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# CURING CHARACTERISTICS OF LOW EMISSION UREA-FORMALDEHYDE ADHESIVE IN THE PRESENCE OF WOOD

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# ABSTRACT

Urea-formaldehyde (UF) resin presents, by far, the most utilized adhesive system in the manufacture of particleboard and fiberboard. At the temperatures above 100°C in the presence of catalyst, this resin undergoes cross-linking reaction and bonding of wood particles in a hot press. In this work the cross-linking of the new type of commercial UF adhesive for E1 type of wood based panels was studied using infra red (IR) spectroscopy and differential scanning calorimetry (DSC). IR spectra of examined UF adhesive showed distinctive characteristics in comparison to the older types of UF adhesives. The influence of different industrial wood species (obtained from beech, fir and poplar) on the curing behavior of wood-flour/adhesive mixtures has been evaluated using DSC method. The peak temperature and enthalpy of the curing reaction were evaluated from scans obtained with different heating rates. The activation energy for the curing reaction of pure adhesive and for wood-flour/adhesive mixtures was calculated using the Kissinger method.

KEYWORDS: Adhesives, wood-based panels, infrared spectroscopy, differential scanning calorimetry, wood flour.

# **INTRODUCTION**

Urea-formaldehyde resin presents one of the most important thermosetting adhesive system of interior class with the largest tonnage consumption in wood processing industry and particularly in wood-based panel (WBP) production. In addition to its low cost, it has several favorable processing features, like the ease of manipulation, good water solubility, low curing

temperature and short pressing time. Having in mind high production capacities of today's wood based panel plants, a great concern is addressed to more effective and efficient utilization of UF resin. Modern UF adhesives are therefore specially tailored to achieve the best possible performance in regard to different technologies and processing conditions in wood-based panel's production.

The adhesion process itself involves many factors, such as wetting, flow, diffusion, adsorption, solidification, chemical reaction, etc. In particleboard (PB) and medium density fiberboard (MDF) production, this is further complicated by the influence of wood component. Wood is a natural material and possesses its own variety of chemical compounds and physical structures, which can differ significantly amongst the wood species and may have different impacts on the curing of UF adhesives. This question was the starting basis of this research.

Some earlier studies have shown that the gel-time of UF adhesive is affected by wood extractives (Albriton and Short 1979). Another study revealed that the gel-time of UF adhesive for a defined temperature is strongly dependent on the pH value and the buffer capacity of wood extracts (Johns and Naizi 1980). Stefke and Dunky (2006) have noticed only slightly retarding effect of cold water wood extractives on curing of UF adhesive. More detailed information about this problem, especially concerning kinetic analysis of UF adhesive curing, was obtained by the differential thermal analysis (DTA) and differential scanning calorimetry (DSC) methods (Mizumachi 1973, Xing et al. 2005, Gao et al. 2008). Mizumachi (1973) used the DTA method to determine the activation energy of UF adhesive mixed with fine wood powders from different wood species. Accordingly, the wood species were classified into two groups; one which had no apparent influence on UF adhesive curing and other group that retarded or inhibited the curing reaction. Bearing in mind such a behavior of UF resin, this study was aimed at investigating the influence of certain industrial wood species on the curing of commercial UF adhesive using advanced DSC equipment.

Curing reactions of UF adhesive lead to formaldehyde (FA) emission. Formaldehyde is necessary to induce hardening; while on the other hand, it causes FA emission during the press cycle as well as subsequent emission from the pressed panels, which have led to changes in UF formulation during the past decades and appearing of the new formulations of UF adhesives (Dunky 1998).

The constant attention and action towards this ecological problem have ensured that modern UF adhesives are still dominant in the production of furniture panels and elements for interior applications (Crnogorac et al. 1995). Formaldehyde to urea ratio has been dramatically lowered to approximately 1.02 to 1 by addition of urea at the end of synthesis and by other methods. Quantity of initial polycondensation metilol forms increased, while formaldehyde shortage decelerated polycondensation. Because of that, curing characteristics of modern low-formaldehyde emission adhesives of so-called E1 (or newly appeared E0) class, have been changed together with necessary curing conditions. In addition, it was found that the FA emission from the panel glued with E1 class UF adhesive can be further reduced through manipulation and adjustments of some manufacturing variables (Petinarakis and Kavvouras 2006). Therefore, it was interesting to perceive again basic thermal characteristics of curing of modern UF formulations in the presence of wood, since every wood species influence adhesive curing in different way. The research consistently included beech, fir and poplar, as the most common industrial wood species. Contemplative thermal research of the last part of polycondensation reactions i.e. of adhesive curing which occurred at the surface and within cellular interspace of wood tissue is necessary knowledge in determination of hot pressing parameters, like the press temperature, pressing time, type and amount of curing catalyst (hardener) in the presence of certain wood species. In such an instance, mentioned parameters determine rate and cost of pressing operation, which in turn might cause significant production savings. The performance of the produced panel is largely dependant on its internal bonding, which further underlines the effectiveness of the adhesion process during hot pressing.

## MATERIAL AND METHODS

#### Urea-formaldehyde adhesive

In this investigation, the commercial urea-formaldehyde UF adhesive (Nafta-Petrochem, Slovenia) was used, having 1:1:1 formaldehyde to urea mole ratio. Basic physic-chemical tests, gave the following data for adhesive: solid content of 67.54 %, density 1.303 g.cm<sup>-3</sup>, pH value 8.16 and viscosity 545 mPa.s (obtained by Brookfield Synchro-lectric viscosimeter LVF). Ammonium chloride (NH<sub>4</sub>Cl) was used as the catalyst (pro-analysis powder, Alkaloid, Skopje, FYRM). Gel time was determined using 50 % diluted emulsion of UF adhesive with different addition of catalyst. The test tube filled with approx. 2 g of adhesive was immersed into boiling water, and constant stirring was applied throughout the test. The elapsed time until the point when no further stirring is possible is defined as the gelation time for a given adhesive sample. Catalyst addition of 0.2 %, 1.0 % and 2.0 % resulted in gel times of 114, 68 and 62 s, respectively.

#### Wood species preparation

Raw wood material of beech, fir and poplar wood species was collected from forest regions in Serbia. The mean densities of oven dried specimens were: 0.65, 0.45 and 0.34 g.cm<sup>-3</sup>, respectively. The logs were cut into boards for kiln drying. Wood shavings, obtained on a planning machine, were further reduced to particles in a laboratory hammer mill and ground into fine wood flour using a Willey mill. Finally, the wood flour was screened and the smaller fraction, passing through a 0.15 mm mesh was used in this study. Wood flour was conditioned under ambient atmosphere ( $20 \pm 1^{\circ}$ C and  $65 \pm 2$  % relative humidity) for approximately 10 days before testing. The moisture content of the wood flour was in the range of 7 - 8 % for all samples.

## **IR** measurement

The infrared (IR) spectra were obtained using a Thermo Nicolet Nexus 670 spectrometer, with DTGS KBr detector and XT-KBr beamsplitter. The cured UF adhesive samples were grounded with KBr, followed by vacuum compression to consolidate the formation of the pellet. Single beam spectra of the samples were obtained after averaging 32 scans in the wavenumber range of 4000 to 500.cm<sup>-1</sup> with a resolution of 4.cm<sup>-1</sup>. The samples of cured UF adhesive and UF adhesive and wood flour mixtures were prepared using sample material cured during DSC scans.

### DSC measurement

Test samples for evaluation of the influence of wood species were obtained by mixing wood flour into the adhesive 24 h prior to DSC testing and stored into refrigerator at 5°C. All calculations of mixture proportions were based on the weight of oven dried (od) materials, i.e. od flour or od catalyst vs. od adhesive. The addition of wood flour was 10 % by weight of oven dried (od) flour vs. od adhesive. For all DSC tests, the UF adhesive was diluted to a concentration of 50 %. Addition of NH<sub>4</sub>Cl was 0.2 % by weight (od catalyst vs. od adhesive), for all DSC measurements intended for evaluation of the activation energy for both UF adhesive alone and the systems with wood flour. Exceptionally, the influence of catalyst on the curing of adhesive

(without addition of wood flour) was obtained with the following content of  $NH_4Cl$ : 0.2, 0.6, 1.0, 1.5 and 2.0 %. The curing reactions of the UF adhesive alone and its mixtures with wood flour were monitored using a differential scanning calorimeter (DSC Q20 TA Instruments, USA). Small amounts of the test samples (approx. 4 to 5 mg) were placed in hermetically sealed aluminum pans. All scans were run in the dynamical regime with different heating rates (5, 10, 15 and 20°C.min<sup>-1</sup>) in the temperature range from 40°C to 200°C. Before the test run, the temperature of the heating block was equilibrated at 40°C. The purge gas was nitrogen. The DSC curves were monitored in real time, showing the generated heat as a function of temperature. The instrument software was set to show the exothermal peaks in the upwards direction. The area under the exothermal curve, presenting the enthalpy of reaction, and the peak temperature were obtained using TA Universal Analysis software procedure.

## **RESULTS AND DISCUSSION**

#### FT-IR spectra of UF adhesive

The obtained FT-IR spectra of commercial UF adhesive with low FA emission examined in this work are given in the Fig. 1 for UF adhesive emulsion and in the Fig. 2 for cured UF adhesive. Spectra of cured UF adhesive mixed with wood flour of beech, fir and poplar has not shown significant differences in regard to the spectrum of cured UF adhesive alone. It was probably due to low addition of wood flour of 10 %. In such way the spectra of adhesive component overlapped the possible chemical influence of wood species. Therefore, the spectra of pure UF adhesive emulsion and cured adhesive are discussed in this paper. In addition, we have compared our results with literature findings and some previous IR spectroscopy research on UF adhesives.

#### Region from1350-1660.cm<sup>-1</sup>

In this region three characteristic bands appeared. The first one is a strong band at 1659.cm<sup>-1</sup> observed on the spectrum of UF adhesive emulsion. It retained almost the same intensity after curing, but shifted to the lower frequency of 1638.cm<sup>-1</sup>. All amides show a strong carbonyl (C=O) absorption band near 1640.cm<sup>-1</sup> when examined in the solid state, while having a higher frequency in the emulsion (Bellamy 1975). In the early research of IR spectra of polyamides the same absorption band was observed (Cannon 1960). Due to its stability, this carbonyl absorption band was used to normalize the other absorbencies within UF spectra (Myers 1981). In the recent research of the UF adhesives of low formaldehyde to urea mole ratio, this mode also presented highly characteristic absorption at the frequency near to 1650.cm<sup>-1</sup> (Zorba et al. 2008). The band at 1548.cm<sup>-1</sup> appears as a strong absorption band in UF adhesive emulsion, while in the cured adhesive its intensity decreases and shifts to a higher frequency of 1559.cm<sup>-1</sup>. The observed frequencies can be attributed to amide II absorption band, which originates from mechanical coupling of C-N stretching and N-H deformation modes (Cannon 1960). This absorption band is characteristic for secondary, non-cyclic (linear) amides, found at the region of 1510-1550.cm<sup>-1</sup> in solution spectra and at 1515-1570.cm<sup>-1</sup> in solids (Bellamy 1975). In addition, observed frequencies have very good agreement with the resulting spectra found in earlier research on UF polymer system, having this band at the range of 1550-1560.cm<sup>-1</sup> (Mayers 1981). Weak band at 1384.cm<sup>-1</sup> in emulsion, becomes sharp and strong after cure. The band with similar characteristics and in the range of 1360-1400.cm<sup>-1</sup> was observed in the recent work on UF adhesive curing (Zorba et al. 2008), while in earlier investigation on the same type of adhesive, this band had medium intensity, slightly decreased in solid state (Mayers 1981). Since this area of UF polymer spectra is usually assigned to C-H mode in CH<sub>2</sub> and CH<sub>3</sub> structures it allows some very interesting considerations when comparing older UF adhesives with the actual adhesives having low formaldehyde to urea mole ratio. Early formulations of UF adhesives used in PB and MDF production did not consider subsequent addition of urea at the end of UF resin synthesis. Addition of urea is characteristic for today's E-1 class UF adhesives. As a matter of fact, this urea starts to react in the curing process (i.e. in the hot press), creating again mono-, di- and trimethylolurea derivatives and acts as a scavenger for free formaldehyde. Methylol derivatives of urea are characterized with high quantity of methylol  $CH_2OH$  groups. Therefore, this band may indicate subsequent addition of urea.

### Region from 1000-1260.cm<sup>-1</sup>

Medium band at 1256.cm<sup>-1</sup> appeared in our spectra of UF adhesive emulsion. It became very strong after cure and slightly shifted to a lower frequency of 1249.cm<sup>-1</sup>. This seems to be characteristic for the new type of UF adhesive (Zorba et al. 2008). Comparing with the former types of UF adhesive, it is having high FA: Urea mole ratio, it is obvious that the band in this region showed medium intensity and disappeared during cure (Chow and Steiner 1975, Mayers 1981). This presents one more distinguished characteristics when comparing new types of E-1 class UF adhesives with the older ones. Concerning the assignment of the observed band, it can be attributed to amide III structure of secondary amides. Band at 1136.cm<sup>-1</sup> appears weak in emulsion spectrum and strong in the spectrum of cured adhesive while shifted to the higher frequency of 1160.cm<sup>-1</sup>. This band might be attributed to both C-O stretching in aliphatic ethers and C-N stretching modes (Bellamy 1975). In the earlier research of UF polymer spectra this band was absent (Mayers 1981). Strong band at 1013.cm<sup>-1</sup> remains strong after cure and becomes sharp at 1038.cm<sup>-1</sup>. In the vicinity of these wave numbers strong band at 1020.cm<sup>-1</sup> appeared in emulsion spectrum of older type of UF adhesives (Mayers 1981), and decreased to medium intensity during cure, while shifting simultaneously to higher frequency of 1040.cm<sup>-1</sup>. This band might be attributed to wide variety of modes in UF spectra (Mayers 1981, Bellamy 1975). Most probably those bands originated from combined methylol C-O stretch and amide C-N stretch modes. This might be another confirmation of subsequent addition of urea in the new types of UF adhesives, pointing on repeated formation of starting olygomers.

Region below 1000.cm<sup>-1</sup> has not been thoroughly examined here. Yet, the interesting band at 647.cm<sup>-1</sup> appeared after cure. The NH deformation mode presents the most probable origin of this band.



Fig. 1: FT-IR spectrum of urea-formaldehyde adhesive emulsion.



Fig. 2: FT-IR spectrum of cured urea-formaldehyde adhesive.

## Influence of the catalyst content on the curing of the UF adhesive

Ammonium chloride (NH<sub>4</sub>Cl) is a commonly used catalyst for UF adhesives designed for the production of particle-board or medium density fiber-board. In order to evaluate its catalytic influence on the curing of UF adhesives, DSC scans with different amounts of NH<sub>4</sub>Cl were run. These scans were performed on adhesive without the addition of wood flour. The DSC scans of the changes of the heat content as the curing reaction progresses at a heating rate 10°C.min<sup>-1</sup> are given in Fig. 3. This figure further presents the influence of the NH<sub>4</sub>Cl content on the curing reaction of the UF adhesive.



Fig. 3: C curves for the curing of UF adhesives with different catalyst  $NH_4Cl$  concentrations obtained at a heating rate at 10 .min<sup>-1</sup>.

Acting as the catalyst in the UF adhesive system,  $NH_4Cl$  reacts with free formaldehyde (and to a lesser extent with methylol groups), forming hexamethylene tetramine, hydrochloric acid and water. The hydrochloric acid lowers the pH of the system thus creating favorable acidic conditions for the polycondensation reaction and final curing of the UF adhesive, which

is significantly accelerated by heat. In the DSC scans (Fig. 3), the curing reaction of the UF adhesive is represented by an exothermic region with a single peak. As expected, the exothermic peak was shifted toward lower temperatures with increasing of  $NH_4Cl$  concentration. On the other hand, the catalytic effect of  $NH_4Cl$  dramatically decreased when its content reaches 0.6 % (based on the adhesive dry content), especially at levels of 1.0 % and more. This is presumably because of the limited quantity of free formaldehyde available for the cross-linking reactions, in the new formulation of E1 class of UF adhesive. In addition, with increasing NH<sub>4</sub>Cl content, the most reactive groups of the adhesive were activated. This leads to the conclusion that after a certain level, further addition of NH<sub>4</sub>Cl is not effective. Based on the obtained thermograms, it was concluded that the critical content of  $NH_4Cl$  catalyst is between 0.6 % and 1.0 %, which roughly concurs with literature data for this new formulated type of adhesive (Gao et al. 2008). When the temperature reaches the region between 135 and 140°C (above the exothermic curing process), an endothermic reaction can be noticed. This may be assigned to a certain amount of degradation of the urea polymer, as this temperature level coincides with the melting temperature for urea, which occurs at a temperature of 132°C. As a mean of lowering formaldehyde emission, urea itself is usually subsequently added at the end of synthesis of UF resins, thus acting as a scavenger for free formaldehyde. Non-reacted, low molecular weight methylol derivatives might be the cause of the endothermic reaction, which, in this particular case, seems to have no effect on the main curing reaction. Subsequent rescans showed no endothermic process, thus confirming former assumption. The  $NH_4Cl$  addition reduced the peak temperature but only slightly reduced the reaction enthalpy ( $\Delta H$ ). The relevant results are given in Tab. 1.

NH <sub>4</sub> Cl content (% based on the dry adhesive content)	Curing peak temperatures T <sub>p</sub> (°C)	Enthalpy of curing reaction ΔH (J.g <sup>-1</sup> )	
0.2	94.6	151	
0.6	88.6	147	
1.0	87.0	141	
1.5	86.1	139	
2.0	85.7	141	

Tab. 1: Data for the obtained peak temperatures and reaction enthalpies for adhesive curing (without wood flour) in presence of different content of  $NH_4Cl$  catalyst.

#### Influence of wood flour on the curing reaction of the UF adhesive

The influence of wood species on curing behavior of the UF adhesive was evaluated by dynamical scanning at different heating rates (5, 10, 15 and  $20^{\circ}$ C.min<sup>-1</sup>). This allowed for calculation of activation energy ( $E_a$ ) for each test sample (pure adhesive and three samples of adhesive with wood flour).  $E_a$  was calculated based on the variation of the peak temperature as a function of the heating rate for a relevant set of DSC curves. The increase of the heating rates shifted the exothermic peak of the DSC scans to higher temperatures. The analytical method adopted by Kissinger (1957) was used for the calculation of the activation energy. With increasing temperature, the reaction rate rise to a maximum value and returns to a zero as the reactant is exhausted. If assumed that the peak temperature on the DSC scan is equal to a temperature where reaction rate is at its maximum, then the Kissinger equation can be expressed in the form:

$$-\ln\left(\frac{\beta}{T_{\rm p}^2}\right) = \frac{E_{\rm a}}{R \cdot T_{\rm p}} - \ln\left(\frac{A \cdot R}{E_{\rm a}}\right)$$

where: T - temperature (K), R - gas constant (8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>) and  $E_a$  - activation energy (kJ.mol<sup>-1</sup>),  $\beta$  is the heating rate,  $T\beta$  is the peak temperature (K), A is the pre-exponential factor (s<sup>-1</sup>).

It is possible to calculate the activation energy  $(E_a)$  from the slope of the straight line  $-\ln(\beta/T_p^2)$  vs.  $1/T_p$ . The same method was used in some previous analyses of curing reactions of UF resins (Mizumachi 1973, Xing et al. 2005, Kim et al. 2006, Gao et al. 2008).



Fig. 4: DSC thermograms for the curing of the UF adhesive and its mixes with wood flour obtained at a heating rate of 10 °C.min<sup>-1</sup> in the presence of catalyst NH<sub>4</sub>Cl (0.2 %).

The most apparent influence of the presence of wood flour was an increase of the peak temperatures of the curing reaction. This holds for all wood species used in this study and is consistent for all employed DSC heating rates. Typical DSC scans for adhesive alone and its mixtures with wood flour, obtained at a heating rate of 10°C.min<sup>-1</sup> are shown in Fig. 4. At this rate, the exothermic peak for the UF adhesive alone was at 94.6°C, while the addition of poplar wood flour resulted in a peak temperature of 100.2°C.

The results of the determination of the activation energy  $(E_a)$  are given in Tab. 2. It is obvious that the  $E_a$  is slightly affected by the addition of wood flour. Possibly, increasing the content of wood flour might yield more significant differences.

Interestingly, the UF adhesive mixed with poplar wood flour resulted in the lowest  $E_a$  (71.0 kJ.mol<sup>-1</sup>), while the highest  $E_a$  was obtained for the system with beech wood flour (77.2 kJ.mol<sup>-1</sup>). Such results for the  $E_a$  contradict the previous results for  $T_p$ , which suggested that poplar wood retarded the curing process the most. This could be due to the physical properties and structure of the wood species. The density of beech wood (0.65 g.cm<sup>-3</sup>) is almost twice that of poplar (0.34 g.cm<sup>-3</sup>). Although the same amount of wood flour per unit weight was added, both the volume and the specific surface of the added particles differed significantly. Therefore, the  $E_a$  results for the UF adhesive mixed with poplar wood flour might have been more affected by adsorption processes, which masked the influence of wood extractives to some extent. Phase change may also influence the curing reaction. The homogeneous solution of UF adhesive when mixed with wood flour becomes a heterogeneous system and the phase will change from a continuous to a dispersive one. Presumably, the UF adhesive may disperse on many spots on the surface of wood flour. The curing reactions of each spot will progress as for the bulk UF adhesive, but they will not be able to link effectively with each other (He and Riedl 2004).

	Peak temperature T <sub>p</sub> (°C)				Function	Energy of activation $E_a$
Heating	5	10	15	20	i unction	
rate	(°C.min <sup>-1</sup> )					(kJ.mol <sup>-1</sup> )
UF adhesive	85.6	94.6	101.3	105.0	y = 8.83x - 14.46 $R^2 = 0.998$	73.4
UF + beech	87.8	97.8	102.7	106.8	y = 9.28x - 15.54 $R^2 = 0.9978$	77.2
UF + fir	87.5	97.1	103.6	107.0	y = 8.85x - 14.37 $R^2 = 0.9978$	73.6
UF + poplar	89.8	100.2	106.2	110.6	y = 8.54x - 13.34 $R^2 = 0.9997$	71.0

Tab. 2: Peak temperatures and activation energy for the curing reaction of UF and UF/wood flour mixes obtained by DSC measurements at different heating rates.

Another possible cause affecting  $E_a$  could be attributed to wood extractives. The extractives of acidic wood species may accelerate the curing reaction by lowering pH value of the UF adhesive when it is mixed with wood flour. On the other hand, extractives from alkaline wood species may buffer the acid (HCl) generated by the addition of NH<sub>4</sub>Cl catalyst. Furthermore, some extractives, such as tannin, may react with free formaldehyde, needed for the cross-linking reactions in the adhesive. Those assumptions regards the curing of UF adhesive on more or less developed sorption surface of wood furnish which can result in different curring kinetics and where wood tissue anatomy might have its own influence. Noncompliance of the  $E_a$  results in regard to results of peak temperatures present interesting point for further research.

# CONCLUSIONS

Influence of wood species on UF adhesive curing could not be observed by IR spectra for the given ratio of wood flour addition used in this research. On the other hand, IR spectra of both UF adhesive emulsion and cured UF adhesive have shown distinctive bands in comparison to IR spectra of older types of UF adhesives. Especially, the strong bands at 1389, 1249 and 1038.cm<sup>-1</sup> in IR spectra of cured UF adhesive could be used to reveal the subsequent addition of urea, as a common procedure in new types of UF adhesives having low formaldehyde to urea mole ratio.

DSC scans have shown that the addition of wood flour increased the temperature of the exothermic peak of the UF curing reaction for all studied wood species. The highest peak temperature of the curing reaction was attained by the addition of poplar flour, for all heating rates, having a mean value of 100.2°C, registered under a heating rate of 10°C.min<sup>-1</sup>. The UF adhesive alone (without wood flour) had the lowest peak temperature of 94.6°C, under the same heating regime. According to peak temperatures, poplar wood flour had the most retarding effect on the curing. The activation energy was the lowest for the UF adhesive with poplar wood flour (71.0 kJ.mol<sup>-1</sup>). The results obtained from this investigation could be of crucial importance for the hot-pressing process in the production of particle-board or medium density fiber-board panels. Even small adjustments in the press parameters, such as processing time and/or temperature, have a significant economic impact, especially in modern high capacity plants.

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