Production of water tolerant melamine-urea-formaldehyde resin by incorporation of sodium metabisulphite

Nádia T. Paiva, João M. Ferra, João Pereira, Jorge Martins, Luísa Carvalho, Fernão D. Magalhães

www.elsevier.com/locate/ijadhadh

PII: S0143-7496(16)30128-2
DOI: http://dx.doi.org/10.1016/j.ijadhadh.2016.06.005
Reference: JAAD1859

To appear in: *International Journal of Adhesion and Adhesives*

Received date: 16 May 2015
Accepted date: 8 June 2016

Cite this article as: Nádia T. Paiva, João M. Ferra, João Pereira, Jorge Martins Luísa Carvalho and Fernão D. Magalhães, Production of water tolera melamine-urea-formaldehyde resin by incorporation of sodium metabisulphit *International Journal of Adhesion and Adhesive* http://dx.doi.org/10.1016/j.ijadhadh.2016.06.005

Production of water tolerant melamine-urea-formaldehyde resin by incorporation of sodium metabisulphite

Nádia T. Paiva[a,b], João M. Ferra[b], João Pereira[a,c], Jorge Martins[a,c], Luísa Carvalho[a,c], Fernão D. Magalhães[a*]

[a]LEPABE, Chemical Engineering Department, Faculty of Engineering, University of Porto, Rua Dr^{o} Roberto Frias, 4200-465, Porto, Portugal

[b]EuroResinas – Indústrias Químicas, S.A., 7520-195, Sines, Portugal

[c]DEMAD – Department of Wood Engineering, Polytechnic Institute of Viseu, Campus Politécnico de Repeses, 3504-510 Viseu, Portugal

*Corresponding author: fdmagalh@fe.up.pt

Keywords: MUF resins, sodium metabisulphite, water dilution capacity

Abstract

The aim of this work was the development of a new MUF resin formulation with high tolerance towards water dilution, and a good overall performance in terms of physico-mechanical properties and formaldehyde emissions. For this purpose, sodium metabisulphite (MTBS) was added during melamine condensation reaction, therefore decreasing its extent by blocking amino groups. It was found that the resins with higher amounts of MTBS have obtained the higher water dilution capacity (a percentage of 6 % of MTBS resulted in a resin with a water tolerance about 60 times higher than the one present in a resin without MTBS incorporation). The molecular weight distribution showed that the resins produced with MTBS have a different polymeric structure. Regarding particleboard production and evaluation, it was possible to conclude that the increase in MTBS addition lowers the internal bond strength and formaldehyde emissions. However, with the resin, having the MTBS addition of 6 %, it was still possible to obtain the panel with internal bond strength higher than the acceptable minimum (0.45 N·mm^{-2}), with a pressing time of 150 s. When compared with commercial MUF resins, the formulation developed in this work presents lower values of formaldehyde emissions, complying to CARB II regulation, even though with somewhat inferior physico-mechanical performances.

1. Introduction

Formaldehyde-based resins are the most commonly used adhesive system in industrial production of wood-based panels. Urea-formaldehyde resins (UF) are predominant, followed by phenol-formaldehyde (PF), melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF). Other synthetic and natural adhesives are employed, but in a significantly lower scale [1, 2]. Formaldehyde-based resins are mostly used in the production of a wide range of board's types such as particleboard (PB), medium density fibreboard (MDF), oriented strand board (OSB) and plywood (PW) [3].

The success of UF resins is due to their high reactivity and good mechanical performance, combined with low cost. However, they have an important disadvantage: low water resistance caused by chemical reversibility of aminomethylene bonds, leading to the release of formaldehyde [4]. MF resins have much higher resistance to water, which is their main advantage when compared with UF resin. However, the higher cost and slightly lower reactivity make MF resins acceptable only for high value-added products. Melamine-based resins are among the most used adhesives for exterior and protected exterior wood-based panels and for the production and bonding of low- and high-pressure decorative laminates and overlay sheets [5].

In order to reduce cost, melamine-urea-formaldehyde (MUF) resins are often used as an alternative to MF, despite the decrease in performance of the final product. MUF resins obtained by copolymerization of the three monomers are superior in performance to those prepared by mixing pre-polymerized UF and MF resins [5]. The relative mass ratios of melamine to urea used in the synthesis are generally in the range between 50:50 and 30:70 [6].

Melamine resins, particularly MUF resins, while useful to produce moisture resistant particleboard, have very poor dilutability in water and therefore are inconvenient to handle in PB and MDF mills [7]. This limitation, which does not occur with UF resins, is a consequence of the methylolation and condensation reactions of formaldehyde with melamine. Formaldehyde first attacks the amino groups of melamine, forming methylol groups. However, this addition occurs in a larger extension than when formaldehyde is reacted with urea. The amino group in melamine accepts easily up to two molecules of formaldehyde and thus the complete methylolation of melamine is possible, which is not the case with urea. Due to melamine's functionality, up to six molecules of formaldehyde can be attached to one molecule and the methylolation step can lead to a series of methylolated compounds. As a consequence, highly hydrophobic compounds are formed early in the reaction [5]. These are responsible for the lower water compatibility of melamine-based resins.

The ability of sodium sulphites to react with aldehydes is well known. Sodium metabisulphite (MTBS), in particular, has actually been described in some studies as an effective formaldehyde scavenger [8, 9]. MTBS, with molecular formula of $Na_2S_2O_5$, forms sodium bisulphite after contact with water (equation 1) [8].

$$Na_2S_2O_5 + H_2O \longrightarrow 2NaHSO_3 \qquad (1)$$

The addition of MTBS in the production of MF and MUF resins reduces the production of the hydrophobic compounds, due to the reaction between sodium bisulphite and methylolmelamines (Fig. 1) [5] producing a sodium salt of bisulphite adduct [10]. This reaction is called sulfonation.

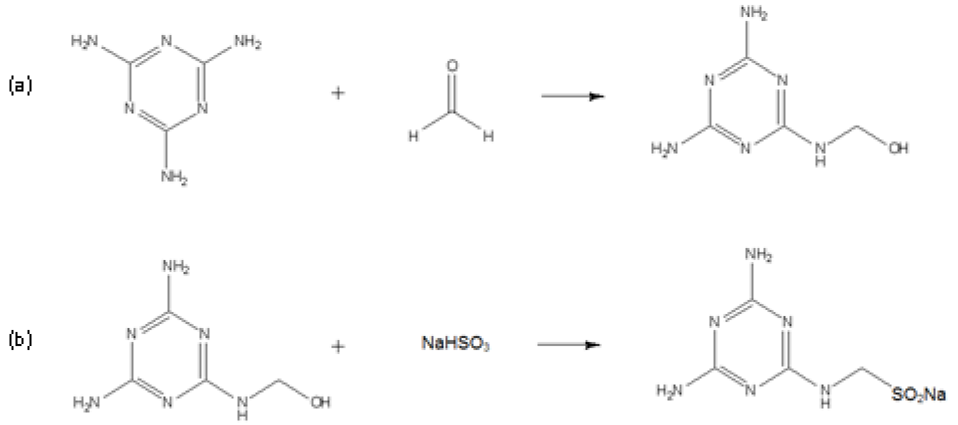

Fig. 1. *The reactions between melamine and formaldehyde giving a mono-methylolmelamine (a) and between mono-methylolmelamine and sodium bisulphite (b)*

Su et al. studied which factors affect sulfonation and condensation of highly-sulfonated melamine-formaldehyde (sodium metabisulphite/melamine, MTBS/M, molar ratio = 1.5) production and concluded that to achieve resins with good water solubility it was necessary to extend the condensation reaction for 24 hours [11]. Gourdarzian and Rabiee used paraformaldehyde for the preparation of sulfonated melamine-formaldehyde and studied the effect of different degrees of sulfonation with several ratios of MTBS/M (0.6-1.2) [12]. The results show that the resins produced with lower values of S/M ratios are more viscous. Decreasing the MTBS/M molar ratio, results in an increase in the viscosity of the final resins [12]. At lower degree of sulfonation, where MTBS/M molar ratio is 0.6, the viscosity of the final solution decreases with a decreasing F/M ratio until gelation takes place at much higher F/M ratios [12]. Both works were directed towards MF application as concrete plasticizer.

Considering MF resins for thermal insulation, Tutin studied addition of MTBS to MF synthesis in proportions between 0.15-0.25 (in terms of MTBS/M molar ratio) with an incorporation of a polyhydroxy compound such as sucrose or sorbitol [13]. Despite the good water dilution capacity observed, in all these studies the resins produced had low solid contents (between 30 and 45 %) and synthesis process times (7 to 10 hours) were excessively high, increasing the cost of the final product.

The incorporation of MTBS on the production of melamine-urea-formaldehyde resins was also studied by Dopico and co-workers in proportions of 0.1 to 0.3 (in terms of MTBS/M molar ratio), along with the incorporation of a urea-formaldehyde prepolymer (UFP) in proportions between 0.1-1 (in terms of

M/UFP) [7]. The synthesis process used was divided in two different steps: first reaction between formaldehyde, MTBS, urea-formaldehyde prepolymer and melamine, and then a new amount of melamine was added along with the formaldehyde. The copolymerization of melamine, urea and formaldehyde therefore occurred only in the first step, along with urea-formaldehyde prepolymer. The resins produced had water dilution capacity (WCD) higher than 20:1 (water/resin). However, this study did not test the incorporation of MTBS alone, and very long reaction times were used.

The main purpose of the current work is to develop a new MUF formulation with high water dilution capacity and good overall performance in terms of physico-mechanical properties and formaldehyde emissions. The addition of MTBS during melamine condensation stage is tested (MTBS/M molar ratio between 0.15 and 0.50). An alkaline-acid synthesis process is adopted in order to promote the copolymerization of melamine, urea and formaldehyde.

2. Materials and Methods

2.1. Materials

2.1.1. Raw Materials

Formaldehyde (55 wt.% solution), urea, melamine and sodium metabisulphite for the production of UF resins were provided by EuroResinas – Indústrias Químicas, S.A. (Sines, Portugal). Wood particles, paraffin and ammonium sulphate were supplied by Sonae Indústria PCDM (Oliveira do Hospital, Portugal) for particleboards production.

2.1.2. Commercial Resins

The three commercial resins analysed in this study were supplied by EuroResinas – Indústrias Químicas, S.A. (Sines, Portugal). These are all melamine-urea-formaldehyde resins with percentages of melamine between 8 and 16 % (CR3 < CR2 < CR1). According to manufacturer´s information, both resins CR1 and CR2 have a final viscosity between 150 and 300 mPa·s, a final pH between 8.5 and 10.0, a solid content around 64 % and a gel time of 80 seconds; while the resin CR3 has a final viscosity between 100 and 200 mPa·s, a final pH around 9.0, a solid content between 61 and 65 % and a gel time of 110 s. All the commercial resins have low water capacity dilution stability, with acceptable values for only 1 to 3 days.

2.2. Methods

2.2.1. Resin Synthesis

Resins were synthesized in a round bottom glass flask, with a volume of 2 L, equipped with mechanical stirring and a thermometer. Both pH and viscosity measurements were performed off-line, on the samples taken from the reaction mixture while temperature control was accomplished with a heating blanket. The resins were synthesized according to the so-called alkaline process, which consists in methylolation and condensation reaction at an alkaline environment followed by a final addition of urea [5].

The synthesis process begins with the methylolation reaction between 50 % formaldehyde solution, urea and melamine, at a basic pH (usually between 7.5 and 9.0), obtained by adding an appropriate amount of base. Urea is added slowly, allowing the heat of reaction to raise the temperature from the initial 60 °C to the values between 80 and 90 °C. The amount of urea and melamine added in this step is sufficient to provide a formaldehyde/amine groups molar ratio ($F/(NH_2)_2$) of 4 to 3.5.

The condensation reaction can be divided in two different steps: initially the reaction proceeds until a viscosity of around 100 mPa·s is obtained. At this point, a second amount of melamine is added in order to provide a $F/(NH_2)_2$ molar ratio of 3.0 to 2.5. Then the condensation reaction continues until a desired viscosity is attained, between 350 and 400 mPa·s, and is terminated by cooling the reaction mixture to a temperature of 60 °C. Hereupon, a given amount of urea is added in order to decrease the $F/(NH_2)_2$ molar ratio to a value between 1.15 and 1.05, which was the same for all productions. The reaction is terminated by cooling the mixture to a temperature of 25 °C.

The major difference between all the produced resins is the amount of sodium metabisulphite added during the condensation reaction.

Resin Properties Determination

At the end of each synthesis, the properties like viscosity, pH, gel time, solids content and water dilution capacity were determined. Viscosity (expressed in mPa·s) was measured with a Brookfield viscometer at 25 ºC. The resin pH was measured using the pH meter with a combined glass electrode. The solids content (expressed in %) was determined by evaporation of volatiles in 2 g of resin for 3 h at 120 ºC. The resin gel time (expressed in seconds) was determined at 100 ºC, after addition of the catalyst (ammonium sulphate). The resin was manually stirred until detecting gelation, and the corresponding time was recorded. Water dilution capacity (WDC) (expressed in %) was determined by the amount of water that is possible to add to 5 g of resin until this solution turns hazy and presents phase separation.

GPC/SEC Analysis

A GPC/SEC equipped with a Knauer RI detector 2300 and a Knauer injector with a 20 µL was used. The columns used were PSS Protema 100 and 300, 5 µm, conditioned at 60 ºC using an external oven. The flow rate was 1 $mL \cdot min^{-1}$ and DMF was used as the mobile phase. Samples for analyses were prepared by dissolving a small amount of resin in DMSO (dimethylsulfoxide), followed by vigorous stirring. Subsequently, the sample was left to rest, and then filtered through a 0.45 µm filter [14, 15].

Particleboard Production

Wood particles were blended with resin, catalyst and a hydrophobic agent (paraffin), added together, in a laboratory glue blender. Surface and core layers were blended separately. However, 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).

After blending, a three-layer particle mat was hand formed in a flexible aluminium container (220 x 220 x 80 millimetres). The amount of wood particles was determined in order to obtain the panels with densities of 650 ± 20 $kg \cdot m^{-3}$. Surface and core layers of the produced panels differed in particle size distribution and moisture content. The mass distribution was 20 % for the upper surface layer, 62 % for the core layer and 18 % in the bottom surface layer. Pressing was performed in a parallel plate hot-press, scheduled in order to simulate a typical particleboard continuous pressing operation. The panels were pressed for 120 or 150 s, at 190 °C. The final thickness of the panels was 16 mm. Five panels were produced for each resin.

Physico-Mechanical Characterization of Particleboards

After pressing, panels were stored in a conditioned room (20 ºC, 65 % RH) and then tested accordingly to the European standards. The following physico-mechanical properties were evaluated: density (EN 323), moisture content (EN 322), internal bond strength (IB) (EN 319 – tensile strength perpendicular to the plane of the board) and thickness swelling (EN 317). For each experiment, four board replicates were obtained. Formaldehyde content was determined according to EN 120 (perforator method) and formaldehyde emission was determined according JIS A 1460 (desiccator method). Panels for the analysis of formaldehyde content and the emission were stored in the sealed plastic bags.

3. Results and Discussion

3.1. Synthesis

A set of resins was synthesized according to the same process, varying only the amount of MTBS added, between 0 wt. % (resin 1) and 6 wt. % (resin 4). Table 1 presents the final properties of the MUF resins produced.

Table 1. *Process variables and final properties of MUF resins*

Properties / Resin	Resin 1	Resin 2	Resin 3	Resin 4
% MTBS	0.0	2.0	3.0	6.0
RM MTBS/M	0.00	0.15	0.25	0.50
Solids content (%)	64.7	65.1	65.6	67.1
Final pH	9.51	9.45	9.85	9.80
Final viscosity (mPa·s)	160	180	190	170
Gel time (s)	55	58	64	65
Density ($kg \cdot m^{-3}$)	1.290	1.296	1.310	1.330

Concerning the final pH and viscosity, the results are very similar for all four synthesized resins. The slight increases in solid content and density occurred because an extra compound (MTBS) was added without adjusting the concentration of the other reactants. Gel time tends to increase (*i.e.* reactivity decreases) with MTBS addition because of the premature consumption of a significant amount of free formaldehyde, which is not available for the final cure reaction. This free formaldehyde reacts with sodium bisulphite producing a sodium salt of the bisulphite adduct [16].

$$NaHSO_3 + CH_2O \longrightarrow NaHOCH_2SO_3 \qquad (2)$$

The viscosity of the resins was monitored during the condensation step, after addition of MTBS together with the second amount of melamine. The results are shown in the Fig. 2. The amount of MTBS added does not affect the reaction progress and all the resins have presented a condensation time of approximately 75 minutes. The last point in the graph corresponds to the viscosity after 30 minutes of cooling down to a temperature of 60 °C.

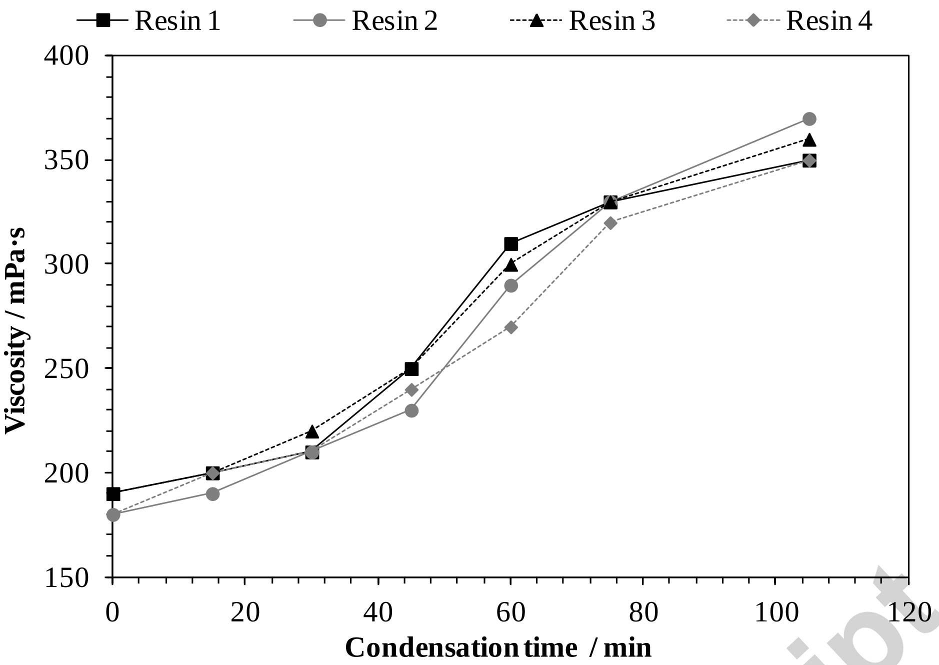

Fig. 2. *The evolution of viscosity of the MUF resins during the condensation reaction, after addition of MTBS*

3.2. Resin Stability

The stability of the four synthesized resins was evaluated during storage for one month at 25 °C. Viscosity, pH and water dilution capacity were measured weekly. The evolution of pH in this period (not shown here) was very similar for all resins and showed a decrease from 10.0 to 8.0. Viscosity and water dilution capacity as a function of storage time are presented in Fig. 3 and Fig. 4, respectively. The change of viscosity with time is analogous for all resins, increasing by about 50 mPa·s after one month. Resins 1 and 4 maintain viscosities lower than the other two, but within the acceptable variability range for this synthesis process.

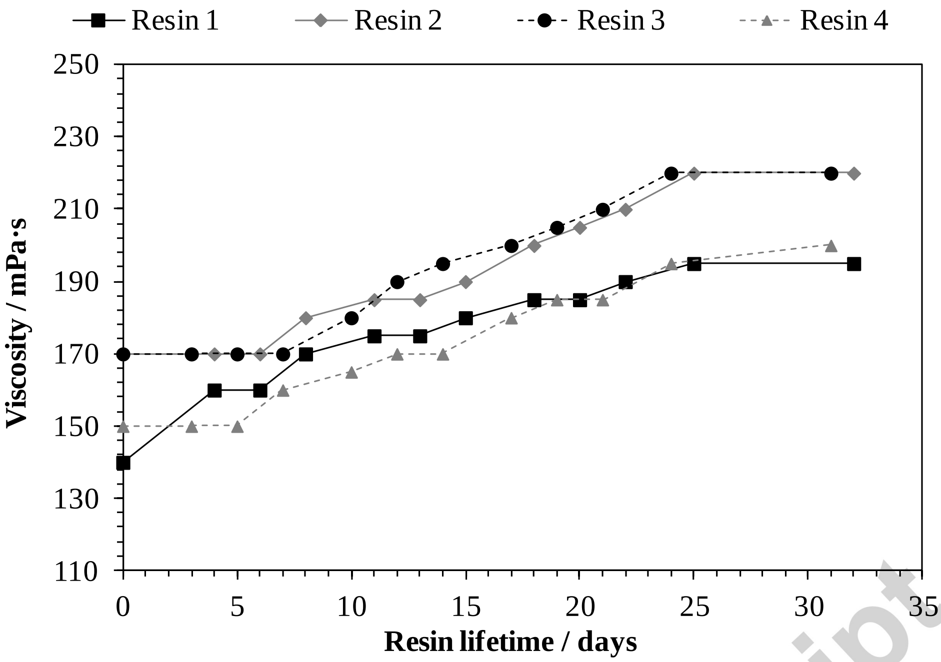

Fig. 3. *The viscosity evaluation of the resins during 1 month of stability tests*

Regarding water dilution capacity, Figure 4 shows that increasing the amount of sodium metabisulphite results in a significant increase in water dilution capacity (WDC) right after synthesis. This translates into longer storage times until reaching WDC lower than 1. The best result was obtained for resin 4, with 6 % of MTBS added, which consistently exhibited WDC above 100 along the entire one month storage period.

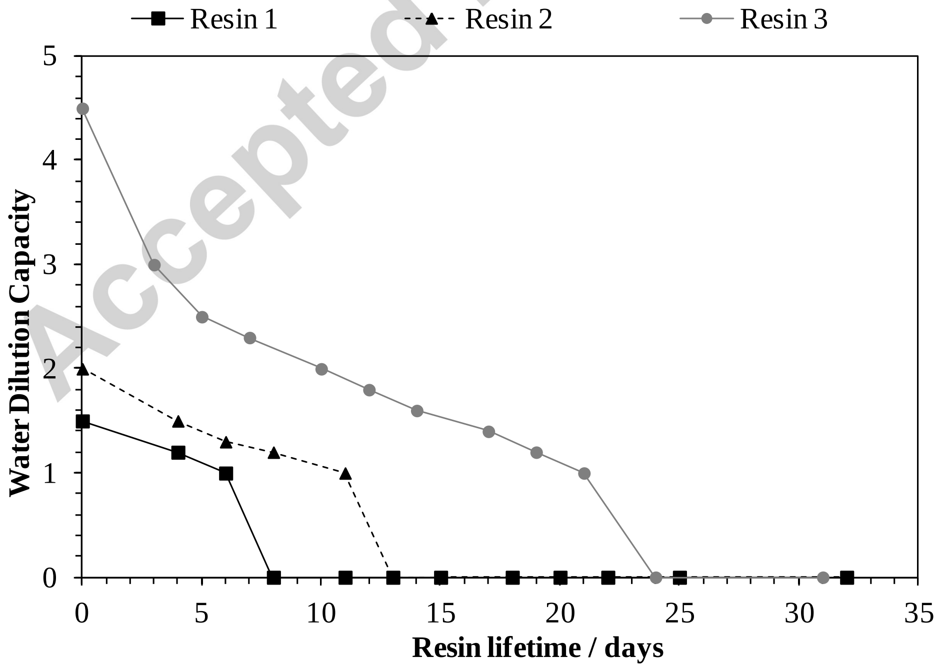

Fig. 4. *The water dilution capacity of the resins during 1 month of stability tests (the graph for the resin 4 are not shown here, since it has the values above 100 for all measurements)*

As previously discussed, the increase of the resin's WDC with addition of sodium metabisulphite is related to a higher sulfonation of methylolmelamines by MTBS. Addition of this compound along with the second melamine addition minimizes condensation of methylolmelamines into hydrophobic products and thus reduces the tendency for precipitation upon water dilution.

The decrease in the resins WDC during the storage period is a consequence of the progressive reaction between methylolmelamines, methylolureas and free melamine, urea and formaldehyde along time. This leads to formation of insoluble colloidal aggregates, originating the observed viscosity increase, and reducing the water dilution capacity [17].

3.3. GPC/SEC Characterization

Figure 5 shows the results for the GPC chromatograms for the four MUF resins synthesized in this study. The first thing that can be noticed is that the resin without MTBS incorporation (resin 1) presents only one peak, for larger retention volumes (RV between 20 and 26 mL). This RV range corresponds to the lower molecular weights, and can be assigned to unreacted urea, methylolureas, methylolmelamines, oligomers and polymer with intermediate molecular weight (< 3000) [15]. The chromatograms for the other three resins are more complex, showing additional peaks at the lower retention volumes (RV between 6-20 mL), which corresponds to the presence of polymer with high molecular weight (>12000) [18]. This difference can be explained considering that the higher molecular weight fraction present in resin 1 does not actually enter the GPC column. This fraction, produced during the condensation reaction, is known to form molecular aggregates that can be retained in the microporous filter with 0.45 μm during sample preparation [14]. In the case of resins 2, 3 and 4, the addition of MTBS reduces the formation of these aggregates, allowing the detection of polymer with higher and intermediate molecular weights (RV between 9 and 20 mL), as seen in Figure 5. The higher the quantity of incorporated MTBS, the higher is the amount of intermediate molecular weight polymer produced, which promotes the displacement to the right of the peak between RV 6 and 20 ml.

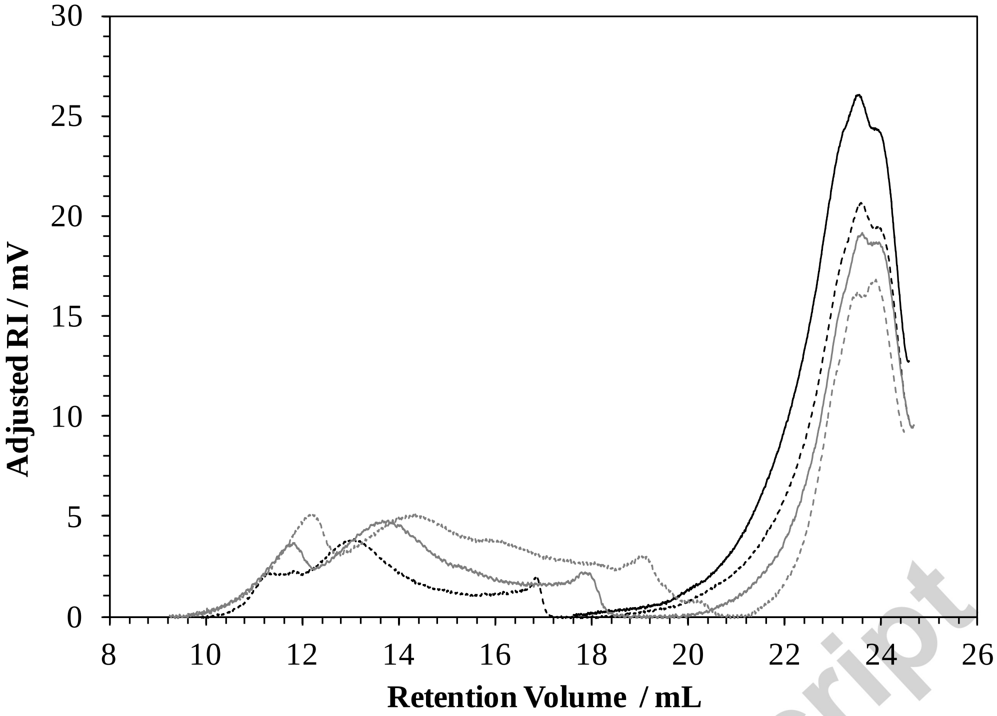

Fig. 5. *The chromatograms of MUF resins (continuous line is resin 1, black dotted - resin 2, grey line - resin 3 and grey dotted - resin 4)*

In order to understand the evolution of the condensation reaction, samples were taken and analysed during the synthesis of the resins 1 and 4. Fig. 6 and Fig. 7 show the evolution of the GPC/SEC chromatograms during the condensation steps for the resins 1 and 4, respectively, in 30 minutes intervals. Fig. 6, in which the evolution of molecular weight distribution for resin 1 (resin without any MTBS incorporation) is present, has only one peak on the lower molecular weight for all samples taken during the condensation. The first two samples were taken before the second melamine addition. After that, the peak corresponding to urea and methylolureas (RV between 23 and 24 mL) suddenly increases (resin 1, sample 3). As the condensation time proceeds (resin 1, samples 4 and 5), this peak decreases, accompanied by an increase in polymer with intermediate molecular weight (RV between 17 and 21). Concerning the higher molecular weight polymer, as it was explained earlier, this was not detected due to their retention on the filter during sample preparation.

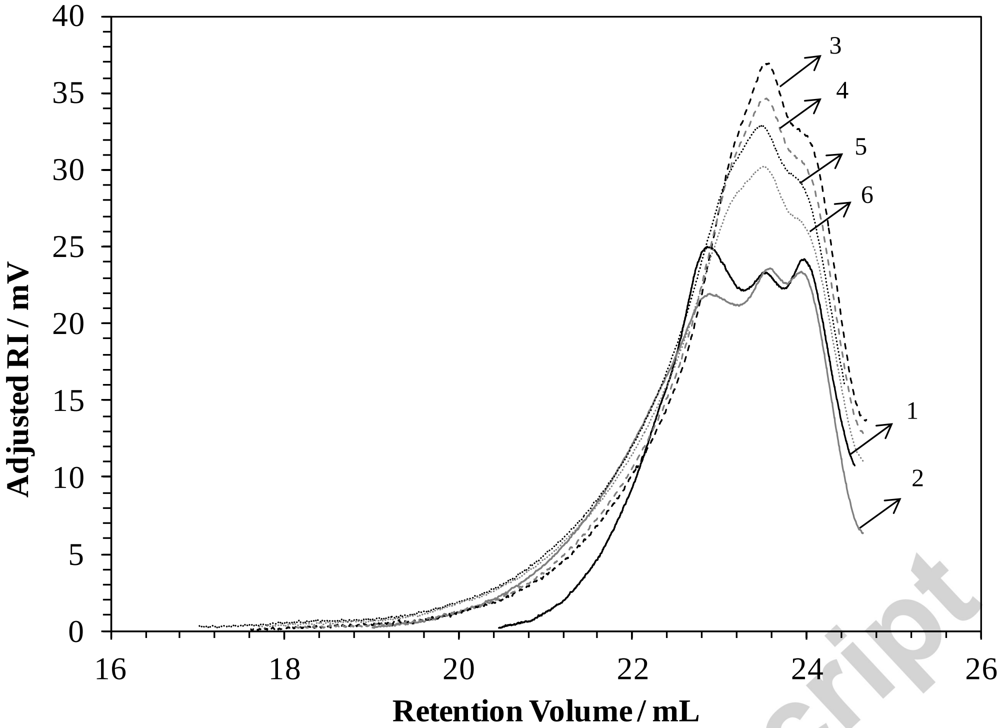

Fig. 6. *The chromatograms of samples taken from Resin 1 during the condensation step (1: 0 min, 2: 30 min, 3: 60 min, 4: 90 min, 5: 120 min and 6: 150 min)*

Fig. 7 presents the evolution in resin 4, with 6 % of MTBS. In this case the samples 1 and 2 were taken before second melamine and MTBS addition, which explains the difference in the intensity of these two samples when compared with the other 4. It is possible to see that as the reaction proceeds, the intensity of the peak between of 20 and 23 mL of RV decreases together with an increase of the peak corresponding to the higher and intermediate molecular weights (RV between 10 and 20 mL). In this case, the peak corresponding to the higher and intermediate molecular weights is detected, with an increase on the intensity of this peak with the condensation time due to the growth of the polymer during this step.

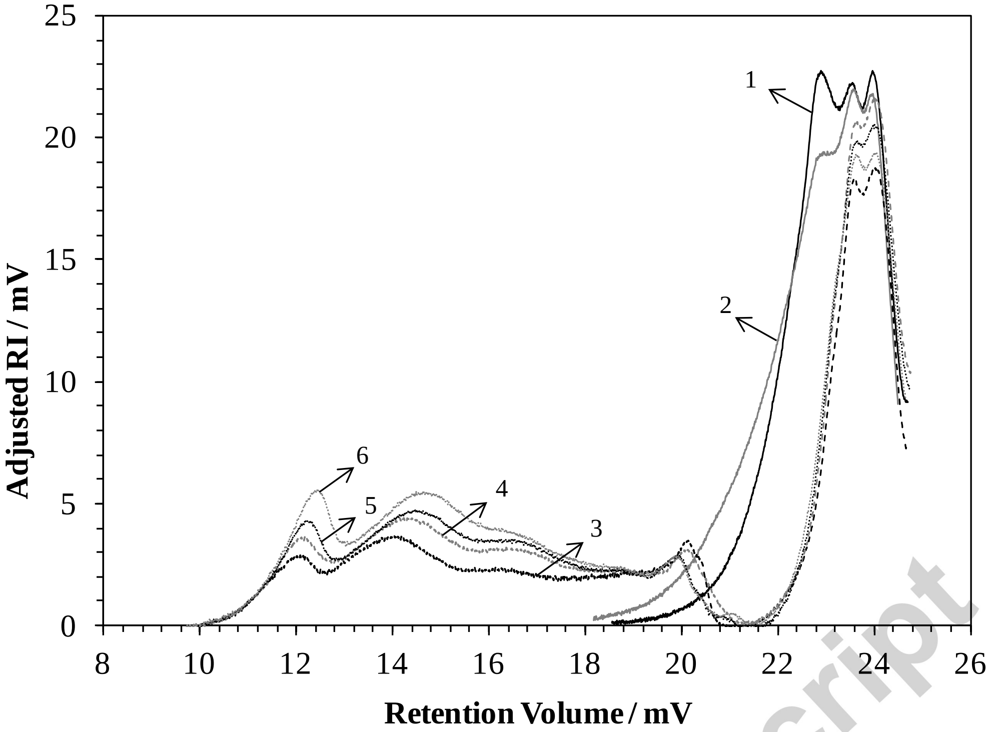

Figure 7*Chromatograms of samples taken from Resin 4 during the condensation step (1 – 0min, 2 – 30min, 3 – 60min, 4 – 90min, 5 – 120min and 6 – 150 min)*

3.3. Particleboard Evaluation

To determine the ideal amount of catalyst (ammonium sulphate) to use in resin cure, gel time tests were carried out using hardener dosages between 1 and 6 wt. % (dry catalyst per solid resin) (Fig. 8). The expected gel time values of for this type of resins, without addition of external agents, are usually around 55 to 60 seconds. Addition of MTBS results in a significant increase in gel time: about 10 seconds from resin 1 to resin 4. Since the lowest values were obtained for the catalyst addition between 3 and 4 %, it was established that the amount of hardener to be used in particleboard production would be 3 %.

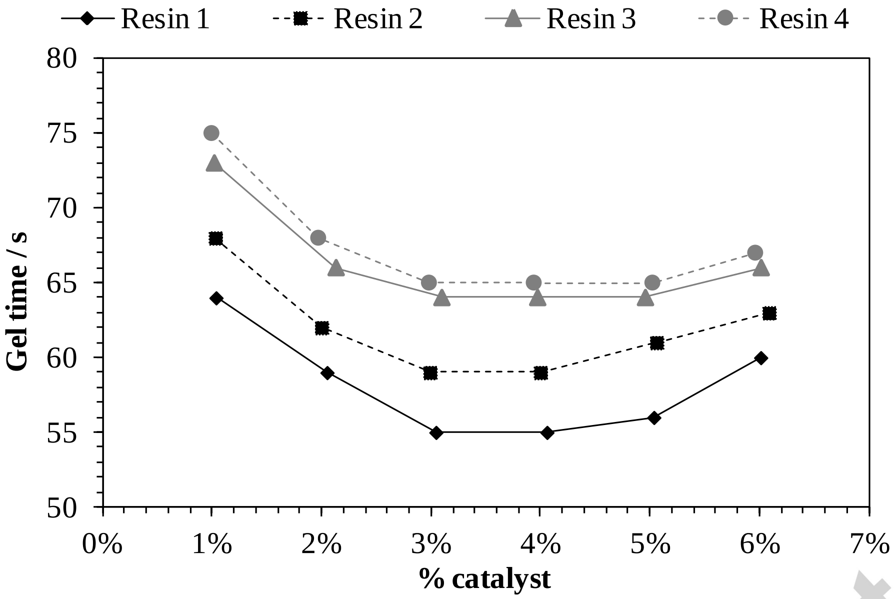

Fig. 8. *The gel time evolution of the resins according to the amount of catalyst*

Table 2 presents the physico-mechanical properties of particleboards produced with the four synthesised MUF resins. The pressing times used were 120 and 150 seconds. In the first case, the values found for density and water content are very similar for all panels. Concerning internal bond strength, most values are higher than the minimum acceptable value of 0.45 N·mm^{-2}, the requirement for type P3 (non load-bearing boards for use in humid conditions) and P5 (load-bearing for use in humid conditions) boards, according to EN 312, except the one produced with Resin 4. On the other hand, regarding formaldehyde content, all the resins are below the limit imposed by CARB II legislation corresponding to an equivalent of perforator value ≤ 5.6 mg/100 g oven dry board [19]. The formaldehyde emissions for all the resins are below the limit imposed by CARB I legislation, corresponding to an equivalent desiccator test value ≤ 1.3 mg·mL^{-1} [19]. Furthermore, it can be observed that increasing the amount of MTBS added to the resin during synthesis decreases the formaldehyde emission and formaldehyde content of the particleboards.

As expected, the increase of the pressing time from 120 s to 150 s results in better properties of the particleboards mainly for the ones produced with resins 3 and 4. With resin 4 it is possible to obtain the panels with internal bond strength higher than the minimum acceptable value of 0.45 N·mm^{-2}. In terms of formaldehyde emission and formaldehyde content, the values are lower than the ones found on the panels produced with the shorter pressing times, and both comply to the limits imposed by CARB II (in terms of formaldehyde content) and CARB I (formaldehyde emission).

Table 2. *The properties of the particleboards produced with synthesized MUF Resins*

Properties / Resin	Pressing time (s)	Resin 1	Resin 2	Resin 3	Resin 4
Density (kg·m^{-3})	120	670	680	674	659
Internal Bond Strength (N·mm^{-2})		0.84	0.77	0.58	0.32
Thickness Swelling (%)		20.7	24.6	27.0	36.3
Moisture Content (%)		5.6	5.2	5.2	5.1
Formaldehyde Content (mg/100g oven dry board)		5.0	4.6	4.2	4.0
Formaldehyde Emission (mg·L^{-1})		1.20	1.11	1.05	0.93
Density (kg·m^{-3})	150	681	706	686	674
Internal Bond Strength (N·mm^{-2})		0.84	0.84	0.70	0.53
Thickness Swelling (%)		22.9	24.4	28.3	33.8
Moisture Content (%)		4.9	4.8	4.9	4.6
Formaldehyde Content (mg/100g oven dry board)		4.2	3.7	3.4	3.3
Formaldehyde Emission (mg·L^{-1})		1.04	1.02	0.87	0.84

3.4. Comparison with other commercial resins

Table 3 shows the physico-mechanical properties of the particleboards produced with resin 4 and three MUF commercial resins with melamine contents varying between 8 and 22 % (CR3 < CR1 < CR2).

Despite the fact that the panels produced with the resin 4 have the lowest values of internal bond strength and the highest values of thickness swelling, they are the only ones with formaldehyde content values below the limit imposed by CARB II legislation, corresponding to an equivalent of perforator value ≤ 5.6 mg/100 g oven dry board, with both pressing times of 120 s and 150 s.

Comparing these four resins in terms of water dilution capacity (Figure 4) and physico-mechanical properties, it is possible to conclude that resin 4 provides the best overall performance.

Table 3. *The properties of the particleboards produced with different commercial MUF resins and with the resin 4*

Properties / Resin	PT (s)	Resin 4	CR 1	CR 2	CR 3
Density (kg·m^{-3})	120	659	666	706	674
Internal Bond Strength (N·mm^{-2})		0.32	0.63	0.73	0.64
Thickness Swelling (%)		36.3	18.6	19.0	21.3
Moisture Content (%)		5.1	7.2	6.9	7.2
Formaldehyde Content (mg/100g oven dry board)		4.0	8.0	-	7.2
Density (kg·m^{-3})	150	674	692	708	681
Internal Bond Strength (N·mm^{-2})		0.53	0.81	0.81	0.89
Thickness Swelling (%)		33.8	20.8	15.1	13.3
Moisture Content (%)		4.6	6.6	6.9	7.6
Formaldehyde Content (mg/100g oven dry board)		3.3	6.5	8.1	5.7

4. Conclusions

This work studied the effect of MTBS addition during MUF synthesis, with the purpose of developing resins tolerant to dilution in water. MTBS was added along with the second melamine addition, during the condensation reaction.

Water dilution capacity was observed to increase significantly with MTBS incorporation. This was attributed to the presence of MTBS minimizing the condensation of methylolmelamines into hydrophobic products. On the other hand, the resin reactivity decreased, due to premature formaldehyde consumption. GPC/SEC results showed that the resins produced with MTBS incorporation present lower molecular weight when compared with the one without MTBS.

Regarding particleboard production and evaluation, MTBS addition lead to lower values of internal bond strength. However, for the MTBS addition of 6 % it was possible to obtain a resin with internal bond strength above the acceptable minimum (0.45 N·mm^{-2}), using a pressing time of 150 s. When compared with other commercial MUF resins, the formulations containing MTBS present lower values of formaldehyde emissions, verifying CARB II criteria, and much higher water tolerance.

Acknowledgements

The authors wish to thank: EuroResinas – Indústrias Químicas, S.A. (Sines, Portugal) and Sonae Indústria PCDM (Oliveira do Hospital, Portugal) for providing the equipment and raw materials needed for this work.

Nádia Paiva wishes to thank FCT – Foundation for Science and Technology and EuroResinas – Indústrias Químicas, S.A. (Sines, Portugal) for the PhD grant with reference SFRH/BDE/51294/2010.

References

[1] Rowell RM, Handbook of Wood Chemistry and Wood Composites. Second Edition. Taylor & Francis: 2012.

[2] Pizzi A, Scharfetter HO. The chemistry and development of tannin-based adhesives for exterior plywood. J Appl Polym Sci 1978; 22: 1745-61.

[3] Carvalho L.H., Magalhães F.D., Ferra J.M., Formaldehyde Emissions from Wood-Based Panels - Testing Methods and Industrial Perspective, in: Chemistry, Applications and Role in Polymerization, : Nova Science Publishers; 2012.

[4] Dunky M. Urea–formaldehyde (UF) adhesive resins for wood.Int J Adhes Adhes 1998; 18: 95-107.

[5] Pizzi A. Melamine-Formaldehyde Resins. In: Handbook of Adhesive Technology, Revised and Expanded. Taylor & Francis: 2003.

[6] Mercer TA, Pizzi A. Considerations on the principles of preparation of melamine-urea-formaldehyde adhesive resins for particleboard. Holzforschung und Holzverwertung 1994; 46: 51-4.

[7] Dopico PG, Wertz SL, Phillips JC, Mirous GE. Melamine-urea-formaldehyde resins modified with cyclic urea prepolymer and sodium metabisulfite.US Patent 6566459: 2003.

[8] Barberá JJ, Metzger A, Wolf M. Sulfites, Thiosulfates, and Dithionites. In: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA: 2000.

[9] Costa NA, Pereira J, Ferra JM, Cruz P, Martins J, Magalhães FD.Sodium metabisulphite as a scavenger of air pollutants for wood-based building materials. I Wood Prod J 2013; 4: 242-7.

[10] Watson W. Practical Synthetic Organic Chemistry, Reactions, Principles, and Techniques. Organic Process Research & Development 2011; 15: 1470.

[11] Su L, Qiao S, Xiao J, Tang X, Zhao G, Fu S. Synthesis and properties of high-performance and good water-soluble melamine–formaldehyde resin J Appl Polym Sci 2001; 81: 3268-71.

[12] Gourdarzian N, Rabiee A. Effect Of Reactant Ratios on Gel Point of Sulphonated Melamine-Formaldehyde Superplasticizer. Iranian Polymer Journal 1996; 5: 24-9.

[13] Tutin KK. Water-soluble sulfonated melamine-formaldehyde resins. US Patent 5710239: 1998.

[14] Ferra JM, Mendes AM, Costa MRN, Magalhaes FD, Carvalho LH.Characterization of Urea-Formaldehyde Resins by GPC/SEC and HPLC Techniques: Effect of Ageing. J. Adhes. Sci. Technol 2010; 24: 1535-51.

[15] Paiva NT, Henriques A, Cruz P, Ferra JM, Carvalho LH, Magalhaes FD.Production of melamine fortified urea-formaldehyde resins with low formaldehyde emission. J Appl Polym Sci 2012; 124: 2311-7.

[16] Caron S. Practical Synthetic Organic Chemistry. Reactions, Principles, and Techniques. John Wiley & Sons: 2011.

[17] Ferra JMM, Mendes AM, Costa MRN, Carvalho LH, Magalhães FD.A study on the colloidal

nature of urea-formaldehyde resins and its relation with adhesive performance. J Appl Polym Sci 2010; 118: 1956-68.

[18] Paiva NT, Pereira J, Ferra JM, Cruz P, Carvalho L, Magalhães FD.Study of influence of synthesis conditions on properties of melamine–urea formaldehyde resins. International Wood Products Journal 2012; 3: 51-7.

[19] Harmon DM. CHANGE - Its Challenges and Opportunities, Technical Formaldehyde Conference. Germany: 2008.