



Effect of the initial F/U molar ratio in urea-formaldehyde resins synthesis and its influence on the performance of medium density fiberboard bonded with them



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ARTICLE INFO

Keywords:

Urea-formaldehyde resin
Formaldehyde to urea mole ratio
Medium density fiberboard
Physico-mechanical properties

ABSTRACT

The formaldehyde to urea molar ratio (F/U) plays an important role on the properties of urea formaldehyde (UF) resins and of the medium density fiber board (MDFs) bonded with them. This work presents a hypothesis that besides the final F/U molar ratio in UF resin preparation, the initial F/U affects both the formaldehyde emission levels and the physico-mechanical properties of the boards. Three initial molar ratios F/U of 1.9, 2.1 and 2.3 in resin synthesis have been examined in this work. The structural changes and thermal curing behavior of UF resins were tracked by ¹³C NMR and DSC, respectively. At parity of final F/U molar ratio, the resin with initial F/U = 2.1 yielded the highest proportion of linear methylol groups, resulted in the best internal bond strength and lowest thickness swelling of the board. A resin synthesized with the initial F/U = 1.9 provided the highest proportion of total methylene linkages, most methylene ether linkage and lowest free formaldehyde, consistently yielding the lowest formaldehyde emission. These results partially explained why UF resins with lower F/U molar ratios showed relatively poor adhesion when used to manufacture wood-based composites. MDFs bonded with a UF resin having the initial F/U = 2.3 had a relatively good performance with the exception of free formaldehyde, but also showed the best storage stability compared to the other resins having lower initial F/U molar ratios.

1. Introduction

Formaldehyde (HCHO) is an extremely versatile building block used for the synthesis of complex compounds and materials in many chemical and industrial processes, especially in the wood panels (WBPs) industry. Urea-formaldehyde (UF) is a major amino plastic resins which is widely used in the modern wood-composite industry due to its good properties, namely fast curing, good internal bond (IB) strength, relatively low price, and a clear color [1].

The wood-composite industry relies strongly on the use of these synthetic resins as adhesives for the bonded products constituting the majority of the wood panels on the market today. Notwithstanding the considerable tonnage of UF resin resins produced yearly, the disadvantages of this resin should not be ignored, like its problematic formaldehyde emission and poor water resistance from the wood boards bonded with it. This results from the low stability of the amino-methylene bridges, as well as its lack of weather resistance, which precludes exterior uses [2–4]. In the past decades, to overcome these

problems, great efforts have focused on modifying the resin synthesis methods by investigating resin manufacturing parameters such as reaction pH, temperature [5–7], different F/U molar ratios [2,8–10] and the use of additives [11–14].

Conversely, resin manufacturing can be manipulated to produce quality urea-formaldehyde (UF) resins as well as better physico-mechanical performance such as the UF resin prepared by using formalin [15] and using different acids (e.g. Ammonium salts) during the synthesis of UF adhesives [16,17].

Studies have indeed provided many useful details about the structures of the polymers, however, they provided limited information about how these structures are formed and why they are different in relation to the different conditions used.

The main objective of the modern resin industry is to produce effective UF resins with very low, if not zero, formaldehyde emissions [18]. Many authors published studied about alternative latent catalysts systems for curing UF resins [19]. Besides, an effective reduction in formaldehyde emission with a remarkable improvement in the

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durability and stability of UF bonded wood panels could further develop the applications and markets for these products.

Many studies suggest that the formaldehyde to urea molar ratio affects the final characteristics of UF resins, such as resin reactivity, degree of condensation during resin synthesis, free formaldehyde content, branching and cross-linking in curing [1]. Previous studies have shown that the F/U molar ratio of the UF resin has a significant impact on the formaldehyde emission during pressing and after manufacturing of the board [20]. The molar ratio also influences the physico-mechanical properties of the boards such as internal bond (IB) strength, modulus of elasticity (MOE), module of rupture (MOR) [21] and thickness swelling (TS) [22].

^{13}C NMR analysis is a well-known technique to examine the changes in the proportions of the compounds formed at different temperatures and F/U molar ratios during resin synthesis [23]. Quantitative ^{13}C NMR analysis has been used to follow the typical three-step preparation of UF resin, aiming at determining the changes in the resin chemical structures [10].

Differential scanning calorimetry (DSC) is widely used to provide easy and fast cure kinetics evaluation for curing reactions of thermosetting resins [24]. A number of studies by DSC have been used to characterize the thermal curing behavior of liquid and solid UF adhesives and show that they are affected by different molar ratios [25,26].

Nevertheless, in spite of such studies on the final F/U molar ratio of UF adhesives, there is still limited information on the influence of the initial F/U molar ratio on the structure, properties of UF resins and of the medium density fiber board (MDFs) bonded with them. On the other hand, there is no extensive information on the thermal analysis (DSC) UF resins synthesized with different initial formaldehyde/urea ratio on the literature search. In this work, the effect of three types of UF resin, prepared by different initial F/U molar ratios, on the curing and chemical structure of the resin itself has been examined extensively. The final molar ratio F/U = 1.14 was selected for synthesizing all of the samples. Quantitative ^{13}C NMR and DSC tests were carried out for analyzing the chemical structure and the thermal curing behavior of the UF resins prepared, respectively. Medium density fiberboard panels were prepared with the sample resins and their physico-mechanical properties were evaluated. This issue has relevance to better understand the relationship between initial F/U molar ratio and the performance of the resin in wood-base panels.

2. Material and methods

2.1. Materials

Urea-formaldehyde condensate (UFC) containing 60% formaldehyde with urea percentage of 25% was supplied by Chassbsaz Company (Sari, Iran). The aqueous solutions of HCOOH and NaOH, used to adjust the pH level during the UF resin synthesis, were supplied by Arvand Petrochemical Company and Guangxi Liucheng Chuandong Fine Chemical Co., Ltd, respectively. Granular industrial urea was obtained by Kermanshah Petrochemical Industries Co. (KPIC), Iran. Industrial Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), purchased from Urmia Petrochemical Company, Iran, was used as curing agent of the resin in MDF production. The chemicals were used as received without further purification. Wood fibers were provided by Arian Sina, Sari, Iran as a fiberboard manufacturer.

2.2. UF resin preparation

The UF resin samples were synthesized according to the alkaline-acid-alkaline process. 1200 g of UFC (60% CH_2O , 24 mol) and (25 wt % urea, 5 mol) along with 450 g H_2O were placed in a 3-L three-neck flask equipped with a condenser, heating, mechanical stirring, cooling devices, and a thermometer. The pH of the solution was adjusted between

Table 1

The addition of urea at different stages during UF resin synthesis.

Resin	UF1	UF2	UF3
Initial F/U for U ₁ stage	1.9	2.1	2.3
U ₁ (g)	457.9	385.7	326.1
U ₂ (g)	505.4	577.6	637.2

8 and 9 using a 30 wt% NaOH solution. The temperature was then raised to 40 °C. Subsequently, the first urea (U1) was then charged to the reactor. After complete urea dissolution, the temperature was raised to 90 ± 1 °C and maintained for 30 min with a constant pH of 8.2. The pH was then adjusted to 4.7–5.1 with formic acid (HCOOH) and the acid-promoted reaction was carried on at 96 ± 1 °C to obtain the desired viscosity. The viscosity of the resulting mixture was measured by a Nr.3 Ford cup (at 50 °C). The reaction mixture was then cooled for 25 min, until a temperature of 60 °C was attained. At this point, a second urea (U2) was added to provide a final F/U = 1.14 M ratio. The reaction mixture was then cooled down to ambient temperature. Table 1 shows the proportions of first and second urea added during resin preparation.

2.3. Resin properties determination

Gelation time, Viscosity, pH, non-volatile solids content, specific gravity and free formaldehyde content were determined at the end of each synthesis. The viscosity of the resins was measured by a Ford cup (Nr.4) at 25 °C. The resins pH was measured with a Metrohm 827 pH-meter. The non-volatile solids content was determined by evaporation of volatiles from measuring approximately 1.5 g of resin in a disposable aluminum dish and taking an accurate weight before and after drying in a convection oven for 2 h at 120 °C. The gel time of the resin, is when 5 g of resin sample after addition of 10% $(\text{NH}_4)_2\text{SO}_4$ (20% aqueous solution) as cure catalyst was converted at 100 °C to a high viscosity gel. The specific gravity values of the liquid resin were obtained by density hydrometer. The storage stability of the synthesized resins was measured by placing the resin samples in a convection oven at 30 °C and checking the viscosity changes daily for 40 days. The formaldehyde analysis was carried out by the Na_2SO_3 titration method to measure the free formaldehyde content in the aqueous resin solution.

2.4. ^{13}C NMR spectroscopy

The ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were acquired with a Bruker AVANCE 400 and 500 MHz instrument using Deuterated dimethyl sulfoxide (DMSO-d6) as the solvent. The 40 mg liquid resin was directly mixed with 10 mL of dimethyl sulfoxide (DMSO-d6) for ^{13}C NMR determination. About 400–600 scans were accumulated for each spectrum. Spectra were internally standardized with tetramethylsilane (TMS). Peaks are recorded in ppm downfield of TMS. All chemical shifts were reported as (ppm) values. The observed chemical structures and chemical shifts were assigned according to the literature [27–31]. The relative contents (%) of all methylene carbons (or molar distribution) were calculated as the ratio of the integral value of each type of methylene carbon over the total value of all methylene carbons, from the following formula:

$$\text{Molar\%} = \frac{A_i}{\sum A_i} \times 100\%$$

The A_i is the integral area of a methylene carbon, and the $\sum A_i$ is the sum of the integral areas of all methylene carbons. The relative content of different carbonyl carbon atoms in urea were also calculated using the same method.

2.5. Differential scanning calorimetry (DSC)

DSC measurements were carried out with a DSC (TA METTLER TGA/STTA 851, Switzerland) equipped with a thermal analysis (TA) system and related software. The sample resins were tested by placing about 3–5 mg of each sample into a hermetic pan. A heating rates of 10 °C/min, and a temperature scan range of 30–220 °C, at a pressure of 4MPa, with nitrogen as the flushing gas were selected during the DSC scanning. As a crosslinking catalyst, 20 wt% solution of (NH₄)₂SO₄ was mixed into the UF resin (2 wt% of the dry salt per solid content of the resin).

2.6. MDFs preparation and determination of properties

The three different UF resins which were synthesized in this work were initially mixed with water to reach a 55 wt% solids content followed by the addition of 2% on total UF resin solids of an oven dry weight (NH₄)₂SO₄ as hardener. The resin samples so prepared were added and mixed well with the fiber at a ratio of 10:90 wt: wt (solid content of resin to dried fiber). Finally, laboratory boards of 25 cm × 25 cm × 10 mm (length × width × thickness) dimensions were prepared under identical conditions, namely hot-pressed for 5 min at 180 °C at a maximum pressure of 3.5 MPa. The MDF panels were prepared at a density of 700 kg/cm³. After pressing, the boards were stored in a conditioned room (at 20 ± 2 °C and relative humidity of 65 ± 5%) [32].

To evaluate the mechanical properties of the panels, the modulus of elasticity (MOE) and modulus of rupture (MOR) (3 samples from each board) were measured according to EN 310: 1999. The internal bond (IB) strength (3 samples from each board) of the manufactured panels were measured according to EN 319:1999. Physical properties such as the thickness swelling (TS) after 24 h soaking in cold water (3 samples from each board) were determined according to the procedure specified in EN 317:1999. Formaldehyde emission from the MDF panels prepared was assessed according to EN 120:1999 (perforator method). Mechanical properties of the MDF panels were measured in an IMAL (IB600) universal testing machine on the premises of the Arian Sina Co. Ltd, Iran. The data reported represent the average of multiple measurements.

3. Results and discussion

3.1. Resin properties

The physicochemical properties of UF resins prepared at different initial F/U molar ratio during resin synthesis are summarized in Table 2. The effect of the initial molar ratio is markedly related to the free formaldehyde content of the resin. The actual formaldehyde concentration in each case was also measured using the titration method mentioned in the experimental section, as shown in Table 2. It can be seen that the high free formaldehyde content in the UF3 resin is caused by the high initial molar ratio (F/U = 2.3). When compared with other resins prepared at different initial molar ratios, the free formaldehyde content decreased with the decrease of the initial molar ratio. In the resin which was prepared with F/U = 1.9, the excess urea reacts with the exiting free formaldehyde, and therefore the free formaldehyde

content of the resin is reduced. Viscosity is one of the most important parameters influencing resin penetration, which is an indicator of advancement of hardening, polymerization, and the number of side branches in the resultant polymer [33,34]. Resins with a higher-viscosity lead to poor resin penetration, while the resins with a lower-viscosity can cause starved bond-lines because of excessive resin penetration.

It must also be noted that the viscosities of the resins prepared under the same acid pH with at the same condensation time were completely different. The condensation potential was increased at the lower initial F/U molar ratio. As a result, the molar mass of the UF resin is increasing towards the point where it passes from liquid to a partly gelled state. The effect of the initial molar ratio was also shown by the measurement of the resin reaction end point determined by the reaction time required to achieve the same cloud (turbidity) point during UF resin synthesis. At higher urea proportions (lower F/U), the condensation stage was faster than at lower proportions of urea (high F/U). This occurs because there are more amine groups available to react with formaldehyde. Furthermore, this accelerates the condensation reactions during resin synthesis.

As expected, the use of different initial molar ratios has significant effects on the resins gel time. In general, the non-volatile solid content of the resin decreased as the F/U molar ratio increased. Differences in resin specific gravity were also non-significant.

The gel time results indicate that the curing reaction of the initial F/U = 1.9 resin is slower than that of the other resins. For a lower initial molar ratio (F/U = 1.9), there is a very limited proportion of free formaldehyde in the system. If a same amount of (NH₄)₂SO₄ hardener is added, the effect of time on the pH will become very limited. When an adequate amount of formaldehyde is not present, the amount of H₂SO₄ released by (NH₄)₂SO₄ is not sufficient to equalize the content of sodium hydroxide (NaOH) in the system as in the other molar ratios.

According to the traditional alkaline-acid-alkaline UF synthesis procedure, the appearance of a cloudy point (turbidity point) indicates that the condensation has reached the end of the acid stage. Table 2 indicates that the reaction end point for an initial F/U = 1.9 UF resin was about 35 min as compared to 85 and 215 min, respectively, for F/U = 2.1 and F/U = 2.3 resins.

3.2. ¹³C NMR spectra

The effect of the initial molar ratio (F/U₁) on resin structure was investigated by ¹³C NMR spectroscopy. The ¹³C NMR spectra of resins prepared at different F/U₁ are shown in Figs. 2–4. Table 3 shows the ¹³C NMR quantitative measurement results for the samples.

The ¹³C NMR spectra form two main groups. The first group illustrates different methylene containing functional groups represented by a wide range of chemical shifts between 40 and 100 ppm, into three distinguished sections, each of which is interpreted in detail later. The methylene bridges can be categorized into three section. The different carbon of the methylene linkages peaks appeared at 46, 53, and 60 ppm. The signal at 60–61ppm is completely absent in all of resins, indicating that the methylene bridge (=N-CH₂-N=) was not formed. The peak of 64–66 ppm is attributed to the hydroxymethyl linkages of the type -NH-CH₂OH. Furthermore, the peaks at 68, 75 and 78 ppm are assigned to the carbon in type I, II, and III methylene-ether groups

Table 2
Properties of UF resins synthesized with different initial F/U molar ratios.

Initial F/U	pH	SPG ^a (gr/cm ³)	Curing time (s)	Viscosity (mPa.s)	Endpoint (min)	Solid content (%)	Free Formaldehyde
1.9	8.4	1.270	59	270	35	65.30	0.22
2.1	8.1	1.269	53	230	85	64.40	0.43
2.3	8.3	1.268	50	170	215	63.80	0.71

^a Specific gravity.

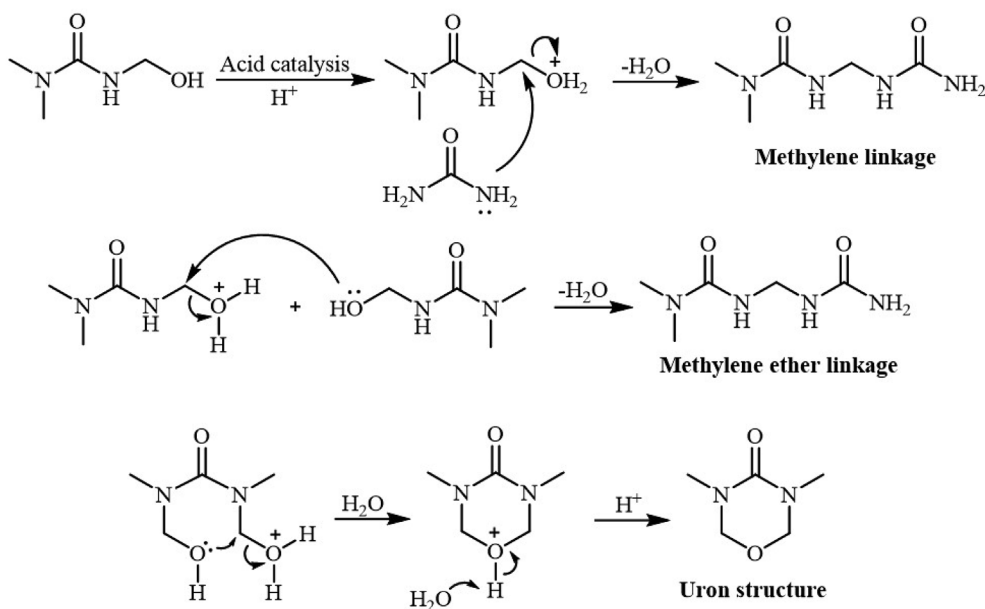


Fig. 1. Proposed formation of methylene, methylene ether linkages and uron structure.

(-CH₂OCH₂-). The peak at 78 ppm refers to the carbon of the -CH₂- groups of uron derivatives. The condensation reaction generates, particularly, methylene-ether group (=N-CH₂OCH₂N= and -CH₂ of the Uron ring) with shift at 77–78 ppm, but the products are minor in relation to the methylene bridge carbons. Weak chemical shifts are found in the 80–90 ppm range this belonging to free formaldehyde in the spectrum of UF resin. As shown in Fig. 1 the increase in molecular weight of the UF resin will result from a combination of reactions leading to the formation of methylene bridges between aminogroups nitrogens (-NH₂) by the reaction of methylol groups in methylolureas and amino groups in urea. Methylene ether linkages are also formed by the reaction of two methylol groups; and uron by the hydration reaction forming stable five-member rings (Fig. 1).

The second group illustrates the carbonyl carbons region between 150–170 ppm, the assignment depending on the different levels of urea substitution. The changes in the carbonyl region of the NMR spectra

cannot be quantitatively explained. The main reason for this is the very strong overlap of signals from different environments. The condensation reaction causes the decrease of the ¹³C signals intensities of carbonyls of methylol ureas (159 and 161 ppm). As the condensation advances this leads to the formation of complicated chemical structures presenting different substitution patterns. This is evident from the relative increase in intensity of signals in the 159–161 ppm region because of the continuing substitution on urea amino groups. Intra-molecular Michael addition [35] of a di or tri-methylolurea can produce cyclic ether structures, like uron. Although the uron structures were observed in all resins, the proportion of uron carbonyls are much lower than those of other carbonyls throughout the whole condensation stage. This result clearly shows that the formation of cyclic ether structure is minor in comparison to other methylene ether linkages.

Fig. 2 shows the spectrum of the sample which is prepared by F/U₁ = 1.9 and the quantitative results are also listed in Table 3. The

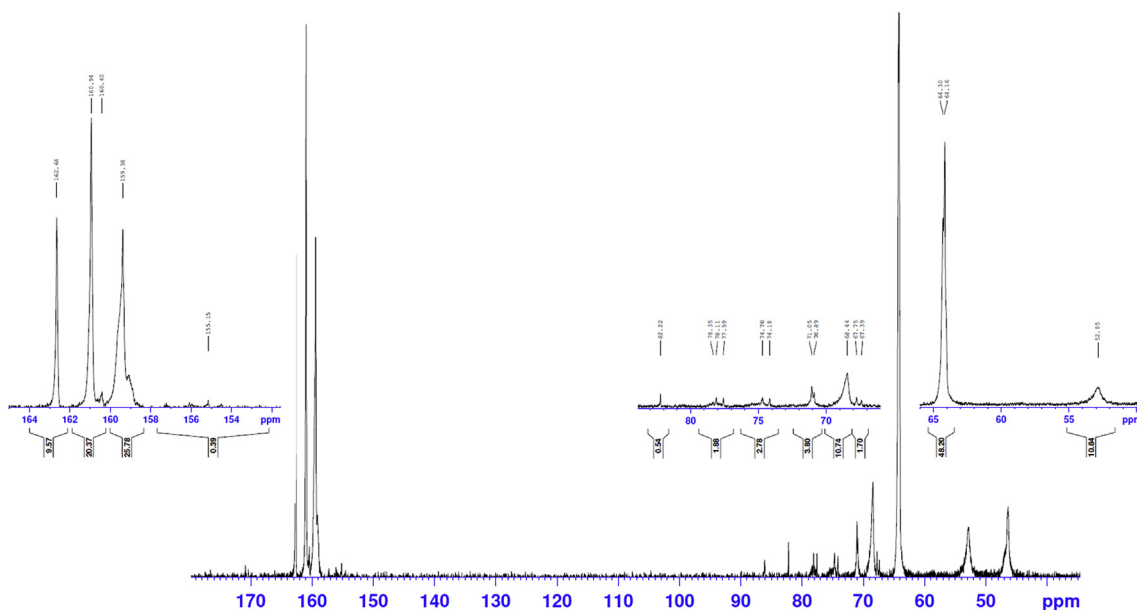


Fig. 2. ¹³C NMR spectrum of UF resin with initial F/U = 1.9.

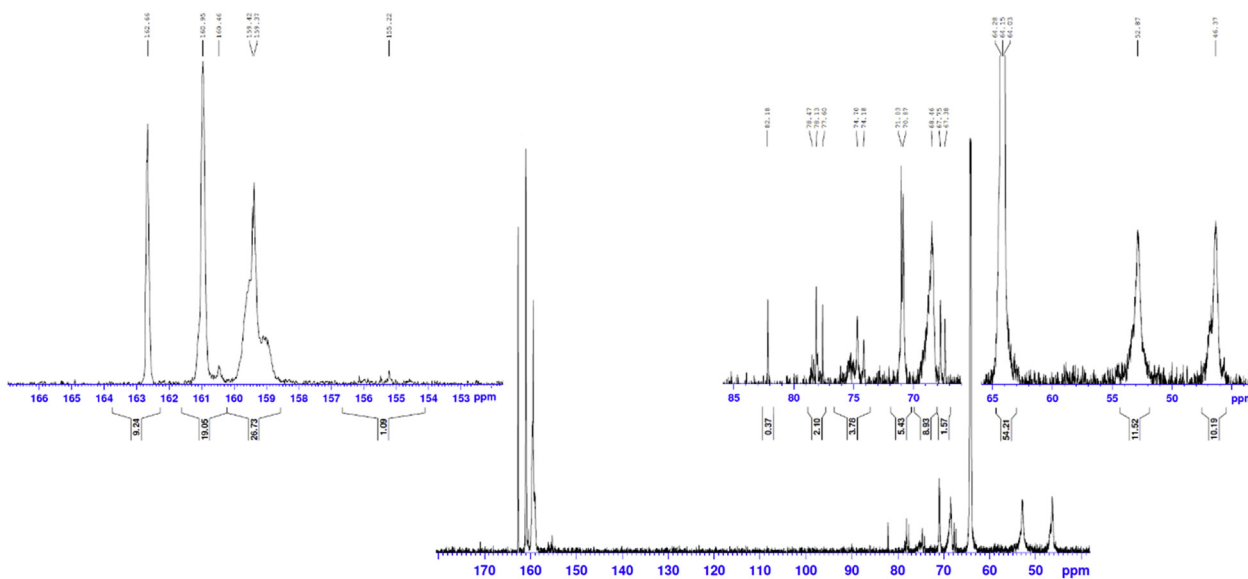


Fig. 3. ^{13}C NMR spectrum of UF resin with initial F/U = 2.1.

resin synthesis by F/U initial molar ratio 1.9 produced the highest proportion of methylene linkages as compared respectively to UF2 and UF3 and also UF1 provided the most methylene-ether groups, but the least total hydroxymethyl linkages ($-\text{NH}-\text{CH}_2\text{OH}$). Thus, the use of low F/U initial molar ratio and extension of the reaction to a higher viscosity point carried out in this study resulted in increasing the linear ether linkages content. In summary, the lower content of methylool linkage (57.07%) are present in F/U = 1.9 compared to 2.1 and 2.3, confirming and explaining the longer gel time in the F/U = 1.9.

As it can be seen from the quantitative results for the UF resin synthesized with initial F/U = 2.1 in Table 3, hydroxymethyl groups maximum ($-\text{CH}_2\text{OH}$) was reached at 61.31% of reaction. At the first stage of polycondensation, the steric barrier suppresses the reaction between two hydroxymethyl groups to form an $\text{N}-\text{CH}_2-\text{N}$ bridge, and accordingly, the formation of methylene ether bridges is faster. The F/U = 2.1 gave the higher proportion of trisubstituted urea

($-\text{NH}-\text{CO}-\text{N}=\text{}$) but the lower amount of monosubstituted urea ($\text{NH}_2-\text{CO}-\text{NH}-$). As shown in Table 3, the urea carbonyls account for 1.94% of the total urea carbonyls, observed in the F/U = 2.1 case, higher than for initial F/U = 2.1 (1.34%) and F/U = 1.9 (0.7%), respectively. The carbon from unbranched methylene bridge at 46–49 ppm accounts for 10.41% and the peak at 53–55 ppm belonging to the methylene carbon of the branched bridge $-\text{NH}-\text{CH}_2-\text{N}=\text{}$, was 11.77%. The total proportion of methylene ether linkages was calculated to be 16.51% specially for the $-\text{NH}-\text{CH}_2\text{OCH}_2-\text{NH}-$ (I) type and for $-\text{NH}-\text{CH}_2\text{OCH}_2\text{OH}$ at 68–70 ppm at most it accounts for 10.73%.

According to data listed in Table 3, the F/U = 2.3 resulted in the highest proportion of monosubstituted urea ($\text{NH}_2-\text{CO}-\text{NH}-$) and disubstituted urea ($-\text{NH}-\text{CO}-\text{N}-$), but the lower proportion of methylene linkages and methylene ether groups than other resins. It can be seen in Table 3 that the type I linear ether linkage at 68–70 ppm only decreased by 1.04% from F/U = 2.1 to F/U = 2.3. During hot pressing wood-

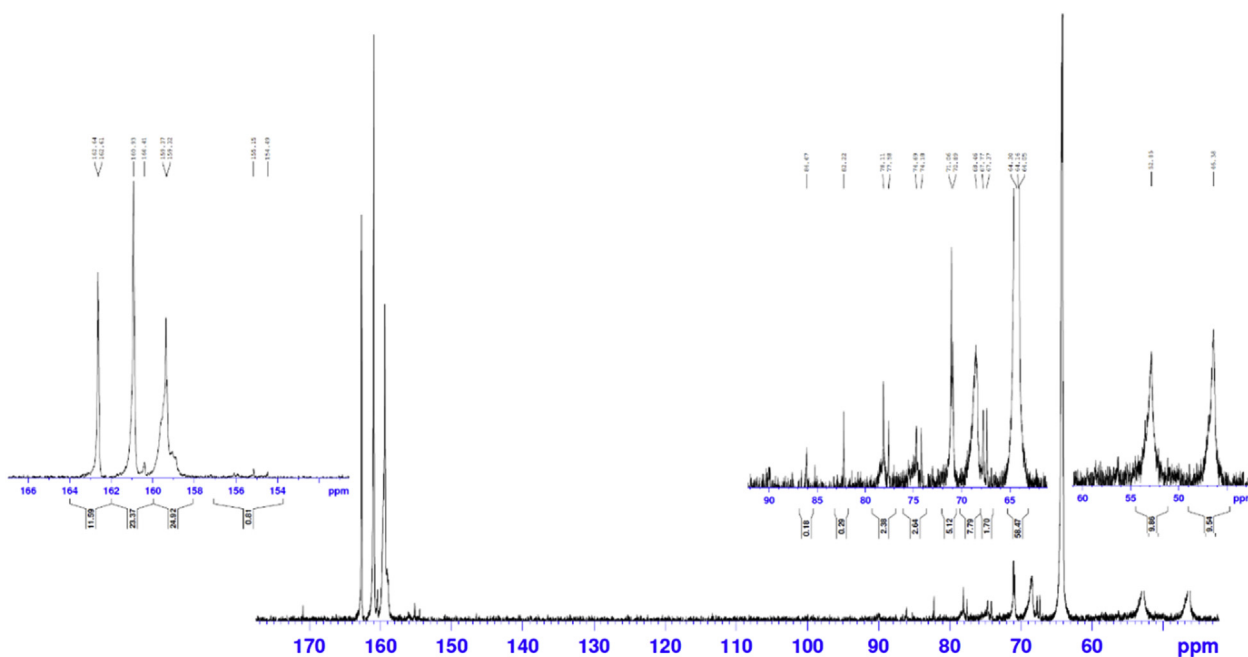


Fig. 4. ^{13}C NMR spectrum of UF resin with initial F/U = 2.3.

Table 3
The relative content of the methylene and carbonyl carbons (%) of UF adhesive samples by ^{13}C NMR.

Structures	Chemical shifts/ppm	Relative peak area	Relative peak area	Relative peak area
		for F/U = 1.9 (%)	for F/U = 2.1 (%)	for F/U = 2.3 (%)
Methylene linkages	Total	24.4	22.18	19.8
-NH-CH ₂ -NH- (I)	46–49	12.60	10.41	9.74
-NH-CH ₂ -N= (II)	53–55	11.80	11.77	10.06
=N-CH ₂ -N= (III)	60–61	–	–	–
Methylene-ether groups	Total	18.53	16.51	14.81
-NH-CH ₂ OCH ₂ -NH- (I)	68–70	13.51	10.73	9.69
-NH-CH ₂ OCH ₂ OH				
-NH-CH ₂ OCH ₂ -N= (II)	75–77	3.01	3.86	2.69
=N-CH ₂ OCH ₂ N= (III)	78–80	2.01	1.92	2.43
Uron-type ether				
Total methylol groups	Total	57.07	61.31	65.39
-NH-CH ₂ OH (I)	64–66	52.35	55.38	59.68
-N(-CH ₂)CH ₂ OH	71–72	4.12	5.55	5.23
HO-CH ₂ -OH	82–84	0.6	0.38	0.3
HOCH ₂ -O-CH ₂ -OCH ₂ OH	86–88	–	–	0.18
Carbonyl groups				
NH ₂ -CO-NH-	162–163	17	16.47	19.10
-NH-CO-NH-	160–162	36.30	33.95	38.50
-NH-CO-N=	158–160	46	47.64	41.06
Uron	154–157	0.7	1.94	1.34

1–2 ppm movement to high field occurred for UF resins because more DMSO-*d*₆ was used.

based composites, and curing, further condensation and re-arrangement, and release of formaldehyde do occur. To scavenge the unreacted formaldehyde and formaldehyde released by the breakage of the condensed resin structures in industrial wood composites during their long-term use, an excess of urea is necessary. Nevertheless, the use of additional urea may influence negatively the UF resin chemical structure and may show poor adhesion performance when applied to the manufacture of wood-based composites. The peak at 46–49 ppm assigned to methylene bridge decreased when increasing the initial F/U ratio, showing that molecular mobility of the UF resin increased with increasing the initial F/U ratio used during its synthesis.

3.3. DSC analysis

Fig. 5 shows typical DSC curves for UF resins which are synthesized with different initial F/U molar ratios at a heating rate of 10 °C/min over a temperature range of 30–220 °C. A dynamic DSC scanning of a UF resin by a controlled heating rate method can provide many information related to resin curing, such as total reaction heat, onset temperature, exotherm peak temperature followed by an endotherm peak temperature.

Table 4 summarizes the DSC thermograms results of the exotherm peaks for the UF resins synthesized with different initial F/U molar ratios (Fig. 5). The exotherm peak appearing before 100 °C belongs to the condensation reaction between primary amide groups of unreacted urea and methylol groups (-CH₂OH). The endothermic heats of reaction vary widely within the temperature range of 100–140 °C as they are certainly related to the evaporation of condensed water, free formaldehyde, and decomposition of the methylene-ether bridges [36]. Enthalpy of the curing reaction (ΔH_{curing}) was measured as the region under the curing transition peak in the DSC analysis. This region also presents the total heat liberated during the curing reaction. According to the isothermal DSC curing curves, the exotherm peak temperatures were 84.8, 86.2 and 88.7 °C and endothermic peak temperatures were 116.4, 110.8 and 120.3 °C, respectively for the initial F/U molar ratios 2.3, 2.1 and 1.9. The UF resin peak temperature span is the peak temperature difference between the exothermic and endothermic peak.

There are some noteworthy results obtained through the DSC test, such as:

- The F/U molar ratio 1.9 provided the highest peak temperatures for both exothermic and endothermic reactions with the highest exothermic heat of reaction, and the biggest peak temperature span.
- The initial F/U molar ratio 2.3 resulted in the lowest peak temperature for the exotherm, but in the highest heat of reaction for both the endotherm and exotherm than the other resins,
- The resin which is synthesized with an initial F/U = 2.1 presented a lower endothermic heat of reaction but an exotherm enthalpy lower than that of the initial F/U = 2.3 resin.
- The enthalpy of the curing reaction ($\Delta H_{\text{exothermic}}$) of the initial F/U = 1.9 ratio UF resin was the lowest, compared to those of the other resins. It was expected that the longer gel time of the UF resin, prepared with F/U = 1.9, could give a greater exothermic heat of reaction, but this was not the case.

3.4. Storage stability

The storage stability of the synthesized resins is as an important property from both an economical and an environmental point. They are shown in Fig. 6. Having low stability during storage is a disadvantage, imposing strict limits in term of allowable shipping distance and storage life. In storage stability tests, the samples have been allowed to stand at room temperature (~24 °C) and the viscosity changes have been checked daily for 50 days.

As it can be observed, the resin with low initial molar ratio (F/U = 1.9) gave the fastest increase in resin viscosity and the lowest shelf life, eventually gelling in about 20 days. This could be related to a higher proportion of methylene-ether bridges, methylene linkages, lower content of hydroxymethyl (-NH-CH₂OH) groups and other factors. The resin with the lower initial molar ratio has the least number of side-chain branches as well as the highest amount of free amino linkages -NH₂ on the UF polymer chain.

The resin synthesized at F/U₁ = 2.3 showed the best storage stability compared with the other initial F/U molar ratios, which can also be related to the results obtained from the ^{13}C NMR analysis.

3.5. Physical and mechanical properties of MDFs

The average value of the mechanical properties and the free formaldehyde emission from the MDFs bonded with the urea formaldehyde resins are shown in Table 5. Results showed that the initial F/U molar ratio in the UF resins was the most significant factor influencing MDFs samples.

According to Table 5, the highest IB, MOR, MOE and the lowest thickness swelling were found for the panels bonded with the UF resin prepared with F/U = 2.1. Initial F/U = 2.1 showed several favorable resin properties, namely; a) adequate methylene bridge proportion for great cohesive strength of cured resin and great resistance to hydrolytic degradation, b) the lowest endothermic heat of curing indicating easier removal of moisture during resin curing.

One of the most significant results of this study is that reducing the initial F/U molar ratio in the UF resins reduces the amount of free formaldehyde in the boards. Table 5 presents the result for free formaldehyde emission. As expected, the formaldehyde content of MDFs made with the resin with F/U initial molar ratio of 2.3 is considerably higher. The formaldehyde emission is determined from different sources: unreacted formaldehyde, hydrolysis of methylene-ether linkages and hydrolysis of hexamine. Moreover, the UF resin with F/U = 2.3 has the highest proportion of hydroxymethyl linkages (mostly -NH-CH₂OH), which causes free formaldehyde emission because of the reversibility of alkaline hydroxymethylation reaction between urea and formaldehyde. The most striking effect of the UF resin with F/U = 1.9 was its lowest free formaldehyde emission. These results may be related

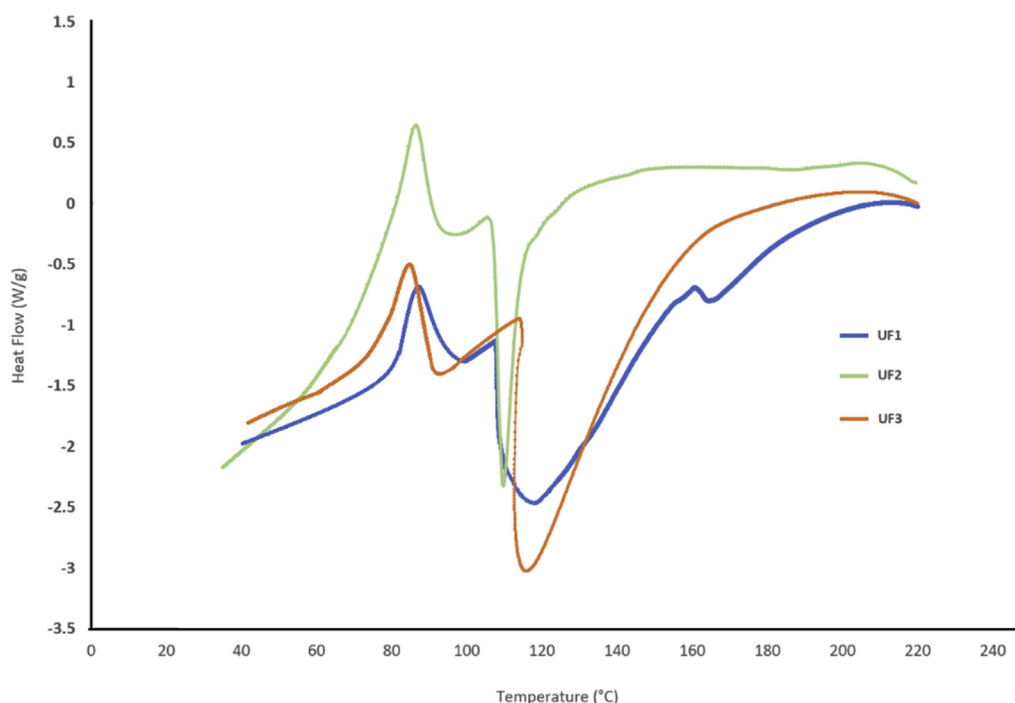


Fig. 5. DSC curves of UF1 (F/U = 1.9), UF2 (F/U = 2.1), UF3 (F/U = 2.3) resins at a heating rate of 10 °C/min.

to the lower free formaldehyde content and hydroxymethyl end groups as well as amino group $-NH_2$ which can react with more free formaldehyde and methylol groups in the condensation step. Many studies investigated the crystalline and domain size of UF resins with different F/U molar ratios. As the F/U molar ratio decreases, the crystallinity of cured UF resins increases. As well as the UF resins with lower F/U molar ratios (about 1) showed crystalline regions, the hydrolytic stability of cured UF resins improved, but decreased when the particle size decreased. Conversely, these crystalline regions did not change, depending on cure temperature and time, hardener type and level, which suggested that the crystalline regions of the cured UF resins were inherently present [37,38]. By decreasing the initial F/U molar ratio, the formaldehyde content of the UF resin so prepared will be lower, which leads to a decrease the proportion of hydroxymethyl groups especially of the $-NH-CH_2OH$. Thus, this condition would influence the physical-mechanical properties of the MDFs produced. MDFs bonded with the initial F/U = 2.3 synthesized UF resin yielded the most methylol groups, monosubstituted and di-substituted urea. Conversely, they presented the lowest proportion of methylene and ether linkages. Table 5 shows that the F/U = 2.3 has relatively good performance.

The poor internal bond (IB) strength of UF resins synthesized under a F/U = 1.9 initial molar ratio, could be explained by the fact that the hydroxymethylol groups proportion of a UF resin decreases with a decrease of the initial F/U ratio. In the other words, a decreased methylol groups proportion in a UF resin induces a greater flexibility (i.e., less rigidity) of the molecular network formed. This could cause a lower cohesive strength, and result in a poorer performance with a lower bond strength and a higher thickness swelling.

4. Conclusions

This study examined the effect of different initial F/U molar ratios in UF resin synthesis and its relation with the properties of the resins and of the MDF bonded with them. The urea-formaldehyde resins were formulated with three different initial F/U molar ratio of 1.9, 2.1 and 2.3, respectively, during resin synthesis while maintaining a final resin molar ratio of F/U = 1.14. These resins have been extensively evaluated by ^{13}C NMR, DSC and storage stability analysis and finally the physical-mechanical properties of the bonded MDFs have been investigated. Resins which are synthesized by an initial F/U = 2.1 resulted in the best MDF performance with the exception of formaldehyde emission. Accordingly, highest IB, MOR, MOE and lowest TS, correlated to the lowest exothermic heat of curing and formation of a tighter cross-linked network in the cured resin. This better performance of MDFs bonded with the resin at initial F/U = 2.1 compared to the other resins can be the consequence of various parameters, such as: a) an increased methylol groups content, enhancing the number of hydrogen bonds between the adhesive and the wood surface and increasing the initial bond strength of the adhesive, b) adequate viscosity due to the higher reactivity, c) lowest exothermic and endothermic peak temperatures and smallest peak temperature span. The resin with an initial F/U = 1.9 yielded significantly higher viscosity and longer gelation time than the other initial molar ratios and also yielded the highest peak temperature for both exothermic and endothermic peaks, with the lowest formaldehyde emission (FE) as confirmed by ^{13}C NMR spectra (lowest proportion of hydroxymethyl groups). The resin with initial F/U = 1.9 ratio negatively affected both physical and mechanical properties of the MDF board, with higher thickness swelling (TS) but lower MOR and MOE as well as IB values. This poor performance could be related to the

Table 4

Peak temperatures for the curing reaction of various initial F/U molar ratios UF resins determined by DSC measurements at 10 °C/min heating rate.

Initial F/U molar ratios	Exothermic Peak	Exothermic ΔH (J/g)	Endothermic Peak	Endothermic ΔH (J/g)	Peak temperature span
1.9	88.7	34	120.3	234	31.6
2.1	86.2	43	110.8	68.83	24.6
2.3	84.8	46	116.4	294	31.6

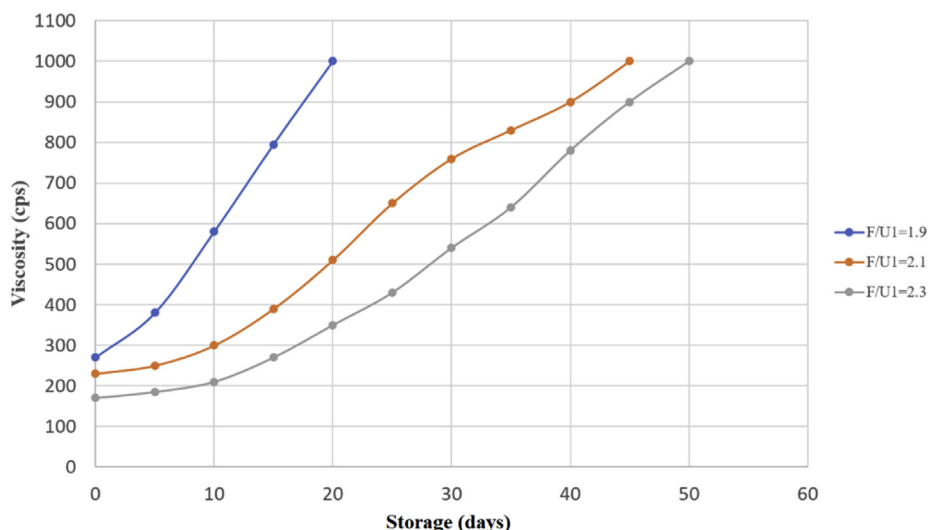


Fig. 6. Storage stability of UF resins with different initial F/U molar ratio.

Table 5

The physical and mechanical analysis of the MDFs produced with different resins.

Properties fiberboards	Unit	F/U = 1.9	F/U = 2.1	F/U = 2.3
IB	MPa	0.45	0.57	0.54
MOE	MPa	2036	2154	2082
MOR	MPa	21.92	22.43	21.97
TS	%	17	13	15
Formaldehyde emission	mg (100 g oven dry board)	6.8	8.5	11

molecular mobility of the cured UF resin network. With the lowest formaldehyde emission, the F/U = 1.9 M ratio resin resulted in the best performance in term of formaldehyde emission. It was observed that the properties of a resin synthesized with an initial F/U = 2.3 M ratio, was rather close to the properties of resins synthesized with F/U = 2.1. Initial F/U = 2.1 and 2.3 M ratio resins produced a decrease in the proportion of methylene and linear ether bridges and an increase in methylol groups. However, the resin synthesized with F/U₁ = 2.3 showed the best storage stability compared with the other initial F/U molar ratio resins.

Acknowledgements

This research was supported by Mr. Ali Saeedi the head of Arian Saeed Industrial Group (ASIG) and the authors are thankful for his invaluable support. Further, special gratitude to all employees in Chassbsaz company for their support in this research.

References

- [1] Dunky M. Urea-formaldehyde (UF) adhesive resins for wood. *Int J Adhesion Adhes* 1998;18:95–107.
- [2] Pizzi A, Lipschitz L, Valenzuela J. Theory and practice of the preparation of low formaldehyde emission UF adhesives. Berlin/New York: Walter de Gruyter; 1994.
- [3] Dunky M. Adhesives based on formaldehyde condensation resins. *Macromolecular Symposia Wiley Online Library*; 2004. p. 417–30.
- [4] Rowell RM. Handbook of wood chemistry and wood composites. CRC press; 2012.
- [5] Tohmura SI, Hse CY, Higuchi M. Formaldehyde emission and high-temperature stability of cured urea-formaldehyde resins. *J Wood Sci* 2000;46(4):303.
- [6] Ferra JM, Henriques A, Mendes AM, Costa MRN, Carvalho LH, Magalhães FD. Comparison of UF synthesis by alkaline-acid and strongly acid processes. *J Appl Polym Sci* 2012;123(3):1764–72.
- [7] Hse CY, Xia ZY, Tomita B. Effects of reaction pH on properties and performance of urea-formaldehyde resins. Berlin/New York: Walter de Gruyter; 1994.
- [8] Zhang SF, Li JZ, Zhang JZ, Li YH, Gao Q. Study on properties of modified low molar ratio urea-formaldehyde resins (I), advanced materials research. *Trans Tech Publ* 2010:2016–20.
- [9] Nuryawan A, Singh AP, Park BD. Swelling behaviour of cured urea-formaldehyde resin adhesives with different formaldehyde to urea mole ratios. *J Adhes* 2015;91(9):677–700.
- [10] Li T, Guo X, Liang J, Wang H, Xie X, Du G. Competitive formation of the methylene and methylene ether bridges in the urea-formaldehyde reaction in alkaline solution: a combined experimental and theoretical study. *Wood Sci Technol* 2015;49(3):475–93.
- [11] Pizzi A. Advanced wood adhesives technology. CRC Press; 1994.
- [12] Luo J, Zhang J, Luo J, Li J, Gao Q. Effect of melamine allocation proportion on chemical structures and properties of melamine-urea-formaldehyde resins. *BioResources* 2015;10(2):3265–76.
- [13] Park BD, Ayilimis N, Kwon JH, Han TH. Effect of microfibrillated cellulose addition on thermal properties of three grades of urea-formaldehyde resin. *Int J Adhesion Adhes* 2017;72:75–9.
- [14] Lubis MAR, Park BD, Lee SM. Modification of urea-formaldehyde resin adhesives with blocked isocyanates using sodium bisulfite. *Int J Adhesion Adhes* 2017;73:118–24.
- [15] Dorieh A, Mahmoodi N, Mamaghani M, Pizzi A, Mohammadi Zeydi M. Comparison of the properties of urea-formaldehyde resins by the use of formalin or urea formaldehyde condensates. *J Adhes Sci Technol* 2018:1–15.
- [16] Dorieh A, Mahmoodi N, Mamaghani M, Pizzi A, Mohammadi Zeydi M. Effect of different acids during the synthesis of urea-formaldehyde adhesives and the mechanical properties of medium-density fiberboards bonded with them. *J Appl Polym Sci* 2019;136:47256.
- [17] Dorieh A, Mahmoodi N, Mamaghani M, Pizzi A, Mohammadi Zeydi M, Moslemi A. New insight into the use of latent catalysts for the synthesis of urea formaldehyde adhesives and the mechanical properties of medium density fiberboards bonded with them. *Eur Polym J* 2019;112:195–205.
- [18] Ghani A, Ashaari Z, Bawon P, Lee SH. Reducing formaldehyde emission of urea formaldehyde-bonded particleboard by addition of amines as formaldehyde scavenger. *Build Environ* 2018;142:188–94.
- [19] Costa N, Pereira J, Martins J, Ferra J, Cruz P, Magalhães F, Mendes A, Carvalho LH. Alternative to latent catalysts for curing UF resins used in the production of low formaldehyde emission wood-based panels. *Int J Adhesion Adhes* 2012;33:56–60.
- [20] Que Z, Furuno T, Katoh S, Nishino Y. Evaluation of three test methods in determination of formaldehyde emission from particleboard bonded with different mole ratio in the urea-formaldehyde resin. *Build Environ* 2007;42(3):1242–9.
- [21] Kim MG, Young No B, Lee SM, Nieh WL. Examination of selected synthesis and room-temperature storage parameters for wood adhesive-type urea-formaldehyde resins by 13C-NMR spectroscopy. *V. J Appl Polym Sci* 2003;89(7):1896–917.
- [22] Myers GE. How mole ratio of UF resin affects formaldehyde emission and other properties: a literature critique. *For Prod J* 1984;34(5):35–41.
- [23] Wang H, Cao M, Li T, Yang L, Duan Z, Zhou X, Du G. Characterization of the low molar ratio urea-formaldehyde resin with 13C NMR and ESI-MS: negative effects of the post-added urea on the urea-formaldehyde polymers. *Polymers* 2018;10(6):602.
- [24] Park BD, Kang EC, Park JY. Differential scanning calorimetry of urea-formaldehyde adhesive resins, synthesized under different pH conditions. *J Appl Polym Sci* 2006;100(1):422–7.
- [25] Nuryawan A, Park BD, Singh AP. Comparison of thermal curing behavior of liquid and solid urea-formaldehyde resins with different formaldehyde/urea mole ratios. *J Therm Anal Calorim* 2014;118(1):397–404.
- [26] Dongbin F, Jianzhang L, An M. Curing characteristics of low molar ratio urea-formaldehyde resins. 2006;7(4):45–52.
- [27] Christjanson P, Pehk T, Siimer K. Hydroxymethylation and polycondensation reactions in urea-formaldehyde resin synthesis. *J Appl Polym Sci* 2006;100(2):1673–80.

- [28] Sun QN, Hse CY, Shupe TF. Characterization and performance of melamine enhanced urea formaldehyde resin for bonding southern pine particleboard. *J Appl Polym Sci* 2011;119(6):3538–43.
- [29] Kibrik ELOJ, Steinhof O, Scherr GN, Thiel WR, Hasse H. On-line NMR spectroscopic reaction kinetic study of urea–formaldehyde resin synthesis. *Ind Eng Chem Res* 2014;53(32):12602–13.
- [30] Steinhof O, Kibrik EJ, Scherr G, Hasse H. Quantitative and qualitative ¹H, ¹³C, and ¹⁵N NMR spectroscopic investigation of the urea–formaldehyde resin synthesis. *Magn Reson Chem* 2014;52(4):138–62.
- [31] Li T, Liang J, Cao M, Guo X, Xie X, Du G. Re-elucidation of the acid-catalyzed urea–formaldehyde reactions: a theoretical and ¹³C-NMR study. *J Appl Polym Sci* 2016;133(48).
- [32] Khonakdar Dazmiri M, Valizadeh Kiamahalleh M, Valizadeh Kiamahalleh M, Mansouri HR, Moazami V. Revealing the impacts of recycled urea–formaldehyde wastes on the physical–mechanical properties of MDF. *Eur. J. Wood Wood Prod.* 2019;77:293–9.
- [33] Park BD, Kim JW. Dynamic mechanical analysis of urea–formaldehyde resin adhesives with different formaldehyde-to-urea molar ratios. *J Appl Polym Sci* 2008;108(3):2045–51.
- [34] Abdullah ZA, Park BD. Hydrolytic stability of cured urea-formaldehyde resins modified by additives. *J Appl Polym Sci* 2009;114(2):1011–7.
- [35] Little RD, Masjedizadeh MR, Wallquist O, Mcloughlin JI. The intramolecular Michael reaction. *Org React* 2004;47:315–552.
- [36] Szesztay M, László-Hedvig Z, Kovacsovics E, Tüdő F. DSC application for characterization of urea/formaldehyde condensates. *Holz Roh Werkst* 1993;51(5):297–300.
- [37] Park BD, Jeong HW. Hydrolytic stability and crystallinity of cured urea–formaldehyde resin adhesives with different formaldehyde/urea mole ratios. *Int J Adhesion Adhes* 2011;31:524–9.
- [38] Nuryawan A, Park BD. Quantification of hydrolytic degradation of cured urea-formaldehyde resin adhesives using confocal laser scanning microscopy. *Int J Adhesion Adhes* 2017;74:1–5.