



Influence of glyoxal on curing of urea-formaldehyde resins

Daria A. Perminova^{a,*}, Viktor S. Malkov^a, Viktor Guschin^b, Norbert Eisenreich^b

^a Laboratory of Organic Synthesis, Tomsk State University, Tomsk 634050, Russia

^b Energetic Systems, Fraunhofer Institute for Chemical Technology ICT, Pfinztal, 76327, Germany



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ABSTRACT

In the present paper, the effect of glyoxal on the gel formation within the adhesive systems based on urea-formaldehyde (UF) resins is shown. A reduction of formaldehyde content in wood-based panels by decreasing the formaldehyde/urea molar ratio in the UF resins leads to increasing of the UF resin gel time, and impairing the qualitative characteristics of the UF-based wood materials. Glyoxal is shown to speed up the crosslinking of the macromolecules as well as significant reduction of gel time of adhesive composition. The first reason is the result of reaction between glyoxal and ammonium ion leading to protons releasing. Another reason is that glyoxal and its interaction products react with macromolecules of the UF resin forming a three-dimension cross-linked structure. The gel time and the pot life of the UF resin are measured by the oscillatory viscometer. Formation of the UF cross-linked resin structure with glyoxal and a curing catalyst (ammonium sulfate) is studied using dispersion Raman scattering spectroscopy. Particleboards (PB) are produced using different amount of glyoxal and formaldehyde/urea molar ratio in the UF resin. The properties are evaluated according to the European Standards and include density, internal bond, thickness swelling moisture content and formaldehyde content.

1. Introduction

Urea-formaldehyde resins are widely used as adhesives in the woodworking industry. UF resin is a product of polycondensation of urea and formaldehyde. In industry, a technology to manufacture urea-formaldehyde resin is usually optimized empirically. Therefore, there are meaningful differences in the values of pH, temperature, urea content used to produce the UF resins [1]. Along with other thermo-setting and condensing binders, the UF resins are cheaper and more available products with high ability of rapid curing in the presence of catalysts, and also relatively high concentration at low viscosity. This provides low shrinkage during the wood board pressing, and allows obtaining materials with acceptable strength values. The main disadvantages of the wood composite boards based on UF binders are high emission of formaldehyde during both production and subsequent exploitation of the boards [2]. International Agency For Research On Cancer (IARC) has included formaldehyde to the list of the first category carcinogens [3]. According to the European standard EN 120, formaldehyde content for particleboards should not exceed 8 mg/100 g oven dry board (class of formaldehyde emission is E1) by perforator method. Therefore, the reduction of the toxicity of wood composite materials remains of importance, and a complex solution is required.

A decrease of the formaldehyde/urea molar ratio is believed to be

the main way to reduce toxicity of the UF resins and materials on the basis thereof [4]. The toxicity can also be reduced by addition of various modifiers, such as amine-like modifiers [5–8]. Due to modification of the UF resins and reduction of the formaldehyde/urea molar ratio in production of the UF resin the reduction of the reactivity of UF adhesive system takes place. Therefore, the gel time of the UF resins increases, influencing on the qualitative features of constructional materials based on the UF resins and resulting in decrease of efficiency of their production.

Latent catalysts, mainly, ammonium salts, are used to accelerate both gel formation and a cross-linking of macromolecules of the UF resins. When the temperature or hold time increase, the ammonium salts are hydrolyzed yielding the acids, which accelerate the curing process of the UF resin [2,9]. On the other hand, the rate of the cross bond formation directly depends on the formaldehyde content because the corresponding acid, accelerating the curing of the UF resin, is formed when formaldehyde interacts with ammonium ions. Formation of hexamethylenetetramine and acid is intensified by the elevation of temperature [2]. A reduction of the formaldehyde/urea molar ratio leads to extremely low free formaldehyde content. Therefore, an increasing of the catalyst amount no longer has any impact on the gelling rate of the adhesive composition [10]. In Refs. [11,12] a limited influence of the catalysts (such as ammonium salts) on the curing rate of

* Corresponding author. Tomsk state university, Laboratory of organic synthesis, Arkadiya Ivanova street, 49, 634050 Tomsk, Russia.

E-mail address: vyatkinadasha@gmail.com (D.A. Perminova).

the UF resin by measuring the activation energy, enthalpy and peak temperature was shown by differential scanning calorimetry. The results indicated that the curing rate of the UF resin increased as the catalyst content increased and reached a maximum value when the catalyst content ranged from 0.5 to 1.0%. Further increases in the catalyst content had no effect on the resin curing rate.

To increase the moisture resistance and decrease the gel time of composite materials based on the UF resin organic salts of melamine are used [13]. Decomposition of the melamine salts results in releasing of organic acids, which act as curing agents. Melamine forms a three-dimensional network with the UF resin. Glutaraldehyde is introduced to the adhesive system as a cross-linker along with the latent catalysts [14]. Addition of glutaraldehyde leads to increasing of the amount of methylene bridges. As a result, the aldehyde is involved in formation of the cross-linking resins. Materials on the basis thereof possess water-resistant properties.

Pizzi et al. showed that glyoxal is a non-toxic nonvolatile substance and green environment-friendly agent, which substitute formaldehyde as a cross-linker and hardener for tannin-, lignin- [15] and protein-based adhesives [16]. Co-condensed glyoxal-urea-formaldehyde resins for wood adhesives with low formaldehyde emission [17] and zero formaldehyde emission urea-glyoxal resin [18] and hardener for its resin [19] were also synthesized.

In the present work, the effect of glyoxal as a cross-linker on the gel formation in the adhesive system based on the UF resin was studied. An influence of glyoxal content on the pH value, pot life and gel time of the adhesive system was considered. The process of cross-bonding of the UF resin was demonstrated using *in situ* Raman spectroscopy. The particleboards based on UF resins with urea/formaldehyde molar ratios 1:1.1 and 1.0 and glyoxal were produced, and their physical-mechanical parameters and formaldehyde content were tested.

2. Materials and methods

2.1. Materials

Commercial urea-formaldehyde resins, wood chips were supplied by Tomlesdrev Company (Russia). The urea/formaldehyde molar ratios were 1:1.1, 1:1.0. Table 1 summarizes the qualitative characteristics of the UF resins. The shelf life of the UF resin samples used for experiments was 3 days. Wood chips with moisture content of $2.5 \pm 0.5\%$ were from 1 to 40 mm in size.

To prepare the different adhesive compositions based on the UF resins, a latent curing catalyst (or hardener) represented by the 20% water solution of ammonium sulfate and 40% water solution of glyoxal (both purchased from Sigma-Aldrich) were used. The amount of ammonium sulfate was from 0.1 to 1.5 wt. % based on liquid resin (calc. to the dried substance). Different portions of glyoxal 0.5–10 wt. % based on liquid resin (calc. to the dried substance) were added to prepare the adhesive composition at room temperature. In Tables 2a and 2b characteristics of adhesive compositions are reported.

Table 1
Qualitative characteristics of UF resin.

| Parameter | Value | |
|---|-------|------|
| Molar ratio F/U | 1.1 | 1.0 |
| Mass fraction of free formaldehyde, wt % | 0.1 | 0.08 |
| Mass fraction of solids at $105 \pm 2^\circ\text{C}$, wt % | 66.4 | 67.6 |
| Viscosity at 20°C , cP | 284 | 261 |
| Maximal water miscibility at 20°C | 1:4 | 1:3 |
| pH | 7.9 | 7.5 |
| Gel time at 100°C , sec | 52 | 56 |

Table 2a
Characteristics of adhesive composition based on UF resin with molar ratio of 1.1, glyoxal and ammonium sulfate.

| Composition of adhesive system, wt % (calc. to the dried substance) | | Viscosity at 20°C , cP | Mass fraction of solids at $105 \pm 2^\circ\text{C}$, wt % |
|---|---------|--------------------------------------|---|
| $(\text{NH}_4)_2\text{SO}_4$ | glyoxal | | |
| 1 | 0 | 189 | 61.15 |
| | 0.1 | 188 | 61.02 |
| | 0.2 | 187 | 60.72 |
| | 0.5 | 180 | 60.52 |
| | 1 | 175 | 59.91 |
| | 2 | 172 | 59.42 |
| | 3 | 168 | 58.88 |
| | 4 | 165 | 58.33 |
| | 5 | 163 | 58.02 |
| | 10 | 117 | 56.37 |

Table 2b
Characteristics of adhesive composition based on UF resin with molar ratio of 1.0, glyoxal and ammonium sulfate.

| Composition of adhesive system, wt % (calc. to the dried substance) | | Viscosity at 20°C , cP | Mass fraction of solids at $105 \pm 2^\circ\text{C}$, wt % | pH | Gel time at 100°C , sec |
|---|---------|--------------------------------------|---|-----|---------------------------------------|
| $(\text{NH}_4)_2\text{SO}_4$ | glyoxal | | | | |
| 1 | 0 | 177 | 62.81 | 6.8 | 56 |
| | 0.5 | 169 | 62.42 | 6.4 | 36 |
| | 1 | 166 | 61.94 | 5.8 | 32 |
| | 2 | 162 | 61.30 | 5.2 | 27 |
| | 3 | 160 | 60.95 | 4.5 | 26 |

2.2. Methods

The evaluation of pot life and rate of gelation of adhesive composition were carried out by measurement of dynamic viscosity using oscillatory viscometer “Reokinetic 2 M” with thermostatic control at 25°C .

The dependence of the UF resin pH value on the contents of catalyst and glyoxal was evaluated using the pH-meter/ionometer (ITAN) at 25°C .

The adhesive composition gel time was measured in a laboratory test tube immersed into the boiling water at constant stirring. The onset of gelation process was fixed by the fluidity loss of the adhesive system.

In situ Raman spectra of the curing of the UF adhesive composition with glyoxal were recorded using an experimental unit comprising Raman spectrometer RAMAN RXN1 (Kaiser) with a scanning range from 200 to 2000 cm^{-1} , a monochromatic light source Invictus TM NIR Laser 785 nm, 400 nW and a temperature- and pressure-resistant fibre-optic probe (NIR Dynisco® Threaded immersion sampling optic from Kaiser Optical Systems). The experiments were carried out at room temperature.

The UF adhesive compositions with wood chips were prepared in a laboratory glue blender IMAL LGB100. Different amounts of glyoxal (0, 0.5, 1.0, 2.0, 3.0 wt%) were mixed with the resins (molar ratios of 1.11 and 1.0) and ammonium sulfate (1 wt%) before the blending with wood chips. The ratio between the amounts of dry resin and wood chips was 1/10. One-layered particleboards were formed in a square section wood mold ($400 \times 400\text{ mm}$). Pressing of the particleboards samples produced on the basis of various UF adhesive systems was carried out using a laboratory press. The pressing conditions corresponded to industrial performance for 16 mm three-layered particle boards. Hot pressing time of plates was 3 min at 180°C , and a 550 kN clamping force was used. After the hot pressing, the boards were stored at room temperature, 55% RH and 10% EMC for 72 h before testing. Three boards samples were used for each series of experiment. The physical-mechanical

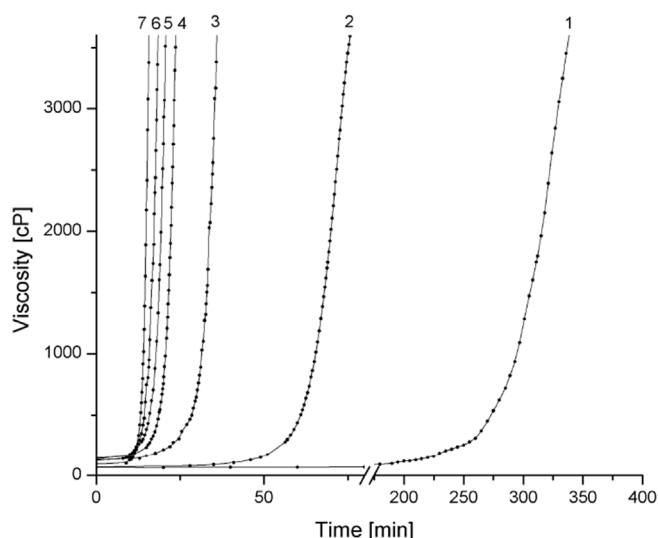


Fig. 1. Viscosity curves of the gelation process corresponding to various glyoxal contents in the UF adhesive composition with molar ratio of 1.1 at 25 °C. Glyoxal content (wt. %): (1) 0, (2) 0.5, (3) 1.0, (4) 2.0, (5) 3.0, (6) 4.0, (7) 5.0.

properties were evaluated according to the testing methods for density (EN 323), internal bond strength (EN 319) by IMAL IBX 600 laboratory testing machine and also thickness swelling (EN 317) and moisture content (EN 322). Formaldehyde content in each sample was determined by perforator method according to EN 120.

3. Results and discussion

3.1. Effect of ammonium salts and glyoxal content on gel time, pot life and pH value of UF resin

Fig. 1 represents the gelation rate curves for various amounts of glyoxal in the adhesive system. One can also judge on the pot life of the glyoxal-modified UF composition using these similarity viscometric curves. The shape of the gelation curves (for isothermal conditions) bear an exponential character reflecting the complex mechanism of the process.

One can see that the induction time, i.e. the time interval when the viscosity is constant, decreases when the glyoxal content increases. The induction time also characterizes the pot life of the UF adhesive composition. The time interval is characterized by the sharp growth of dynamic viscosity followed by the gelation. Thus, the increasing of glyoxal content in the UF composition leads to decreasing of the pot life of UF binder.

Dependences of the gel time and adhesive composition pH value on the amount of the catalyst (ammonium sulfate) and glyoxal are shown in **Fig. 2a** and **b**.

Decreasing of the pH value of the adhesive composition leads to reduction of the gel time. The pH values for the UF resins remain constant after addition of 0.5 wt. % of the hardener. Reduction of the gel time and pH also takes place, when the glyoxal content in the adhesive composition increases. When up to 2% of glyoxal are added, a sharp decrease of the gel time takes place. Subsequent increase of glyoxal content slightly changes the gel time. It is noteworthy that the UF resins possess the highest reactivity in a pH range between 4.5 and 6.

As demonstrated in section 1 [5,9,10], when hydrolyzed, ammonium salts reduce the pH and speed up gel of the UF resins due to proton release (**scheme 1A**). This leads to acceleration of the UF resin gel. On the other hand, formaldehyde reacts with ammonium ions to give hexamethylenetetramine releasing protons (**scheme 1B**).

In Ref. [8] it was shown that the increasing of the amount of

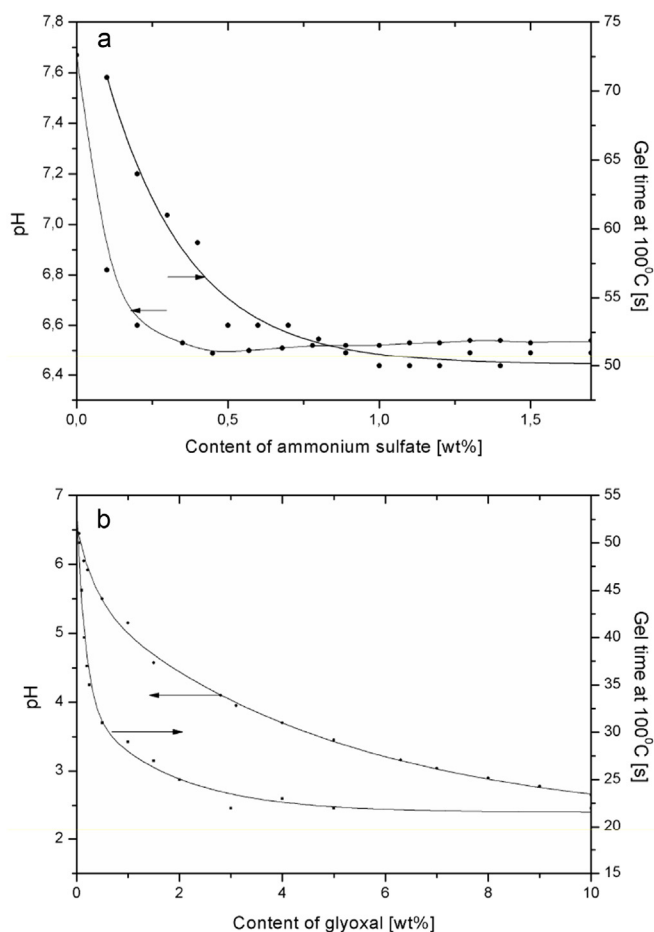
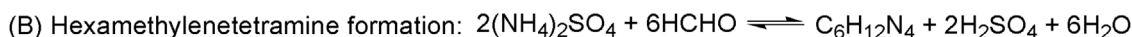
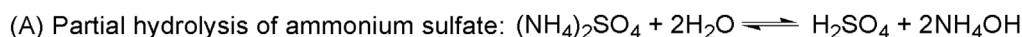


Fig. 2. a. Dependence of the gel time and pH value of the UF adhesive composition with molar ratio of 1.1 on ammonium sulfate content. b. Dependence of the gel time and pH value of the UF adhesive composition with molar ratio of 1.1 on the content of glyoxal.

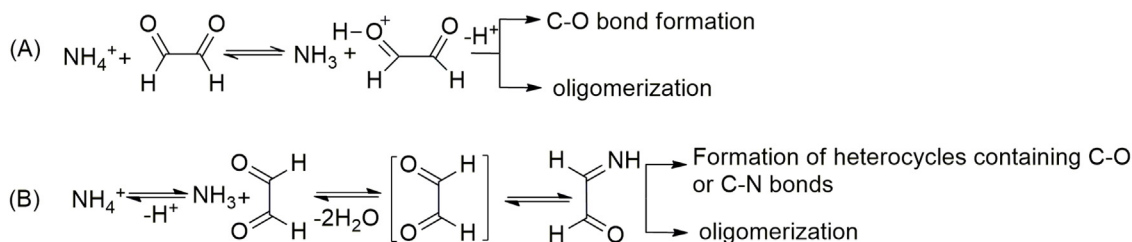
ammonium salts leads to reduction of the pH value and gel time. This is connected with the fact that the UF resins possess high formaldehyde/urea molar ratios and large amounts of free formaldehyde. However, the UF resins described in the present article and elsewhere [9–11] have both low molar ratio and free formaldehyde amount. Thus, the additional amount of the catalyst (~1 wt.%) has no influence on either pH value or gel time of the adhesive composition. Glyoxal addition to adhesive system leads to increasing of the amount of released protons as it can be seen from a decrease of pH value (**Fig. 2b**). As a result, a gel time decreases.

It is known [20,21] that in the presence of ammonium ions glyoxal is able to oligomerize and also form C–O bonds according to the classical mechanism of acidic catalysis, when the ammonium ion acts as a Brønsted acid. On the other side (**scheme 2A**), protonated glyoxal can undergo a nucleophilic attack by the ammonium ion followed by the loss of water and formation of the corresponding iminium intermediate, which is activated for further transformations, including formation of heterocycles and oligomerization reactions (**Scheme 2B**).

Thus, the interaction of glyoxal and ammonium ion probably leads to release of additional protons increasing the rate of cross-bonding between macromolecules of the UF resin. From the other hand, the intermediate products of interaction between glyoxal and ammonium ions as well as oligomerization products or protonated glyoxal can react with both macromolecules of the UF resins and a cross-linker to form three-dimensional branched structures.



Scheme 1. Main pathways to release protons.



Scheme 2. Glyoxal Reactions catalyzed by ammonium ions.

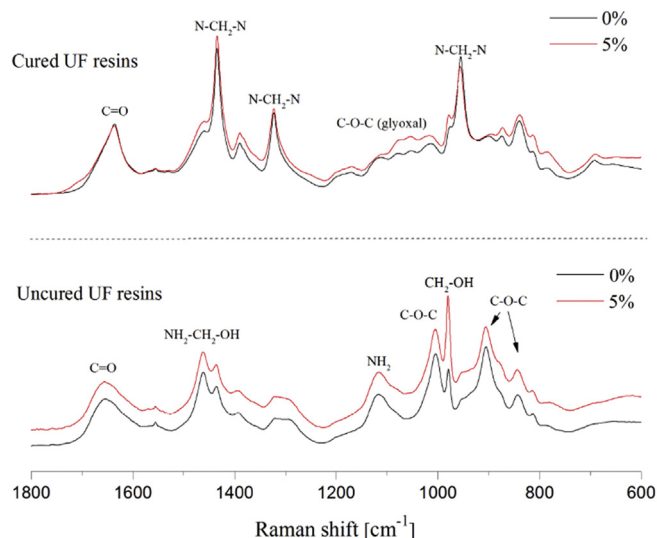


Fig. 3. Raman spectra of the UF adhesive composition with molar ratio of 1.1 before and after the curing (glyoxal amount was 0 and 5 wt %).

3.2. Raman spectroscopy of curing process of mixed UF resin, catalyst and glyoxal

In Fig. 3 Raman spectra of the adhesive compositions containing curing catalyst and glyoxal are presented for comparison. The spectra are identical to those taken before the curing. The bands specific for methylol ($\text{CH}_2\text{-OH}$) and methylene ether (C-O-C) groups at 905, 1080–1000 and 1460 cm^{-1} are the dominated ones (see Table 3). The curing process is accompanied by the formation of the cross-linked $> \text{N-CH}_2\text{-N} <$ bonds and three-dimensional structures [22,23].

Table 3

Assignment of Raman spectra bands in UF adhesive systems.

| Raman Shift (cm^{-1}) | Signals | Assignment | Notes |
|----------------------------------|----------------|--|--|
| 3500–3400 | weak | $-\text{NH}_2$ | |
| 3340–3330 | Medium: strong | $-\text{NH}-$, $-\text{NH}_2$, Amide CONH_2 , CONH | |
| 3000–2800 | medium | $\text{CH}_3\text{-O-}$ (2800) | $> \text{N-CH}_2\text{-N} <$ (2900) weak |
| 1650–1630 | weak; medium | C=O (carbonyl group) | |
| 1480–1440 | Medium, weak | $-\text{CH}_2\text{-O-}$, ($> \text{N-CH}_2\text{-OH}$), $-\text{CH}_2\text{-O-CH}_2\text{-}$ | CH_2 bending in |
| 1436–1430 | Medium, weak | $> \text{N-CH}_2\text{-N} <$ | CH_2 bending in |
| 1330–1300 | Medium, weak | $> \text{N-CH}_2\text{-N} <$ | CH_2 bending in CH_2 deformation |
| 1120–1110 | Strong, medium | $-\text{NH}_2$ | |
| 1000–990 | Strong, medium | CH_2OH , $-\text{C-O-C-}$ | |
| 960 | Strong, medium | $> \text{N-CH}_2\text{-N} <$ | |
| 905 | | $-\text{C-O-C-}$ | |

The spectrum of the UF resin cured with glyoxal has a low intensity broad band in the region of $1000\text{--}1100\text{ cm}^{-1}$ which is specific for ether group (C-O-C) forming via the interaction of glyoxal or its oligomerization products with the UF resin macromolecule [24–26].

In Fig. 4 kinetic curves containing the band intensities characterizing $> \text{N-CH}_2\text{-N} <$ bonds in the UF resin are shown. The proton-catalyzed cross-linking of the UF resin is shown in Scheme 3. At the first stage, a polycondensation takes place (Fig. 4) and is characterized by formation of the linear and branched structures. A slight increase of the molecular weight occurs. This does not result in viscosity increase and is characterized by the induction period (Fig. 1).

Then the formation of the cross-linked structures with small amount of the cross-bonds takes place. The process is characterized by the significant viscosity rise. After UF resin transition to gel state, formation of enforced network occurs [22,27,28].

Probably, glyoxal and the products of its interaction with ammonium ions, e.g. imine, incorporate into the oligomeric chain via reaction with methylol and amino groups. The branched structure of the macromolecule is formed. Formation of a three-dimensional cross-linked structure is accelerated (Fig. 4). The appearance of additional methylene ether groups is observed, when glyoxal content is high (Fig. 3).

3.3. Evaluation of physical-mechanical characteristics and formaldehyde content in particleboards

The particleboard samples were prepared and their physical-mechanical characteristics and formaldehyde content measured to evaluate the glyoxal performance as a cross-linking agent for the UF adhesive system with 1.11 and 1.0 M ratio U/F. For each of experiments three boards with four replicates of each test were used. The results are presented in Tables 4 and 5. As can be seen, the reduced molar ratio

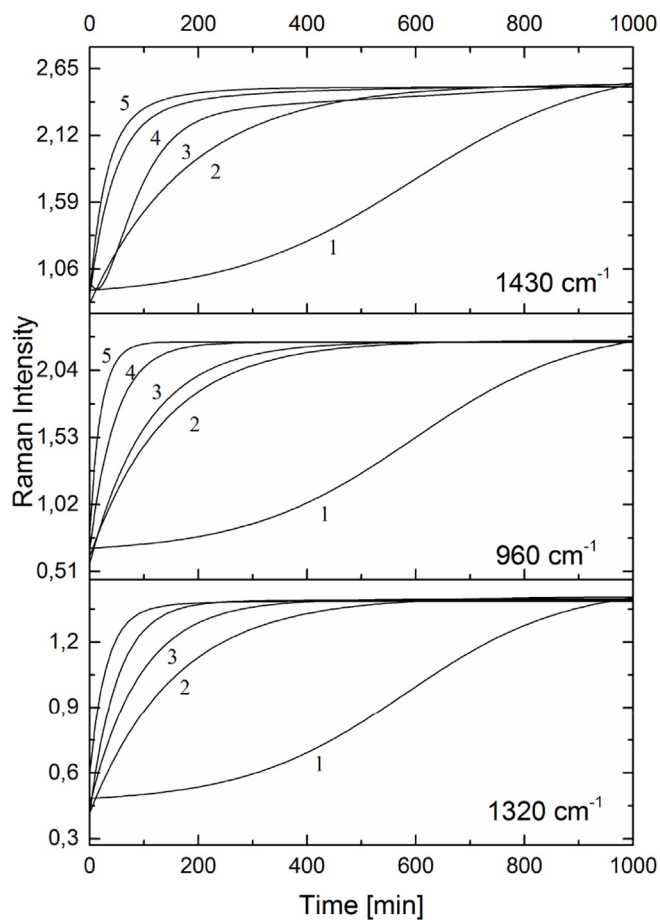


Fig. 4. Influence of glyoxal on the rate of $>N-CH_2-N<$ group formation in UF resin with molar ratio of 1.1. Ammonium sulfate amount was 1 wt %. Glyoxal content (wt %): (1) 0, (2) 0.5, (3) 1.0, (4) 2.0, (5) 3.0.

leads to degradation of physical-mechanical properties. The thickness swelling is slightly declined, while the internal bond strength slightly increased, when up to 2% of glyoxal is added. This is related to the sharp decrease of the gel time in this interval as previously discussed. Moreover, glyoxal improves physical-mechanical characteristics of the boards based on UF resin with 1.0 F/U molar ratio then in the boards based on UF resin with 1.11 F/U molar ratio. However, glyoxal addition exceeding 2% increases the frequency of the cross-linkages, the amount of methylene ether and the acceleration of formation of $>$

$N-CH_2-N<$ groups and reduces the amount of methylol groups, which participate in the formation of chemical bonds with wood particles. Thus, an increasing of particleboards fragility and reducing of resistance to water is observed. Also the high curing rate of adhesive system with glyoxal amount above 2% leads to the pre-curing process of the wood resin compositions. This is the reasons for lower physical-mechanical characteristics of the wood adhesive materials.

Addition of glyoxal to adhesive composition with UF resins does not lead to reduced formaldehyde content. Thus, glyoxal is not a scavenger of formaldehyde and only accelerates the curing process.

4. Conclusions

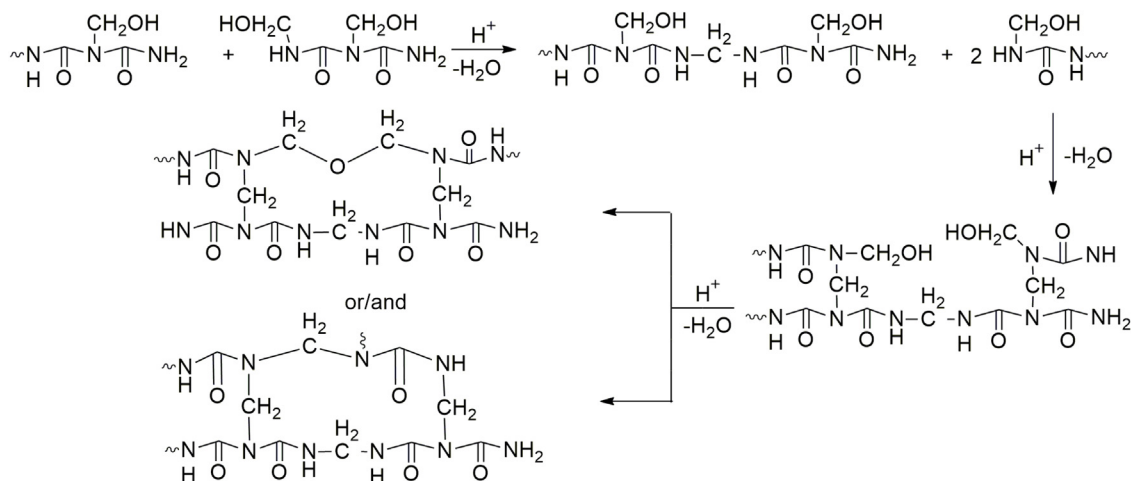
The opportunity to use glyoxal as a cross-linking agent to accelerate the formation of the three-dimensional cross-linked structures in the UF resin was shown. Glyoxal reduced the pot life of the UF resin and accelerated the gel formation process. On the one hand, the influence of glyoxal was caused by the reaction with ammonium ions, which resulted in additional protonation of the adhesive system. This hypothesis was supported by a decrease of the pH value of glyoxal-containing adhesive composition, reduction of the induction period for viscometric curves, and increasing of the rate of $>N-CH_2-N<$ bond formation.

On the other side, glyoxal and its condensation products formed a three-dimensional cross-linked structure with the UF resin. However, the appearance of additional band characteristic to methylene ether group occurs, when the glyoxal content is high. This process of interaction of glyoxal and its condensation products with the UF resin was not studied in details and will be investigated in the further work.

The particleboards based on the UF adhesive system with up to 2% of glyoxal possess water resistance and internal bond strength, which is better than those of the reference sample. Moreover, glyoxal influence on internal bond and water resistance is strengthened at reducing of U/F molar ratio to 1.0. However, the physical-mechanical characteristics of the particleboards are impaired as glyoxal amount exceeds 2%. Glyoxal addition in UF binders does not affect the formaldehyde content in particleboards on the basis thereof. Thus, the U/F molar ratio decreasing and glyoxal addition to the UF adhesive system allows achieving a reducing of formaldehyde content at satisfactory physical-mechanical characteristics of the particleboards.

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Scheme 3. Formation of three-dimensional cross-linked structures.

Table 4

Physical-mechanical characteristics of the particleboards produced from the UF resins with molar ratio of 1.1 different glyoxal content.

| Glyoxal content (wt. %) | Moisture content (%) | Density (kg/m ³) | Thickness swelling (%) | Internal bond (N/mm ²) | Content formaldehyde, mg/100 g oven dry board |
|-------------------------|----------------------|------------------------------|------------------------|------------------------------------|---|
| 0 | 2.3 | 770 ± 20 | 36.0 ± 2.4 | 0.35 ± 0.02 | 8.0 |
| 0.5 | 2.2 | 746 ± 15 | 32.8 ± 1.8 | 0.40 ± 0.02 | 7.5 |
| 1 | 2.5 | 750 ± 22 | 30.4 ± 1.9 | 0.42 ± 0.01 | 7.6 |
| 2 | 2.4 | 769 ± 21 | 28.1 ± 2.2 | 0.40 ± 0.01 | 7.7 |
| 3 | 2.7 | 760 ± 14 | 34.9 ± 2.0 | 0.36 ± 0.03 | 7.8 |

Table 5

Physical-mechanical characteristics of the particleboards produced from the UF resins with molar ratio of 1.0 different glyoxal content.

| Glyoxal content (wt. %) | Moisture content (%) | Density (kg/m ³) | Thickness swelling (%) | Internal bond (N/mm ²) | Content formaldehyde, mg/100 g oven dry board |
|-------------------------|----------------------|------------------------------|------------------------|------------------------------------|---|
| 0 | 3.1 | 780 ± 20 | 38.1 ± 1.2 | 0.26 ± 0.01 | 6.0 |
| 0.5 | 3.6 | 750 ± 20 | 32.9 ± 1.0 | 0.42 ± 0.02 | 5.5 |
| 1 | 2.5 | 760 ± 25 | 30.8 ± 1.9 | 0.41 ± 0.03 | 5.6 |
| 2 | 3.8 | 750 ± 28 | 34.1 ± 1.2 | 0.34 ± 0.02 | 5.8 |
| 3 | 2.2 | 766 ± 10 | 36.6 ± 1.0 | 0.36 ± 0.02 | 5.9 |

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