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# Water resistance evaluation of a MFU resins with different molar ratio catalyzed with citric acid

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ABSTRACT

Urea, in either solid form or in solution, is an additive commonly used to control the viscosity or act as a scavenger in MF (melamine-formaldehyde) and MUF (melamine-urea-formaldehyde) resins for particleboard production.

The aim of this work was to evaluate the influence of adding urea to MF (melamine-formaldehyde) resin in terms of the water-resistance of the final particleboards. FTIR-ATR spectroscopy, adhesive bonding evaluation system (ABES) and gravimetric techniques were used. MF and MFU (melamine-formaldehyde-urea) resins were prepared. Urea was introduced as an additive, in different percentages (0, 10, 20, and 30% (on adhesive, dry basis), and citric acid was used as catalyst. Beech veneer strips were bonded together with these formulations and then tested in dry conditions and after immersion in water for 24 h. The effect of urea load on the resin curing reaction in dry and humid joints was studied. Particleboards were produced with MF and MFU (melamine formaldehyde urea) resins with different urea loads and using industrial recycled wood particles as raw material. Particleboard evaluation indicated that the water resistance of the final particleboards decreased linearly with urea addition.

## 1. Introduction

Melamine-Urea-Formaldehyde (MUF) is the most common resin used as an exterior-grade adhesive in the wood-based panels industry. It is commonly synthesized by copolymerization of melamine and urea with formaldehyde. The percentage of melamine used in the resin synthesis is associated with increased water resistance properties, due to the better hydrolysis resistance of the C–N bonding between the melamine ring and the methylene bridge [1] in comparison with the C–N bonds in urea-formaldehyde (UF) resins. Despite its hygroscopicity, urea is added as an additive to amino resins, due to its properties as a formaldehyde scavenger [2]. Urea can also be used to adjust resin viscosity, due its ability to disrupt hydrogen bonding between resin molecules, and confers better storage stability [3].

Nowadays, the industry demands wood-based panels with high performance, mainly for construction and furniture applications, such as kitchen worktops, flooring and structural components in humid conditions, for which MUF resins are used as binders with good properties [4].

Particleboard water resistance will depend on wood raw material, resin type and water-repellent additives used in its production [5].

The aim of this work was to evaluate the influence of added urea on the water resistance of particleboards produced with melamine formaldehyde (MF) resin, using FTIR-ATR spectroscopy, adhesive bonding evaluation system (ABES) and gravimetric techniques. For this purpose, a MF resin was laboratory synthetized and melamine formaldehyde urea resins (MFU) were prepared mixing the MF resin with different percentages of urea (0, 10, 20, 30%) and using citric acid as catalyst.

Citric acid was used as a catalyst to avoid the influence of the free formaldehyde on the catalyst reaction, when a latent catalyst is used [2]. Recent studies have shown that citric acid is a good crosslinking agent in the formulation of bio-based adhesives to be used in the production of wood products, mainly with carbohydrates such as starch [6] or sucrose

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[7–11], or in combination with tannins [12,13]. Reactions between wood components (lignin and carbohydrates) and citric acid were also studied [14]. Its use in amino resins was tested before by other authors, but with urea-formaldehyde resins [2,15], and recently in the synthesis of a MUF resin used to study the valorisation of Pinus Pinaster by-products on the particleboard production [16].

The first studies done using citric acid with amino resins [2] indicated that low stability resins tended to be produced. To overcome this, citric acid was mixed with the urea solution to increase the stability of the adhesive [17]' following the same procedure used in other studies by the authors [16].

The influence of urea percentage added to the resin was evaluated by adhesive bonding evaluation system (ABES). Beech veneer strips were bonded together with these formulations and then tested in dry conditions and in wet conditions after immersion in water for 24 h. The effect of urea load on the resin curing reaction of dry and wet joints was studied. Particleboards with MF and MFU resins with different urea loads were produced and evaluated, using industrial recycled wood particles as raw material.

## 2. Materials and methods

### 2.1. Materials

Formaldehyde (37 wt % solution), melamine, sodium hydroxide (10 wt % solution), along with urea were furnished by Euroresinas, Indústrias Químicas, S.A. (Sines, Portugal). Citric acid was supplied by PanReac AppliChem (Barcelona, Spain.

### 2.2. Resin synthesis

Melamine-formaldehyde (MF) resin was produced in a 2 L round bottom flask equipped with a mechanical stirrer and an immersed thermometer. A heating mantle was used to heat the flask. MF resin was prepared by condensation of melamine, and formaldehyde with a final formaldehyde/melamine (F/M) of 1.80. Melamine and formaldehyde aqueous solution (at 37 wt % solution) was first charged into the round bottom flask, and the pH value was adjusted to 8.5–9.0 using NaOH solution 10% in water. The mixture was then heated to 90–100 °C, upon which it became a clear solution. Subsequently, the reaction proceeded until a water tolerance of 200% was attained. At this point, the mixture was cooled until room temperature. The MF resin synthesized was then mixed with solid urea, till a final resin solid content by weight of 57%.

### 2.3. Solid content

For the determination of the solids content of the resin samples, 2 g of each sample was heated in an oven at 120 °C for 3 h until a constant mass. Analyses were performed in triplicate and the results were averaged.

### 2.4. Water tolerance

For the evaluation of resins water tolerance (wt), 5 mL of resin (at 25 °C) was introduced into a test tube and distilled water was added until the resin solution become cloudy. Water tolerance is reported following the equation (Eq. (1).):

$$WT\ (\%) = \frac{V}{V'} * 100 \quad (1)$$

Being $V$ the water added (mL), and $V'$ the complete sample volume (mL).

The increase in the degree of condensation is measured by reducing the water tolerance resin.

**Table 1**
Synthetized MF resin properties.

| pH | Solid content (%) | Water tolerance (%) | Density (kg/m$^3$) |
|---|---|---|---|
| 9.7 | 56.7 ± 0.1 | 200 ± 5 | 1255 ± 2 |

### 2.5. Fourier transform infrared spectroscopy (FTIR) assay

FTIR spectra were recorded on a VERTEX 70 FTIR spectrometer (BRUKER, Billerica, MA, USA) in transmittance mode with a high sensitivity DLaTGS detector, at room temperature.

Samples were measured in ATR mode, with a single reflection diamond ATR accessory.

The spectra were recorded from 4000 to 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. All spectra were recorded and processed with OPUS 7.0 software.

### 2.6. Automated Bonding Evaluation System (ABES) assay

An ABES instrument (Adhesive Evaluation Systems, Corvallis, Oregon, USA) was used to evaluate the maximum strength of the wood-adhesive-wood system at defined temperature and time conditions [18,19].

The wood veneer samples (Fagus sylvatica L., thickness 0.7 mm) were stored in a conditioned chamber for one week at 20 °C and 53% relative humidity before testing. Probes were cut into 117 mm × 20 mm strips using a pneumatically-driven sample cutting device for ABES sample preparation (supplied by Adhesive Evaluation Systems, Corvallis, Oregon, USA).

Two peeled wood veneer strips were glued along the fiber direction with a 100 mm$^2$ overlap using 10 mg of adhesive. Analyses were conducted at 120 °C and over 30, 60, 90, and 120 s time frames. Measurements were repeated five times for each data point.

To evaluate the water influence on the adhesion properties, samples glued were introduced in water at 25 °C, during 24 h. The samples were glued with the MF resin with 3% of citric acid as catalyst alone and with 10, 20 and 30% of urea.

Samples were air-dried and evaluated 24 h after with the same equipment.

### 2.7. Residual rate

The adhesives prepared with MF resin citric acid and 0–30% of urea (2 ± 0.005) g were oven-dried at 120 °C (for 30 and 180 min) and the initial dry weight was measured ($W_0$). The dried samples were immersed in water (100 mL) and maintained at 25 °C for a week.

Subsequently the samples were oven-dried at 120 °C for 180 min, and cooled to room temperature in a desiccator, and then the residual weight was measured ($W_{RR}$).

The residual rate ($RR$) of the adhesive was determined by the equation (Eq. (2)):

$$RR = 100 \times \left(1 - \frac{W_0 - W_{RR}}{W_0}\right) \quad (2)$$

## 3. Results and discussion

To evaluate the influence of the free urea addition on MF properties, first a MF resin was laboratory synthetized, following the same method used previously [20]. The MF resin was characterised based on its physical properties and the results are shown in Table 1.

The influence of urea addition to MF resin on its reactivity, on its physicochemical characteristics, and on the properties of the particleboards produced with these resins was studied by FTIR-ATR spectrometric technique.

The first step was the evaluation and quantification of the urea

**Table 2**
Molar ratio (*MR*) of the MF and MFU resins evaluated.

| RESIN | Melamine (% mass respect resin, dry basis) | Urea (% mass respect resin, dry basis)) | Formaldehyde (% mas respect resin, dry basis) | Citric acid (% mass respect resin, dry basis) | *MR* |
|---|---|---|---|---|---|
| MF | 35.0 | 0 | 14.2 | 3.8 | 1.85 |
| MF10 | 31.5 | 9.5 | 12.8 | 3.8 | 1.14 |
| MF20 | 28.0 | 18.9 | 11.4 | 3.8 | 0.78 |
| MF30 | 24.5 | 28.4 | 9.94 | 3.8 | 0.56 |

content on the catalyzed (with citric acid) liquid resin by FTIR-ATR.

MF resin was mixed with 0, 10, 20 and 30% (g solid urea/g solid MF resin) of urea, and 3% of citric acid as catalyst (respect urea + MF solids). The adhesives were prepared and evaluated 1 h after preparation. For all the adhesives essayed, the solid content was fixed at (57.0 ± 0.5) %, using distilled water for adjustment.

The final Molar ratio (*MR*) of the resin was calculated taking into account the influence of citric acid as acid catalyst and as formaldehyde replacement component, following the subsequent equation (Eq. 3):

$$MR = \frac{F + CA(OH)}{M + U\ (NH_2)} \quad 3$$

Where:

- *F* is the molar fraction of formaldehyde on the resin.
- *CA* is the molar fraction of citric acid on the resin.
- *M* is the molar fraction of melamine on the resin.
- and *U* is the molar fraction of urea.

Table 2 shows the molar ratio (*MR*) values and the percentage (in mass, dry basis) of the main components of the adhesive evaluated.

In typical MF synthesis, the formaldehyde to melamine ratio (F/M) is generally around 2.0 [21]. Usually, lowering this ratio at the synthesis stage has the handicap of causing problems in the dissolution of melamine in the formaldehyde solution. The replacement of MF resin by urea affects the molar ratio and the proportion of free OH to react with $NH_2$ groups. Previous studies have shown that molar ratio and melamine content, have a significant effect on the properties of MUF resins [22–24]. The *MR* of UF and MFU resins has been slowly decreased over the years from its initially high value, mainly looking to reduce the

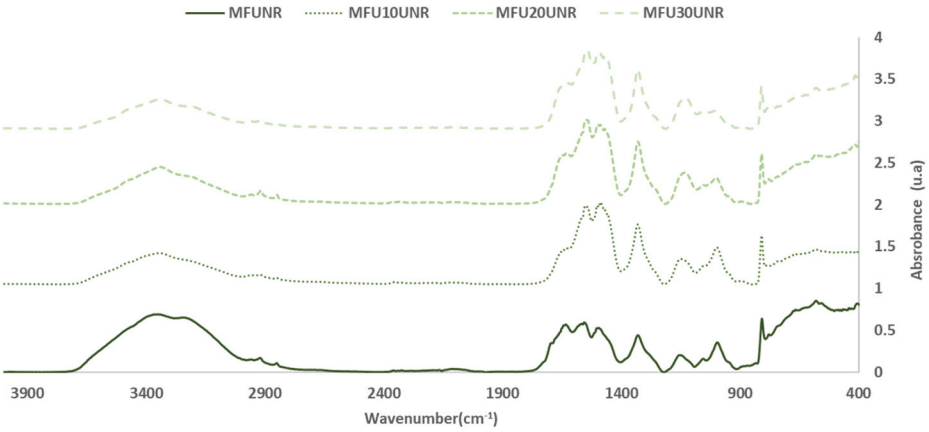


**Fig. 1.** FTIR spectra of MF resins with 0–30 (%) urea (400-4000 $cm^{-1}$).

**Table 3**
IR spectral data of MF and MFU liquid resins with 10–30 (%) urea and citric acid.

| MF | | MFU10 | | MFU20 | | MFU30 | | Group | Range |
|---|---|---|---|---|---|---|---|---|---|
| $cm^{-1}$ | Intensity | $cm^{-1}$ | Intensity | cm-1 | Intensity | $cm^{-1}$ | Intensity | | |
| 1695 | 58.0 | | | | | | | C=O stretching, citric acid [28] | 1693 |
| | | 1645 | 74.3 | 1652 | 61.2 | 1649 | 102 | C=O stretching, secondary amine –N-H- (methylol and methylene urea); -N-H- triazine ring | 1644 |
| 1632 | 90.6 | | | | | | | -N-H (primary amine) bending [27]; | 1629 |
| | | | | 1622 | 69.3 | 1628 | 107 | -N-H (secondary amine) methylol and metilene melamine bending [25] | 1625 |
| 1553 | 94.0 | | | | | | | -NH- (secondary amine); bending (of melamine) | 1556 |
| | | 1548 | 146 | 1539 | 114 | 1539 | 162 | -N-H- (secondary amine, methylol and methylene urea) bending [27]; | 1544 |
| | | 1513 | 130 | | | 1514 | 142 | N–C–N of a proper methylene bridge (-$CH_2$-) [27] | 1513 |
| 1495 | 85.0 | 1487 | 151 | 1487 | 122 | 1487 | 156 | C–H deformation vibration of –$CH_2$-OH | 1480–1410 |
| | | | | 1472 | 122 | | | triazine ring "semicircle" stretching | 1469 |
| | | | | | | 1464 | 151 | CH- deformation; asymmetric in –$CH_3$ and –$CH_2$- | 1460 |
| 1331 | 71.9 | 1331 | 118 | 1331 | 118 | 1331 | 131 | $C_{AR}$-N asymmetric stretching of substituted melamine. | 1360–1320 |
| 1155 | 35.2 | 1151 | 56.8 | | | | | $C_{AR}$-N stretching and asymmetric C–O–C stretching | 1150 |
| | | | | 1136 | 85 | 1132 | 78.1 | Symmetric C–O–C of –$CH_2$-O-$CH_2$ stretching between melamines | 1135 |
| 1055 | 27.9 | 1055 | 42.4 | 1057 | 71.9 | | | Symmetric C–O–C stretching in –$CH_2$-O-$CH_2$- | 1040 |
| | | | | 1033 | 72.4 | 1059 | 47.6 | $C_{AR}$-H in plane deformation | 1030–1035 |
| 995 | 59.0 | 999 | 78.9 | 1001 | 79.1 | 1007 | 48.3 | C–O stretching in –$CH_2$OH | 990 |
| 944 | 20.1 | 944 | 24.9 | 941 | 58.2 | 945 | 15.9 | C–O stretching, citric acid [28] | 943 |
| 808 | 100 | 810 | 100 | 810 | 100 | 810 | 100 | triazine ring (melamine) | 810 |
| 779 | 73.5 | 787 | 44.0 | 783 | 80.7 | 787 | 54.9 | CO wagging; $NH_2$+CO out of plane wagging; $NH_2$ wagging or rocking | 790–786 |
| 746 | 87.2 | 746 | 51.8 | 747 | 87.7 | 747 | 58.5 | C–H bending | 735–775 |

$C_{AR}$: Aromatic Carbon.

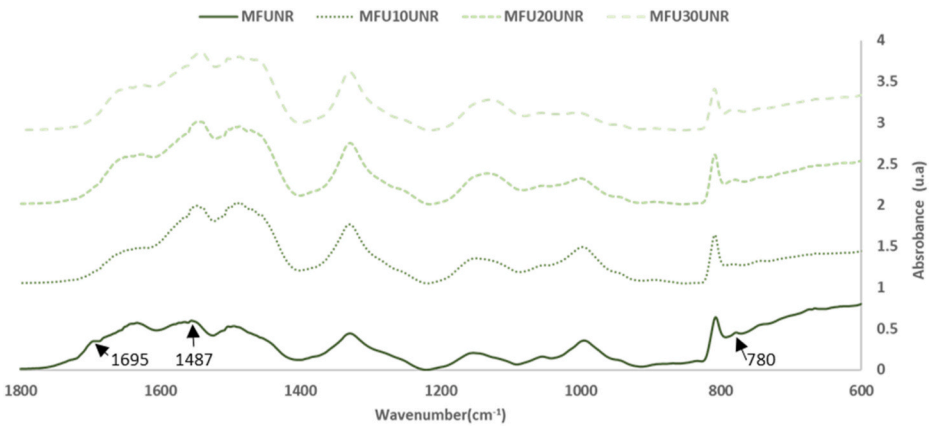


**Fig. 2.** FTIR spectra of MF resins with 0–30 (%) urea (600-1800 $cm^{-1}$).

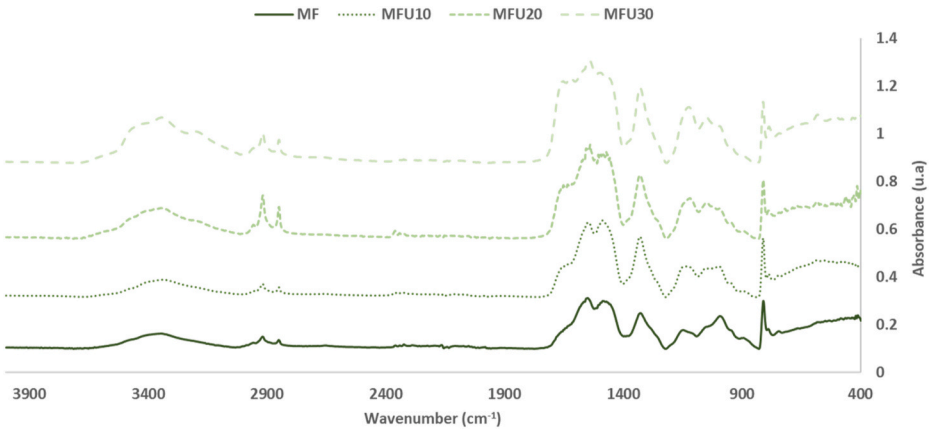


**Fig. 3.** FTIR spectra of MF resins with 0–30 (%) urea reacted at 120 °C for 180 min (400-4000 $cm^{-1}$).

formaldehyde emission of the products produced with this resin. Nowadays, it is possible to produce resins with *MR* values of around 1 [24]. In this study, very low *MR* values were used due to the free urea addition as a replacement of the MF resin especially in the formulation of the MFU30 resin. This formulation condition was tested to evaluate the influence of a high amount of free urea on the resin, in the adhesive properties.

### *3.1. Evaluation of urea influence on MF curing reaction and on the resin water resistance by FTIR-ATR*

Samples of MF and MFU resins with citric acid as catalyst and different urea contents, were analysed with FTIR-ATR, and the spectra obtained are shown in Fig. 1.

FTIR band assignment is summarized in Table 3, and was done based on previous studies ([25–27]). For the analysis, FTIR spectra were normalized, based on the triazine ring vibration band at 810 $cm^{-1}$. In this case, the analysis was focused on the fingerprint region, which is a

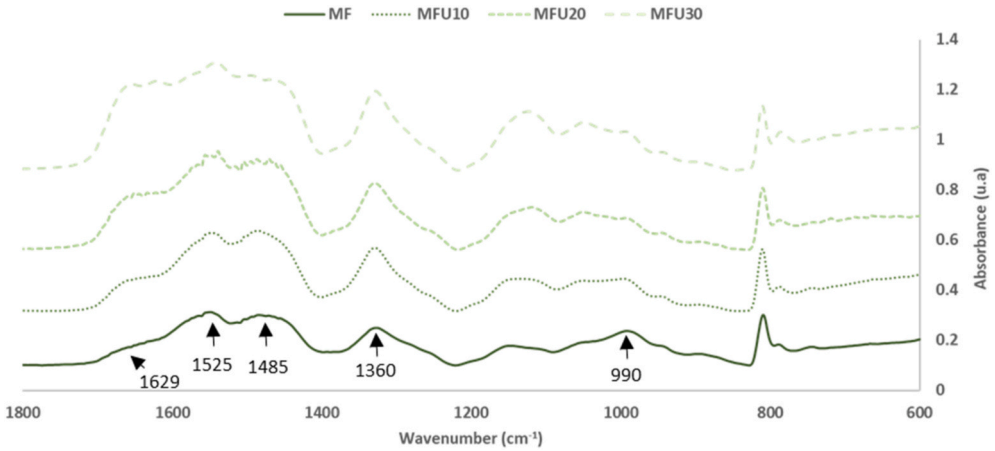


**Fig. 4.** FTIR spectra of MF resins with 0–30 (%) urea reacted at 120 °C for 180 min (600-1800 $cm^{-1}$).

**Table 4**
IR spectral data of MF and MFU resins with 10–30 (%) urea and citric acid reacted at 120 °C for 180 min.

| MFR | | MFU10R | | MFU20R | | MFU30R | | Group | Range |
|---|---|---|---|---|---|---|---|---|---|
| $cm^{-1}$ | Intensity | $cm^{-1}$ | Intensity | $cm^{-1}$ | Intensity | cm-1 | Intensity | | |
| | | 1643 | 55.3 | 1644 | 91.1 | 1651 | 130 | -NH- triazine ring | 1644 |
| | | | | | | 1616 | 135 | -NH. (secondary amine) methylol and metilene melamine bending | 1625 |
| 1547 | 105 | 1541 | 125 | 1547 | 145 | | | -NH- (secondary amine) bending | 1556 |
| | | | | 1539 | 151 | 1537 | 159 | C=N (ring vibration) stretching | 1520–1530 |
| | | 1485 | 128 | 1487 | 139 | 1492 | 143 | C–H deformation vibration of $–CH_2$-OH | 1480–1410 |
| 1468 | 98.4 | | | 1472 | 141 | | | triazine ring "semicircle" stretching | 1469 |
| | | | | 1456 | 132 | 1462 | 137 | CH- deformation; asymmetric in $–CH_3$ and $–CH_2$- | 1460 |
| | | | | | | 1377 | 37.0 | C–H wagging of $CH_2$–OH | 1390–1280 |
| 1327 | 75.2 | 1329 | 90.7 | 1329 | 107 | 1329 | 121 | $C_{AR}$-N asymmetric stretching of substituted melamine. | 1360–1320 |
| 1150 | 39.8 | 1146 | 52.2 | | | | | $C_{AR}$-N stretching and asymmetric C–O–C stretching | 1150 |
| | | | | 1126 | 71.0 | 1128 | 92.2 | $-NH_2$ rocking and twisting in primary aromatic amines | 1120 |
| 1050 | 46.2 | 1053 | 50.9 | 1051 | 63.4 | 1051 | 76.4 | Symmetric C–O–C stretching in $–CH_2$-O-$CH_2$- | 1040 |
| 993 | 69.0 | 998 | 54.1 | 990 | 53.5 | 992 | 62.3 | C–O stretching in $–CH_2OH$ | 990 |
| 944 | 39.5 | 943 | 24.8 | 943 | 29.6 | 942 | 29.6 | C–O stretching, citric acid [28] | 943 |
| 810 | 100 | 810 | 100 | 810 | 100 | 810 | 100 | triazine ring (melamine) | 810 |
| 790 | 42.2 | 789 | 41.2 | 787 | 50.3 | 787 | 61.6 | CO wagging; $NH_2$+CO out of plane wagging; $NH_2$ wagging or rocking | 790–786 |
| 746 | 37.6 | 746 | 38.9 | 747 | 47.0 | | | C–H bending | 735–775 |

**Table 5**
FTIR-ATR evaluation of urea influence on the MFU adhesives curing reaction.

| Resin | 1600 $cm^{-1}$ (-$NH_2$) (Area band reduction on cure %) | 1360 $cm^{-1}$ (Car-N) (Area band reduction on cure %) | 1525 $cm^{-1}$ (C=N ring vibration) (Area band reduction on cure %) |
|---|---|---|---|
| MF | 24.3 | 22.9 | 16.4 |
| MFU10 | 52.1 | 43.6 | 34.2 |
| MFU20 | 65.8 | 63.3 | 55.8 |
| MFU30 | 68.2 | 64.5 | 54.8 |

more sensitive spectral region (Fig. 2).

Regarding the spectrum of the MF resin (with CA) and the resins with free urea (MFU10, MFU20 and MFU30), the main differences were found in the band around 1695 $cm^{-1}$ due to the presence of carbonyl groups of the citric acid. The absence of this band on the spectrum of the adhesives formulated with urea was due to the reaction between the urea and citric acid, which produces urea citrate [17]' justifying the improved stability of these resins. In addition, a band around 1487 $cm^{-1}$ was observed in the spectra of the MFU resins, which is due to the increase of $–CH_2OH$ groups in the resin. The increase in the methylol groups could be due to intermediate reaction compounds between urea and citric acid, or the formation of methylolureas. Finally, the band at 780 $cm^{-1}$ in the MF spectra shifts to higher wavenumber values in the spectra of the MFU10-30 resins due to the presence of more free $NH_2$ groups from the unreacted urea.

The influence of the urea percentage added to the MF resin in the chemical curing reaction was evaluated by FTIR-ATR, for that the MF resin with different urea content were cured at 120 °C for 180 min, cooled and subsequently were analysed. The FTIR spectra of the cured resins are shown in the Fig. 3 and Fig. 4.

To analyse the spectra of the cured resins, the same strategy was followed with the uncured resins and the peak assignment is summarized in Table 4.

The main changes observed due to the curing reaction were found in the bands around 1629 and 1525 $cm^{-1}$ of primary amine $–NH_2$, which reduces its intensity due to the reaction of these groups with the free –OH groups. The band at 1360-1320 $cm^{-1}$ due to Car-N stretching vibration shifts to lower wavenumber values due to the transition of methylol groups to methylene ether or methylene bridges.

The intensity of the band at 990 $cm^{-1}$ is due to the C–O stretching vibration in $–CH_2OH$ decreases. In the case of MFU resins, the band in 1485 $cm^{-1}$ due to the deformation of CH vibration of $–CH_2$-OH, reduces its intensity in the curing reaction. This decrease was dependent on the amount of urea added; being very slight in the MFU30 resin, showing that in this case, a significant percentage of the added urea remained as free urea in the cured resin.

Regarding the most sensitive FTIR-ATR bands involved in the curing reaction, it was possible to evaluate the influence of the urea addition on the curing reaction.

Table 5 shows the area band reduction of this bands due to the curing reaction process.

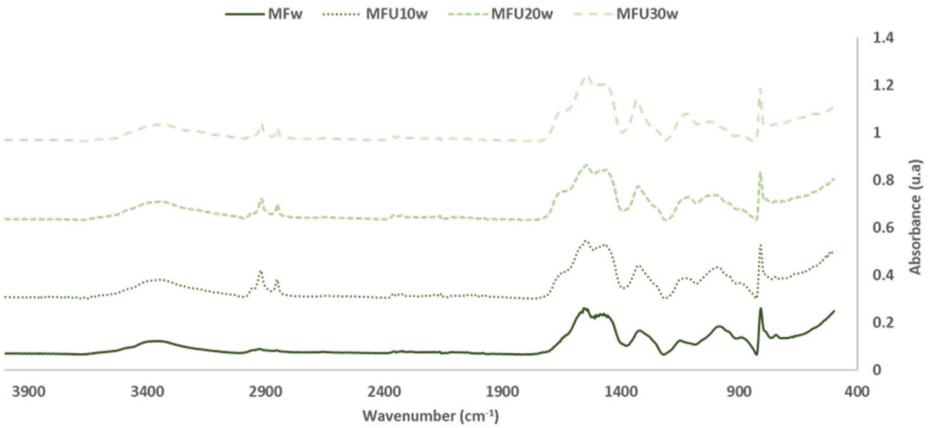


**Fig. 5.** FTIR spectra of MFw and MFU10w, MFU20w, and MFU30w resins reacted at 120 °C for 180 min (400-4000 $cm^{-1}$) after the water treatment.

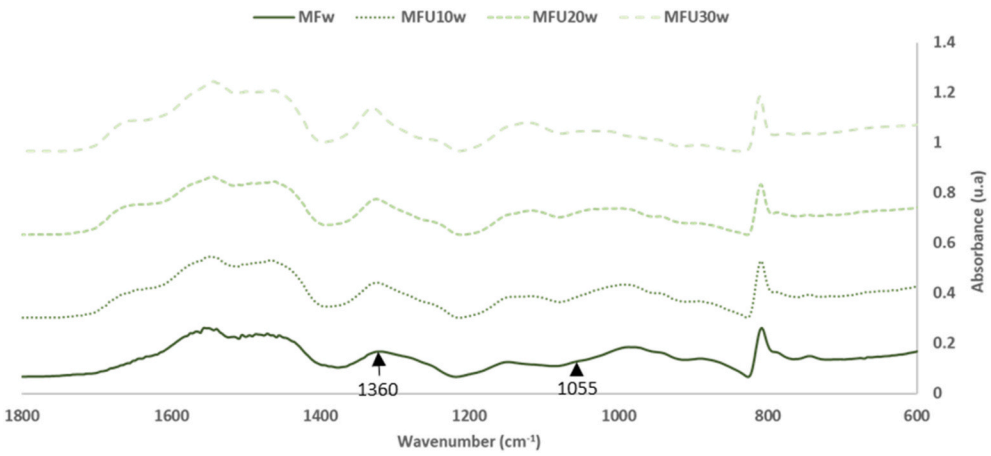


**Fig. 6.** FTIR spectra of MFw and MFU10w, MFU20w, and MFU30w resins reacted at 120 °C for 180 min (600-1800 $cm^{-1}$) after the water treatment.

**Table 6**
IR spectral data of MFw and MFUw resins with 10–30 (%) urea and citric acid reacted at 120 °C for 180 min and subjected to water hydrolysis treatment.

| MFw | | MFU10w | | MUF20w | | MUF30w | | Group | Range |
|---|---|---|---|---|---|---|---|---|---|
| $cm^{-1}$ | Intensity | $cm^{-1}$ | Intensity | cm-1 | Intensity | cm-1 | Intensity | | |
| 1642 | 38.4 | 1644 | 50.7 | 1647 | 61.2 | 1653 | 57.4 | -NH- triazine ring | 1644 |
| 1622 | 46.5 | 1633 | 52.2 | 1625 | 63.1 | 1625 | 62.3 | -NH. (secondary amine) methylol and metilene melamine bending | 1625 |
| 1555 | 100 | 1547 | 108 | 1543 | 116 | 1543 | 125 | -NH- (secondary amine) bending | 1556 |
| 1517 | 82.6 | 1513 | 91.7 | 1509 | 100 | 1509 | 107 | C=N (ring vibration) stretching | 1520–1530 |
| 1485 | 88.1 | 1485 | 98.1 | 1491 | 104 | 1492 | 109 | C–H deformation vibration of $–CH_2$-OH | 1480–1410 |
| 1471 | 88.9 | | | | | | | triazine ring "semicircle" stretching | 1469 |
| 1464 | 85.9 | 1467 | 102 | 1461 | 106 | 1461 | 110 | CH- deformation; asymmetric in $–CH_3$ and $–CH_2$- | 1460 |
| 1436 | 73.5 | 1440 | 86.3 | 1439 | 90.4 | 1439 | 94.0 | triazine ring "semicircle" stretching | 1435 |
| 1322 | 53.1 | 1325 | 62.9 | 1326 | 72.2 | 1330 | 79.7 | $C_{AR}$-N asymmetric stretching of substituted melamine. | 1360–1320 |
| 1149 | 31.5 | 1150 | 36.4 | 1148 | 41.0 | | | $C_{AR}$-N stretching and asymmetric C–O–C stretching | 1150 |
| | | 1119 | 38.8 | 1122 | 49.3 | 1122 | 53.6 | $-NH_2$ rocking and twisting in primary aromatic amines | 1120 |
| | | | | 1039 | 51.5 | | | Symmetric C–O–C stretching in $–CH_2$-O-$CH_2$- | 1040 |
| 986 | 62.1 | 990 | 59.3 | 999 | 53.7 | | | C–O stretching in $–CH_2$OH | 990 |
| 944 | 51.2 | | | | | | | C–O stretching, citric acid [18] | 943 |
| 808 | 100 | 809 | 100 | 809 | 100 | 811 | 100 | triazine ring (melamine) | 810 |
| 788 | 51.9 | 787 | 46.0 | 786 | 45.6 | 771 | 33.5 | CO wagging; $NH_2$+CO out of plane wagging; $NH_2$ wagging or rocking | 790–786 |
| 744 | 43.9 | 745 | 41.4 | 744 | 40.5 | 745 | 34.3 | C–H bending | 735–775 |

Regarding the percentage of area reduction of the different bands used to study the curing reaction, it was observed that in terms of reactivity the replacement of the MF resin by urea (with CA as catalyzed agent) was possible up to 20%. When this value was exceeded, the added urea did not react with the MF resin (due to the low *MR*) and remained as free urea in the cured resin.

These results are in correlation with the intensity of the bands at 2919 and 2849 $cm^{-1}$ due to the stretch vibration modes of the $CH_2$ groups. The percentage of these functional groups increases in the curing reaction due to the formation of methylene bonds, and their intensity peaks increase with the addition of urea until reaching the value of 20%.

Subsequently, the cured samples of the adhesives MF, MFU10, MFU20 and MFU30, were subject to a water treatment, and after were oven dried and reanalyzed by FTIR-ATR (MFw, MFU10w, MFU20w and MFU30w), to evaluate the influence of water on MF and MFU resins. Fig. 5 and Fig. 6, shows the spectra of the dry samples after the water treatment.

To analyse the influence of water treatment on the cured resin, the FTIR-ATR spectra were evaluated focusing on the finger-print region and the peak assignment is summarized in Table 6.

FTIR-ATR essay allows to evaluate the chemical changes produced in the resins, due to influence of water. Comparing the spectra before and after water treatment, some differences appear. In the case of MF resin, the most important changes correspond to the $CH_2$ bands at 2919 and 2849 $cm^{-1}$. The intensity of these bands decreases in the spectra of the sample that was subjected to water treatment, due to the degradation by water hydrolysis of the methylene bridges present in the resin. The band around 1055 $cm^{-1}$, of the symmetric C–O–C stretching vibrations of the ether bonds also decrease slightly its intensity in MFw resin, indicating that a percentage of the ether bonds were broken due to the hydrolysis promoted by water.

The band at 1360-1320 $cm^{-1}$ due to Car-N stretching vibration is a very X-sensitive absorption band (highly dependent on groups linked to the aromatic triazine ring) [20,29].

The normalized intensity (respect the triazine ring band at 810 $cm^{-1}$) of the band around 1320 $cm^{-1}$, ascribed to the methylene bridges, is a good parameter to evaluate the degree of condensation and the cross-linking of the resin [20]. Regarding the intensity decrease of the bands, it is possible to evaluate the water hydrolysis effect on MF resin and MFU10, MFU20 and MFU30. The hydrolysis effect (decreasing on band intensity) increases with the percentage of urea added to the MF resin.

### *3.2. Evaluation of urea influence on MF curing reaction and on resin water resistance by Automated Bonding Evaluation System (ABES)*

The curing of an adhesive in contact with wood can be evaluated by ABES. This method evaluates how fast the bond strength develops under controlled hot-pressing conditions. The press time (15–120 s) at a

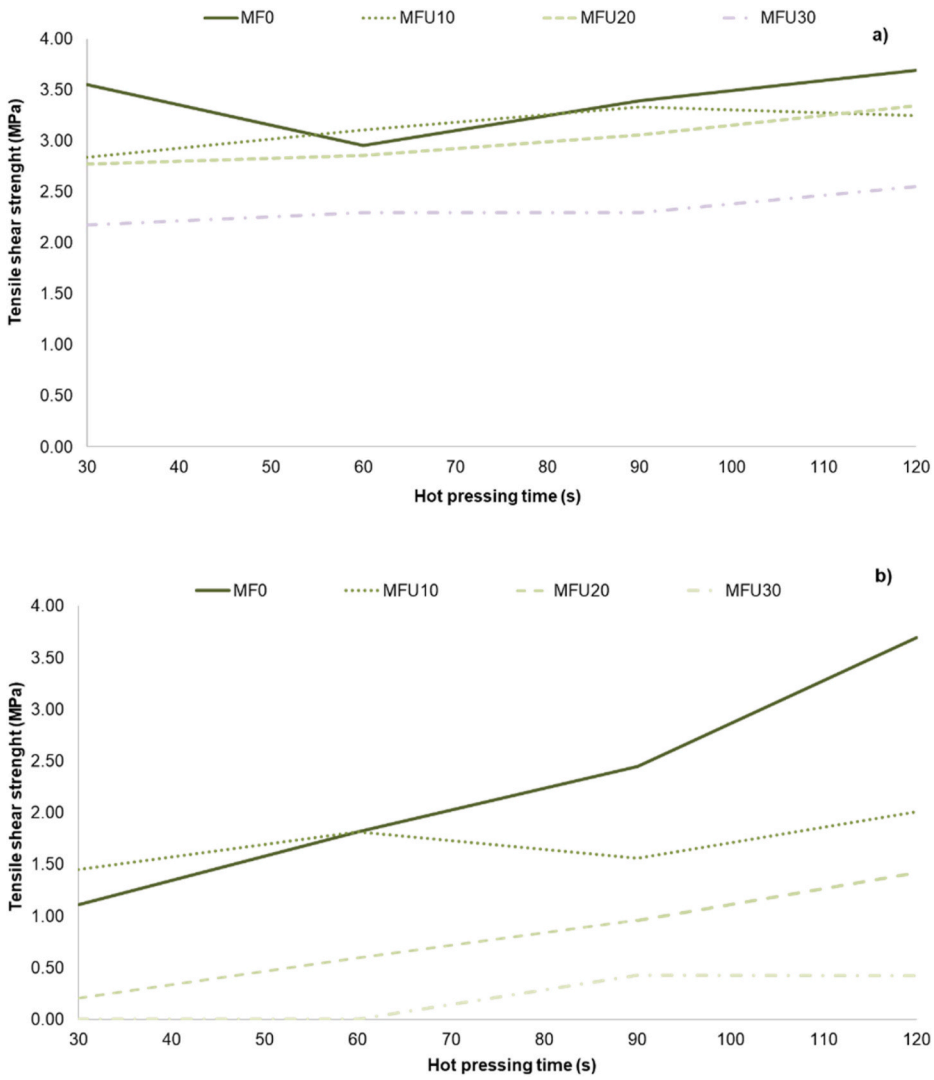


**Fig. 7.** Development of shear strength as a function of hot-pressing time for MF and MUF with urea (0–30 (% on adhesive weight, dry basis)) at 120 °C a) dry essay b) wet after water-treatment.

constant temperature (120 °C) effect was analysed (Fig. 7).

By ABES, the influence of the urea percentage in the MF resin in the dry samples and in the samples subjected to the water-immersion treatment was evaluated.

Regarding the results obtained in the dry essays, it was demonstrated that at the press conditions studied the replacement of the MF adhesive by urea (using CA as catalyst and copolymer) did not have a significant influence in the adhesive performance until 30% of urea was used.

However, when the evaluation was performed in wet conditions, the ABES method allow to predict the urea influence on water resistance of the beech wood-adhesive system, and the adhesive development in wet conditions was conditioned by the amount of urea added to the MF adhesive.

### 3.3. Evaluation of resin hydrolysis by gravimetric methods

The residual rate (RR) is a parameter commonly used as an indicator to assess the hydrolytic stability of a cured wood adhesive [30]. It can be calculated by using the weight difference between the original weight of an adhesive and its non-hydrolysable portion after a specific hydrolysis treatment [31].

In this case, the influence of cure time on resin hydrolysis resistance was also evaluated and two curing conditions were tested:

**Table 7**
Residual rate of MF and MFU10, MFU20 and MFU30 resins.

| Adhesive | MF | MFU10 | MFU20 | MFU30 |
|---|---|---|---|---|
| RR1 (%) (T1) | 88.24 ± 0.11 | 81.16 ± 0.06 | 72.26 ± 0.18 | 51.75 ± 0.15 |
| RR2 (%) (T2) | 99.89 ± 0.05 | 93.18 ± 0.36 | 81.69 ± 0.09 | 54.53 ± 0.32 |

- T1: 120 °C 30 min
- T2: 120 °C 180 min

The results obtained for the residual rate as shown in Table 7.

The percentage of urea added to the MF resin showed a great influence on the water resistance properties of the resin, appearing a relationship between the decrease in the residual rate and the percentage of urea added to the MF resin.

These parameters followed the subsequently linear relations:

$$y_1 = -1.18x + 91.11 \ (R^2 = 0.933)$$

$$y2 = -1.48x + 104.46 \ (R2 = 0.908)$$

Where y1 and y2 are the residual rate values RR1 and RR2 (%) and $x$ is

**Table 8**
Results for 21 × 21 cm particleboards bonded with MF resin and MUF with 10–30% of urea and citric acid as catalyst.

| Resin | Density (kg/m$^3$) | -Dry- IB strength (MPa) | −24 h Thickness Swelling (%) |
|---|---|---|---|
| MF | 680 ± 6 | 0.72 ± 0.07 | 16.2 ± 0.6 |
| MF10 | 697 ± 5 | 0.68 ± 0.09 | 21.2 ± 2.2 |
| MF20 | 696 ± 3 | 0.63 ± 0.05 | 29.4 ± 0.8 |
| MF30 | 668 ± 8 | 0.41 ± 0.06 | 39.0 ± 1.9 |
| EN 312 Requirement (type P2) | ≥0.35 | | ≤14% |

Values are presented as mean ± standard deviation (n = 6); IB=Internal Bond; Particleboard dimensions 21 × 21 cm.

the quantity of urea (%) added to MF resin.

The cure time influenced the water resistance properties of the resin. The shorter cure time led to lower hydrolysis resistance, mainly when urea was added to the MF resin.

This influence disappeared when 30% urea was used, demonstrating that, above the value of 20% addition, the urea will remain in the free state in the adhesive system, regardless of the reaction time used.

As the proportion of urea increases, the residual rate shows a decreasing trend, showing that the incorporation of more than 10% of free urea in the MF resin produced an important amount of easily hydrolysable components in the adhesive mixture.

### 3.4. Evaluation of particleboard properties

Particleboards were produced with adhesives prepared with the synthetized MF resin alone and with 10–30% of urea, catalyzed with citric acid.

Table 8 shows the results obtained for density and internal bond strength of dry boards. In addition, the thickness swelling values (%) after 24 h water immersion are shown for the particleboards produced based on the percentage of urea used.

For internal bond values, the best results were obtained when 0–10% or urea was used. It was found that the increase in the quantity of urea added to the MF resin decreased in all the cases studied the values of the internal bond strength (Table 8). But this IB decrease was not so important until the replacement of MF resin by free urea achieved 30%. This effect was expectable due to the resin *MR* (molar ratio) decrease (Table 2).

However, the influence of the quantity of urea in the resin had shown a great influence on resin water resistance properties, showing a linear relation between water swelling increase and free urea added to the MF resin. This relation can be described as $y = 0.77x + 14.96$ ($R^2 = 0.982$), where $y$ is the thickness swelling (%) and $x$ is the quantity of urea (%) added to MF resin.

Regarding the values of thickness swelling, it was also found a relationship between the FTIR-ATR essays and the particleboard water resistance properties. These parameters followed the linear relation:

$$y = 1.189x - 11.007\ (R^2 = 0.989)$$

where $y$ was the particleboard thickness swelling (%) and $x$ was the decreasing of intensity (%) of the 1320 cm$^{-1}$ band calculated as follow (Eq. 4):

$$X = (100\ \frac{I_r - I_w}{Ir}\ )$$

Where:

$I_r$: Normalized intensity of the dry cured resin before the water treatment

$I_w$: Normalized intensity of the dry cured resin after water treatment.

Independently of the quantity of urea added to the MF resin (0–30%), all the particleboards tested comply with the minimum IB of the European standard EN 312 for boards type P2 for indoor use in dry conditions (≥0.35 MPa).

The water resistance of a particleboard will depend on the resin water resistance (mainly to the hydrolysis) and on the particleboard hydrophobicity properties that avoid the water penetration (usually increased with the paraffin addition).

Finally, to analyse the influence of the added urea to MF resins, on particleboards surface characteristics, the wettability of particleboards produced with the resins: MF, MUF10, MFU20 and MFU30 was evaluated. Fig. 8 shows the water contact angles on particleboard samples made with MF and MFU resins.

Equilibrium water contact angles on particleboards surface, produced using MF and MFU10 resin are similar, but the hydrophobicity of the particleboards decreased when the MFU20 resin and, especially, when MFU30 resin were used as binders. This shows the influence of the added urea on the particleboard hydrophobicity. The higher reduction on surface hydrophobicity of particleboards produced with the MFU30 resin showed that, as observed in FTIR-ATR spectra, a considerable amount of free urea continues in the resin and its hygroscopicity

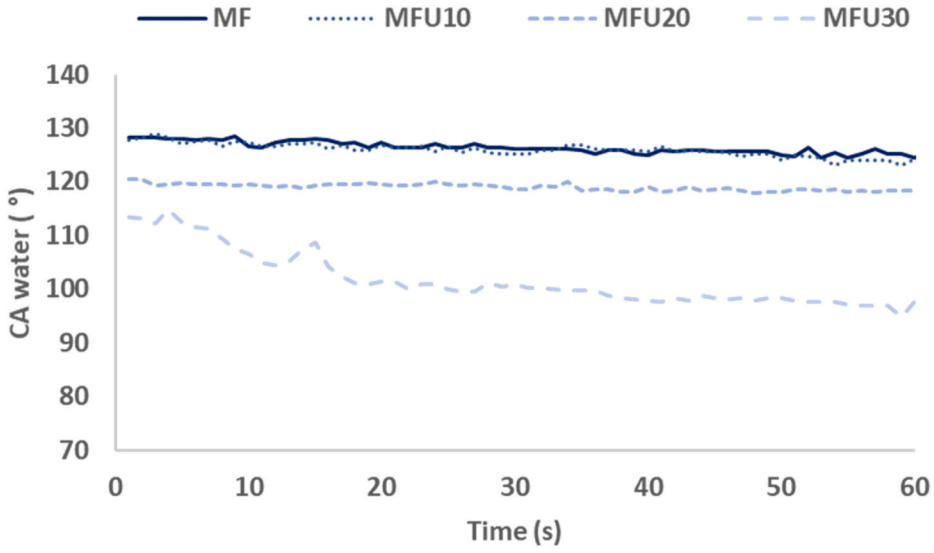


**Fig. 8.** Evolution of contact angles of water on the surface of MF and MFU particleboards.

modifies the particleboards' surface wettability.

## 4. Conclusions

This study shows the important influence of the added urea on the reactivity and hydrolysis resistance of MFU resins obtained by mixing with MF resins.

The incorporation of free urea in the MF resin has the advantage of reducing the formaldehyde molar ratio, allowing to obtain MFU resins with a very low molar ratio and a low percentage of free formaldehyde. Furthermore, increasing the percentage of urea added to the MF resin will decrease the amount of melamine used in the formulation, improving the economic viability of the product.

FTIR-ATR spectroscopy, adhesive bond evaluation system (ABES) and gravimetric techniques proved to be very useful tools to evaluate the water resistance of a new adhesive formulation and to predict the water behaviour of the particleboard produced with these adhesives.

By ABES and FTIR-ATR, it was demonstrated that it is possible to replace 20% of a synthesized MF resin with free urea, achieving a similar degree of crosslinking and dry adhesive performance.

To our knowledge, the viability of using citric acid, mixed with urea, as a catalyst agent and copolymer in MF and MFU resins was demonstrated for the first time.

A linear relationship was obtained between the amount of added urea and the water resistance properties of the MFU resin, as well as with the properties of particleboards produced with these resins.

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