 g o.d.b.)
Resin 1	1.10	0.51 ± 0.06	660 ± 8	32 ± 1	7.1 ± 0.6	5.1
	1.18	0.53 ± 0.07	653 ± 7	31 ± 1	7.0 ± 0.3	6.7
	1.25	0.69 ± 0.07	653 ± 7	26 ± 2	7.0 ± 0.1	8.8
Resin 4	1.10	0.36 ± 0.04	645 ± 18	30 ± 3	6.1 ± 0.1	6.0
	1.18	0.54 ± 0.07	649 ± 7	27 ± 2	6.2 ± 0.1	6.4
	1.25	0.61 ± 0.04	649 ± 12	25 ± 0	6.2 ± 0.1	9.3
Resin 5	1.10	0.36 ± 0.06	616 ± 5	33 ± 2	6.2 ± 0.2	5.8
	1.18	0.42 ± 0.02	635 ± 22	28 ± 2	6.1 ± 0.1	6.6
	1.25	0.58 ± 0.05	656 ± 5	27 ± 2	6.3 ± 0.1	9.3
Resin 6	1.10	0.35 ± 0.06	636 ± 23	30 ± 1	7.2 ± 0.0	4.9
	1.18	0.49 ± 0.04	649 ± 8	28 ± 1	7.1 ± 0.2	6.9
	1.25	0.53 ± 0.04	649 ± 15	31 ± 3	7.0 ± 0.1	8.7

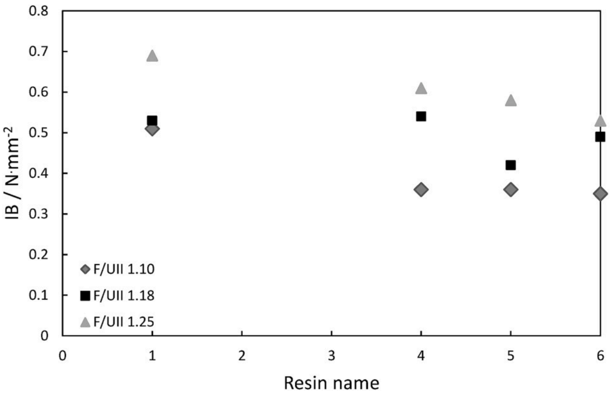


Fig. 6. IB values for Resin 1, Resin 4, Resin 5 and Resin 6 for different F/U_{II} molar ratios.

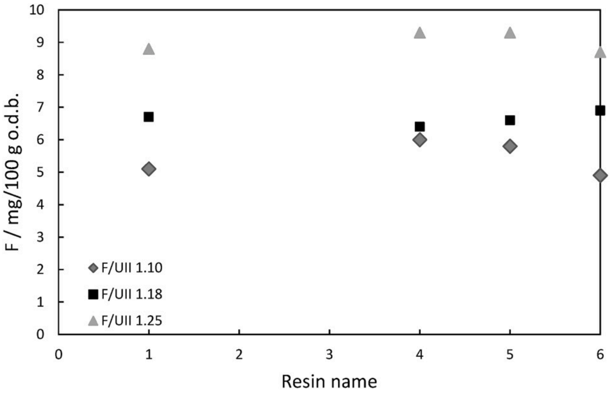


Fig. 7. F values for Resin 1, Resin 4, Resin 5 and Resin 6 for different F/U_{II} molar ratios.

(150–300 mPa s). The pH value is within the intended range ($7.5 < \mathrm{pH} < 9.0$), for all resins and for all F/U_{II} molar ratios. The density and solids content are also within the target values (1265–1270 kg m^{-3}). Gel time directly depends on the F/U_{II} molar ratio (61–64 s for $F/U_{II} = 1.10$; 58–59 s for $F/U_{II} = 1.18$; 50–54 s for $F/U_{II} = 1.25$).

For urea feed rate, as proved below for the statistical analysis, differences are not significant.

3.2.2. *Gel permeation chromatography/size exclusion chromatography (GPC/SEC)*

Fig. 4 shows the gel chromatograms of the synthesized resins. As observed previously, low and high molecular weight polymer regions were detected for all resins. The same trend is observed when the different F/U_{II} molar ratios are compared. The values are similar showing that the U feed rate during the methylolation step does not seem to have any major influence on the high MW fraction. Moreover, in the region of lower MW, the lowest value corresponds to Resin 1. With these results, it is possible to conclude that variations of the U feed rate during the methylolation step in the alkaline phase do not influence the molecular structure of the final resin, because the final polymeric structure is determined in the acidic condensation phase.

3.2.3. *High-performance liquid chromatography (HPLC)*

The amount of unreacted monomers is shown in Fig. 5. Increasing the F/U_{II} molar ratio, the amount of unreacted U decreases. This result was expected because for a higher F/U_{II} value a smaller amount of U was added at the end, as previously mentioned. The percentage of MMU and DMU is almost the same for different F/U_{II} molar ratios.

3.3. *PB properties*

PB properties were measured for both synthesis parameters under investigation: F/U molar ratio at condensation step and U feed rate during the methylolation step. The final amount of U added depends on the molar ratio during the acidic condensation phase as well as on the final F/U molar ratio (F/U_{II}).

3.3.1. *F/U_I molar ratio*

Table 4 summarizes the PB properties for the series with variation of the first molar ratio F/U_I and the final molar ratio F/U_{II}. The D values are within the expected range for all PBs, but nevertheless show some variation; however, no connection between D and the two parameters in the investigation are given. As expected the boards with the resins with lower F/U_{II} molar ratio present the lowest F content. This dependence is well known and can be expected since more F was consumed by the increased content of U [17]. The IB decreases with lower F/U_{II} molar ratio, as this also was to be expected; thickness swelling did not show clear dependence from the two parameter in investigation. The MC is similar for all first and final molar ratios. Comparing the IB achieved using the various F/U_I molar ratios it is possible to conclude that the values are similar with just slight differences. It is important to note that according to the statistical analysis presented below, the IB is not significantly affected by F/U_I molar ratio. In turn, it can be observed that for Resin 1 (i.e. prepared using the highest condensation molar ratio) the IBs are higher for all the final molar ratios (F/U_{II}). Comparing the two lower F/U_I molar ratios there is no clear result. This difference can be explained by the higher viscosities of Resin 2 and Resin 3, which may limit resin penetration in the wood during gluing and remain on the surface as opposed to what tends to happen when the resin presents a low viscosity and can easily penetrate into the wood particles.

From our long term experience in PB production, high values of IB are obtained when higher final molar ratios are used. This might be related with the higher proportion of free formaldehyde of methylolated monomers and oligomers. Conversely, for a lower F/U_{II} molar ratio, the proportion of the methylolated species decreases and therefore a detriment on IB is verified.

The free F of the panels (for perforator value) is higher for a higher first molar ratio i.e. F Resin 1 > F Resin 2 > F Resin 3 for all three final molar ratios. Resin 1 prepared using the highest first molar ratio shows higher F values compared to the other resins. This is rather surprising and not so easy to explain. The higher the first molar ratio, the higher is

Table 6
ANOVA p-value and significance level (*5%, **1%, ***0.1%).

	Intercept	F/U_I molar ratio	F/U_{II} molar ratio	U feed rate (min)	Condensation time (min)
Final viscosity (mPa·s)	0.8764	0.7300	0.0024**	0.5292	0.6986
Final pH	0.7812	0.0876	0.5816	0.0236*	0.0478*
Gel time (s)	0.0191*	0.2367	<0.0001***	0.3264	0.2000
Density (kg·m^{-3})	<0.0001***	0.0569	0.0025**	0.0584	0.0276*
Solids content (%)	<0.0001***	0.0171*	<0.0001***	0.0326*	0.0142*
IB (N·mm^{-2})	0.9109	0.4045	<0.0001***	0.7996	0.2528
TS (%)	0.0585	0.3573	0.0026**	0.2335	0.4266
F (mg/100 g o.d.b.)	0.7421	0.2884	<0.0001***	0.1549	0.2208

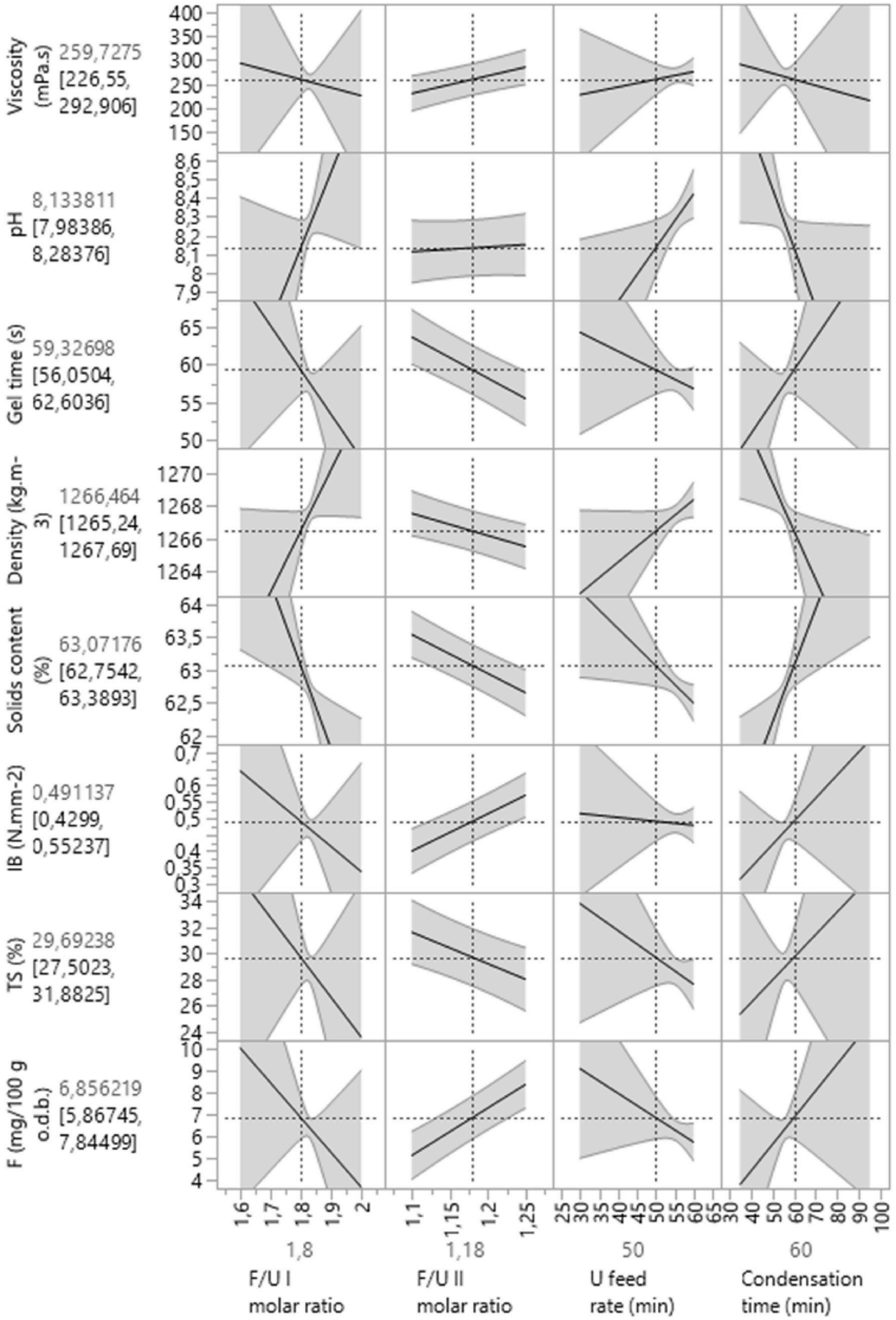


Fig. 8. Prediction profile for different responses with confidence intervals (The values presented on the left side represent the values obtained for each factor studied).

Table 7
Characterization of Resin 1 with $F/U_{II} = 1.18$ after 24 h and 15 days.

Resin	Final Viscosity (±10 mPa s)	Final pH (25 °C) (±0.20)	Gel time (±3s)	Density (±1 kg m^{-3})
Resin 1	170	8.03	50	1268
Resin 1–15 days	230	7.62	49	1269

Table 8
PBs properties at a pressing time of 90 s for Resin 1 after 24h and 15 days.

Resin	IB (N·mm^{-2})	D (kg·m^{-3})	TS (%)	MC (%)	F (mg/100 g o.d.b.)
Resin 1	0.53 ± 0.07	653 ± 7	31 ± 1	7.0 ± 0.3	6.7
Resin 1–15 days	0.52 ± 0.05	659 ± 14	31 ± 1	6.2 ± 0.1	5.2

the addition of second urea, hence, the content of free urea in the final resin should be lower; on the other hand resins with higher first molar ratio have higher methylol group contents, but not all of them then react with the second urea so the best results were obtained for Resin 1 related to IB however, if the goal is to reduce the F value, a better choice would be Resin 2 or Resin 3. Yet, it is important to note that for Resin 2, the value for F is lower than expected which suggests the measurement could be wrong.

As expected, the F value increases when higher final molar ratios are used and this is actually in agreement with our long term experience.

3.3.2. U feed rate

Table 5 summarizes the properties of the PBs at a pressing time of 90 s for resins prepared with varying urea feed rate at the alkaline methylation step. The D values of PBs are within the expected range. As observed above, the IB and F increase with higher F/U_{II} molar ratio. Resin 1 prepared using the lowest feed rate yields the best IB in most cases; the other three resins prepared using increasing feeding rates do not show a clear picture regarding the IB values. The results obtained using the different resins are plotted in Fig. 6. As observed, the IB is similar for Resin 4, Resin 5 and Resin 6 and higher for Resin 1. Indeed, according to the statistical analysis presented below, the IB is not significantly affected by urea feed rate. However, it is important to study this parameter. These results also agree with the observation by Pizzi et al. and Kumar et al., who reported that an increase in the number of additions of U during the synthesis increases the IB, even though those authors studied the urea feed rate for different steps of the process [29, 30]. As mentioned above when discussing the effect of F/U_I molar ratios, the TS presents lower values at higher IBs. In turn, as illustrated in Fig. 7 the F content is similar for all the panels prepared using resins with the same F/U_{II}, possibly due to the fact that a faster addition of U during the methylolation step favours the formation of methylene diU as illustrated in Fig. 1 (a) which is highly reactive towards F. Nevertheless, it is important to note that all panels prepared using resins with F/U_{II} molar ratios of 1.10 and 1.18 are below the minimum acceptable for E1 class ($F \leq 8$ mg/100 g o.d.b.).

3.4. Statistical analysis

Table 6 presents the ANOVA p-value and significance level for the results obtained (characterization of the resins and PB) and Fig. 8 represents the effect of factor levels (prediction profiler) for the same results. According to ANOVA results, the final viscosity is significantly affected by F/U_{II} molar ratio (p-value = 0.0024**). This value is associated with the different amounts of final U added for different F/U_{II} molar ratios. From Fig. 8, the final viscosity increases with the increase of F/U_{II} molar ratio. High values of F/U_{II} molar ratio imply that less U was added to achieve a high final viscosity. The addition of final U increases the solid content of the resin yet, due to the small size of these molecules, the viscosity drops. The final pH is significantly affected by U feed rate (p-value = 0.0236*) and condensation time (p-value = 0.0478*). The final pH (between 7.5 and 9.5) increases with the increase of U feed rate and the reduction of condensation time. Gel time is also significantly affected by the F/U_{II} molar ratio (p-value < 0.0001***) and other factors such as temperature or the pH during the condensation or methylolation step (intercept p-value = 0.0191*). Gel time, as a measurement of resin reactivity, presents higher values when the quantity of the last U added increases, *i.e.* when the F/U_{II} molar ratio decreases. Another explanation may be that more U simply reacts with the free F, hence hindering the reaction of the latter with the hardener to create the acid necessary to promote the hardening reaction. Density is significantly affected by F/U_{II} molar ratio (p-value = 0.0025**) and condensation time (p-value = 0.0276), however, other factors (p-value < 0.0001***) also influence density. According to this study, the solids content is significantly affected by all the factors studied. In particular, by the first molar ratio because urea in this stage reacts, whereas the final urea remains mainly as free urea in the resin and will get lost during the determination of the solid content. As regards the effect on the characteristics of the ensuing PBs, IB is significantly affected by F/U_{II} molar ratio (p-value < 0.0001***). A high F/U_{II} molar ratio leads to a high IB value. TS decreases with the increase of F/U_{II} molar ratio. TS is generally related to IB. When the bonds are strong, the TS decreases. In addition, the bonds can restrain wood swelling and in this way the entry of water is difficult. F increases with the increase of F/U_{II} molar ratio. At high F/U_{II} molar ratio more free formaldehyde as well more methylol groups are present, this increases curing speed, but at the same time more formaldehyde and methylol groups will remain unreacted and will therefore contribute to the F value.

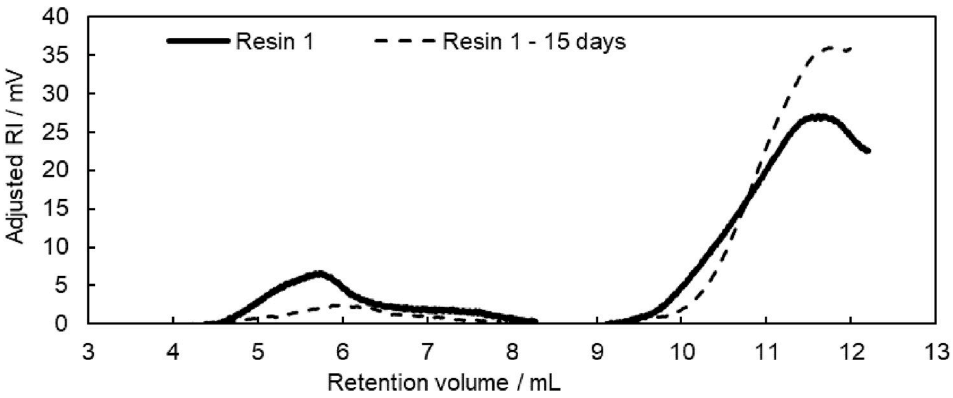


Fig. 9. GPC/SEC chromatograms for Resin 1 after 24 h and 15 days.

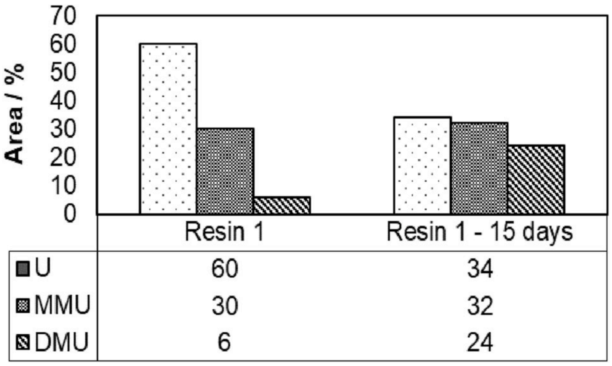


Fig. 10. Peak areas of unreacted U, MMU and DMU for Resin 1 after 24 h and 15 days.

3.5. Aged resin

The resin prepared using the molar ratio F/U$_{II}$ = 1.18 (Resin 1) was analyzed after ageing, using GPC/SEC and HPLC techniques as well as by viscosity, pH, gel time and density. After 15 days, the viscosity increases and the pH decreases due to the Cannizzaro reaction. The gel time and density do not change significantly (Table 7).

Fig. 9 shows the chromatograms for Resin 1 after 24 h and 15 days. According to Ferra et al. no significant changes in the molecular weight distributions were observed until 12 days of storage time [31]. However, the results here presented, for 15 days are different. On analyzing the chromatograms, it is possible to observe that the retention volume between 9 and 12 mL for intermediate polymer and oligomers, decreases with ageing. Related to high retention volume, an increase in this volume is observed with ageing.

Fig. 10 shows the evolution with ageing of the fractions of U, MMU and DMU for Resin 1 after 24 h and 15 days, respectively. The fractions of U and DMU decrease significantly after 15 days whilst the fraction MMU is almost unchanged. Similar results were observed by Ferra et al. [31], who have reported that the amount of U decreases with ageing and DMU increases. These results indicate that the free F reacts with U and mostly with MMU forming DMU. In brief these results indicate that reactions between F, U and methylolureas continue during the storage of the resin which is in agreement with Kim et al., who have reported that the amount of MMU during storage could increase or decrease depending on the amount of free F present in the resin [32].

Table 8 presents the PB test results for the fresh and the aged resins at a pressing time of 90 s. D, TS, and IB are more or less equal; the minimum acceptable IB for panels type P2 ($\geq$0.35 N mm^{-2}) according to EN 312 is fulfilled. The main difference between these panels is related to F content. After 15 days the F content is lower (5.2 mg/100 g o.d.b) comparing with that of the same resin after 24 h (6.7 mg/100 g o.d.b.). This result can be explained by the ageing of the resin, during which free F is consumed. Therefore, the panels produced after 15 days presented less F content.

4. Conclusions

This paper has considered the effect of two crucial synthesis parameters for the alkaline-acid process: (i) the condensation F/U molar ratio and (ii) the U feed rate during the alkaline methylolation step; both, the various resins themselves as well as PBs produced using those resins have been investigated. Additionally, the effect of resin ageing of one of the resins was also evaluated.

As regards the F/U$_I$ molar ratio, it can be observed that for Resin 1 (i.e. with the highest condensation molar ratio) the IBs are higher at all final molar ratios. In turn no clear result was obtained for Resins 2 and 3 prepared using lower condensation molar ratios.

In what regards the feed rate during the methylolation step, the impact on IB varies depending on the final molar ratio used: for the highest final molar ratio IB decreases with higher feed rate; for the medium final molar ratio (Resin 1 and 6) the same IB is obtained, with variation up and down in between depending on the feed rate; for the lowest final molar ratio variations of the feed rate do not cause any difference on the IB values obtained (Resins 4–6, but all of them are much lower compared to the IB value obtained for Resin 1.

Concerning F content resins 2 and 3 show an advantage, but the IB values are lower. However, a lower F can be also achieved using lower final molar ratio whilst obtaining high IB values as it was the case for Resin 1 prepared using a final molar ratio of 1.10. Furthermore, it was also concluded that a higher feed rate of U leads to panels with lower IB.

In brief, with this study it was possible to conclude that small changes in some synthesis parameters may result in differences in the final resin properties and consequently on the PBs produced. Moreover, the statistical analysis allowed understanding which synthesis parameters have a significant effect on the resins' properties. F/UII molar ratio presented significance on almost all the resins' characteristics, but the other parameters (F/UI molar ratio, U feed rate and condensation time) had minor impact on those properties.

Furthermore, the results obtained for PBs produced using Resin 1 after 15 days ageing showed equally good performance as with the fresh resin but a significantly lower F value proving that resin ageing is not a problem and can actually be an advantage regarding F emissions.

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