Partial replacement of melamine by benzoguanamine in MUF resins towards improved flexibility of agglomerated cork panels

Ana Antunes[a], Margarida Duarte[b], Nádia Paiva[a], João Ferra[a], Jorge Martins[b,c], Luísa Carvalho[b,c], Ana Barros-Timmons[d], Fernão D. Magalhães[b,*]

[a] EuroResinas – Indústrias Químicas, S.A., 7520-195 Sines, Portugal
[b] LEPABE – Faculdade de Engenharia, Universidade do Porto, rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[c] DEMAD – Department of Wood Engineering, Polytechnic Institute of Viseu, Campus Politécnico de Repeses, 3504-510 Viseu, Portugal
[d] CICECO – Aveiro Institute of Materials and Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

ABSTRACT

Melamine-urea-formaldehyde (MUF) resins are highly effective adhesives for lignocellulosic materials. However, their high stiffness hinders applications where flexibility is desired. In this work, MUF resins were modified with benzoguanamine by partially replacing melamine in two different steps of the synthesis. The purpose was to obtain a less densely crosslinked, and hence more flexible, structure after cure. All modified MUF resins were characterized using gel permeation chromatography (GPC). Results suggest that benzoguanamine and its derivatives were integrated into the polymer structure. FTIR and ^{13}C-NMR analysis confirmed the presence of benzoguanamine in the modified resins. The addition of benzoguanamine to the MUF resin synthesis significantly improved the flexibility of agglomerated cork panels bound with modified resins. The minimum mandrel diameter on which the panels could be bent by 180° without failure decreased from 18 mm to 12 mm diameter, while the remaining key properties of the panels were maintained (tensile strength and boiling water resistance). The formaldehyde content of the panels (determined according to EN120) corresponds to E1 class.

1. Introduction

Melamine-urea-formaldehyde (MUF) resins are thermosetting polymers characterized by high stiffness, absence of color, high gloss, high water resistance, very good adhesive performance, and very low cost when compared to other adhesives for paper, wood and cork [1–3]. MUF resins have lower cost than melamine-formaldehyde (MF) resins, while still having better hydrolysis resistance than urea-formaldehyde (UF) resins [1,2].

The stiffness and brittleness of MUF resins, however, may be a limiting factor when they are used as binders for products where flexibility is desired. Such an example is agglomerated cork panels. These are produced using granulate wastes from the natural cork industry and have applications in a wide variety of areas (construction, decoration, fashion, transportation). The cork granules are mixed with a binder and fed into a mold with parallelepiped or cylindrical shape, which is then closed and heated for curing [3,4]. The cured product is then laminated into panels with varying thickness, and then stocked. Polyurethane binders, which are highly flexible, allowing the panels to be easily stocked as rolls – the optimal form for storage and transportation. On the other hand, if the panels are bonded with MUF resins, they are prone to fracture upon bending, due to the high stiffness of the cured binder. However, since MUF resins are highly competitive in relation to polyurethanes in terms of cost, it is a pertinent challenge to find an approach to chemically modify these resins, allowing production of sufficiently flexible agglomerated cork panels.

Some general information can be found in the literature suggesting that benzoguanamines can be used as a partial substitute of melamine in order to improve some characteristics of MUF resins [5–8]. The only work containing detailed information was authored by Henriques et al. [7], describing significant improvement of storage stability of a melamine-formaldehyde resin modified with benzoguanamine. The new resin was used to impregnate decorative paper, and the properties of the high pressure laminate produced with it were equivalent to those obtained with the standard resin. Chang [9] patented the use of benzoguanamine in polyester crosslinking in order to obtain flexible coatings. Benzoguanamine has a similar chemical structure to melamine, but has lower functionality and is less reactive because one NH_2 group is replaced with a benzene ring. By incorporating benzoguanamine in the polymer structure, the obtained resin should present lower crosslink

* Corresponding author.
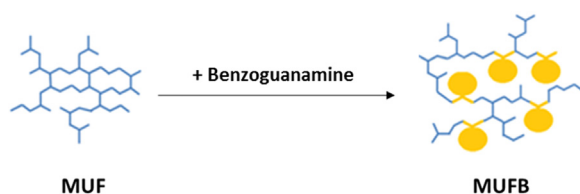 *E-mail address:* fdmagalh@fe.up.pt (F.D. Magalhães).

Fig. 1. Schematic representation of the densely crosslinked MUF resin (left) and the MUF resin containing benzoguanamine (right).

density, resulting in a modified resin with higher flexibility (Fig. 1) than standard MUF. Replacing melamine with another guanamine raises the price of the adhesive. However, the product is still viable when compared to much higher priced polyurethanes.

The purpose of this work is to study the most effective approach for introducing benzoguanamine in a standard formulation of melamine-urea-formaldehyde resin, and to evaluate the properties of the resulting adhesive. Agglomerated cork panels are used as an application example, since the flexibility of the final product is not adequate when standard MUF resins are employed.

2. Materials and methods

2.1. Materials

For melamine-urea-formaldehyde resins preparation, industrial-grade raw materials were provided by EuroResinas – Indústrias Químicas S. A. (Sines, Portugal): melamine (M), urea (U), formaldehyde (F) 53% solution, sodium hydroxide (NaOH) 50% solution and ammonium sulphate ($(NH_4)_2SO_4$) 30% solution. Benzoguanamine was purchased from Sigma-Aldrich, USA. Cork oak (Quercus suber) bark granules with 0.5–1.0 mm diameter were provided by Amorim Cork Composites, S.A. (Santa Maria da Feira, Portugal).

2.2. Synthesis of MUF and MUFB resins

The MUF resins were prepared in a three-necked 2500 ml glass flask under atmospheric pressure adapting the alkaline process [10]. Formaldehyde 53% solution at 50–60 °C was charged into the reactor and the pH value was adjusted to 7.5–9.0 using sodium hydroxide solution. Urea and melamine were slowly added, allowing the heat to raise the temperature from initial temperature up to values between 80 and 90 °C. For the condensation step, a second load of urea and melamine was added and the reaction was carried out until a desired viscosity between 500 and 700 mPa s was obtained. This reaction was stopped by cooling the subsequent mixture to a temperature of 60 °C. Finally, a given amount of urea was added in order to decrease the F/(NH$_2$)$_2$ M ratio to a value between 1.05 and 1.15. The reaction was ended by cooling the mixture to a temperature of 25 °C and pH was adjusted to 8.5–10.0.

The major differences between all produced resins were the amount of benzoguanamine added to the reaction mixture and the reaction step where this was done. A fraction of equivalent moles of the first and/or second melamine load were replaced by benzoguanamine. Table 1 describes the synthesized melamine-urea-formaldehyde-benzoguanamine (MUFB) resins. Samples were named according to the fraction of melamine replaced in the synthesis step, and ordered in Table 1 according to the total amount of benzoguanamine introduced.

2.3. Characterization of MUFB resins

The solid content (%) was determined by evaporation of volatiles in two grams of resin for three hours at a temperature of 120 °C in an oven. The solid content was determined by the mass ratio of the sample before and after drying.

Table 1
Composition of the synthesized MUFB resins.

Resin	Replaced fraction and addition step
R_1/4_0	1/4 of first melamine + 0 of second melamine
R_2/4_0	2/4 of first melamine + 0 of second melamine
R_0_1/3	0 of first melamine + 1/3 of second melamine
R_3/4_0	3/4 of first melamine + 0 of second melamine
R_1/4_1/3	1/4 of first melamine + 1/3 of second melamine
R_4/4_0	4/4 of first melamine + 0 of second melamine
R_2/4_1/3	2/4 of first melamine + 1/3 of second melamine
R_0_2/3	0 of first melamine + 2/3 of second melamine
R_3/4_1/3	3/4 of first melamine + 1/3 of second melamine
R_1/4_2/3	1/4 of first melamine + 2/3 of second melamine
R_2/4_2/3	2/4 of first melamine + 2/3 of second melamine
R_3/4_2/3	3/4 of first melamine + 2/3 of second melamine
R_0_3/3	0 of first melamine + 3/3 of second melamine

Viscosity of MUF and MUFB resins were measured with a Brookfield viscometer at 25 ± 1 °C and expressed in mPa s.

The resin pH was measured using a combined glass electrode.

The density (kg/m^3) of the resins was measured using a hydrometer.

Gel time is the time needed for resin gelation under hot and catalysed environments. This time was measured in a laboratory test tube immersed in boiling water with resin prepared in a 3 wt% of ammonium sulphate 30% solution.

Storage stability was evaluated by comparing the pH and viscosity of MUFB at 25 °C until the resin viscosity was equal or superior to 500 mPa s. Viscosity and pH were measured as described above.

2.4. Determination of free formaldehyde of MUFB resins

Determination of free formaldehyde in amino groups was done according to European standard EN 1243. This test takes into account the reaction of the free formaldehyde with sodium sulfite, in the presence of a measured excess of acid, in accordance with the reaction (Eq. (1)):

$$CH_2O + Na_2SO_3 + H_2O \rightarrow CH_2(OH)SO_3Na + NaOH \qquad (1)$$

and alkaline titration of the unreacted excess acid. The acid-sulfite mixture provides an essentially neutral buffered system, which prevents hydrolysis of condensed formaldehyde. A reaction temperature close to 0 °C helps to ensure the absence of side reactions. The free formaldehyde content is calculated using (Eq. (2)):

$$Free\ formaldehyde(\%) = \frac{(V_2 - V_1) \times M \times 3.002}{m} \qquad (2)$$

where V_1, is the volume (ml) of 0.1 M sodium hydroxide solution used for the adhesive test; V_2 is the volume (ml) of 0.1 M sodium hydroxide solution used for the blank test; M is the molarity of sodium hydroxide solution; m is the mass (g) of the adhesive test portion.

2.5. Gel permeation chromatography/size exclusion chromatography analysis of MUFB resins

GPC/SEC equipped with a Knauer RI detector 2300 and a Knauer injector with a 20 μl volume was used. The columns used were PSS PolarSil with a pore size of 30 Å and a particle size of 100 μm, conditioned at 60 °C using an external oven. The flow rate was 1 ml/min and dimethylformamide (DMF) was used as the mobile phase. Samples for analysis were prepared by dissolving a small amount of resin (100 mg) in DMSO (dimethylsulfoxide), followed by vigorous stirring for 1 min. Subsequently, the sample was left to rest (10 min), filtered through a 0.45 μm nylon filter and then injected. The universal calibration was done using poly(styrene) standards from PSS, with molecular weight between 162 and 66,000 g/mol.

2.6. Fourier transform infrared spectroscopy of MUFB resins

FTIR studies were performed in a Bruker Vertex 70 spectrophotometer. The samples were scanned using a Platinum-ATR single reflection diamond ATR module. Spectra were recorded at wavenumbers of 4000–500 cm^{-1} by signal averaging of 64 scans at a resolution of 4 cm^{-1}. The evaporation technique was used to prepare the films of resin samples. Approximately 50 g of resin was poured into a PTFE-coated mold and then cured in an oven at 120 °C.

2.7. ^{13}C-NMR analysis of MUFB resins

About 40 mg of liquid sample was directly mixed with 0.75 ml DMSO-d6 and the mixture was placed in an NMR tube. The high concentration of the samples allowed very good signal/noise ratios. The spectra were obtained on a Bruker Avance III 400 NMR spectrometer using a repetition delay of 10 s. The quantitative analysis was performed through a decoupling process of proton–carbon interactions without introducing the Nuclear Overhauser Effect (NOE) on the peak intensities. A 5 s pulse interval was sufficient to allow the relaxation of all carbons and to obtain reliable spectra, as seen from the measurement of the spin-lattice relaxation time T1. The quantitative spectra were obtained at 400 MHz with 3200 scans and took about 10 h to accumulate. Chemical shifts in DMSO-d6 solution were calculated by defining a ^{13}C chemical shift of DMSO-d6 at 39.5 ppm. All results were discussed after being normalized by carbonyl's urea signal.

2.8. Thermal gravimetric analysis of MUFB resins

Thermogravimetric analysis (TGA) was performed in a simultaneous thermal analyser STA 449 F3 Jupiter (NETZSCH). About 10 to 15 mg of a sample of cured resin was placed in an alumina crucible for each scan. The heating rate was 10 °C/min, under nitrogen flow (30 ml/min) from room temperature to 500 °C.

2.9. Dynamic mechanical analysis of MUFB resins

Dynamic mechanical measurements of resins were performed using a DMA model Tritec 2000 (Triton Technology) in material pocket support mode, in the temperature range from − 100 to 200 °C. The heating rate was 2 °C/min and a gaseous nitrogen stream was used to keep a controlled atmosphere inside of the sample container. The frequencies used were 1, 5 and 10 Hz with a maximum dynamic force of 2 N and maximum strain amplitude of 10 μm. Glass transition temperatures were identified as corresponding to the peak on the damping coefficient (tan δ) curve. The material pocket support mode, with the samples in powder form, was used because films of uniform thickness and without air bubbles could not be obtained for use in tension or bending test modes.

2.10. Production of cork agglomerates

Resins were added to granulated cork and the mixture was prepared by manual stirring during 5 min at room temperature. The addition of solid resin was 6% based on dry cork mass. The catalyst level was 3 wt% of ammonium sulphate 30% solution.

After blending, the agglomerated cork panel was hand formed in a deformable aluminium mold (2 × 450 × 250 mm^3). The cork amount was determined in order to obtain boards with target densities of 600 kg/m^3. Panels were pressed in a laboratory batch hot-press at 150 °C and 12 bar during 1.5 min. Three panels were produced for each resin tested.

2.11. Physical-mechanical characterization of cork agglomerates

2.11.1. Tensile strength of panels

After production, boards were hermetically conditioned until performance evaluation at (23 ± 2) °C and a relative humidity of (50 ± 5) % for 48 h. Stress-strain tests were based on ISO 7322:2000 (E), which describes cork composites test methods. Three samples with dimensions 100 × 15 × 2 mm^3 were tested for each production condition in a Mecmesin MultiTest-1-d testing machine equipped with a Mecmesin BFG 1000 dynamometer, at a crosshead speed of 300 mm/min under room temperature, as specified in the standard. At least three replicates were made for each measurement.

2.11.2. Resistance to boiling water of panels

The resistance to boiling water was done according to ISO 7322:2000(E). Three samples with dimensions of 50 × 50 × 2 mm^3 were tested for each resin. The specimens were placed in boiling water for 3 h. After the test, the samples were visually examined and classified as disaggregated or not.

2.11.3. Flexibility of panels

The flexibility of agglomerated cork panels was measured according to ASTM F147-87. The method consists in bending the material 180° around a mandrel. The mandrels have diameters ranging from 3 to 48 mm, corresponding to designations F1 to F16. The flexibility of the specimen corresponds to the minimum mandrel diameter about which the specimen could be flexed without exhibiting any signs of failure. A flexibility designation of F1 would therefore correspond to maximum flexibility in this test (specimen does not fracture when bent around a 3 mm diameter mandrel).

2.12. Formaldehyde emission content of panels - perforator method (EN120)

Formaldehyde content of agglomerated cork panels was determined according to perforator method (EN 120). Perforator method measures the formaldehyde emissions content of the specimen potentially emitted under forceful conditions. Formaldehyde was extracted from 110 g of test pieces by means of boiling toluene and then transferred into distilled or demineralized water. The formaldehyde content of this aqueous solution was determined photometrically by the acetyl acetone method.

3. Results and discussion

The reaction schemes involving urea, melamine, benzoguanamine and formaldehyde are schematized in Figs. 2 and 3.

3.1. General properties

Thirteen resins were synthesized using the same process, but varying the fraction of melamine replaced by benzoguanamine, and the moment of addition during the synthesis. The nomenclature used to describe the formulations was described in Table 1. Table 2 presents the final properties of the MUFB resins and of the reference MUF resin.

The synthesis of resins R_4/4_0 and R_0_3/3, involving total substitution of melamine by benzoguanamine in each reaction phase, were not terminated. These resins gelled inside the reactor after the introduction of the final urea load, *i.e.* there was a very large increase in the viscosity of the reaction medium. The excessive amount of benzoguanamine used may have resulted in a water-intolerant product [11].

Concerning the final pH, viscosity, solid content and density, the results were very similar for all resins. Incorporation of benzoguanamine increased the storage stability, with the exception of resins R_3/4_1/3, R_1/4_2/3 and R_3/4_2/3, which were less stable than the reference MUF resin. All MUFB resins presented a longer gelling time than
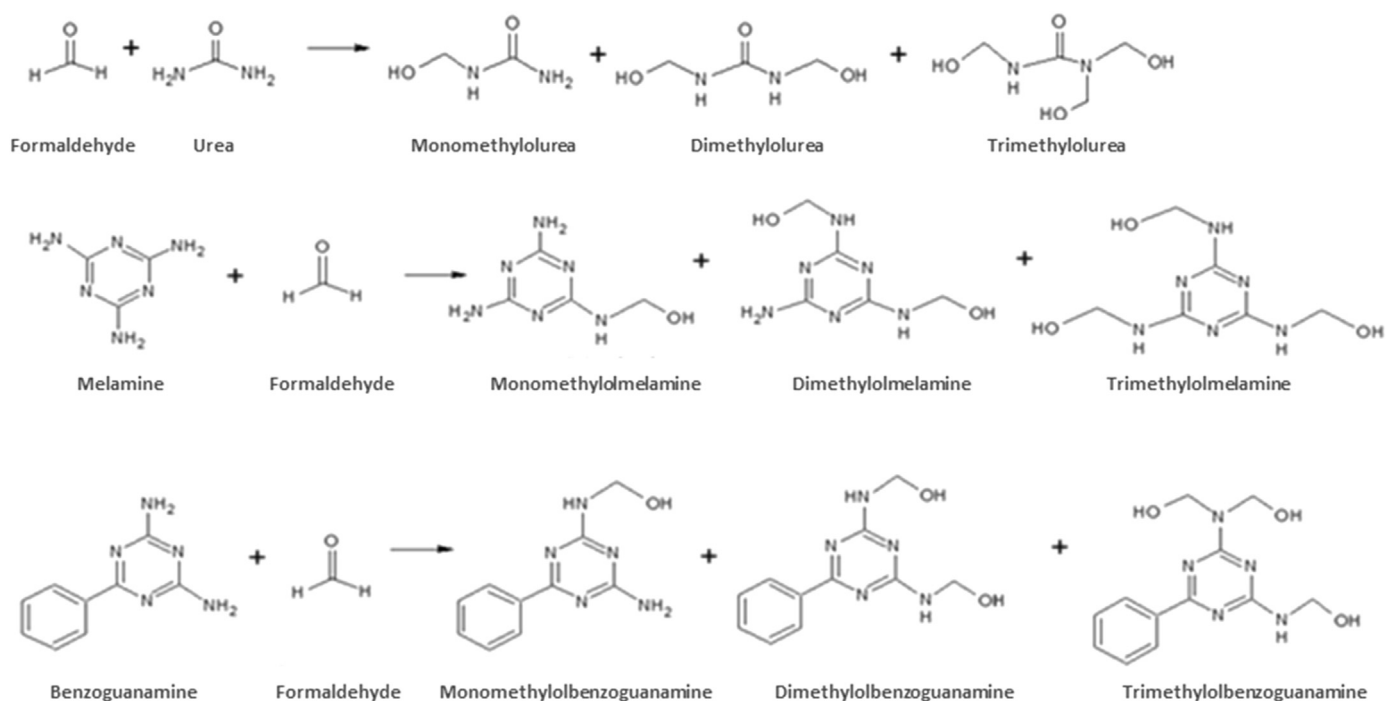
Fig. 2. Methyolation reaction of urea, melamine and benzoguanamine with formaldehyde, forming methylolureas, methylolmelamines and methylolbenzoguanamines, respectively.

MUF. Gel time could not be determined for resins R_3/4_1/3 and R_3/4_2/3 because polymer precipitation occurred after the addition of the aqueous catalyst solution. This was due to the decrease in the water tolerance of resins containing the highest amount of first melamine replaced by benzoguanamine and combined with 1/3 and 2/3 of second melamine [11].

Free formaldehyde content was equivalent or lower than the values observed in the standard resin. This is a surprising result, considering that benzoguanamine was added replacing equivalent moles of NH_2 of melamine, therefore it would be expected that the free formaldehyde content of MUFB would be identical to that of the MUF resin, or actually higher, in case benzoguanamine did not react with it. The lower values obtained may be associated to measurement errors, inherent to the analysis method that is based on visual identification of equivalence point.

3.2. Gel permeation chromatography/size exclusion chromatography analysis

Gel Permeation Chromatography (GPC) has been commonly used for qualitative comparison of MUF resin formulations [10,12]. Fig. 4 shows the GPC chromatograms obtained for MUFB resins synthesized in this study, as well as for the standard MUF resin and benzoguanamine.

All synthesized resins, including the standard MUF resin, exhibit a common peak in the retention volume range of 12.5 to 13.0 ml. This range corresponds to low molecular weight compounds and can be assigned to unreacted urea, methylolureas, methylolmelamines and oligomers [10,12]. The retention volume range between 11.7 and 12.5 ml corresponds to the benzoguanamine peak. Resins with benzoguanamine incorporation present one notorious peak to the left of this peak, between 11.5 and 12.5 ml, which is not visible in the MUF resin. This corresponds to methylolbenzoguanamine derivatives with higher molecular weight than the original monomer. When benzoguanamine was added replacing the second melamine (resins R_0_1/3 and R_0_2/3), the peak of the retention volume between 11.5 and 12.5 ml was more intense compared to the resin with benzoguanamine added only in the initial step. Although resin R_3/4_0 had a higher amount of

benzoguanamine relative to resin R_0_1/3, the peak was less intense in the retention volume between 11.5 and 12.5 ml. This suggests that the reaction of benzoguanamine and its derivatives occurs to a greater extent when the compound was introduced replacing the first melamine.

All resins presented in Fig. 4B show a pronounced peak of benzoguanamine derivatives, since in all of them benzoguanamine was added replacing the second melamine.

3.3. Fourier transform infrared spectroscopy

According to the literature [7,13,14] characteristic absorptions bands of MUF resin are observed at 3400–3300 cm^{-1} (NH stretching of primary aliphatic amines and stretching of OH mode of C-OH group), 2970–2950 cm^{-1} (C-H stretching vibration in C-H of methylol group), 1650–1630 cm^{-1} (C=O stretching of urea), 1560–1530 cm^{-1} (C=N stretching of secondary amines in triazine ring), 1500–1380 cm^{-1} (C-H stretching vibration in CH_2 and CH_3), 1380–1330 cm^{-1} (C-N stretching of CH_2-N), 1250–1200 cm^{-1} (stretching of C-N), 1130–1120 cm^{-1} (C-O stretching of aliphatic ether), 1050–1030 cm^{-1} (C-N or NCN stretching of methylene linkages (NCH_2N), 1022–1005 cm^{-1} (C-O stretching aliphatic ether), 890–860 cm^{-1} (C-H deformation out of plane), 814–812 cm^{-1} and 781–771 cm^{-1} (triazine ring stretching) and 750–700 cm^{-1} (N-H bending of secondary aliphatic amines (R_1–CH–NH–CH_2–R_2)).

The two resins with the highest amount of benzoguanamine added in each step (R_3/4_0 – benzoguanamine partially replacing 1st melamine, and R_0_2/3 – benzoguanamine partially replacing 2nd melamine) were analyzed by FTIR. The spectra obtained are shown in Fig. 5, together with the spectrum for the MUF resin.

As expected, since the reagents used and the bonds formed are of the same type, the two MUFB resins show spectra very similar to MUF. However, one band can be seen at 702 cm^{-1} only in MUFB resins, corresponding to out-of-plane deformation of C-H of monosubstitued benzene [7]. This indicates the presence of benzoguanamine in these resins.
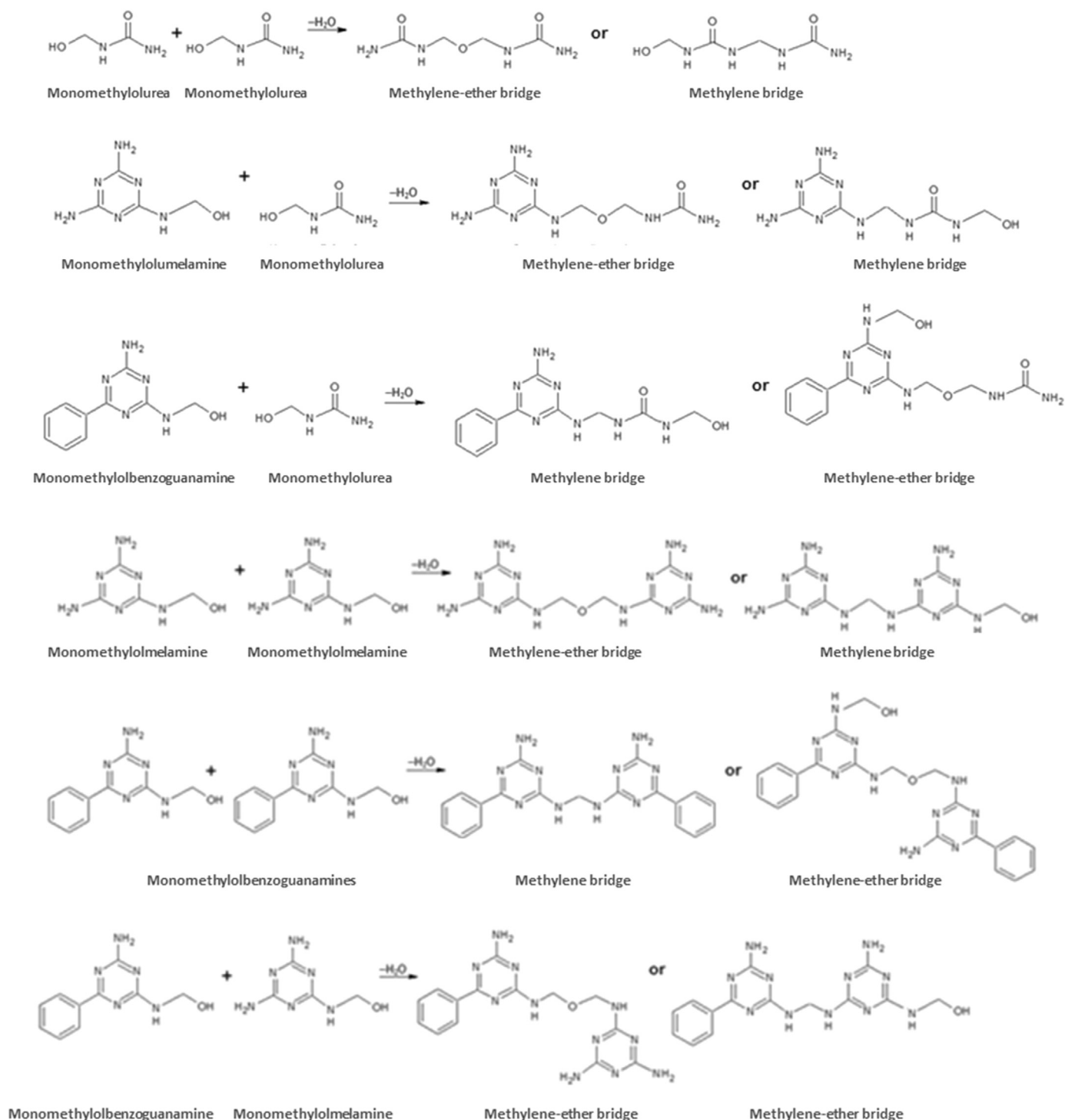
Fig. 3. Condensation reaction of methylolureas, methylolmelamines and methylolbenzoguanamines forming methylene and methylene-ether bridges.

3.4. ^{13}C-NMR analysis

^{13}C-NMR was applied to standard MUF resin and MUFB R_3/4_0 and R_0_2/3. Each signal observed in the spectra was identified according to chemical shifts reported in the literature [7,15–19]. The ^{13}C-NMR spectra and the structural assignments of chemical shifts of standard MUF and MUFB resins are shown in Fig. 6.

The spectra of analyzed resins can be split into five main areas. The following signal attributions can be made: signals from 160.0 to 170.0 ppm correspond to substituted and unsubstituted benzoguanamine's and melamine's triazines and urea carbonyl groups, from 138.0

to 128.0 ppm to carbons in the benzene ring of benzoguanamine, from 67.0 to 70.0 ppm to methylene-ether linkages, from 64.2 to 63.5 ppm to methylol groups, and from 48.8 to 45.5 ppm to carbons on the methylene group.

It should be noted that the three resins have the same functional groups, so the chemical shifts shown are quite similar. The exception is the standard MUF resin, which does not show the signal between 128 and 138 ppm, corresponding to chemical displacement of the benzene ring carbons.

^{13}C-NMR does not show the presence of free formaldehyde, polyoxymethylene oligomers or trioxane isomers (80 to 90 ppm),

Table 2
Properties of the synthesized MUFB resins.

Resin	pH	Viscosity (mPa s)	Gel time (s)	Solid content (%)	Density (kg/m³)	Storage stability (days)	Free formaldehyde (%)
MUF	8.7	235	61	64.4	1.29	19	0.12 ± 0.01
R_1/4_0	9.4	180	80	63.0	1.28	37	0.11 ± 0.01
R_2/4_0	9.9	185	97	63.9	1.28	36	0.07 ± 0.00
R_0_1/3	8.5	185	80	64.3	1.28	29	0.11 ± 0.01
R_3/4_0	8.6	165	70	65.0	1.25	31	0.07 ± 0.01
R_1/4_1/3	9.0	175	81	63.5	1.27	36	0.09 ± 0.01
R_4/4_0	[a]						
R_2/4_1/3	10.4	170	87	64.5	1.27	45	0.07 ± 0.02
R_0_2/3	9.2	245	73	64.7	1.27	25	0.09 ± 0.01
R_3/4_1/3	10.0	180	[b]	63.6	1.27	11	0.06 ± 0.00
R_1/4_2/3	9.3	255	75	65.0	1.26	15	0.08 ± 0.01
R_2/4_2/3	9.4	190	68	64.9	1.26	23	0.08 ± 0.01
R_3/4_2/3	8.6	245	[b]	65.2	1.26	8	0.04 ± 0.01
R_0_3/3	[a]						

[a] Resin gelled inside the reactor during synthesis.
[b] The test could not be performed.

corroborating the previous discussion that indicated low free formaldehyde content. When comparing to R_3/4_0, resin R_0_2/3 shows higher amount of carbons from benzene ring, and from the triazine ring bonded to the benzene ring. This is in agreement with the fact that R_0_2/3 has a greater amount of benzoguanamine, and possibly also of methylolbenzoguanamine derivatives, as verified in the GPC/SEC analysis.

3.5. Thermogravimetric analysis

The thermal stability of cured resins is shown in Fig. 7. Three degradation steps can be observed in all the analyzed resins. In stage I, between 30 and 230 °C, weight loss is mainly caused by the escape of volatile gases like moisture and free formaldehyde. In stage II, between 230 and 380 °C, weight loss is due to breakage of methylene ether bridges into more stable methylene bridges, consequently releasing formaldehyde. In stage III, between 380 and 500 °C, scission of methylene bonds takes place, originating from lower molecular weight species [15,20,21].

Both MUFB resins present a higher final weight loss than MUF. One justification, coherent with GPC results, is the presence of benzoguanamine derivatives in resin R_3/4_0 and resin R_0_2/3. These low molecular weight species are more easily decomposed. It is noteworthy that resin R_0_2/3 corresponds to the higher weight loss and has the higher content of benzoguanamine derivatives in GPC analysis.

3.6. Dynamic mechanical analysis

The loss factor (tan δ) of cured R_3/4_0, R_0_2/3 and MUF resins, in powder form, was measured by DMA as a function of temperature, as seen in Fig. 8.

In the thermogram of standard MUF resin it is possible to observe one peak in tan δ approximately centered at 140 °C. This probably corresponds to the glass transition (Tg) of cured MUF, according to the works of Arab and Shokuhfar [22], who identified the Tg of cured urea-formaldehyde resin between 150 and 170 °C, and of Hanstrand and Klason [23], who identified the Tg of cured melamine-formaldehyde resin between 130 and 180 °C. It is interesting to note that resin R_3/4_0 shows lower Tg (tan δ peak centered at around 100 °C) than MUF and R_0_2/3. This decrease in the glass transition temperature may be a consequence of a less crosslinked, more mobile, polymer structure, obtained when benzoguanamine replaces the first melamine load. A second peak is visible in resin R_3/4_0, centered at 170 °C, which can be attributed to a particular transition in the molecular structure of the MUFB resin, but we cannot identify its origin. Resin R_0_2/3 does not show this peak because benzoguanamine was introduced in the condensation step and the reaction does not occur to the same extent as shown in GPC. Also, resin R_0_2/3 does not show a decrease in glass transition but similar values to standard MUF instead.

Both resins containing benzoguanamine show a small peak between 0 and 50 °C, which probably is a β transition associated with rotation of
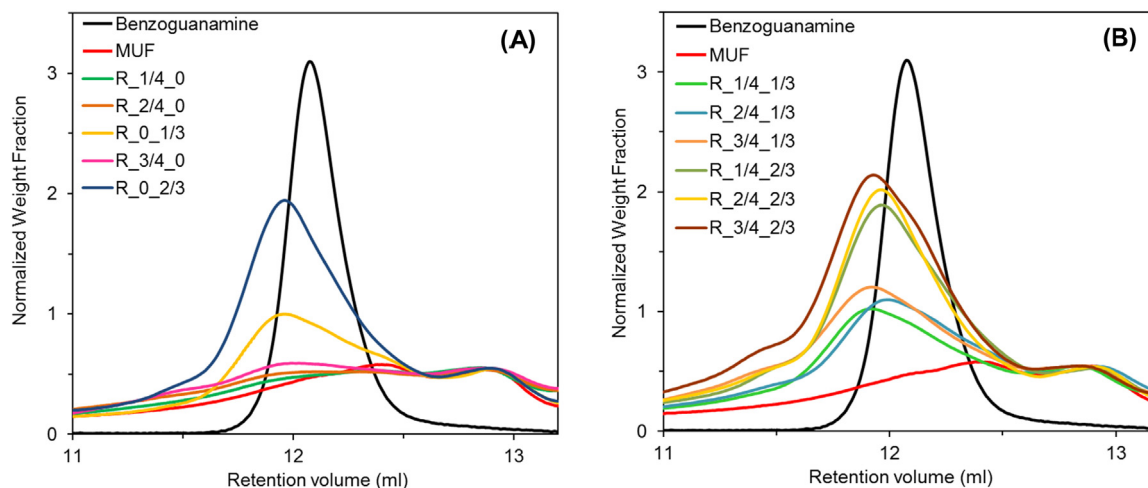

Fig. 4. Chromatograms of MUFB resins where benzoguanamine was added replacing 1st or 2nd melamine (A) and MUFB resins where benzoguanamine was added replacing 1st and 2nd melamine simultaneous (B).
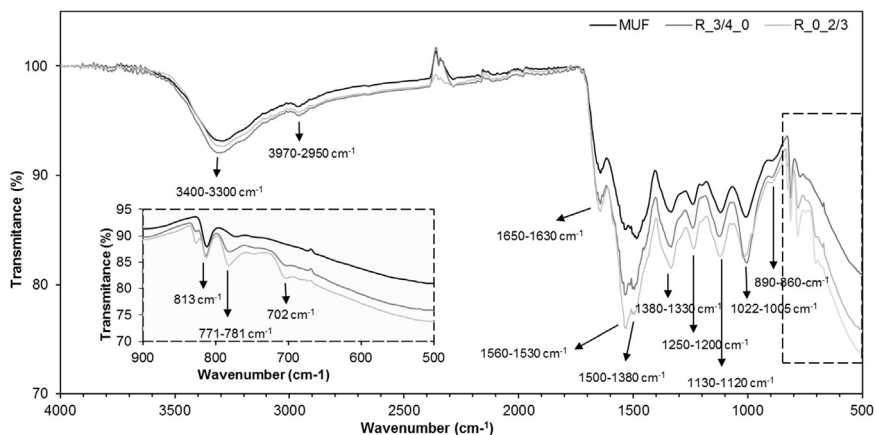
Fig. 5. IR spectrum of MUF and MUFB resins.

the phenyl group in benzoguanamine [24].

3.7. Physical-mechanical characterization of agglomerated cork panels

Cork panels were produced with all synthesized resins (except resin R_3/4_1/3 and R_3/4_2/3 because of water intolerance as mentioned above). Table 3 shows the mechanical properties obtained.

The tensile strength results show that the 0.2 MPa limit required by

APCOR specifications [25] for cork agglomerate panels is achieved for all panels. Addition of benzoguanamine does not therefore impair the adhesion strength of the resins. In addition, it must be noted that all specimens produced with MUFB resins passed the required boiling water resistance test, indicating good cohesion even under extreme moisture conditions.

The mandrel results presented in Table 3 demonstrate that the in-corporation of benzoguanamine in the formulation effectively increases
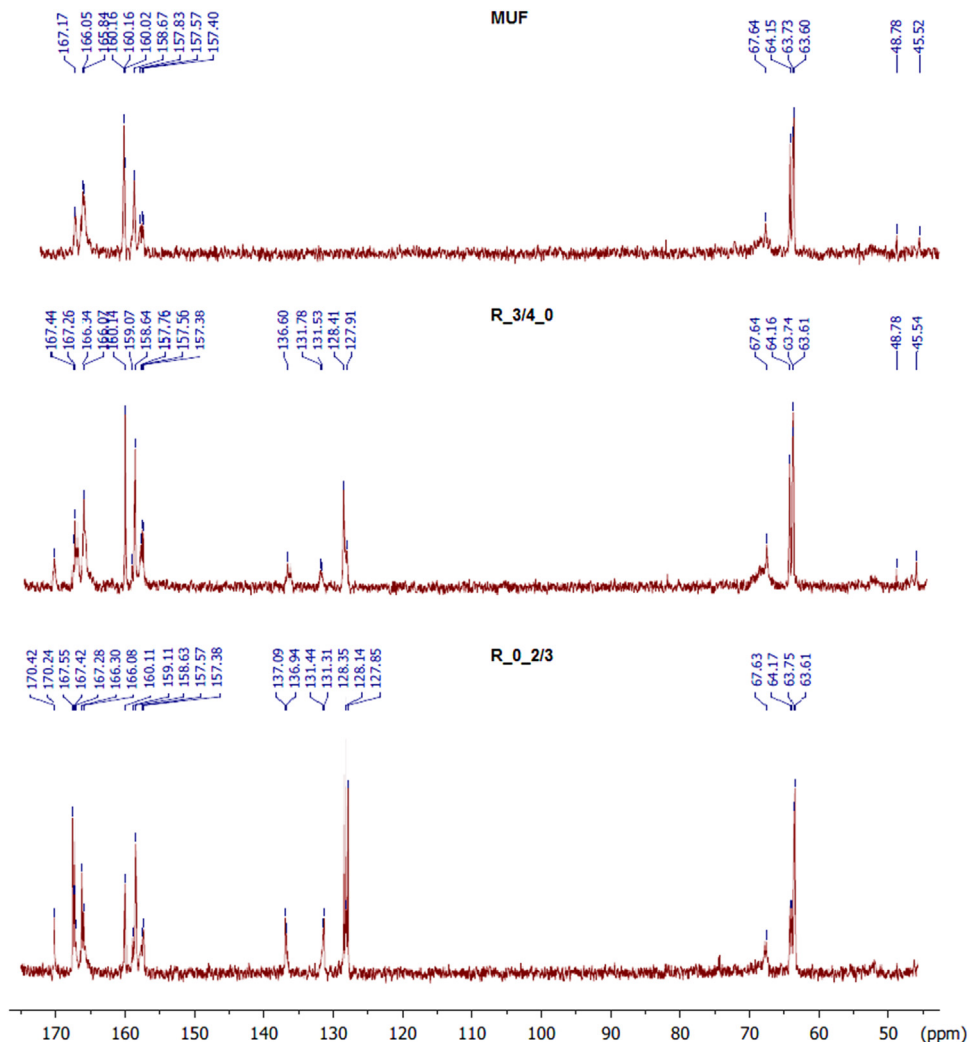
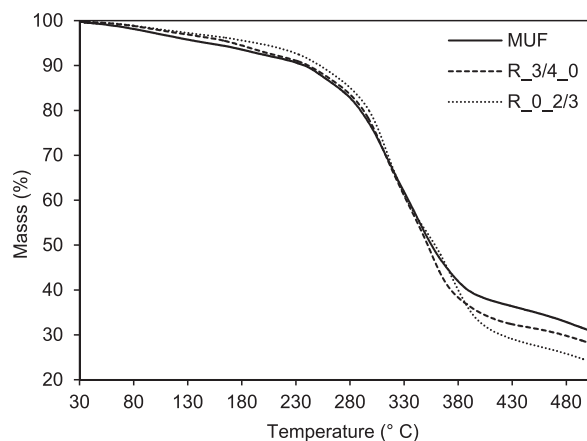**Fig. 6.** ^{13}C-NMR spectra obtained in the region between 200 and 40 ppm for MUF and MUFB resins.

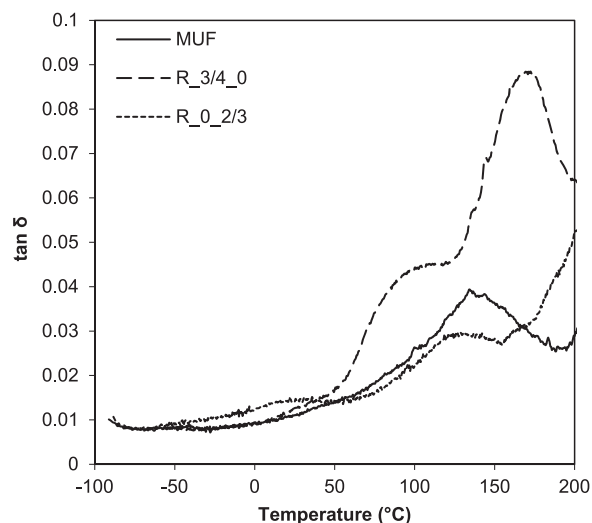**Fig. 7.** Thermogravimetric analysis results of MUF and MUFB resins.

Fig. 8. Loss factor, tan δ, as a function of temperature for MUF and MUFB resins (1 Hz).

Table 3
Mechanical properties of cork-based panels produced with MUF and MUFB resins: maximum tensile strength and higher mandrel value that caused rupture.

Resin	σ máx (MPa)	Flexibility (mandrel value)		
		Sample 1	Sample 2	Sample3
MUF	2.85 ± 0.17	F6	F7	F6
R_1/4_0	3.08 ± 0.20	F5	F4	F4
R_2/4_0	2.35 ± 0.14	F4	F5	F4
R_0_1/3	2.56 ± 0.25	F6	F5	F6
R_3/4_0	2.46 ± 0.15	F4	F4	F4
R_1/4_1/3	2.70 ± 0.23	F5	F4	F4
R_2/4_1/3	2.74 ± 0.23	F5	F5	F6
R_0_2/3	2.38 ± 0.36	F4	F4	F5
R_3/4_1/3	a	a	a	a
R_1/4_2/3	2.95 ± 0.23	F5	F4	F4
R_2/4_2/3	2.31 ± 0.23	F4	F4	F5
R_3/4_2/3	a	a	a	a

^a The test could not be performed.

the flexibility of the cork panels. The effect is more evident when benzoguanamine replaces the first melamine load (resin R_3/4_0), as the minimum mandrel value decreases from F7–F6 (21–18 mm diameter) to F4 (12 mm diameter) yielding the most consistently flexible

cork panel. The small amount of benzoguanamine replacing the first melamine became fully incorporated in the polymer structure, as verified in the GPC results. Furthermore, this modifies significantly the final polymer, as seen by DMA, improving the mobility of the cured resin structure. However, when benzoguanamine replaces the second melamine, the same effect is not observed as seen by GPC. Resin R_0_1/3 yielded the worst mandrel score (F6) of the modified resins.

Regarding formaldehyde content values, MUF and resin R_3/4_0 present 4.4 and 3.8 mg/100 g oven-dry panel, respectively. These results indicate low formaldehyde content, according to the standard for wood-based panels for construction (EN 13986). The panels can therefore be classified as E1 taking into account the limit value for formaldehyde content (≤ 8 mg/100 g oven-dry panel).

4. Conclusions

Melamine-urea-formaldehyde resins modified with benzoguanamine were successfully synthesized. Benzoguanamine was added at various amounts during the standard synthesis procedure, replacing the first and/or second melamine loads. GPC analysis suggested that the incorporation of benzoguanamine in the polymer structure was more effective when the monomer was added to replace the first melamine load. FTIR and ¹³C-NMR analysis confirmed the presence of benzoguanamine in MUFB resins. DMA analysis showed that the replacement of the first melamine load by benzoguanamine decreases the glass transition of the cured resin, therefore improving the chain mobility. The modified resins afforded agglomerated cork panels with appropriate mechanical properties, according to current standards. Panels produced using resin with 3/4 of first melamine replaced by benzoguanamine exhibited significantly better flexibility (minimum mandrel of F4) than the standard resin (F6). This work showed that benzoguanamine is a promising compound for the improvement of flexibility of MUF resins, making them appropriate for use as binders in materials where flexibility is a relevant property, like agglomerated cork panels.

References

[1] Pizzi A. Melamine–formaldehyde adhesives. In: Handbook adhesive technology. 2nd ed., Taylor & Francis Group, LLC; 2003, p. 653–80.
[2] Magnusson A. Synthesis of new MUF resins and analysis of the curing in the glue joint. KTH Royal Institute of Technology; 2015.
[3] Gil L. "Cork". In: Materials for construction and civil engineering. Springer; 2015, p. 585–628.
[4] Gil L. Cork composites: a review. Materials 2009;2:776–89.
[5] Crews GM, Chemicals M, States U. "Melamine and guanamines," Ullmann's encyclopedia of industrial chemistry. Wiley-VCH Verlag GmbH & Co. KGaA; 2005.
[6] Kanbara Y Tomoo T. Benzoguanamine compound having aminomethyl group or salt thereof, and method for manufacturing same. US9458116 B2; 2016.

[7] Henriques A, Paiva N, Bastos M, Martins J, Carvalho L, Magalhães FD. Improvement of storage stability and physicochemical properties by addition of benzoguanamine in melamine-formaldehyde resin synthesis. J Appl Polym Sci 2017;134(32):45185. [1–11].

[8] Poth U. Automotive coatings formulation: chemistry, physics und practices. Vincentz Network; 2008.

[9] Chang W-H. High solids polyester coating composition. US3994851 A; 1976.

[10] Paiva NT, Ferra JM, Pereira J, Martins J, Carvalho L, Magalhães FD. Production of water tolerant melamine-urea-formaldehyde resin by incorporation of sodium metabisulphite. Int J Adhes Adhes 2016;70:160–6.

[11] Ross AJ. Resinous blend of a benzoguanamine-formaldehyde resin and a melamine-formaldehyde resin. US3506738 A; 1970.

[12] 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. Int Wood Prod J 2012;3(1):51–7.

[13] Ambrose D, Abdala AA, Merline DJ, Vukusic S, Abdala AA. Melamine formaldehyde: curing studies and reaction mechanism. Polym J 2013;45(4):413–9.

[14] Cao J, Yan H, Shen S, Bai L, Liu H, Qiao F. Hydrophilic molecularly imprinted melamine–urea–formaldehyde monolithic resin prepared in water for selective recognition of plant growth regulators. Anal Chim Acta 2016;943:136–45.

[15] Siimer K, Christjanson P, Kaljuvee T, Pehk T, Lasn I, Saks I. TG-DTA study of malamine-urea-formaldehyde resins. J Therm Anal Calorim 2008;92(1):19–27.

[16] No BY, Kim MG. Syntheses and properties of low-level melamine-modified urea – melamine – formaldehyde resins. J Appl Polym Sci 2004;93(6):2559–69.

[17] Mercer AT, Pizzi A. A 13C NMR analysis method for MF and MUF resins strength and formaldehyde emission from wood particleboard. I. MUF resins. J Appl Polym Sci 1996;61(10):1687–95.

[18] Slonim YA, Alekseyeva SG, Arshava BM, Matvelashvili GS, Romanov NM, Potseluyeva NV, Bashta NI. An NMR study of the synthesis of benzoguanamine-formaldehyde resins. Polym Sci 1985;27(12):2843–51.

[19] Tohmura S. Influence of the melamine content in melamine-urea-formaldehyde resins on formaldehyde emission and cured resin structure; 2001, p. 451–7.

[20] Khorasani SN, Ataei S, Neisiany RE. Microencapsulation of a coconut oil-based alkyd resin into poly(melamine-urea-formaldehyde) as shell for self-healing purposes. Prog Org Coat 2017;111:99–106.

[21] Jovanović SS, Jovanovič V, Konstantinović S, Marković G, Marinović-Cincović M. Thermal behavior of modified urea–formaldehyde resins. J Therm Anal Calorim 2011;104(3):1159–66.

[22] Arab B, Shokuhfar A. Molecular dynamics simulation of cross-linked urea-formaldehyde polymers for self-healing nanocomposites: prediction of mechanical properties and glass transition temperature. J Mol Model 2013;19:5053–62.

[23] Resins M, Klason C, Ab P. Rheokinetical behavior of melamine-formaldehyde resins. Polym Eng Sci 1999;39(10):2019–29.

[24] Young RJ, Lovell PA. Transitions and polymer structure. In: Francis T, editor. Introduction to Polymers. 3rd ed.Boca Raton: CRC Press; 2011. p. 502–3.

[25] APCOR-Associação Portuguesa da Cortiça. [Online]. Available: ⟨http://www.apcor.pt/⟩. [Accessed 20 March 2016].