Production of Melamine Fortified Urea-Formaldehyde Resins with Low Formaldehyde Emission

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ABSTRACT: Melamine can be incorporated in the synthesis of urea-formaldehyde (UF) resins to improve performance in particleboards (PB), mostly in terms of hydrolysis resistance and formaldehyde emission. In this work, melamine-fortified UF resins were synthesized using a strong acid process. The best step for melamine addition and the effect of the reaction pH on the resin characteristics and performance were evaluated. Results showed that melamine incorporation is more effective when added on the initial acidic stage. The condensation reaction pH has a significant effect on the synthesis process. A pH below 3.0 results on a very fast reaction that is difficult to control. On the other hand, with pH values above 5.0, the condensation reaction becomes excessively slow. PBs panels produced with resins synthesized with a condensation pH between 4.5 and 4.7 showed good overall performance, both in terms of internal bond strength and formaldehyde emissions. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2311–2317, 2012

Key words: urea-formaldehyde resins; melamine; strongly acid process; GPC/SEC; formaldehyde emissions; internal bond strength

INTRODUCTION

Urea-formaldehyde (UF) resins are the most used type of adhesives used in wood-based panels (WBP) industry.[1] Worldwide, these resins represent 80% of the total production in the aminoresins class.[2] The remaining 20% correspond mainly to melamine-formaldehyde (MF) resins, with a small percentage of resins synthesized from other aldehydes and/or other amino compounds.[3] According to SRI Consulting,[4] the global production of UF resins in 2008 was 14 mT. Their consumption increased 2.8% in 2008, and is expected to grow an average 3.2% per year from 2008 to 2013, and just under 2% per year from 2013 to 2018.

UF resins are thermosetting polymers that, before cure, consist of an aqueous solution/dispersion of unreacted monomers, linear or branched oligomeric, and polymeric molecules.[1] They are condensation products of aldehydes with compounds containing amino groups. Their success on the market is mostly because of high reactivity, good performance, and low cost. However, the hydrolytic degradation of UF polymers causes a significant weakening of resin bonds and is a source of formaldehyde emissions.[5] Another cause of formaldehyde emission from WBP produced with these resins is the presence of free (unreacted) formaldehyde.[1]

In 2006 the International Agency for Research on Cancer (IARC), has classified formaldehyde as "carcinogenic to humans."[6] The new classification has led the industry to find strategies to limit formaldehyde emission levels from WPB. The most common approaches consist in: decreasing the F/U (formaldehyde/urea) molar ratio, incorporation of other comonomers in the synthesis and adding formaldehyde scavengers to the particles/fibers before or after resin blending.[7] The F/U molar ratio has been slowly decreased over the years from its initially high value, but causes the manufacturing processes to be more sensitive to perturbations in operating conditions and leads to particleboards (PBs) with lower physical and mechanical properties.[8] Current commercial resins have typical F/U values between 0.9 and 1.1.

The incorporation of a small percentage of melamine to UF resins improve moisture/water resistance and therefore decrease formaldehyde emissions. The aminomethylene bonds in UF resins are quite susceptible

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of hydrolytic attack. However, more stable bonds are obtained when a methylene carbon is linked to an amide group from a melamine ring, instead of nitrogen from urea. This is especially true at high temperatures, probably due to the quasiaromatic ring structure of the melamine. In addition, the slower pH decrease in the bond line due to the buffer capacity of melamine could also explain the higher stability of the bonds in melamine-urea-formaldehyde (MUF) resins.[1] However, this lower decrease in pH also causes an increase in gel time and consequently, higher pressing times.

The wide range of formulations for MUF resins originates different properties, performances, and durabilities.[2,3] One can distinguish two particular cases: MUF resins, where the melamine content is above 5%, and melamine-fortified UF resins, with melamine content below 5%. In both cases, the production can be performed in different ways: cocondensation of all monomers, melamine, urea and formaldehyde, in a multistep reaction; mixing of separately synthesized MF and UF resins; and postaddition of melamine, in various forms (pure melamine, MF/MUF powder resin or melamine acetates) to an UF resin during the preparation of the glue mix.[9]

Melamine-fortified UF resins are now a conventional alternative to UF resins for application as adhesives in WBP, such as PB and medium density fiberboard (MDF). These allow reducing formaldehyde emissions and improving the physical properties of the panels. However, the costs for these fortified products are higher due to the higher price of melamine compared to urea.[1] When added to the reaction mixture, melamine can enter in any of these steps[5]: initial methylolation step (before or after the addition of the first urea), condensation step (before or after the addition of the second urea), or final urea addition. The best procedure depends on the particular process used. The studies by Shiau and Smith [5], using an alkaline-acid process, showed that melamine addition is more effective in the methylolation step. On the other hand, Hse studied melamine addition in a strongly acid process, and concluded that the best results were obtained for melamine addition during acidic condensation (pH between 4.5 and 6.5).[10] This author essentially studied the melamine reaction with a UF prepolymer formed in a strongly acid environment, the final MUF resin produced had a F/U molar ratio of 1.2, with 4.39% (weight basis) maximum melamine content.

Previous studies have shown that the melamine content has a very significant effect on both the resin and PB properties. An increase in melamine content results in an increase in gel time, solid content, and internal bond strength. On the other hand, there is a decrease in thickness swelling, water absorption, and formaldehyde emission.[11]

MUF resins are produced according to the same procedures as UF resins. The most common approach is the alkaline-acid process.[9] The process consists in an initial alkaline methylolation (hydroxymethylolation) step followed by an acidic condensation. An alternative strategy is the strongly acid process.[8] In this case the initial reaction is carried out under strongly acidic environment, in which the methylolation and condensation reactions occur simultaneously. The methylolation step consists in the reaction between urea, melamine, and formaldehyde to form the so called methylolureas and methylolmelamines (Fig. 1). At this low pH, however, these species react almost instantly to form linear and/or branched polymers linked by methylene-ether and methylene bridges (Fig. 2). The released heat is sufficient to drive the reaction to the desired condensation level, and can be controlled by a programmed addition of urea to the acidified formaldehyde solution. This process may reduce the reaction time by 30% in relation to the alkaline-acid process, with much lower energy consumption.[8] The disadvantage of this process lies in the difficulty in controlling the highly acid condensation step, due to its exothermic character.[12]

The present study investigates the best procedure for incorporation of melamine in the synthesis of UF resins, producing a MUF copolymer in the first reaction stages. The general goal is the production of a melamine fortified UF resin with a molar ratio F/U of 0.98, with good internal bond strength and low thickness swelling and formaldehyde emission.

MATERIALS AND METHODS

Resin preparation

All the resins were synthesized in the laboratory reactor. The synthesis was carried out in 2.5 and 5 L round bottom flasks, equipped with mechanical stirring and thermometer. Temperature control of the reactor is performed using a heating mantle. The resins were synthesized using the so-called strongly acid process, which is based on the occurrence of methylolation and condensation reactions simultaneously.[13]

The process begins with the methylolation/condensation reaction between a 50% formaldehyde solution and urea, at very low pH—between 0.5 and 2.5—by adding an appropriate amount of a sulfuric acid. This reaction consists essentially in the addition of one to three formaldehyde molecules to a urea molecule, to form the so-called methylolureas. The UF polymer builds up when the methylolureas react with free urea and formaldehyde, producing linear and partly branched molecules with medium to high molecular weights.[1] Urea is added slowly, allowing the heat of reaction to raise the temperature from
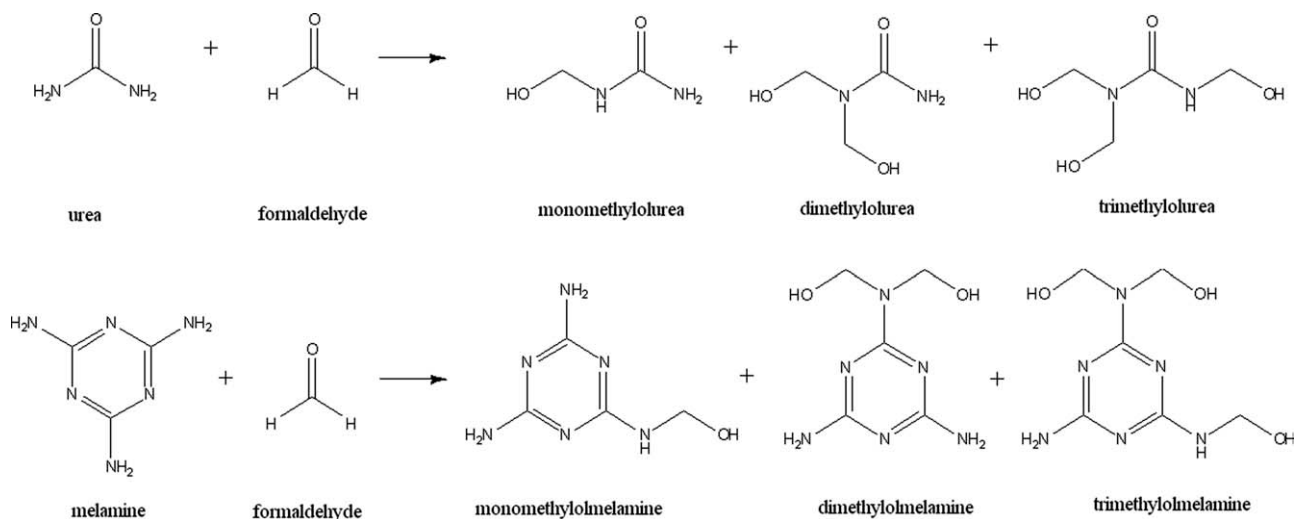
Figure 1 Formation of methylolureas and methylolmelamines (mono-, di- and tri) by the addition of formaldehyde to urea and melamine.

the initial 60°C to values between 80 and 90°C. The amount of urea added to the formaldehyde solution during this initial step is sufficient to provide an F/U molar ratio of 3.5 to 3. If melamine is added in this step, the reaction then proceeds until a desired viscosity of 500 cP is reached.

The second step consists in the methylolation reaction of additional urea with free formaldehyde still present in the reaction mixture. To make sure that only this reaction takes place, and the condensation is inhibited, it is necessary to adjust the pH to a neutral or slightly basic value, by adding sodium hydroxide solution. The additional urea added in this step must be enough to provide an F/U molar ratio of 2.5 to 1.5. If melamine is to be added in this step, the gain in reaction mixture viscosity is expected to occur after this addition.

Afterwards, the reaction mixture is cooled during 30 min, until a temperature of 50°C is attained. At this point, a final amount of urea is added to provide a final F/U molar ratio of 0.98. The reaction is terminated by cooling the mixture to a temperature of 25°C.

Viscosity, pH reactivity, and solid content were determined at the end of each synthesis. Viscosity was measured with a Brookfield viscometer at a constant temperature of 25°C. The resin pH was measured using a combined glass electrode. The solid content was determined by evaporation of volatiles in 2 g of resin for 3 h at 120°C. The resin reactivity was determined by measuring the gel time of a resin sample at 100°C, after addition of a cure catalyst (ammonium sulfate or ammonium nitrate).

As described the synthesis is divided in three different steps. Melamine can be added to the reaction
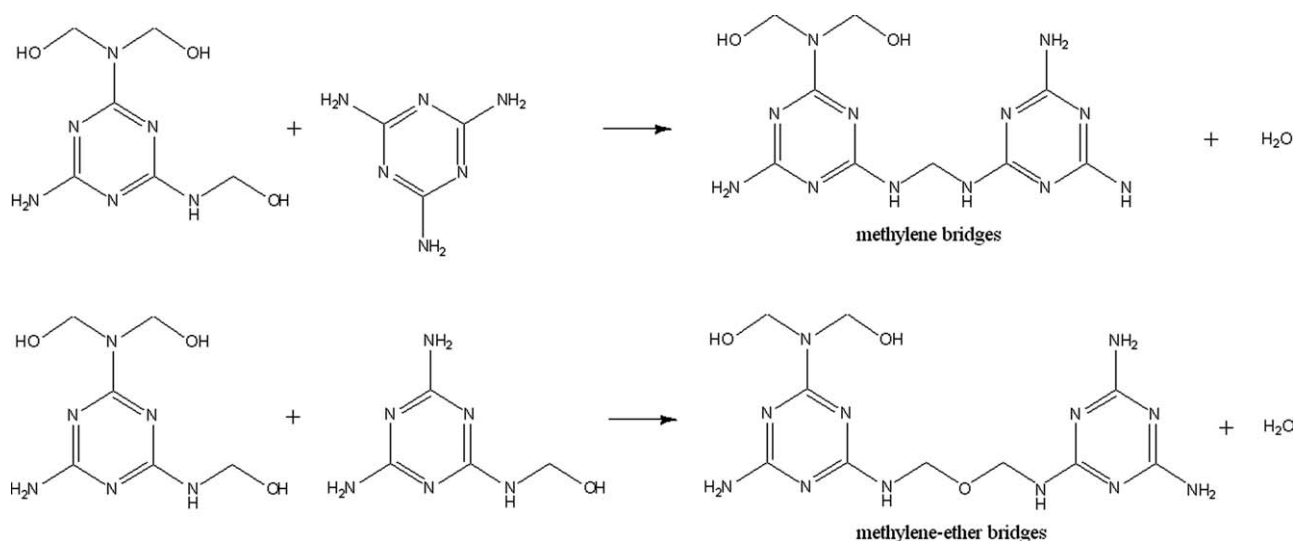

Figure 2 Condensation of the methylolureas and methylolmelamines to form methylene-ether bridges and methylene bridges.

mixture in any of these steps: in the initial methylolation/condensation step (before or after the addition of the first urea), in the methylolation step (before or after the addition of the second urea), or with the final urea. The first two alternatives were studied here. In all cases, the amount of melamine added was 3% relative of final mass of resin.

GPC/SEC analysis

A GPC/SEC equipped with a Gilson Differential RI detector and a Rheodyne 7125 injector with a 20 μL was used. The columns used were PSS Protema 100 and 300; 5 μm, conditioned at 60°C using an external oven. The flow rate was 1 mL/min. Samples for analyses were prepared by dissolving a small amount of resin in DMSO (dimethylsulfoxide), followed by vigorous stirring. Subsequently, the sample is left to rest, and then it is filtered through a filter of 0.45 μm.[14]

Particleboard production

The production of PBs is essentially divided into four stages: preparation of raw materials, blending, mat formation, and pressing. Wood particles were provided by a PB manufacturer (Sonae Indústria, Oliveira do Hospital). Standard mixtures were used for the core and face layers, which are composed of different proportions of pine, eucalyptus, pine sawdust, and recycled wood. The moisture content of the standard mixtures was checked before blending, using an infrared balance. The average of the moisture content of the face and core layers particles was 2.5 and 3.5%, respectively. Wood particles were then blended with the resin, catalyst and paraffin in a laboratory glue blender. The gluing factor was 6.3% resin solids in the face and 6.9% in the core, based on the oven-dry weight of wood particles. The resin was more catalyzed in the core layer (3% solids based on oven-dry weight of resin) than in the face layer (1% solids based on oven-dry weight of resin). The paraffin level was 0.15% solids (based on oven-dry weight of wood).

Three-layer PB was hand formed in an aluminum container with $220 \times 220 \times 80$ mm³. The total percentages of board mass were: 20% for the upper face layer, 62% for the core layer, and for 18% bottom face layer. The pressing of PB panels was carried out in a hot-press, controlled by computer and equipped with four thermocouples, a displacement sensor (LVDT), a load cell, and a pressure transducer. Pressing cycle (stage duration, press closing time, platen temperature) was scheduled to simulate a typical PB continuous pressing operation. The glued particles were pressed at 190°C with a pressing time of 150 s. The target thickness was 16 mm. The

TABLE I
Operation Conditions for the First Four Synthesis Attempts

Resin	Melamine addition	pH before melamine addition	Final pH	Final viscosity (mPa/s)
UF 1	First step	0.5–2	8.83	60
UF 2	Second step	7–8	7.81	142
UF 3	First step	0.5–2	8.90	210
UF 4	First step	5–7	8.82	64

average density of the final boards was 630 ± 20 kg/m³. The thickness of the panels is measured in five points (center and each corner) after pressing.

Physic-mechanical characterization of particleboard

After pressing, boards were stored in a conditioned room (20°C, 65% RH) and then tested accordingly to the European standards. The following physic-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). Panels for the analysis of formaldehyde content were stored in sealed plastic bags.

RESULTS AND DISCUSSION

This study essentially consisted in five distinct approaches for the synthesis strategy. The difference between them consists essentially in the timing and pH for melamine addition. The first four attempts, listed in Table I, resulted in nonviable processes or inappropriate resin performance.

For these formulations the solid content was about 63% in all cases. It must be noted that there is a major difference between synthesis 1 and 3, which results in different ending viscosities. In the first one, the pH was increased to 7 after melamine addition, by adding sodium hydroxide solution, and then the second urea was added (second step). In resin UF 3, on the other hand, the base was not added after melamine addition, and there was only a waiting time for allowing the pH to increase until stabilizing. The final pH before the second step was therefore between 5 and 6.

In resin UF 2, melamine addition occurs in the second step (methylolation at neutral pH). It was observed that the resin did not gain viscosity after the addition, suggesting that the addition of melamine in a neutral to alkaline phase only promotes the formation of methylolmelamines.

TABLE II
Particleboard Properties Obtained in the First Four Synthesis Attempts

Resin	Density (kg/m^3)	Internal bond strength (N/mm^2)	Thickness swelling (%)	Moisture content (%)	Formaldehyde content (mg/100 g oven dry board)
UF 1	666	0.38	28.1	6.3	3.2
UF 2	642	0.18	38.1	6.1	2.7
UF 3	633	0.43	28.6	4.7	3.4
UF 4	627	0.28	33.2	6.0	3.0

Finally, in resin 4 the melamine was added in the first step, after the addition of the first urea and at a pH between 5 and 7 (this value is obtained with the addition of an appropriated base).

Table II shows the results for the PB properties obtained with the first four resins. The results obtained for the resins 2 and 4 explain values out of specification with regard to IB strength (lower than 0.35 N/mm^2, the requirement for type P2 boards, according to EN 319) and thickness swelling, especially in procedure 2. Comparing the results for the UF resin 4 with the results for the UF resins 1 and 3 it is possible to observe that higher condensation pH results in the decrease of PB properties.

The panels produced with resins UF 1 and 3 present a high performance, namely high IB strength and low formaldehyde emission. However, the synthesis processes were very unstable (the increase of the viscosity is too fast during the condensation step), making these strategies unviable for industrial use without rigorous on-line control of the degree of condensation.

In the ensuing approach (fifth synthesis strategy) melamine was added to the initial formaldehyde solution at its normal pH (between 3 and 3.5), instead of decreasing it to 0.5–2.5 as before. After a 5 min stabilization period, pH was raised to 4.5–6, and only then the first urea was added. The second and third steps were then performed as previously described in synthesis described earlier. The major difference between this approach and the previous is the initial formation of methylolmelamines, that posterior react with methylolureas and urea.

Table III summarizes the four syntheses that compose this fifth approach. The fundamental difference between them is the pH set for the addition of the first urea. For all the synthesis it was observed that lower pH implied faster viscosity increase (higher

reaction rate). It is possible to conclude that more acidic conditions favor the condensation of the methylolmelamines and methylolureas produced in the methylolation reaction, instead of a methylolation reaction between the unreacted urea and free formaldehyde. The synthesis of UF 5.4 resin was slightly different. During the methylolation/condensation reaction the resin did not gain the desired viscosity (500 cP) after one and a half hours of reaction time. The temperature was therefore raised to 95°C and the second urea was added immediately. In these conditions the reaction progressed and the viscosity increased. The reaction mixture was then cooled to 60°C and the final urea was added. This synthesis was therefore different because both the first and second urea amounts were present in the methylolation/condensation step.

In conclusion, we can suggest that for this synthesis process for pH higher than 5.5 the condensation reaction does not occur at low temperature and high F/U molar ratio.

Table IV presents the physic-mechanical properties of the PB produced with the four resins. In general, the values are favorable for all features. Increasing the methylolation/condensation reaction pH decreases the IB strength of the panels. However, all the IB strength values are higher than the minimum acceptable value of 0.35 N/mm^2. Regarding formaldehyde emissions, all resins are below the limit imposed by CARB II legislation corresponding to an equivalent of perforator value of $\leq$4.0 mg/100 g oven dry board,[15] all resins having emissions below 3 mg/100 g oven dry board. The other properties are not sensitive to the reaction pH.

To understand the impact of the development of this resin in relation to existing commercial products, Table V shows the results for physical-mechanical properties of panels produced with three resins

TABLE III
Properties of UF Resins Produced in Fifth Synthesis Attempt

Resin	pH before 1st urea addition	Final pH	Final viscosity (mPa/s)	Solid content (%)	Gel time (s)
UF 5.1	4.50	8.21	430	63.40	75
UF 5.2	4.70	7.78	100	62.25	68
UF 5.3	5.00	9.18	140	63.41	110
UF 5.4	6.00	8.80	95	64.17	48

Properties of Particleboards from UF Resins Produced in Fifth Synthesis Attempt

Resin	Density (kg/m³)	Internal bond strength (N/mm²)	Thickness swelling (%)	Moisture content (%)	Formaldehyde content (mg/100 g oven dry board)
UF 5.1	637	0.44	28.9	5.4	2.7
UF 5.2	622	0.44	30.9	4.7	2.8
UF 5.3	634	0.35	29.6	5.0	2.5
UF 5.4	641	0.36	29.9	5.1	2.7

produced by different processes and with different melamine contents. Resins 1 and 2 are produced by the alkaline–acid process, having a melamine incorporation of 0 and 0.3%, respectively. Resin 3 is produced by a basic process and has 3% melamine. The panels and characterization procedures were performed in our lab in the same conditions as the previous ones.

The formaldehyde content for resin 5.1 is significantly lower than for the other resins. Internal resistance is lower than for resin 1, but still acceptable and similar to the values obtained for the other two resins. The other properties are also very similar for these four distinct resins.

Figure 3 shows the GPC/SEC chromatograms obtained for fifth approach resins. In this type of distribution the peaks with larger retention volume (retention volume between 20 and 26 mL) corresponds to free urea, methylolureas, methylolmelamines, and oligomers (molecular weight <3000) and the peaks with lower retention volume (retention volume between 6 and 14 mL) correspond to polymer with high molecular weight (molecular weight >12,000). Considering the high molecular weight fraction of the chromatograms (retention volume between 7 and 12 mL), it can be seen that increasing pH leads to higher molecular weight polymer, for resins 5.1, 5.2, and 5.3. Resin 5.4 is an exception, since the synthesis process was modified as discussed above: the methylolation/condensation step could only be carried after the addition of the second urea and increase of temperature. Since, the F/U molar ratio is lower; the polymer condensation does not progress as much as for the other three resins. This occurs because the free formaldehyde reacts with the methylolureas and methylolmelamines, and also with this new urea.

In the lower molecular weight region (retention volume between 20 and 26 mL) it is noticeable that resin 5.3 shows a lower shoulder (21 to 23 mL), which may be related to the higher degree of condensation, obtained at the expense of oligomeric species.

The resin 5.4 present the lower reactivity (see Table III), which is in agreement with the lower extension of the polymerization at the end of the reaction. The gel time values for resins 5.1 and 5.2 are very close and are essentially equivalent. Resin 5.3 shows the highest reactivity, which is once again relatable to the presence of higher molecular weight material.

CONCLUSIONS

Resins UF fortified with melamine have been developed for upgrading the performance of UF bonded PBs with low formaldehyde emissions. A strongly acid process was used for the resin synthesis. The addition of melamine was tested in the two main synthesis steps: acidic methylolation/condensation and slightly basic methylolation. Results indicated that the first step is the most appropriate for melamine addition. The effect of pH at this step was also studied. Very low or high pH values are not beneficial. Low pH (lower than 3) results in a very unstable reaction, as the resin gains viscosity very quickly. A high pH value (higher than 5) results in a very slow condensation reaction.

The PBs produced with the several resins showed that an increase in the pH of the first reaction step results in lower values of IB strength. Regarding formaldehyde content, all the resins in this study showed very low formaldehyde emissions.

This work describes a new synthesis strategy for UF resins fortified with melamine. Moreover, this process yields resins with good mechanical performances in

Properties of Particleboards Produced with Different UF Resins

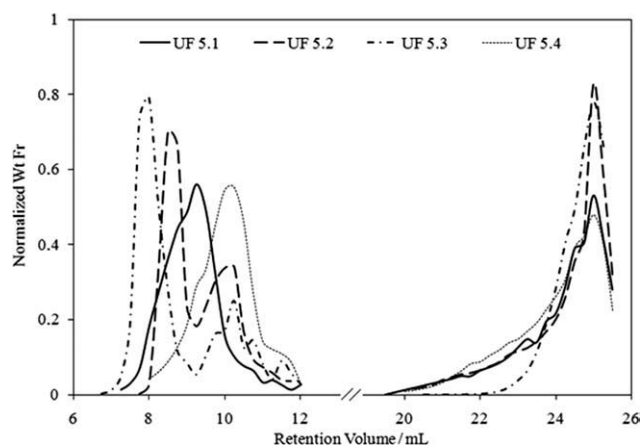| Resin	Density (kg/m³)	Internal bond strength (N/mm²)	Thickness swelling (%)	Moisture content (%)	Formaldehyde content (mg/100 g oven dry board)
Resin 1	641	0.52	25.7	6.3	5.3
Resin 2	675	0.39	32.0	6.2	3.4
Resin 3	656	0.49	24.7	5.8	4.6
UF 5.1	637	0.44	28.9	5.4	2.7

Figure 3 Chromatograms of UF resins produced in fifth synthesis attempt.

terms of IB strength and formaldehyde emissions. The novelty of this approach lies on the melamine addition during the acidic step, promoting its reaction with formaldehyde prior to the introduction of urea. This yields a MUF copolymer with strong bonds, instead of only urea-formaldehyde and MF polymers.

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