

# Curing kinetics of two commercial urea-formaldehyde adhesives studied by isoconversional method

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## Abstract

Differential scanning calorimetry (DSC) was used to evaluate the curing kinetics of two commercial urea-formaldehyde (UF) adhesives having different formaldehyde to urea (F/U) ratio of 1.112 (UF1) and 1.086 (UF2). DSC measurements were done in dynamic scanning regime with heating rates of 5, 10, 15 and 20 °C/min in order to determine the activation energy for each adhesive. Obtained data were analyzed using isoconversional methods with application of Ozawa–Flynn–Wall and Kissinger–Akahira–Sunose kinetic models. In addition, different catalyst levels were tested at the heating rate of 10 °C/min. The results showed that the adhesive with higher F/U ratio achieved higher activation energy, while having lower peak temperature of curing reaction. It was also noticed that the increase of catalyst level influenced the increase of reaction enthalpy of the adhesive with lower F/U ratio.

**Keywords:** UF adhesives; curing kinetics; DSC method; isoconversional models.

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Urea-formaldehyde (UF) resin presents the favorite adhesive system for the production of interior grade wood based panels, such as particleboards and medium density fiberboards used for furniture, cabinet making and interior construction elements. For example, in the European Union and Norway this area of wood industry utilizes approximately 95% of total UF resin consumption, which amounts to more than 5 million metric tons of UF resins per year [1]. Its relatively low costing, and excellent processing features enable the production of panels with required performances and competitive price. The main characteristics of UF resins are their high reactivity and water solubility, which make them very suitable for industrial use. On the other hand, the reversibility of aminomethylene link causes in poor resistance to moisture and water, especially at higher temperatures, thus preventing the use of UF resins for the exterior applications.

In chemical terms, the UF resin is a duromer and belongs to the group of thermosetting aminoplastic resins produced by condensation reactions between its main components, urea and formaldehyde (FA). The reactions between urea and FA are very complex and by applying different reaction conditions and preparation procedures, a variety of condensed structures can be formed [2,3]. This allows a specific tailoring of UF resin

in order to meet the requirements of different processing regimes in wood based panels manufacturing. Its synthesis generally proceeds in two stages. The first stage is usually an alkaline methylation performed at initially high formaldehyde to urea (F/U) mole ratio (1.8–2.5). It is followed by polycondensation reactions, which for practical purposes occur in acidic conditions at a pH value of 4.5–5.0. These reactions involve methylolureas, urea and free FA still present in the system, resulting in a linear and partially branched polymer. Subsequent addition of urea usually proceeds in one or more steps during the acid condensation stage. Finally, the reaction mixture is cooled down and neutralized at pH 7–8 and the water is removed in order to adjust the resin solid content to about 67–69% [4]. Such resin is still soluble in water and ready for use in particleboard and fiberboard factories. During its application, *i.e.*, consolidation of resinated mat in the hot press, the polycondensation reaction proceeds also in acid conditions, resulting in the formation of three-dimensional network in cured UF resin.

In 1970s, the problem of subsequent FA emission from the boards bonded with UF resin has become a matter of increasing ecological concern. The first actions towards limiting of FA emission were taken in the USA by national agencies such as Housing and Urban Development (HUD) and the Environmental Protection Agency (EPA), which mostly affected the particleboard industry at that time. This was followed by the introduction of ecological classes of the produced panels, with the emission levels regulated within the national

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and international standards. Today, the E1 class is mandatory in the most countries of the world. There are several factors that cause the FA emission from the boards bonded with UF resins. FA can be found inside the board structure as a trapped gas or dissolved in water (moisture content of the board). Another cause is the hydrolysis of weakly bonded FA from amino-methylene groups. Also, methylene ether bridges can rearrange into the methylene bridges by splitting the FA. All these factors present the major sources and generative processes for long term FA emission.

The task of decreasing the FA emission was partially dealt within the panel industry, through the processing innovations and improved manufacturing controls. Yet, the main challenge had to be taken by the producers of UF resin. One of the most prominent solutions for the FA emission was to lower the F/U molar ratio. Nowadays, it is common practice to add monomeric urea acting as a scavenger of free or weakly bonded FA during adhesive cure. The problem with this approach lies in the fact that the properties of UF resin are significantly affected by F/U ratio [5]. Lowering this ratio results in lower reactivity of the resin and thus decreasing production efficiency or products performances. In practice, this solution proved to be successful through constant improvements of UF resin technology. Initially, the F/U mole ratio was lowered from 1.6 to 1.25 in 1980s [4]. Today, this ratio can be low as 1.08 to 1.03 but with the same resin performances required by wood based panel's producers [2]. The resilient competitiveness of UF resin on the World market is the result of constant strive towards the improvements in its performances and presents the unique benefit of numerous research and development activities. On the other hand, it offers a wide area of applicative research, always actual and necessary for the characterization of resin performances.

One of the methods that are thoroughly used in the characterization of resins is differential scanning calorimetry (DSC). From its introduction during 1960s, DSC has become one of the most popular techniques in thermal analysis. Amongst its various applications in polymer science, DSC provides easy and fast kinetic evaluation of curing reaction of thermosets. The onset temperature, temperature at exothermic or endothermic peak, slope of the upward curve and enthalpy of the reaction are all readily accessible through the instrument software. In addition, various methods are developed for the calculation of activation energy of curing reaction obtained from DSC scans [6–10]. DSC method can provide valuable data both for the UF resin producers and consumers. For instance, the assessment of resin performances through DSC measurements can be very useful for optimizing the processing parameters in the hot press operation, which presents

the crucial stage in particleboard and MDF production lines. During one press cycle, the wood furnish blended with resin, consolidates into the final panel product under increased pressure and temperature. At the same time, there are many phenomena that occur inside the panel, such as the heat and mass transfer, mechanical deformation of wood component and the chemical reaction of the resin. Their intensity and interaction may significantly affect the properties of produced panels. In that aspect, the understanding of resin behaviour during cure in the hot press can assist in the process simulation and improve production efficiency, also reducing the need of costly trial and error tests.

This work was aimed at the investigation of curing kinetics of two commercial UF adhesives used in particle board production. Having in mind that the particle board producers are the leading consumers of UF resins, it makes such investigations very actual. In addition, it was interesting to evaluate the application of isoconversional methods in analysis of DSC data and thus to achieve a more accurate insight on curing kinetics of tested UF adhesives.

## EXPERIMENTAL

### Materials

Two commercial UF adhesives having different formaldehyde to urea (F/U) mole ratio were obtained from Nafta-Petrohem, Lendava, Slovenia. For the purpose of this research they are designated as UF1 and UF2. The F/U mole ratio of UF1 adhesive was 1.112, while UF2 adhesive had a slightly lower F/U ratio of 1.086. General characteristic of these two adhesives are given in Table 1. In addition, the results of the gel time tests are shown in Figure 1. Ammonium chloride (NH<sub>4</sub>Cl) was used as the catalyst (pro-analysi powder, Alkaloid, Skopje, FYRM), both for the purpose of DSC measurements and for the gel time tests.

Table 1. General characteristics of UF1 and UF2 adhesives

Property	UF1	UF2
Solid content, %	67.54	66.25
Viscosity at 20 °C, mPa s	545	455
Density, kg m <sup>-3</sup>	1303	1335
pH Value	8.16	7.83

Gel time was determined on UF adhesives emulsion diluted to 50% solid content and with the catalyst addition ranged from 0.2 to 2% per weight. The test tube filled with approx. 2 g of prepared 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 gel time for a given adhesive sample. The results of

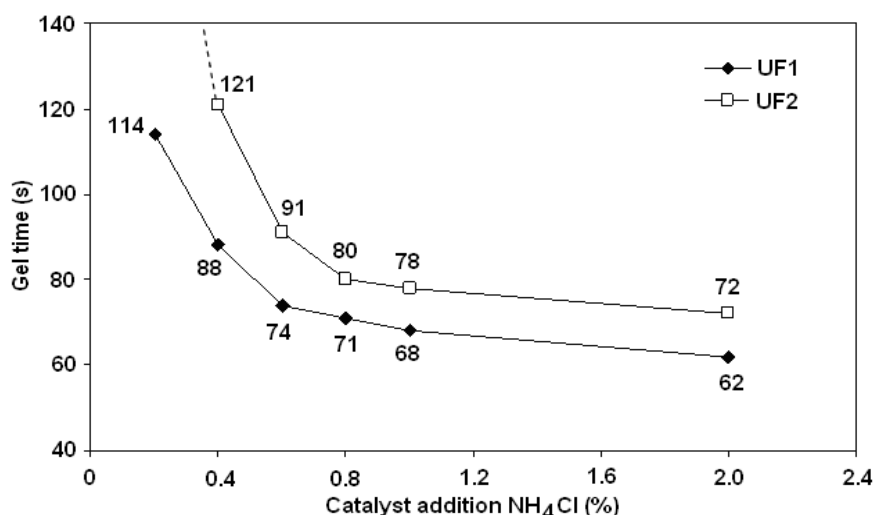


Figure 1. Influence of the catalyst amount on the gel time of the UF1 and UF2 adhesives (at 100 °C).

the gel time tests at the temperature of boiling water (Figure 1) clearly show that the curing reaction of UF1 adhesive occurs faster than for the UF2 adhesive having lower F/U ratio.

#### DSC measurement

UF adhesive samples were diluted to the concentration of 50%. Addition of NH<sub>4</sub>Cl was 0.2 mass%, for all DSC measurements intended for evaluation of the activation energy for both UF adhesives. The curing reactions of the UF adhesives were monitored using 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 dynamical regime with different heating rates (5, 10, 15 and 20 °C/min) in the temperature range from 40 to 200 °C. Before the test run, the temperature of the heating block was equilibrated at 40 °C. The purge gas was nitrogen. Additionally, the catalyst influence on the adhesives curing was obtained with the following content of NH<sub>4</sub>Cl: 0.2; 0.6; 1.0; 1.5 and 2.0% and at the heating rate of 10 °C/min. 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 reaction enthalpy, and the peak temperature were determined using TA Universal Analysis software procedure.

#### Curing kinetics methods

At high reaction rate of resin curing, the isothermal DSC technique is not always suitable for the determination of kinetic data [11]. In addition, using simple methods for the calculation of single activation energy does not offer complete information about characteristics of the relevant curing process [12]. Therefore,

several methods were developed in order to obtain kinetic parameters of the curing reaction with the application of only dynamic DSC runs. The curing reactions of UF1 and UF2 adhesives were compared using model-free isoconversional methods of Ozawa–Flynn–Wall (OFW) and Kissinger–Akahira–Sunose (KAS), which proved to be suitable for the characterization of curing reaction of various thermosetting resins and adhesive systems [11–15].

The degree of curing reaction,  $\alpha(T)$ , was obtained from DSC measurements as proportional to the enthalpies of the exothermic events in the temperature range from 60 to 130 °C. The degree of curing reaction,  $\alpha(T)$ , is defined as:

$$\alpha(T) = \frac{\int_{T_0}^T (dH/dT) dT}{\int_{T_0}^{T_\infty} (dH/dT) dT} \quad (1)$$

where,  $dH/dT$  is the reaction enthalpy at an infinitesimal temperature,  $T_0$  the initial curing temperature,  $T_\infty$  final curing temperature, and  $T$  temperature at an arbitrary time.

The isoconversional methods employed in this work (OFW and KAS) are based on dynamic analysis by DSC. The equation of reaction rate, employed to study the kinetics curing of resin, can be expressed, in general as:

$$\frac{d\alpha}{dt} = k_0 e^{-Ea/RT} f(\alpha) \quad (2)$$

where  $k_0$  is the pre-exponential factor ( $s^{-1}$ ),  $Ea$  the activation energy ( $J mol^{-1}$ ),  $R$  the ideal gas constant ( $8.314 J mol^{-1} K^{-1}$ ),  $t$  the reaction time (s),  $T$  the temperature of reaction (K) and  $\alpha$  the degree of curing. By

introducing the heating rate  $\beta = dT/dt$  ( $K s^{-1}$ ) in Eq. (3), one obtains:

$$\beta \frac{d\alpha}{dT} = k_0 e^{-Ea/RT} f(\alpha) \quad (3)$$

In this way, the integral form of the rate equation can be expressed as:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^t k_0 e^{-\frac{Ea}{RT}} dt \quad (4)$$

Ozawa–Flynn–Wall isoconversional method was applied to calculate the kinetic parameters of resin mixtures curing from dynamic DSC curves. OFW method is based on the following expression:

$$\log \beta = A' - 0.4567 \frac{Ea}{RT} \quad (5)$$

and  $A'$  can be expressed as:

$$A' = \log \left[ \frac{k_0 Ea}{Rg(\alpha)} \right] - 2.315 \quad (6)$$

The isoconversional OFW principle is based on the assumption that the reaction rate at a given degree of conversion is only a function of the temperature. Therefore, for different heating rates at a constant degree of conversion,  $\alpha(T)$ , a linear relationship is observed by plotting  $\log \beta$  versus  $1/T$ , and the activation energy,  $Ea$ , is obtained as the slope of the straight line. Another expression similar to a proposal by Ozawa–Flynn–Wall was the Kissinger–Akahira–Sunose model, which is described by Eq. (7). In both cases, the conversion-dependence function ( $f(\alpha)$  or  $g(\alpha)$ ) are not required.

$$\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{RA}{Eag(\alpha)} \right) - \frac{Ea}{RT} \quad (7)$$

Therefore, if Kissinger's assumptions are correct, a plot of  $\ln(\beta/T^2)$  versus  $1/T$  (Eq. (7)) should be linear and the activation energy might be obtained from the slope ( $-Ea/R$ ).

## RESULTS AND DISCUSSION

Effects of catalyst (ammonium chloride) addition on kinetic parameters obtained under dynamic DSC runs at the heating rate of  $10^\circ C/min$  are given in Figures 2 and 3. Figure 2 shows the decrease of exothermic peak temperatures of curing reaction with the increase of the catalyst addition (in the range of 0.2–2.0%), for both UF1 and UF2 adhesives. It could be also noticed that the addition of ammonium chloride at the levels above 0.6–1.0% is not as much effective, which probably results in conditions when the most of the reactive groups of the adhesive were activated and when further addition of ammonium chloride only slightly affects the peak temperatures. Figure 2 also shows that the UF1 adhesive has lower peak temperatures in regard to UF2, suggesting to its higher reactivity. This is probably due to higher F/U ratio of UF1 adhesive, as it was found that the increase in F/U mole ratio increases the reactivity of UF adhesive [19].

Another interesting observation is the influence of catalyst addition on the reaction enthalpy presented in Figure 3. The curing reactions of UF resins are typically exothermic, so it can be assumed that the reaction enthalpy,  $\Delta H$ , will be proportional to the degree of conversion,  $\alpha$ , during the curing process. The increase of  $\Delta H$  with the increase of catalyst content was noticed in the previous research on UF adhesive cure and was explained by the catalyst effect on decreasing of pH value resulting in the increased adhesive reactivity [17]. Our results showed similar behavior for UF2 adhesive, but only at the lower levels of catalyst addition, up to 1%. Contrary, UF1 adhesive, having higher F/U molar ratio,

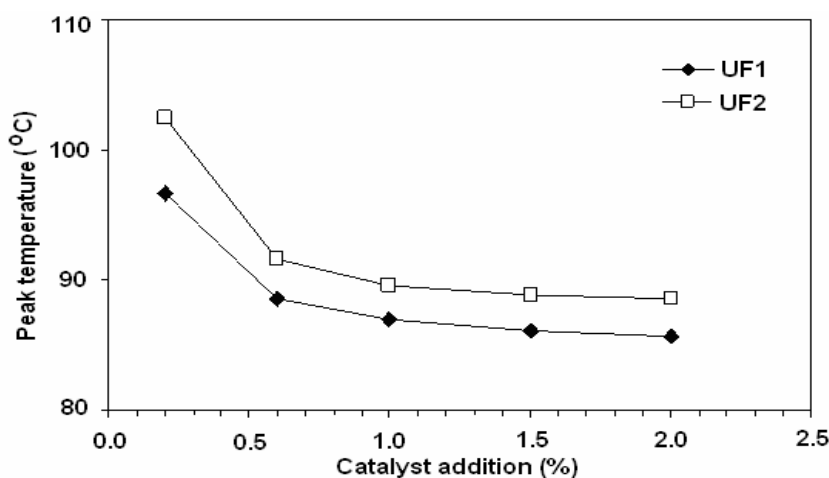


Figure 2. Influence of the catalyst amount on the peak temperatures of curing reaction for UF1 and UF2 adhesives, obtained by DSC runs at the heating rate of  $10^\circ C min^{-1}$ .

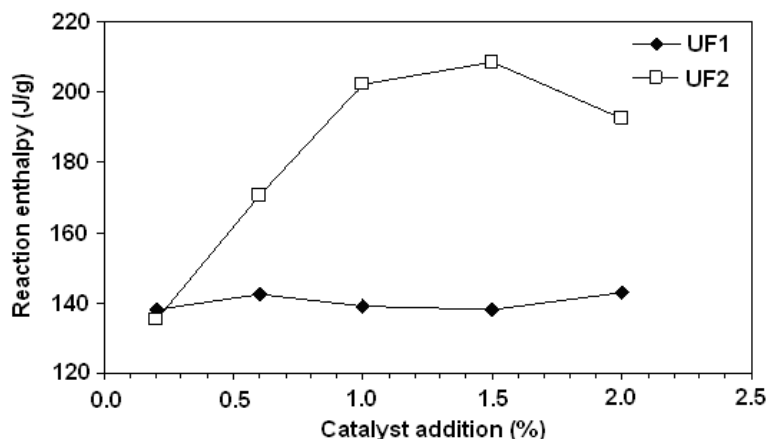


Figure 3. Influence of the catalyst amount on the reaction enthalpy during cure of UF1 and UF2 adhesives, obtained from DSC runs at the heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .

has shown no significant change in  $\Delta H$  in regard to catalyst addition.

In addition, UF1 adhesive has lower values of  $\Delta H$  in regard to UF2 adhesive for all levels of catalyst content, except for the lowest applied addition of ammonium chloride (0.2%), at which point no significant difference was noticed. This complex behavior of  $\Delta H$  might be further explained by the subsequent addition of monomeric urea into the resin. Presumably, the urea addition was higher for UF2 adhesive, which may result in the increase of the exothermic peak of reaction, as it was noticed in earlier research [5]. It also explains the lower F/U ratio of UF2 adhesive in regard to UF1.

Figure 4 presents the thermographs of UF1 and UF2

adhesives in dynamic scanning regimes at the discrete heating rates. Corresponding onset and peak temperatures ( $T_o$  and  $T_p$ , respectively) of the exothermic reaction are given in Table 2, as well as the activation energy,  $E_a$ , calculated using the simple Kissinger kinetic model [6].

DSC data (Table 2) clearly show that the curing reaction of UF1 adhesive occurs at the lower temperatures in regard to UF2 adhesive. Also, lower activation energy of curing reaction was obtained for the UF1 adhesive. Both the onset and peak temperatures, as well as activation energy, suggest that the UF1 adhesive has higher reactivity and can be regarded as a “faster curing adhesive”. The reason might be the higher F/U mole ratio of

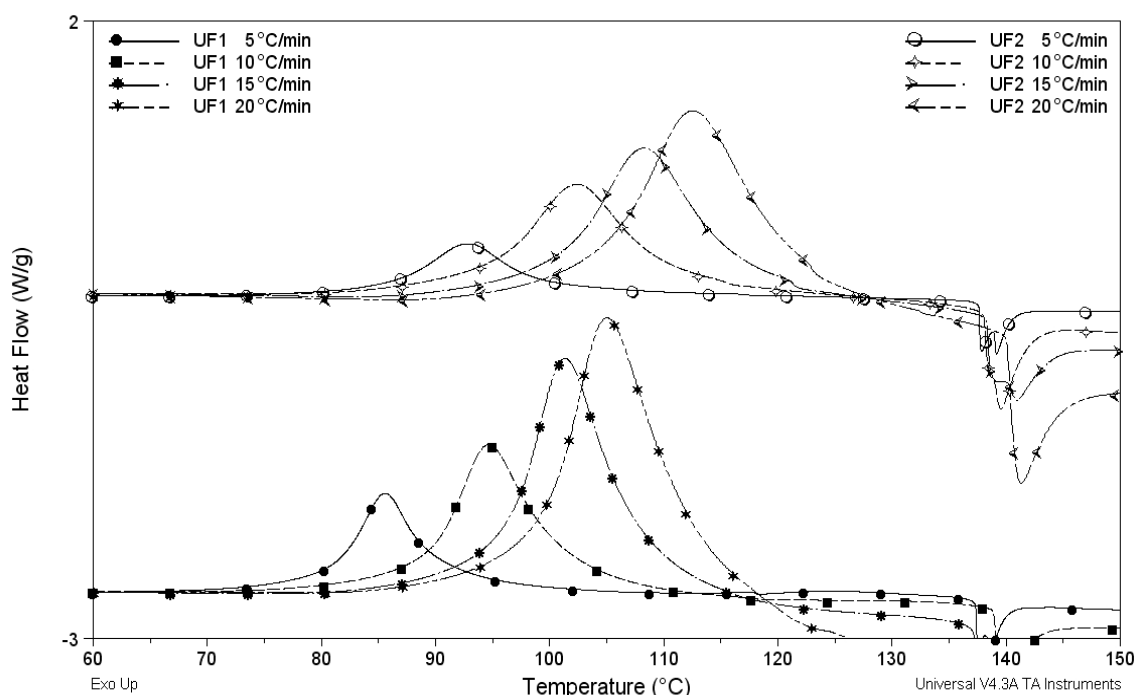


Figure 4. DSC dynamic scans of UF1 and UF2 adhesives recorded at the heating rates of 5, 10, 15 and  $20\text{ }^{\circ}\text{C min}^{-1}$ ; addition of  $\text{NH}_4\text{Cl}$  was 0.2% for all measurements.

Table 2. Onset, peak temperatures and activation energy for the curing reaction of UF1 and UF2 adhesives obtained by DSC measurements at different heating rates

Adhesive	Heating rate $\beta / ^\circ\text{C min}^{-1}$	Onset temperature $T_o / ^\circ\text{C}$	Peak temperature $T_p / ^\circ\text{C}$	Activation energy $E_a / \text{kJ mol}^{-1}$
UF1	5	80.72	85.62	73.35
	10	88.96	94.64	
	15	95.59	101.33	
	20	98.82	105.02	
UF2	5	85.63	93.13	77.71
	10	94.12	102.44	
	15	100.22	108.27	
	20	103.99	112.53	

UF1 adhesive in regard to UF2. The F/U ratio is one of the parameters that govern the resin performances, with its higher values favor the reactivity of the resin in general.

Except the exothermic peaks addressed to the curing reaction of UF adhesives, the Figure 4 also shows the presence of endothermic reaction occurring at the temperatures between 135 and 140 °C. Since the DSC measurements were conducted under the pressure, the apparent phenomenon might be addressed to a certain amount of degradation of the urea polymer, as this temperature level coincides with the melting temperature for urea. In earlier research, the endothermic reaction at 137 °C was addressed to decomposition of urea rings [18].

#### Application of isoconversional methods

The apparent curing degree curves of UF1 and UF2 adhesives versus temperature are shown in the Figures

5 and 6, where each curve presents different heating rate. Normally, the heating rate has a great influence on the curing process, with the exothermic peaks having lower temperatures at lower heating rates.

The application of the isoconversional methods requires the determination of the absolute temperature at which a fixed degree of curing from the several DSC curves is recorded at different heating rates. The conversion range between 0.05 and 0.95 was investigated. Accordingly, the data were analyzed by both Ozawa–Flynn–Wall (OFW) and Kissinger–Akahira–Sunose (KAS) isoconversional models, and the results are given in Tables 3 and 4, respectively.

The correlation coefficients of linear regression were very high, from 0.990 to 0.999. As, both OFW and KAS models show that the activation energy,  $E_a$ , de-

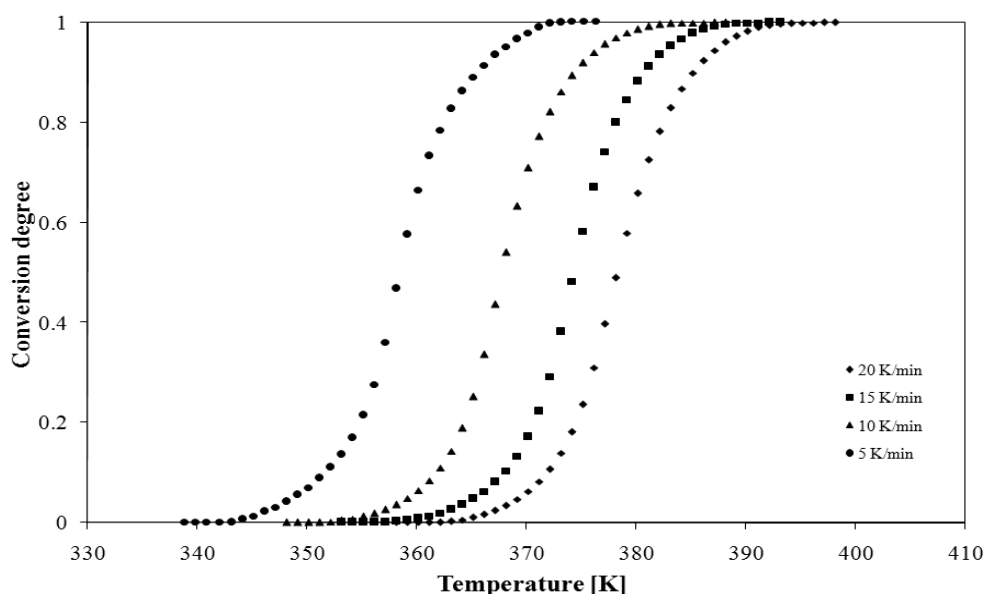


Figure 5. Conversion degree of UF1 versus temperature.

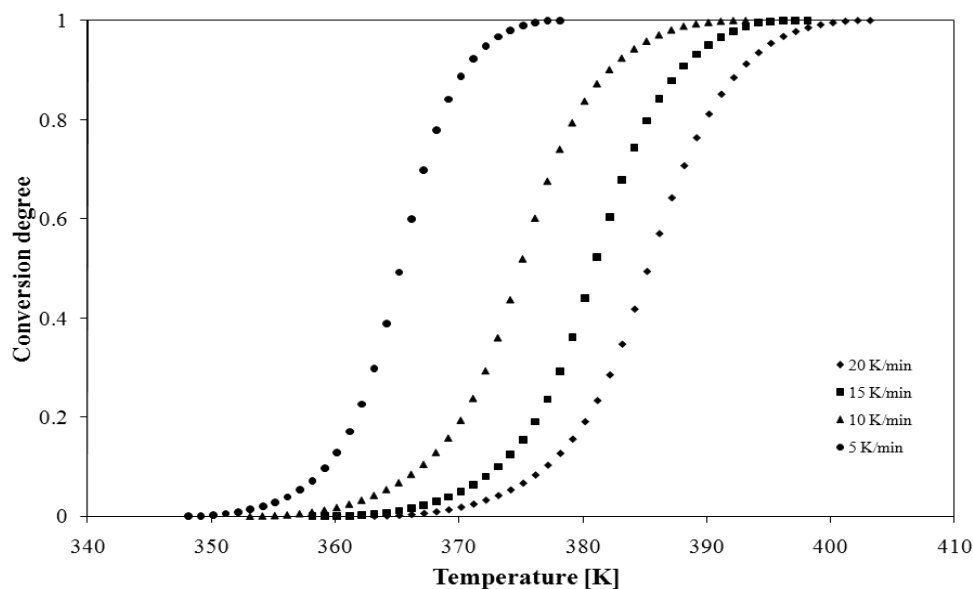


Figure 6. Conversion degree of UF2 versus temperature.

Table 3. Kinetic parameters of UF1 and UF2 curing at different conversion degrees determined by Ozawa–Flynn–Wall isoconversional method

$\alpha / \%$	UF1				UF2			
	$A'$	$Ea / \text{kJ mol}^{-1}$	$A$	$R^2$	$A'$	$Ea / \text{kJ mol}^{-1}$	$A$	$R^2$
5	11.44	68.25	-22.66	0.999	13.75	84.72	-27.77	0.991
10	11.69	70.42	-23.21	0.999	13.39	82.97	-26.97	0.996
20	12.07	73.47	-24.04	0.999	12.89	80.21	-25.83	0.999
30	12.16	74.35	-24.23	0.998	12.66	79.05	-25.31	0.999
40	12.12	74.30	-24.14	0.999	12.47	78.07	-24.90	0.999
50	12.11	74.45	-24.11	0.999	12.29	77.03	-24.49	0.999
60	12.04	74.19	-23.96	0.999	12.12	76.16	-24.12	0.999
70	11.98	74.00	-23.81	0.999	11.94	75.14	-23.71	0.999
80	12.16	75.61	-24.22	0.999	11.70	73.80	-23.17	0.998
90	12.50	78.47	-24.96	0.998	11.37	72.03	-22.44	0.997
95	12.72	80.48	-25.44	0.998	11.17	71.04	-22.00	0.995

Table 4. Kinetic parameters of UF1 and UF2 curing at different conversion degrees determined by Kissinger–Akahira–Sunose isoconversional method (KAS)

$\alpha / \%$	UF1		UF2	
	$Ea / \text{kJ mol}^{-1}$	$R^2$	$Ea / \text{kJ mol}^{-1}$	$R^2$
5	65.81	0.999	83.01	0.990
10	68.05	0.999	81.13	0.995
20	71.21	0.999	78.19	0.998
30	72.10	0.998	76.94	0.999
40	72.03	0.999	75.88	0.999
50	72.17	0.999	74.78	0.999
60	71.89	0.999	73.84	0.999
70	71.66	0.999	72.75	0.999
80	73.32	0.998	71.31	0.999
90	76.28	0.998	69.41	0.997
95	78.35	0.998	68.34	0.994

depends on the degree of curing reaction,  $\alpha$ , it was interesting to notice a different behavior of kinetic models between the adhesive systems used in this research. At the beginning of UF1 adhesive cure, the increase of reaction degree (crosslinking) up to 30% resulted in the increase of  $E_a$ . With the progression of curing reaction from 30 to 70%  $E_a$  remained at constant values, but increased again toward the end of curing reaction (Figure 7). This suggests that at the final stage of curing process of UF1 adhesive, the activation energy increases due to the diffusion-controlled reaction, rather than to follow the kinetic factor [13,16]. UF1 adhesive has slightly higher F/U mole ratio, but the DSC data clearly show its higher reactivity in regard to UF2 adhesive. This might influence the more intensive increase in molecular weight of UF1 adhesive during cure, which also might hinder the required mobility of the molecules with high degree of polymerization at the later stages of resin cure and thus increasing the activation energy.

of the curing reaction was  $73.4 \text{ kJ mol}^{-1}$  for UF1 and  $77.7 \text{ kJ mol}^{-1}$  for UF2 adhesive. Thus, it might be assumed that the UF1 has performed as a "faster" adhesive system, which in terms of wood based panel production may allow for shorter press cycles in regard to UF2 adhesive. Another interesting observation concerns the influence of catalyst level. The increase of catalyst addition resulted in the increase of the reaction enthalpy for the UF2 adhesive. Contrary, this influence was not registered for UF1 adhesive. For both UF adhesives, the optimal level of catalyst addition might be at 0.6 and 1.0% since its further increase has caused lesser effects.

KAS and OFW kinetic models showed similar curing patterns, but with slightly lower  $E_a$  values calculated by KAS method. The results imply that the  $E_a$  depends upon the conversion degree,  $\alpha$ . In that aspect, it was interesting to notice different behavior between the two tested adhesives. In general, the results for UF1 adhesive have shown the increase of  $E_a$  at the lower

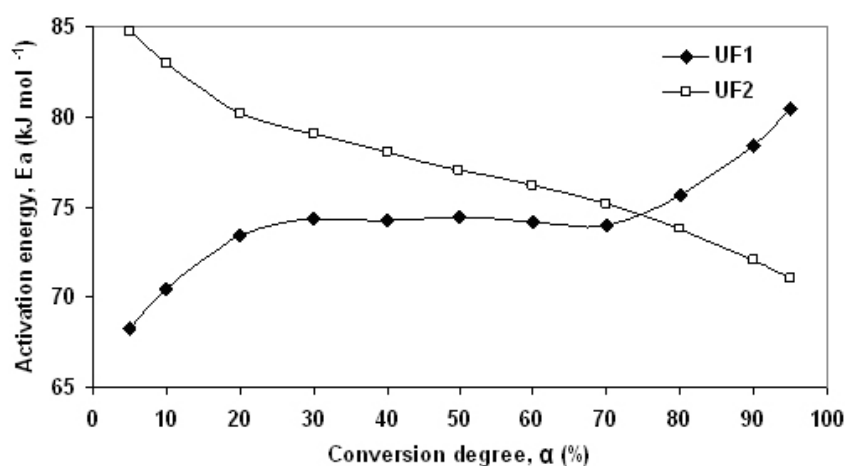


Figure 7. Activation energy dependence on degree of curing reaction for UF1 and UF2 adhesives (Ozawa–Flynn–Wall model).

Quite opposite behavior can be observed for the curing of UF2 adhesive. Its curing reaction starts at higher temperatures and its activation energy decreases as the curing process proceeds. The reason for such behavior of UF2 adhesive might be explained by its lower F/U ratio. This could probably influence the insufficiency of formaldehyde needed for both cross-linking reactions (amino-methylene links) and for the creation of hexamethylenetetramine and hydrochloric acid in the reaction with ammonium chloride as catalyst.

## CONCLUSIONS

UF1 adhesive, having higher F/U molar ratio of 1.112, showed significantly lower values of onset and peak temperatures compared to UF2 adhesive with 1.086 F/U ratio. In addition, the activation energy,  $E_a$ ,

and at the higher conversion degrees, while in the range between 30–70% no significant changes in  $E_a$  occurred. This might be explained by the presence of diffusion controlled reaction at the beginning and at the end of adhesive curing. On the other hand, the curing of UF2 caused constant decrease of  $E_a$ .

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## IZVOD

## IZUČAVANJE KINETIKE UMREŽAVANJA DVA KOMERCIJALNA UREA-FORMALDEHIDNA ADHEZIVA PRIMENOM METODE IZOKONVERZIJE

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Metoda diferencijalne skanirajuće kalorimetrije (DSC) upotrebljena je za određivanje kinetike umrežavanja dva komercijalna urea–formaldehidna adheziva sa različitim molskim odnosom formaldehida i uree (F/U). Merenja su obavljena u dinamičkom režimu pri brzinama zagrevanja od 5, 10, 15 i 20 °C·min<sup>-1</sup>. Na osnovu vrednosti temperature maksimuma na egzotermnom piknu DSC krive vidi se da adheziv UF1 umrežava na nižim temperaturama (adheziv sa višim molskim odnosom F/U), što odgovara nižoj izračunatoj vrednosti energije aktivacije,  $E_a$ , za isti adheziv koja iznosi 73,4 kJ·mol<sup>-1</sup> u poređenju sa 77,7 kJ·mol<sup>-1</sup> za adheziv UF2. Dobijeni podaci takođe su analizirani pomoću modela izokonverzije OFW (Ozawa–Flynn–Wall) i KAS (Kissinger–Akahira–Sunose). Oba primenjena modela ukazuju na uticaj stepena umrežavanja na energiju aktivacije, pri čemu je KAS kinetički model pokazao nešto niže vrednosti energije aktivacije. Zanimljivo je uočiti različito ponašanje ispitivanih adheziva tokom njihovog umrežavanja. Rezultati ispitivanja pokazuju rast energije aktivacije sa porastom stepena konverzije kod adheziva UF1, dok je konstantno smanjenje  $E_a$  tokom reakcije umrežavanja karakteristično za adheziv UF2. Pored navedenog, obavljena su DSC merenja pri različitom dodatku amonijum-hlorida kao katalizatora i pri brzini zagrevanja od 10 °C·min<sup>-1</sup>. Rezultati merenja ukazali su da povećanje dodatka katalizatora od 0,2 do 1,0% utiče na povećanje entalpije reakcije kod adheziva UF2, dok isti uticaj nije zabeležen kod adheziva UF1.

*Ključne reči:* UF adhezivi • Kinetika umrežavanja • DSC metoda • Modeli izokonverzije