Effects of Poly(diallyldimethylammonium chloride) addition on the curing kinetics of urea-formaldehyde adhesives for particleboards

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Abstract

Addition of poly(diallyldimethylammonium chloride) (PDDA) on the performances of urea-formaldehyde (UF) adhesives was evaluated in this work. Three types of UF adhesives were prepared, one without PDDA addition, and two types with PDDA addition of 1 and 3 wt.% per dry UF adhesive mass. These UF adhesive systems were used for producing experimental particleboard panels. The addition of PDDA decreased the thickness swelling of the panel samples, while the internal bond of the particleboards increased significantly only at the highest PDDA content (3 wt.%). Differential scanning calorimetry (DSC) was applied to address the influence of PDDA on UF adhesive curing kinetics. DSC scans were performed in non-isothermal regimes using different heating rates (5, 10, and 20 °C·min^{-1}). The activation energy (E_a) of the curing reaction showed slightly lower values for the UF adhesive systems containing PDDA. However, the peak temperatures and enthalpy of reaction did not change significantly. The Kissinger-Akahira-Sunose and Friedman iso-conversional methods were applied to investigate the effects of PDDA addition on the UF adhesive curing process.

Keywords: polyelectrolyte; thermoset adhesive; differential scanning calorimetry; iso-conversion method; properties of wood-based panels.

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1. INTRODUCTION

Poly(diallyldimethylammonium chloride) (PDDA) is a positively charged linear polyelectrolyte (Fig. 1), which can be regarded as both the conducting and ion exchange polymer. It is often used in water purification and wastewater treatment, as a coagulation and flocculation agent, as well as in a papermaking process as a pitch control and sizing agent.

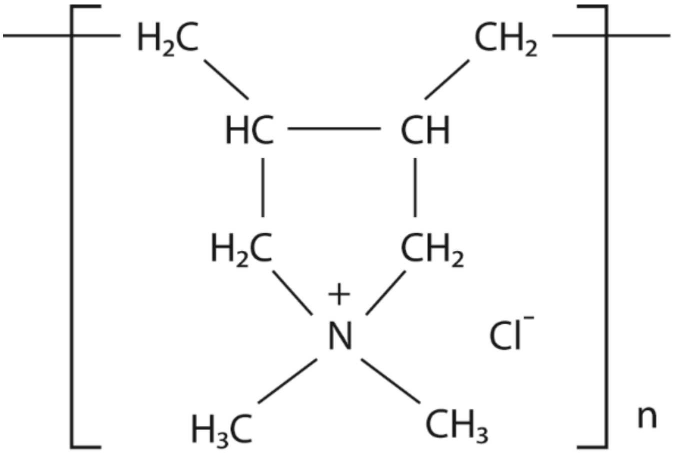

Figure 1. The chemical structure of poly(diallyldimethylammonium chloride) (PDDA)

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However, a growing number of studies have shown successful applications of PDDA in other areas. It can be a functional, reducing and stabilizing agent in the preparation of graphene based composites for use in highly selective electrochemical sensors for various substances, such as esculetin [1], 4-chlorophenol [2], paracetamol, and diclofenac [3], β-nicotinamide adenine dinucleotide [4] and levofloxacin [5]. PDDA is used as a dispersive agent to obtain supermagnetic Fe_3O_4/PDDA nanocomposites [6]. Furthermore, its application for enhancing anion exchange membranes has shown promising results in redox flow batteries [7] and microbial fuel cells [8,9].

Addition of PDDA is an efficient and simple method for improving adhesion between a coating and a substrate because it creates a nano-structural functional surface. Hence, it is used as a linking agent to prepare nanocomposite films based on lignocellulosic materials [10,11], PDDA/sodium-silicate films with superhydrophobic surfaces [12], and silver/PDDA nanocomposites [13].

Since the PDDA polymer consists of positively charged ammonium groups across its chain, it can adsorb onto negatively charged surfaces [14]. Conveniently, the main chemical constituents of wood consist of anionic groups, such as carboxyl acid groups and ionisable hydroxyl groups [15]. In papermaking industry, PDDA acts as a bridging agent, attaching the wood resin particles onto cellulose fibres [16]. Hence, it was interesting to investigate the ability of PDDA polymer to enhance the adhesion of wood particles in the process of particleboard production. Another goal of this work is to evaluate the effects of the PDDA addition on the curing reaction of urea-formaldehyde (UF) adhesives. The UF adhesive, itself, is still highly used as an adhesive in the wood-based panels industry, specifically for the production of interior classes of particleboards and fibreboards.

2. EXPERIMENTAL

2. 1. Materials

PDDA (Poly(diallyldimethylammonium chloride) solution, 409014, Sigma-Aldrich, St. Louis, USA) used in the present study had the molar mass of 8,000 g mol^{-1} and the pH value of the solution of 5.0 to 7.0. The basic characteristics of the commercial UF adhesive used in the present study were as follows: dry matter content was 66.92% [17]; viscosity was 432 mPa·s, determined by the rotational viscometer method [18]; pH was 7.98 [19] and density was about 1270 kg m^{-3} (determined in the present study by an areometer).

The UF adhesive was prepared with the addition of $(NH_4)_2SO_4$ (Superlab, Beograd), as a hardener, in the amount of 0.5 % dry weight per dry weight of the adhesive. Similarly, two UF adhesive mixtures with the PDDA polyelectrolyte were prepared with the same hardener addition. In this case, the polyelectrolyte solution was mixed directly with the UF adhesive first. The additions of PDDA to UF adhesive were 1.0 and 3.0 %, based on the dry weight of both components. The concentration of the UF adhesive and the UF adhesive systems with PDDA were lowered to 50 % by adding the distilled water during the adhesive preparation prior to the $(NH_4)_2SO_4$ addition.

Wood particles were obtained from the Kronospan factory in Lapovo (Serbia), presenting the fraction used for surface layers of industrially produced particleboard panels.

2. 2. Preparation of particleboard panels

Three types of experimental particleboard panels were made, distinguished only by the applied adhesive system: one type was made with the UF adhesive without PDDA addition (control), and two types were made with modified UF adhesives having 1 and 3 % of PDDA (per dry adhesive weight), designated here as UF-PE1 and UF-PE3, respectively.

The application of UF adhesive systems onto wood particles was performed in the laboratory blender equipped with the Multispray 940 nozzle (SCHLICK, Germany). The adhesive was added at the concentration of 10 % of dry adhesive per dry wood particles, for all panel types.

The experimental particleboards were produced in a laboratory hot press, under the maximum specific pressure of 2 N·mm^{-2}, and at the temperature of hot plates of 200 °C. All particleboard types had the nominal thickness of 9 mm, format of 450 × 450 mm, and the targeted density was 700 kg·m^{-3}.

Standard test methods were used to determine the following properties of experimental panels: moisture content [20], density [21], thickness swelling [22] and internal bond strength [23]. Dimensions of all test pieces were 50 × 50 mm × thickness. Total of 8 test pieces from a single panel were used for determination of the moisture content, while each of the other properties was evaluated by using 10 test pieces. Before each measurement, test pieces were conditioned to constant mass in the standard atmosphere (65 % and 21 °C) inside a desiccator with saturated solution of ammonium nitrate (NH_4NO_3). The analysis of variance (ANOVA) was used to compare the test results between the panel types. Statistical comparison was performed at the confidence level of 95 %.

2. 3. DSC measurements

Differential scanning calorimetry (DSC) was used to evaluate the time dependant thermal response of the adhesive systems. The tests were performed with a DSC Q20 instrument (TA Instruments, New Castle, DE, USA). All DSC scans were run in non-isothermal regimes, in the temperature range of 30 - 200 °C, and at the constant heating rates of 5, 10 and 20 $°C\cdot min^{-1}$, thus providing the values of heat flow ($W\cdot g^{-1}$) plotted against the temperature (°C). The instrument software (TA Universal Analysis, New Castle, DE, USA) was used for determination of the peak temperature and enthalpy. The methodology of DSC measurements is the same as described in the previous work [24].

2. 4. Iso-conversional methods

Model-free kinetic methods of Kissinger-Akahira-Sunose (KAS) and Friedman were applied to further analyse the data obtained from DSC measurements. Both methods follow the basic iso-conversional principle that the reaction rate ($d\alpha/dt$) at a certain conversion (α) depends on the temperature, and thus allowing the determination of the activation energy (E_a) as a function of conversion [25,26]. The KAS method uses the Coats-Redfern approximation and it is classified as the integral method [27,28], presented by the following equations:

$$\ln\left(\frac{\beta}{T^2}\right)=A'-\frac{E_a(\alpha)}{RT} \tag{1}$$

$$A'=\ln\left(\frac{AR}{E_a(\alpha)}\right)-\ln g(\alpha) \tag{2}$$

where β is the heating rate ($K\cdot min^{-1}$), E_a is the activation energy ($kJ\cdot mol^{-1}$), A is the preexponential factor and R is the gas constant. By using the multiple heating rates, the activation energy can be found from the slope of the straight line obtained by plotting $\ln(\beta/T^2)$ *vs.* $1/T$.

The Friedman method presents a differential iso-conversional method and does not use any mathematical approximation [27,29]. The relevant equations are given as follows:

$$\ln\left(\beta\frac{d\alpha}{dT}\right)=A'-\frac{E_a(\alpha)}{RT} \tag{3}$$

$$A' = \ln A + \ln f(\alpha) \tag{4}$$

The activation energy at a certain conversion $E_a(\alpha)$ can be obtained by linear regression after plotting the $\ln(\beta d\alpha/dT)$ *vs.* $1/T$ for different values of α [26].

Using data from non-isothermal DSC scans, the Friedman model was also applied for isothermal predictions, *i.e.* to predict the conversion rate of UF adhesive curing with time at the given temperature. Hence, the reaction time t_α at a certain degree of conversion α can be calculated according to Eq. 5 [28].

$$t_\alpha=\int_0^\alpha \frac{e^{\frac{E_a(\alpha)}{RT}}}{e^{A'(\alpha)}}d\alpha \tag{5}$$

3. RESULTS AND DISCUSSION

Basic properties of the experimental particleboards, such as the panel thickness, density and moisture content are given in the Table 1. The statistical evaluation of these results showed insignificant differences between the panel types, thus suggesting that the PDDA addition did not influence these properties.

Table 1. Thickness, density, and moisture content of experimental panels

Property	Control panel (UF adhesive)	UF-PE1 panel (UF + 1 % PDDA)	UF-PE3 panel (UF + 3 % PDDA)
Thickness, mm	8.80 ± 0.13	8.73 ± 0.12	8.77 ± 0.18
Density, kg·m^{-3}	723.6 ± 49.22	728.8 ± 29.13	731.8 ± 37.77
Moisture content, %	8.78 ± 0.24	8.83 ± 0.45	9.00 ± 0.24

ANOVA test did not find significant differences at the confidence level of 95 %

Results of the thickness swelling and internal bond strength are graphically presented in Figure 2 and are statistically compared in Table 2. Since paraffin (wax) was not used in the production phase, all of the panel types were characterised by remarkably high values of thickness swelling, clearly exceeding the upper limit of 17 %, as stated by the standard EN 312 for the P3 class of particleboards [30]. The statistical comparison between the panel types has shown a significant difference only between the control type and the panel type with the addition of 3 % of PDDA (UF-PE3). However, the general trend suggests that the thickness swelling decreases with the addition of PDDA.

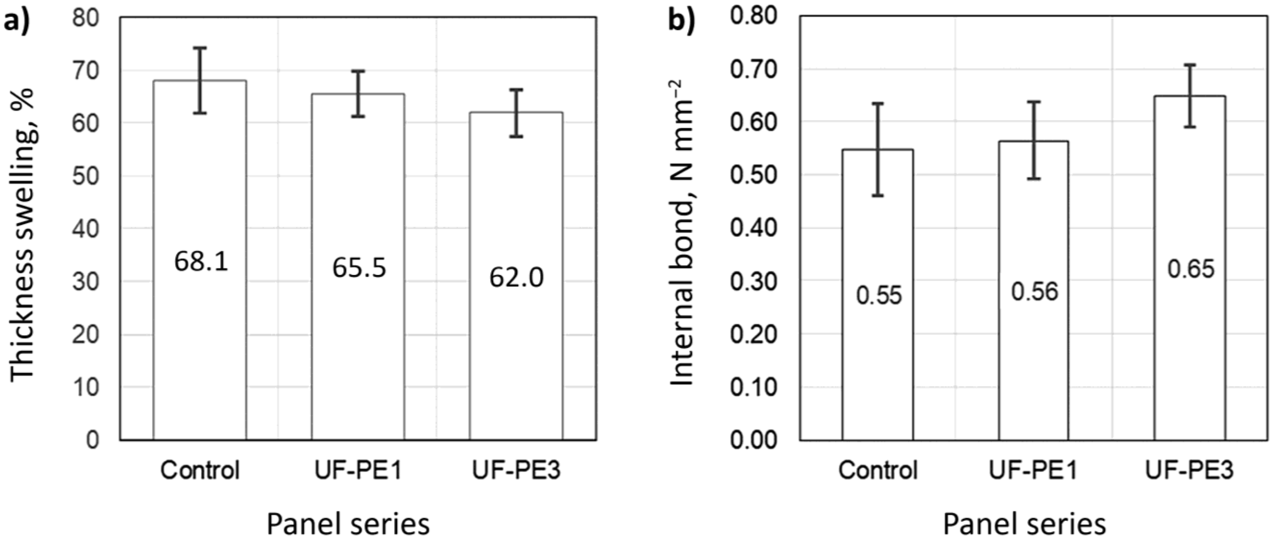

Figure 2. Thickness swelling (a) and internal bond (b) of the control panel and the panels made with UF adhesives containing 1% and 3% of PDDA (vertical error bars show standard deviations)

In contrast to thickness swelling, the internal bond test showed satisfactory results for all panel types. The internal bond strength values were well above 0,40 N·mm^{-2}, a minimum requirement for P2 class of particleboards according to standard EN 312 [30], for all specimens. Although significant differences were not found between the control type and the UF-PE1 panels, the statistically highest value was recorded for the UF-PE3 panel type (Table 2), which again suggests that the addition of PDDA had a beneficial effect in terms of the internal bond strength.

Table 2. Statistical comparison of the thickness swelling and internal bond values for the particleboards obtained with the control UF adhesive and the UF adhesive containing 1 % (UF-PE1) and 3 % (UF-PE3) of PDDA polyelectrolyte (per dry adhesive weight)

Property	Thickness swelling			Internal bond		
Between groups	*F*	*p*-value	*F* crit	*F*	*p*-value	*F* crit
Control / UF-PE1	0.9440	0.3477	4.6001	0.2002	0.6609	4.5431
Control / UF-PE3	5.2067*	0.0387	4.6001	8.3564*	0.0112	4.5431
UF-PE1 / UF-PE3	2.6001	0.1292	4.6001	7.5263*	0.0144	4.4940

*denotes a statistically significant difference at the confidence level of 95 %

3. 1. Curing kinetics of UF adhesive systems

Figure 3 shows the characteristic thermographs of DSC tests, performed in this research. The curing reaction of each UF adhesive system (the control UF adhesive, and the UF-PE1 and UF-PE3 adhesives, having PDDA contents of 1 and 3 wt.%, respectively) are presented by three distinct curves in regard to the heating rate (5, 10, and 20 °C·min^{-1}). The exothermal region of the curve, representing the curing reaction, shifts towards the higher temperature zone as the heating rate increases. In addition, the DCS curves also feature an endothermic region, occurring above the temperature of around 135 °C. This could be attributed to the melting and decomposition of urea which starts to occur at 133 °C [31].

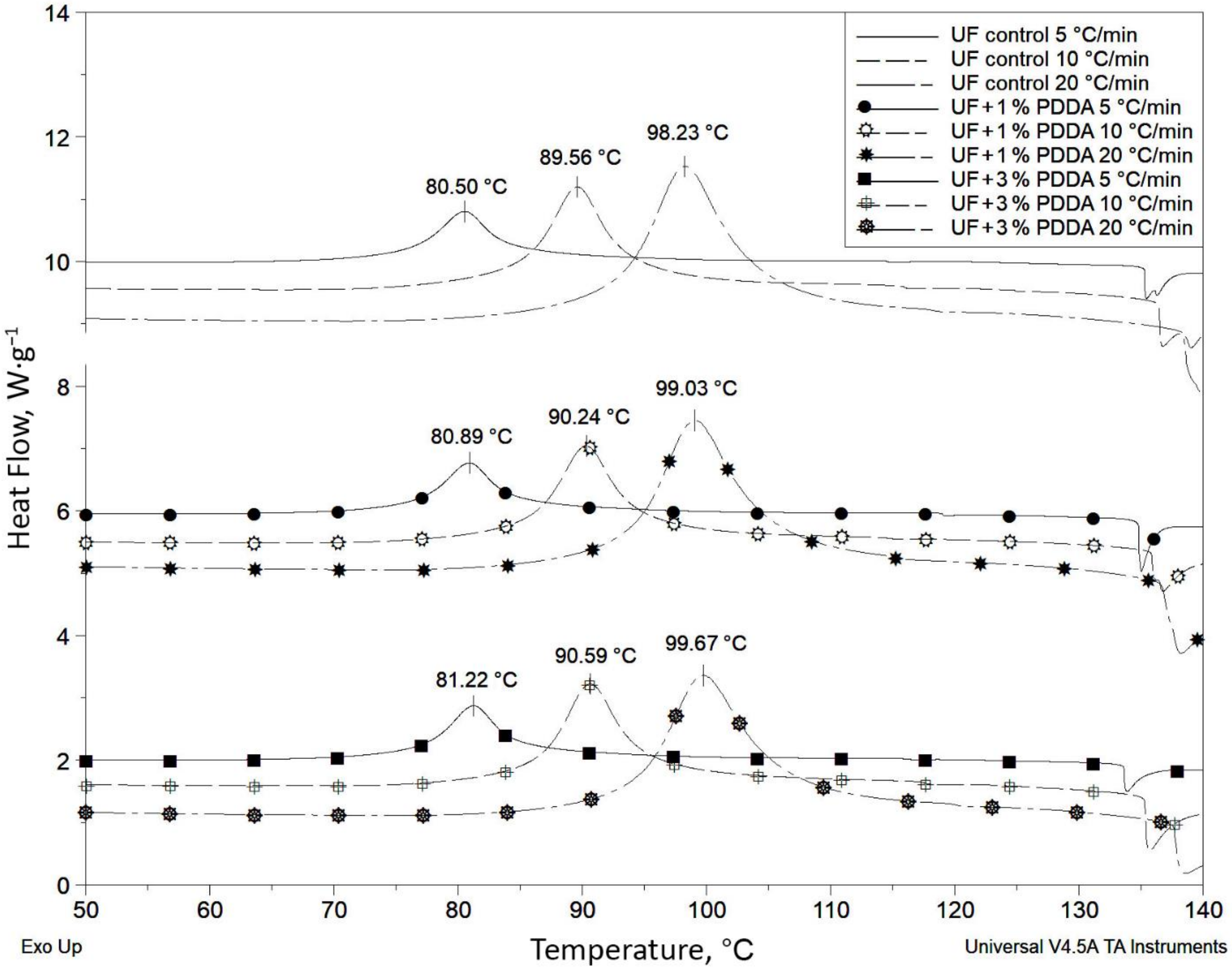

Figure 3. DSC thermographs of the curing reaction of pure (control) UF adhesive and the UF adhesives with PDDA contents of 1 and 3 wt.%, obtained at the heating rates of 5, 10 and 20 °C/min

Tables 3 and 4 present basic parameters of curing reactions of the control UF adhesive and its systems with PDDA. Peak temperatures of the curing reactions do not significantly differ between the UF adhesive types, as shown in Table 3. However, the apparent activation energy, calculated by the general Kissinger model, slightly decreases with the addition of PDDA.

Values for the enthalpy integrals in regard to the heating rate are given in Table 4. It is interesting to notice that the enthalpy of curing reaction decreases as the heating rate increases, which is observed for all of the UF adhesive types. This phenomenon might be attributed to the shorter reaction time available for the complete crosslinking of the adhesive at higher heating rates [28]. However, no apparent influence of the PDDA addition on the enthalpy integrals could be observed.

Table 3. Peak temperatures at different heating rates (β) and activation energy (E_a) of the curing reaction of the control UF adhesive and UF adhesives with PDDA contents of 1 wt.% and 3 wt.%

Sample	Peak temperature, °C			E_a / kJ·mol^{-1}	r^2
	β = 5 °C·min^{-1}	β = 10 °C·min^{-1}	β = 20 °C·min^{-1}		
UF (control)	80.5	89.56	98.23	79.29	0.9992
UF / 1 wt.% PDDA	80.89	90.24	99.03	77.60	0.9988
UF / 3 wt.% PDDA	81.22	90.59	99.67	76.44	0.9994

Table 4. Enthalpy (ΔH) of the curing reaction at different heating rates (β) of the control UF adhesive and UF adhesives with PDDA contents of 1 and 3 wt.%

Sample	ΔH / J·g^{-1}			ΔH / J·g^{-1}
	β = 5 °C·min^{-1}	β = 10 °C·min^{-1}	β = 20 °C·min^{-1}	
UF (control)	76.62	75.92	72.02	74.85 ±2.48
UF / 1 wt.% PDDA	75.31	71.34	67.47	71.37 ±3.92
UF / 3 wt.% PDDA	77.2	75.4	65.19	72.60 ±6.48

The selected iso-conversional methods were applied to determine the activation energy dependence on the conversion for the investigated UF adhesive systems. The results are given in Tables 5 and 6 as well as in Figure 4.

Table 5. Kinetic parameters of the curing reaction of UF adhesives obtained by the KAS iso-conversional model

α / %	UF control			UF-P1 (1 % PDDA content)			UF-P3 (3 % PDDA content)		
	E_a / kJ·mol^{-1}	r^2	A'	E_a / kJ·mol^{-1}	r^2	A'	E_a / kJ·mol^{-1}	r^2	A'
5	84.55	0.9999	-19.25	79.04	0.9991	-17.30	76.52	0.9995	-16.37
10	81.86	0.9999	-18.12	77.89	0.9992	-16.72	76.05	0.9995	-16.03
20	79.68	0.9999	-17.18	77.15	0.9994	-16.28	75.77	0.9996	-15.77
30	78.59	0.9999	-16.71	76.68	0.9994	-16.02	75.37	0.9997	-15.54
40	77.96	0.9999	-16.42	76.28	0.9995	-15.81	74.95	0.9998	-15.33
50	77.39	1.0000	-16.17	75.79	0.9997	-15.59	74.42	0.9999	-15.10
60	76.80	1.0000	-15.91	75.24	0.9999	-15.35	73.83	1.0000	-14.84
70	76.28	0.9999	-15.66	74.88	1.0000	-15.15	73.45	1.0000	-14.64
80	76.35	0.9994	-15.56	75.41	0.9999	-15.21	74.1	0.9999	-14.74
90	76.88	0.9976	-15.51	77.23	0.9989	-15.59	76.4	0.9997	-15.28
95	76.42	0.9954	-15.16	78.77	0.9979	-15.89	78.21	0.9997	-15.68

Table 6. Kinetic parameters of the curing reaction of UF adhesives obtained by the Friedman iso-conversional model

α / %	UF control			UF 1 % PE (1 % addition of PDDA)			UF 3 % PE (3 % addition of PDDA)		
	E_a / kJ·mol^{-1}	r^2	A'	E_a / kJ·mol^{-1}	r^2	A'	E_a / kJ·mol^{-1}	r^2	A'
10	69.78	0.9998	-26.49	72.36	0.9997	-27.32	73.65	0.9995	-27.78
20	69.61	0.9992	-26.95	73.49	0.9998	-28.24	74.35	1	-28.56
30	69.16	0.9998	-27.3	72.36	0.9999	-28.37	71.33	0.9998	-28.05
40	70.09	0.9998	-27.9	70.9	0.9998	-28.16	69.2	0.9985	-27.61
50	68.99	0.9975	-27.65	68.12	0.9975	-27.35	65.81	0.9975	-26.58
60	68.25	0.9914	-27.34	66.83	0.9912	-26.85	64.35	0.9956	-26.01
70	70.35	0.9817	-27.74	70.51	0.9857	-27.78	68.82	0.994	-27.19
80	77.23	0.9756	-29.47	79.89	0.9829	-30.33	79.84	0.9945	-30.27
90	79.71	0.9766	-29.47	85.87	0.986	-31.48	87.64	0.9976	-32.01
95	75.12	0.9734	-27.15	86.94	0.9892	-31.01	87.85	0.9994	-31.26

Application of the KAS method shows slight and uniform decrease of E_a as the curing reaction progresses until 80 % of the conversion. This pattern is similar for all UF adhesive systems, with the control UF adhesive achieving the highest E_a levels and the UF adhesive with 3 % of PDDA having the lowest E_a levels. After the conversion degree (α) of 80 %, both UF adhesive systems with PDDA exhibited a slight increase in the activation energy. In comparison to the KAS method, application of the Friedman method has shown quite different E_a dependences on the conversion for the investigated UF adhesive systems. All UF adhesive systems featured a steep increase of E_a after reaching 60 to 70 % of the conversion. The increase in E_a at the later stage of conversion is probably caused by the diffusion controlled reaction [32]. This increase was most noticeable for the UF adhesive systems with PDDA, and it was also depicted by the KAS method at the very end of conversion.

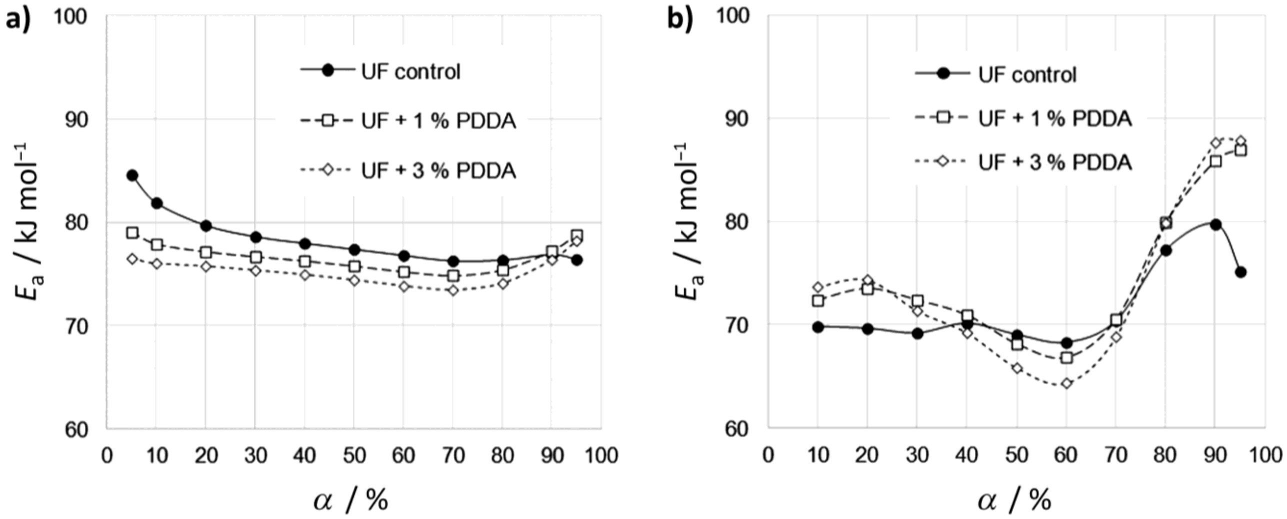

Figure 4. Energy of activation (E_a) dependence on the conversion (α) for different UF adhesives, according to KAS (a) and Friedman (b) iso-conversional models

The Friedman iso-conversional method was used to predict the curing mechanism at isothermal conditions (at the constant temperature), expressing the conversion degree (α) as a function of time. Hence, the Figure 5 presents predictions for the investigated UF adhesive systems at the curing temperatures of 60, 80, 100, and 120 °C. According to this model, the addition of PDDA seems to have different impacts on the curing behaviour of the UF adhesive at different curing temperatures. Thus, in regard to the control UF adhesive, the curing reaction of UF/PDDA systems was slower at lower temperatures (T_{iso} <80 °C), while having similar or shorter curing times at the temperatures above 100 °C.

4. CONCLUSION

The addition of PDDA into the UF adhesive showed positive effects concerning thickness swelling and internal bond strengths of experimental particleboards. Both of these properties were improved with the application of the higher PDDA content of 3 % per dry UF adhesive.

DSC measurements showed that the addition of PDDA into the UF adhesive did not affect significantly peak temperatures and enthalpy of the curing reaction. However, application of the general Kissinger model showed that the 3 % PDDA addition into the UF adhesive slightly decreased its activation energy to 76.4 kJ·mol^{-1} in comparison to 79.3 kJ·mol^{-1} determined for the control UF adhesive.

The dependence of activation energy on the curing degree for each of the UF adhesive systems was determined by application of the KAS and Friedman methods. Both methods depicted the increase in activation energy values at the end of conversion, related to the UF systems with PDDA.

The curing reactions of UF adhesive systems were modeled for isothermal conditions using the Friedman iso-conversional method, *i.e.* showing the conversion degree as a function of time at the constant temperature. It was interesting to notice that the conversion rate for the UF adhesive systems with PDDA was lower for the curing temperatures below 80 °C, while curing of these adhesives was faster at 120 °C in comparison to the control UF adhesive.

The positive effects of the PDDA polymer addition into the UF adhesive have been observed in this work through the improvement of thickness swelling and internal bond of the experimental panel samples. In general, we may suggest that the application of this method could improve physical and mechanical properties of particleboards manufactured in the real processing conditions and in capacities of modern particleboard factories. The addition of PDDA have also showed a possible increase of the reaction rate of the UF adhesives, at the temperatures above 120 °C, which in turn may lead to an increase of the production rate during the hot press operation in the particleboards manufacturing process.

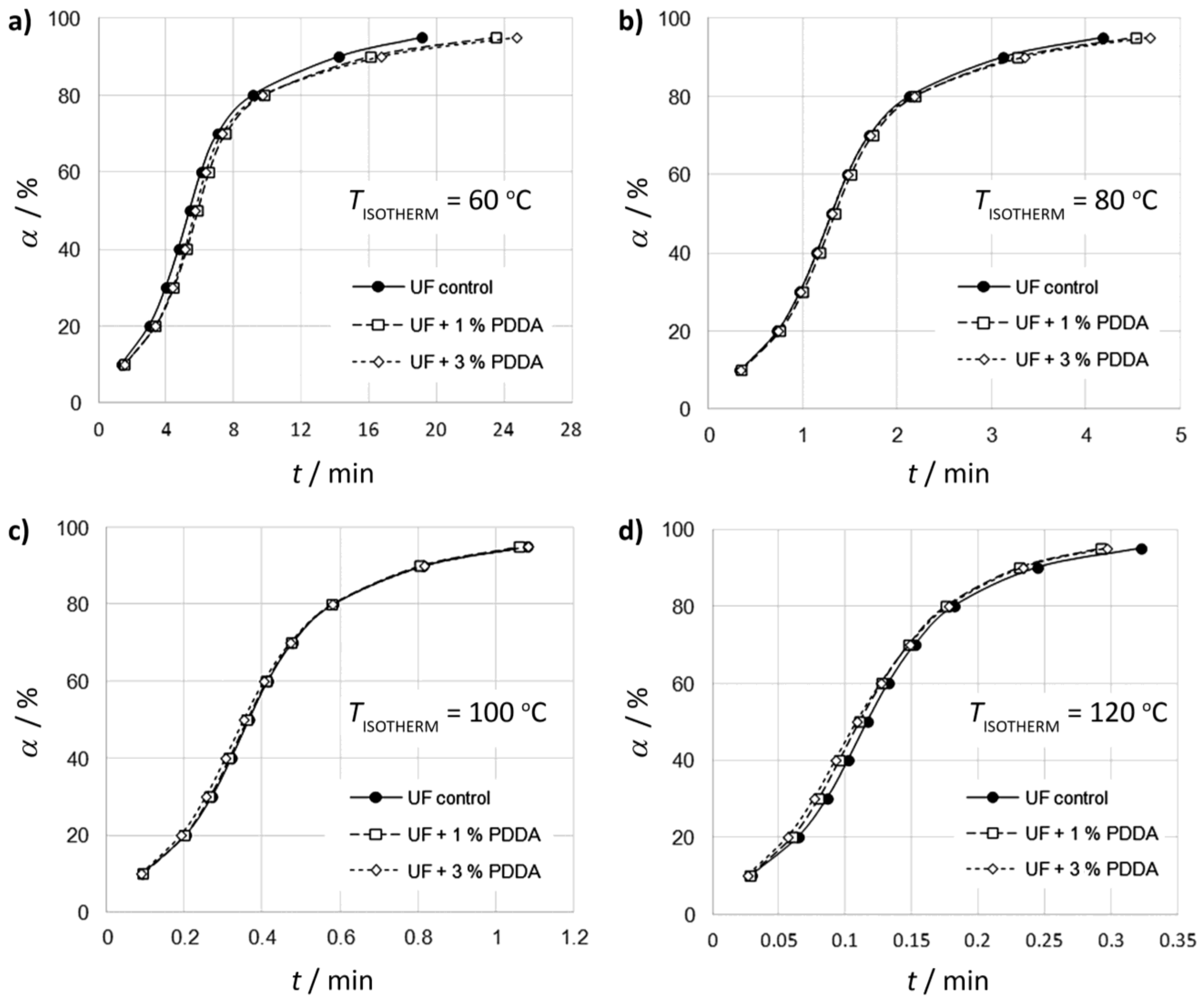

Figure 5. Conversion degree of UF adhesive samples (α) as a function of time by the Friedman model at constant temperatures: a) 60 °C, b) 80 °C; c) 100 °C and d) 120 °C

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Uticaj dodatka poli(dialildimetilamonijum hlorida) na kinetiku očvršćavanja urea-formaldehidnog adheziva za ploče iverice

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Izvod

U ovom radu ispitan je uticaj dodatka poli(dialildimetilamonijum hlorida) (PDDA) na performanse urea-formaldehidnog (UF) adheziva. U tom cilju pripremljene su tri serije UF adheziva: bez dodatka PDDA i sa dodatkom PDDA od 1 i 3 % suve supstance po masi suve supstance adheziva. Dodatak PDDA smanjio je debljinsko bubrenje uzoraka eksperimentlano dobijenih ploča iverica, dok je zatezna čvrstoća upravno na površinu ploče značajno povećana tek pri dodatku PDDA od 3 %. Metoda diferencijalne skeirajuće kalorimetrije (*engl.* differential scanning calorimetry, DSC) primenjena je u cilju ispitivanja uticaja dodatka PDDA na kinetiku očvršćavanja UF adheziva. DSC merenja sprovedena su u dinamičkom režimu korišćenjem različitih brzina zagrevanja (5, 10 i 20 °C·min^{-1}). Povećanje koncentracije PDDA uticalo je na smanjenje vrednosti energije aktivacije očvršćavanja UF adheziva, izračunate po opštem Kisindžerovom modelu. Zavisnost energije aktivacije u odnosu na stepen konverzije određena je za sva tri ispitivana adhezivna sistema korišćenjem izo-konverzionih modela (*Kissinger-Akahira-Sunose* i *Friedman*), što je omogućilo detaljniji uvid u uticaj PDDA na tok reakcije očvršćavanja UF adheziva.

Ključne reči: polielektrolit; termoreaktivni adheziv; diferencijalna skeirajuća kalorimetrija; izokonverziona metoda; svojstva ploča na bazi drveta