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THE INFLUENCE OF WOOD EXTRACTS ON THE CURING KINETICS OF UREA-FORMALDEHYDE ADHESIVE STUDIED BY ISO-CONVERSIONAL METHOD

Mladjan POPOVIĆ
Assist.prof.dr. - University of Belgrade - Faculty of Forestry
Address: Kneza Višeslava 1, 11030 Belgrade, Serbia
E-mail: mladjan.popovic@sfb.bg.ac.rs

Milanka DJIPOROVIĆ-MOMČILOVIĆ
Assoc.prof.dr. - University of Belgrade - Faculty of Forestry
Address: Kneza Višeslava 1, 11030 Belgrade, Serbia
E-mail: milanka.djiporovic@sfb.bg.ac.rs

Jaroslava BUDINSKI-SIMENDIĆ
Prof.dr. - University of Novi Sad - Faculty of Technology
Address: Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia
E-mail: jarkamer@gmail.com

Mirjana JOVIČIĆ
Assistant dr. - University of Novi Sad - Faculty of Technology
Address: Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia
E-mail: jovicic.mirjana@gmail.com

Ivana GAVRILOVIĆ-GRMUŠA
Assist.prof.dr. - University of Belgrade - Faculty of Forestry
Address: Kneza Višeslava 1, 11030 Belgrade, Serbia
E-mail: ivana.grmusa@sfb.bg.ac.rs

Abstract:

The influence of wood species on the curing kinetics of commercial urea-formaldehyde (UF) adhesive was investigated with differential scanning calorimetry (DSC) by mixing the prepared adhesive with the hot water extracts of beech, fir and poplar. 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/extract mix and the adhesive alone. The addition of extracts showed a general retarding effect on the curing reaction of UF adhesive, in such a way that the higher acid buffer capacity of extracts have increased the peak temperature and activation energy for the relevant adhesive mixes, and in regard to UF adhesive alone. Obtained data were additionally analysed using isoconversional methods with application of Ozawa – Flynn – Wall and Kissinger – Akahira – Sunose kinetic models. The results showed a different behaviour of adhesive/extract mixes during cure. The appearance of diffusion controlled curing reaction, at the higher reaction rates (α>75%), were noticed for the UF adhesive mixes with poplar extracts, having the lowest pH values and the highest acid buffer capacity.

Key words: *UF adhesive, wood extracts, differential scanning calorimetry, isoconversional model*

INTRODUCTION

The UF resins present the most common adhesive systems in wood industry, largely used for the production of interior wood based panels. Its major issues in the final product, such as the low moisture resistance and formaldehyde release, especially at the increased temperature and humidity, are all well studied. Certain attention was also given to its sensitivity to wood species. The importance of this problem lies in the real hot pressing environment, when the adhesive is in the close contact with wood substrate (particles, strands, fibers or veneer) and subjected to an increased temperature and pressure. In such conditions, the moisture from wood material dissolves some of its chemical constituents, and then easily reaches the interface region and mix with the adhesive itself. Having in mind that the UF resin require acid condition for its curing reaction, the question arise of how strong is the effect of the unique chemical composition of wood and the acidity of its extract. It was found that the pH value and the buffer capacity of hot water extracts, obtained from different wood species, do have a significant influence on the gel time of the UF adhesive (Johns and Naizi 1980). Thus, we can assume that the variation of chemical compostion among the wood species reflects the change in their acidity, which in turn, can alter the acid conditions required for the optimal UF adhesive curing reaction.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) present possibly the most influential techniques used in the studies of curing reaction of thermoset adhesives. Both methods are methodologically similar and may offer a series of measured and calculated data, such as the onset and peak temperatures (T_o and T_p), enthalpy (ΔH) and activation energy (E_a) of the adhesive curing reaction. The urea-formaldehyde (UF) resin was not the exception, and both methods have been thoroughly used to investigate its performance in regard to the catalyst addition or the formaldehyde to urea molar ratio (Chow and Steiner 1975, Šebenik *et al*. 1982, Siimer *et al*. 2003, Park *et al*. 2006). Various aspects of UF adhesive modifications were also investigated (Kim *et al*. 2006, Lei *et al*. 2008). Very important area of research involved the effects of wood species on the behavior of UF adhesive during cure. The possibility to monitor curing reaction at the controlled temperature regimes, while the adhesive is in the close contact with wood material, may provide some valuable information for the wood based panels industry. Such studies involved the measurements on the UF adhesive mixed with wood flour (Mizumachi 1973, Xing *et al*. 2004) but also the effects of wood extracts on the UF adhesive cure (Gao *et al*. 2007). In this latter research, DSC method was used for evaluation of the effects of pH and buffer capacity of the wood extracts on the kinetics of curing reaction of UF adhesive. Wood species have been categorized in three distinctive groups: 1) with no catalytic influence on curing reaction; 2) with positive catalytic influence and 3) with negative catalytic influence. However, the authors have stated that the activation energy did not fully explained the cure of the UF resin mixed with some wood extracts, and thus have suggested that other kinetic parameters, such as the pre-exponential factor, should also be taken into consideration.

Having in mind limited number of literature data on the said problem, this work presents the study of the pH and buffer capacity of wood extracts and their influence on the kinetics of curing reaction of UF adhesive. In order to achieve more complete insight in the UF adhesive behavior during cure, the isoconversion models of Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) were applied.

MATERIALS AND METHODS

Preparation of extracts

Three wood species used in this work were selected among the main industrial species growing in Serbia: beech (*Fagus moesiaca / Domin, Maly / Czeczott.*), poplar (*Populus x Euroamericana 'I-214'*) and fir (*Abies alba / Mill*). Air dried wood particles were grounded in the laboratory hummer mill and subsequently in the Willey mill. The fraction of wood flour that passed the 1.0mm screen and collected on 0.5mm screen was chosen for the extraction. The air dry wood flour, of equivalent quantity of 25g dry material, was suspended in 250ml distilled water inside the 500ml Erlenmeyer flask. The flask was placed in the water bath and connected to the cooling unit. After reaching the boiling point (100^{o}C), the extraction process followed the 2h period, after which the extracts were cooled and filtered using vacuum pump.

Samples for DSC measurements were further treated in lyophilization process in order to obtain dry extract.

The measurements of pH value and buffer capacity

Before the titration, the pH meter (ISKRA) with glass electrode was calibrated with standard buffer solutions of pH 4 and pH 7. The extract solutions were not further diluted, and the amount of 50ml was used for initial pH measurements and subsequent titration. The acid buffer capacity was obtained by titration of 50ml extract solution with 0.025N H_2SO_4. Another quantity of 50ml extract solution was titrated with 0.025N NaOH for determination of alkaline buffer capacity. The amount of sulfuric acid needed to reach pH 3 defined the acid buffer capacity, while the amount of sodium hydroxide, consumed until pH 8, defined the alkaline

buffer capacity. In addition, the difference between the acid and alkaline buffer capacities was defined as the absolute acid buffer capacity.

UF adhesive

The UF adhesive used in this research was obtained from PETROHEM, Lendava, Slovenia. Supplied adhesive emulsion had a molar ratio of F/U = 1.12, with the following characteristics: dry matter content = 67.54% (SRPS EN 827); density = 1303kg/m^3 (SRPS EN 542); viscosity = 505mPa·s (SRPS EN 12092) and pH value = 8.16 (SRPS EN 1245).

DSC measurements

UF adhesive samples for the evaluation of the effects of wood species were prepared by adding 1% of extracts per adhesive dry matter. Extract solutions were obtained by dissolving the dry extracts in the amount of water needed to adjust the concentration of adhesive emulsion to 50%. Plane distilled water was added for the control UF adhesive samples. The addition of hardener (NH_4Cl) was 0.2% per adhesive dry matter for all tests.

Relatively small amount of UF adhesive samples (approximately 4 to 5mg) were placed in the aluminum pans. The mass of an empty pan and the pan with sample was measured with analytical scale with the precision of 0.1mg, after which the pan was hermetically sealed. All DSC measurements were carried out in dynamic scanning regime, and in the temperature range from 40°C to 200°C, using DSC Q20 (TA Instruments, USA). In order to obtain kinetic parameters, four constant heating rates (β) were used: 5, 10, 15 and 20°C/min. Before each scan, the heating blocks inside the DSC instrument were adjusted to 40°C, and the nitrogen was used as a purge gas. The instrument software, TA Universal Analysis, was used to calculate peak temperatures and the enthalpy of reaction, with the exothermic peak plotting in upward direction.

Isoconversion kinetic models

At the higher rates of curing reaction, the application of isothermal DSC scanning regime may not present suitable for determination of kinetic parameters (Jovicic et al. 2008). Hence, there are several methods developed for processing the kinetics data of the curing reaction, obtained exclusively from the dynamic DSC scans. Some of the relatively novel isoconversion methods of Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS), proved to be suitable for the characterization of the curing behavior of thermoset resins and relevant adhesive systems (Gabilondo 2007, Bianchi et al. 2008, Perez et al. 2009).

OFW isoconversional model for calculating the kinetic parameters from the adhesive curing reaction is based on the following equation:

$$\log\beta = A' - 0.4567 \cdot \frac{Ea}{R \cdot T} \quad (1)$$

β - heating rate, in °C/s,
E_a - activation energy, in J/mol,
R - ideal gas constant, 8.314 J/(mol·K),
T - reaction temperature, in °C,
α - reaction degree.

Factor A´ in the equation (1) can be expressed as:

$$A' = \log\left[\frac{k_0 \cdot Ea}{R \cdot g(\alpha)}\right] - 2.315 \quad (2)$$

k_0 - the pre-eksponential factor, in 1/s.

The OFW isoconversional model assumes that the reaction rate is a function of temperature, at a given degree of conversion (α(T)). Then, using different heating rates and plotting the logβ vs. 1/T it is possible to obtain a linear function. The slope of the straight line is used for the calculation of activation energy (E_a).

The KAS model is described by the following equation:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{R \cdot A}{Ea \cdot g(\alpha)}\right) - \frac{Ea}{R \cdot T} \quad (3)$$

For the Kissinger's assumptions to be correct, a plot of $\ln(\beta/T^2)$ vs. $1/T$ (equation 3) should present a linear function and the activation energy might be obtained from its slope ($-E_a/R$).

RESULTS AND ANALYSIS

The results of pH measurements and the acid and alkaline titration are presented in the table 1. It can be noticed that the pH of fir extracts has a significantly lower value than those of the beech and poplar. The lower pH in fir extracts might originate from the higher ratio of uronic acids in xylenes, which is common in coniferous species (Janežić 1993). The acids such as α - i β-D-galacturonic and 4-O-methyl-ether-α-D-glucuronic acid, can be easily extracted in the hot water and thus contribute to the overall acidity of the fir extracts.

Table 1

pH value and buffer capacities of beech, fir and poplar hot water extracts

Wood Species	Statistical value	pH	Acid buffer capacity (mmol/l)	Alkaline buffer capacity (mmol/l)	Absolute acid buffer capacity (mmol/l)
Beech	Mean value	**5.46**	**5.61**	**1.78**	**3.83**
	St. deviation	0.069	0.170	0.051	0.145
	Variance	0.0047	0.0289	0.0026	0.0211
Fir	Mean value	**4.88**	**2.64**	**1.08**	**1.46**
	St. deviation	0.068	0.087	0.040	0.060
	Variance	0.0047	0.0076	0.0016	0.0036
Poplar	Mean value	**5.59**	**7.07**	**1.26**	**5.81**
	St. deviation	0.091	0.395	0.040	0.431
	Variance	0.0083	0.1557	0.0016	0.1861

UF adhesive systems cure in the acid conditions, therefore, it is very important that wood component does not interfere the effects of a catalyst. It is expected that the wood species with lower buffer capacity interfere less in the curing reaction and as such they should be more suitable for the production of wood based panels. The results for acid and alkaline buffer capacities, as well as for the absolute acid bufer capacity, are given in Tabel 1. Characteristic titration diagrams for all three wood species are shown in the Fig. 1.

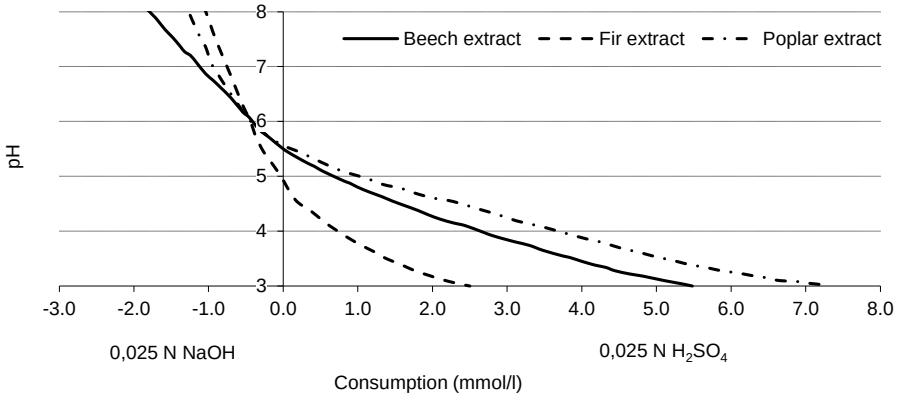

Fig. 1
The pH, acid, and base buffering potential for selected wood species.

The fir extracts have showed the lowest acid buffer capacity, approximately 2.7 times less then poplar and 2.15 times less then beech extracts. The similar trend has been noticed for the absolute acid buffer capacity values, for all three wood species. The lowest acid buffer capacity in fir extracts correlates well with its low pH value. On the other hand, the acid buffer capacity of beech extracts had significantly lower values then for poplar extracts, even though their pH values were similar. However, it is expected that the poplar extracts, having higher acid buffer capacity, will have a higher retarding effect on the adhesive curing reaction.

Curing kinetics

The Fig. 2 presents the characteristic thermographs of the UF adhesive control sample (with 0.2% NH_4Cl and without the addition of extracts), obtained by the DSC scans in the non-isothermal (dynamic) regime. It can be noticed, that the increase in the heating rate (β) from 5 to 20°C/min has influenced the increase in the temperature maximum of the curing reaction (T_p) from 85.6°C to 105.0°C, respectively.

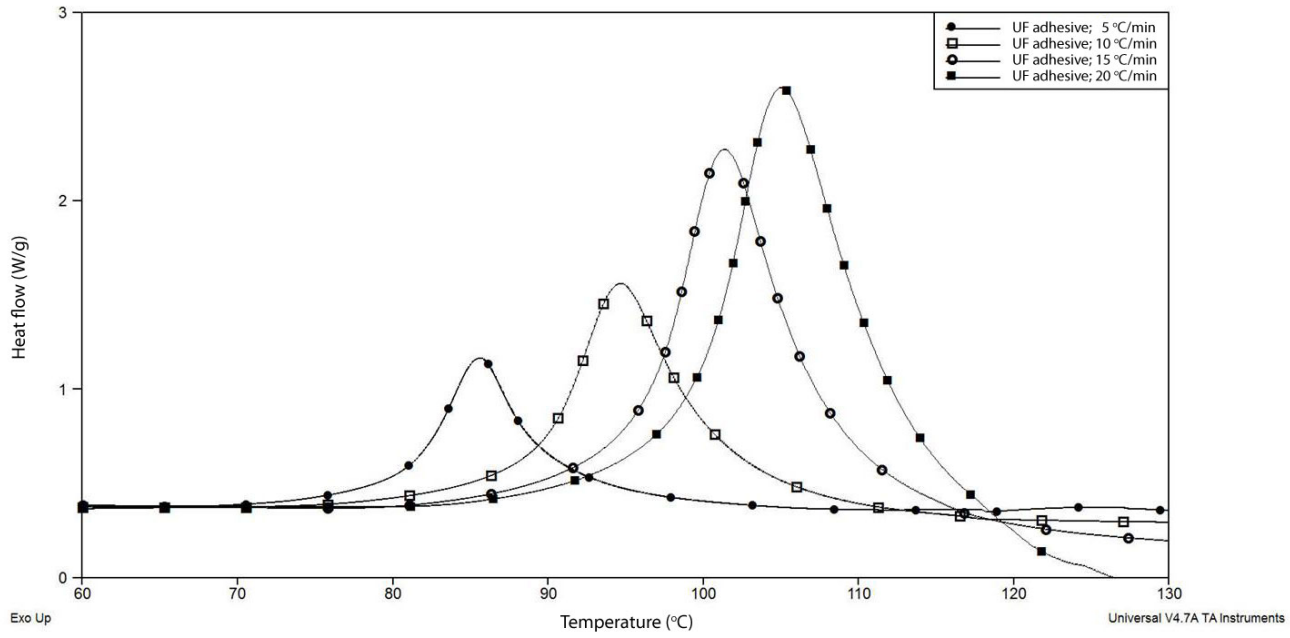

Fig. 2
DSC thermograms of UF adhesive (+0,2% NH_4Cl) without the addition of wood extracts, at the heating rates of 5, 10, 15 i 20°C/min.

Table 2 presents the results for the peak temperatures (T_p) at different heating rates, the enthalpy of reaction (ΔH) and activation energy (E_a) for the control UF adhesive and for the UF adhesive mixes with wood extracts of selected wood species. Fig. 3 presents the relevant linear functions of $\ln(\beta/T^2)$ vs. $1/T$, used for the calculation of E_a based on the general Kissinger assumption.

Several other authors have examined the curing reaction of the commercial UF adhesives. The apparent E_a for the UF adhesive control sample obtained in this research (73.6kJ/mol) is very similar to the E_a value for the commercial UF adhesive (75.28kJ/mol) determined by Gao *et al.* (2007), but with significantly higher catalyst addition (0,97% NH_4Cl). With the catalyst addition of 0.2% (NH_4Cl), the Xing *et al.* (2005) have obtained the significantly lower E_a (43.5kJ/mol), but slightly higher T_p values in regard to the results of this research. Contrary, Mizumachi (1973) have used DTA method to monitor the curing of commercial UF adhesive without the catalyst addition, and have obtained the E_a value of 121kJ/mol.

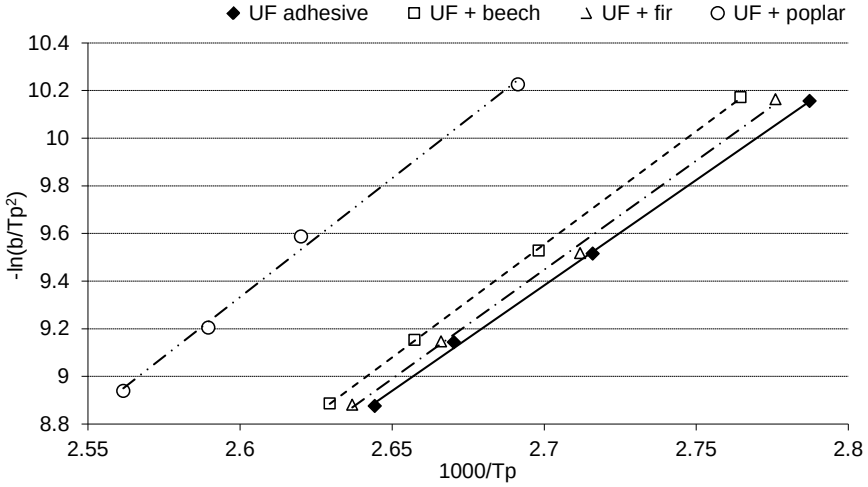

Fig. 3
The plots of ln (β/T2) vs. 1000/T for the control UF adhesive sample and different UF adhesive mixes with 1% of wood extracts per adhesive dry mass
(all the samples have the addition of 0.2% of NH4Cl per dry adhesive mass).

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Table 2

Maximum temperature (T_p), enthalpy (ΔH) and activation energy (E_a) of the curing reaction of the control UF adhesive sample and different UF adhesive mixes with wood extracts (all the samples have the addition of 0.2% of NH_4Cl per dry adhesive mass)

	T_p (°C)				ΔH (J/g)	Function	E_a (kJ/mol)
β (°C/min)	5	10	15	20			
UF adhesive	85.6	95.0	101.3	105.0	**158.63**	$y = 8.856x - 14.53$ $R^2 = 0.9991$	**73.6**
UF + beech[1]	88.6	97.5	103.2	107.2	**135.02**	$y = 9.29x - 15.55$ $R^2 = 0.9979$	**79.0**
UF + fir[1]	87.1	95.6	101.9	106.1	**157.31**	$y = 8.84x - 14.33$ $R^2 = 0.9981$	**76.3**
UF + poplar[1]	98.4	108.5	113.0	117.2	**84.18**	$y = 8.527x - 13.31$ $R^2 = 0.9996$	**83.0**

[1]1% of wood extract per dry adhesive mass

According to the E_a values, presented in the Table 2, the addition of extracts had the retarding effect on the Uf adhesive curing reaction in general. However, the poplar extracts had the most significant influence, resulting in the 12.8% higher E_a of the relevant UF adhesive mix in regard to the control UF adhesive sample. The same UF adhesive mix also had the highest T_p values. Extracts of beech and fir had much lower influence on the UF adhesive curing reaction, especially concerning the T_p results. Their effects on the E_a were somewhat different. The UF adhesive mixed with beech extracts had 7.3% higher E_a in regard to the control UF adhesive sample, while the fir extracts had negligible effects on E_a.

Different effects that the extracts from different wood species had on the UF adhesive curing reaction, originates mostly from their chemical composition, unique for each of the selected wood species. Extraneous material from poplar wood prove to have the most retarding effect which is probably due to its high acid buffer capacity, which might interfered in the catalyst actions in providing the optimal acid conditions for the adhesive cure.

It is important to notice that the beech and poplar extracts had very similar pH values, but with different effect on the UF adhesive cure. Therefore, the pH might not be the reliable parameter in describing the influence of wood species on the UF adhesive curing behaviour. In that aspect, the absolute acid buffer capacity had the highest influence on the UF adhesive cure, as shown on the Fig. 4 and 5.

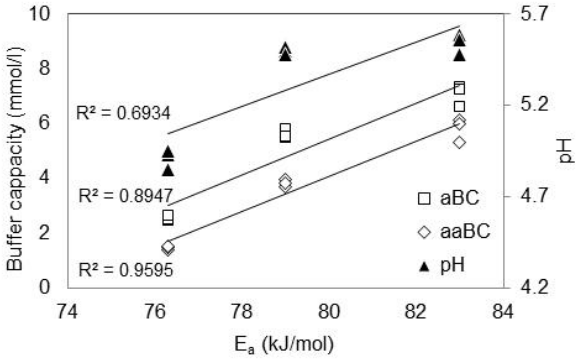

Fig. 4

The influence of the pH and the buffer cappacity of wood extracts on the activation energy (aBC - acid buffer cappacity; aaBC - absolute acid buffer cappacity).

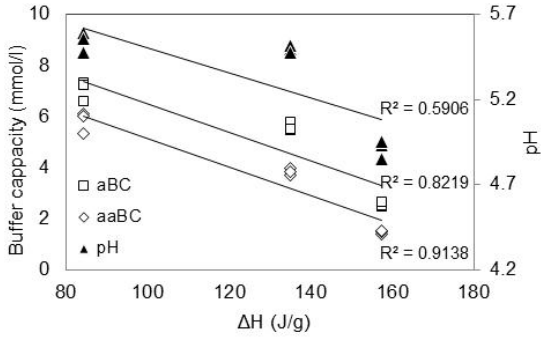

Fig. 5

The influence of the pH and the buffer cappacity of wood extracts on the enthalpy of reaction (aBC - acid buffer cappacity; aaBC - absolute acid buffer cappacity).

Concerning the enthalpy of the curing reaction (*ΔH*), the fir wood extracts showed no significant effects. On the other hand, the addition of poplar extracts resulted in the lowest *ΔH* value of the relevant UF adhesive mix, which is almost two times lower in regard to the *ΔH* of the control UF adhesive sample. Again, the pH of the extracts showed to have less influence in the UF adhesive cure then the acid or absolute acid buffer capacity, with the later having the highest correlation factor. Generally, the increase in the buffer capacity of the wood extracts has decreased the *ΔH* values of the UF adhesive cure. The question arises if this decrease in *ΔH* also presents the retarding effect of the extracts, which should be the case, regarding the earlier mentioned effects of the buffer capacity on the activation energy and peak temperatures. It is possible that the reaction of some extraneous compounds with the catalyst or with the adhesive could be the reason for the loss of heat energy. For instance, tannins, often found in wood extracts, could react with the free formaldehyde or methyl groups from the adhesive needed for the crosslinking reaction (Popovic 2012).

Isoconversional analysis of the results from DSC measurements

The Fig. 2 presents the conversion profiles for the UF adhesive control sample (a) and the UF adhesive mixes with different wood extracts (b, c and d). The apparent conversion rates are given for all four heating rates used in the relevant DSC measurements.

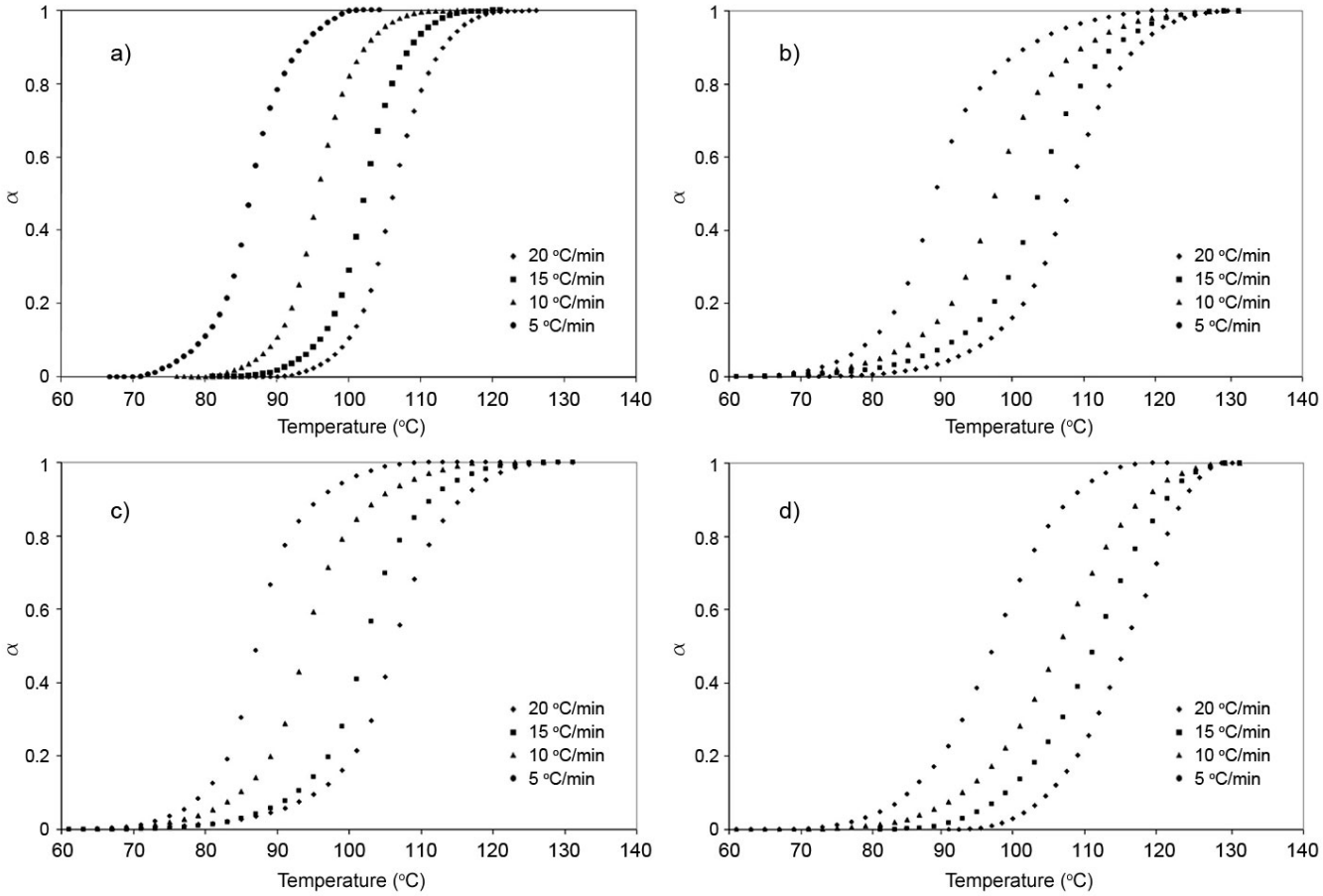

Fig. 6

Conversion profiles of the urea-formaldehyde adhesive samples (+0.2% NH_4Cl) at different heating rates (β = 5, 10, 15 and 20 °C/min): a - UF adhesive control sample; b - UF adhesive with 1% of beech extracts; c - UF adhesive with 1% of fir extracts and d - UF adhesive with 1% of poplar extracts.

The apparent activation energy calculated by OFW and KAS isoconversional models are given in the Tables 3 and 4, respectively. It could be noticed that the E_a values obtained by both methods are quite similar, with OFW method showing slightly higher values. This suggests that the both methods reflects the mechanics of the UF adhesive cure in the same way, and that each of them could be used independently in the case of UF adhesive systems. The results also show the high correlation coefficient of E_a values, obtained by both isoconversional methods. The correlation coefficients were generally in the range of 0.92 - 0.99.

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Table 3

Activation energy of the UF adhesive control sample and the adhesive/extract mixes, at different conversion rates obtained by Ozawa-Flynn-Wall (OFW) method

α [%]	UF adhesive		UF + beech[1]		UF + fir[1]		UF + poplar[1]	
	Ea [kJ/mol]	R^2	Ea [kJ/mol]	R^2	Ea [kJ/mol]	R^2	Ea [kJ/mol]	R^2
5	68.25	0.999	87.25	0.923	70.69	0.995	64.10	0.951
10	70.42	0.999	85.82	0.966	73.24	0.997	67.03	0.958
20	73.47	0.999	82.94	0.989	75.79	0.997	74.31	0.972
30	74.35	0.998	81.45	0.995	76.15	0.997	79.23	0.982
40	74.30	0.999	80.14	0.998	76.08	0.997	82.85	0.985
50	74.45	0.999	78.48	0.999	75.71	0.997	86.56	0.986
60	74.19	0.999	77.72	0.999	75.20	0.996	89.80	0.987
70	74.00	0.999	76.19	0.999	75.00	0.995	94.52	0.986
80	75.61	0.999	74.37	0.999	74.97	0.992	102.66	0.986
90	78.47	0.998	72.04	0.999	75.97	0.982	115.98	0.98
95	80.48	0.998	71.13	0.998	77.77	0.971	123.81	0.972

[1]1% of wood extract per dry adhesive mass

Table 4

Activation energy of the UF adhesive control sample and the adhesive/extract mixes, at different conversion rates obtained by Kissinger-Akahira-Sunose (KAS) method

α [%]	UF adhesive		UF + beech[1]		UF + fir[1]		UF + poplar[1]	
	Ea [kJ/mol]	R^2	Ea [kJ/mol]	R^2	Ea [kJ/mol]	R^2	Ea [kJ/mol]	R^2
5	65.81	0.999	85.72	0.912	68.34	0.995	61.37	0.942
10	68.05	0.999	84.14	0.961	70.98	0.996	64.40	0.951
20	71.21	0.999	81.14	0.988	73.63	0.997	71.99	0.968
30	72.10	0.998	79.54	0.995	73.99	0.996	77.11	0.979
40	72.03	0.999	78.14	0.997	73.89	0.997	80.89	0.983
50	72.17	0.999	76.38	0.998	73.49	0.996	84.72	0.983
60	71.89	0.999	75.56	0.999	72.93	0.995	88.13	0.985
70	71.66	0.999	73.94	0.999	72.70	0.994	93.03	0.984
80	73.32	0.998	72.00	0.999	72.63	0.991	101.51	0.984
90	76.28	0.998	69.51	0.999	73.65	0.978	115.48	0.978
95	78.35	0.998	68.53	0.998	75.49	0.966	123.71	0.969

[1]1% of wood extract per dry adhesive mass

Fig. 7 shows the activation energy dependence on conversion degree of the adhesive samples curing reaction, obtained from OFW method. It actually presents the graphical expression of the results from Table 3.

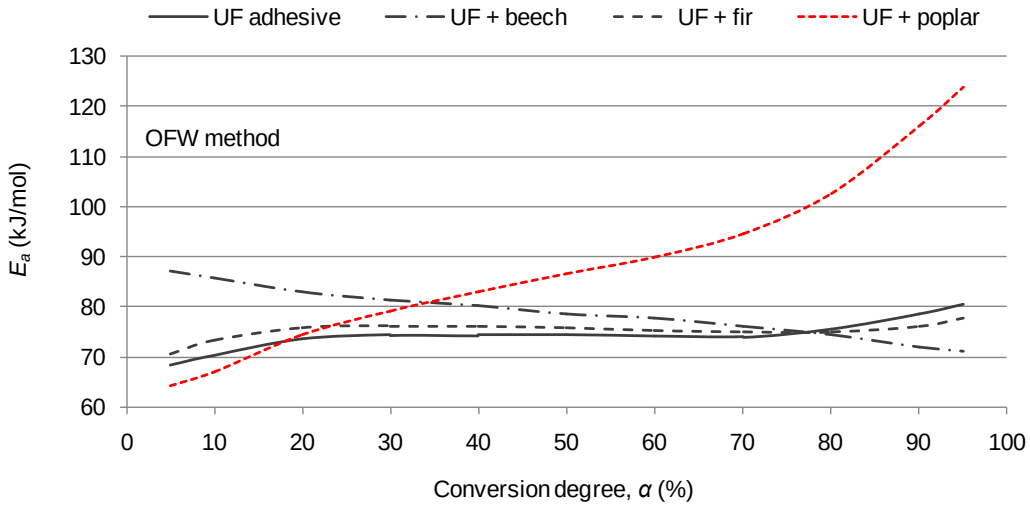

Fig. 7

Dependance of the activation energy on the conversion degree of the curing reactions for the UF adhesive control sample and the adhesive / extract mixes obtained by Ozawa-Flynn-Wall (OFW) method (all the samples have the addition of 0.2% of NH4Cl per dry adhesive mass).

The addition of the fir extract has showed no significant influence in the mechanics of the UF adhesive curing reaction. UF adhesive mix with the beech extracts has started the reaction at the relatively high E_a value of 87kJ/mol, but has followed the constant decrease toward the end of the cure, when the E_a was 71kJ/mol.

It was very interesting to observe the influence of the poplar extracts on the curing behaviour of the relevant UF adhesive sample. The curing reaction of this sample was characterised by the lowest E_a value of all the adhesive samples used (64kJ/mol). With the progression of the curing reaction, the constant and significant increase of the E_a was recorded, which was not the case with the other adhesive samples. At the conversion degree range of 20-35%, the E_a of the UF adhesive mixed with poplar extract passes above the E_a of other adhesive samples. After the conversion degree of 75%, its increase in E_a becomes even steeper, reaching the value of 124kJ/mol at the end of cure. Recorded increase in the E_a suggests that the extraneous chemical substances form poplar wood had the most significant retarding effect on the UF adhesive curing reaction. Presumably, they have contributed to the diffusive controlled reaction and possibly inhibited the crosslinking and formation of the molecules with higher molar mass, at the ending phases of the curing process.

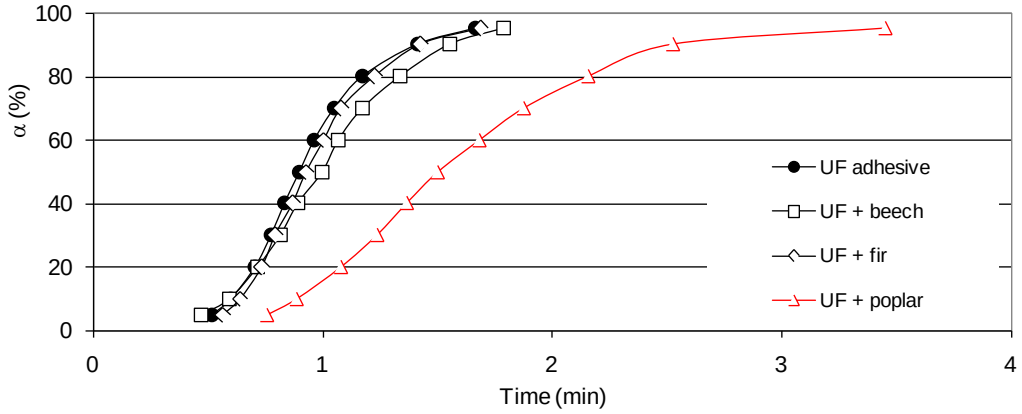

Fig. 8
Conversion degree of the curing reactions for the UF adhesive control sample and the adhesive/extract mixes obtained by Ozawa-Flynn-Wall (OFW) method and for the curing temperature of 100°C (all the samples have the addition of 0.2% of NH4Cl per dry adhesive mass).

The Fig. 8 presents the application of OFW model for transfering the data obtained from dynamic DSC scans into the apparent conversion degree of the adhesive samples curing reaction in the isothermal conditions. The figure presents the characteristic diagram of the conversion degree time dependance during UF adhesive samples cure at the temperature of 100°C. Again, the influence of the fir extracts is neglegible. Contrary, the addition of poplar extracts have showed the obvios retarding effect of this wood species. Achieving the conversion degree of 80% for the UF adhesive mix with poplar extract requires almost two times longer period then for the UF adhesive control sample, at the temperature of 100°C. Such findings corelates well with the high acidic buffer capacity of poplar extracts.

CONCLUSIONS

From the selected wood species, the fir extracts showed the lowest pH of 4.9, while the beech and poplar extracts has the pH value of 5.5 and 5.6, respectively. Fir extracts also had the lowest acid and absolute acid buffer capacities, while the same properties were the highest for the poplar extracts.

Differential scanning calorimetry was used to evaluate the effects of the extracts from the selected wood species on the curing reaction of urea-formaldehyde (UF) adhesive with the catalyst addition of 0.2% (NH_4Cl):

- The thermographs obtained from dynamic scans have showed the single characteristic exothermic peak of the UF adhesive curing reaction for all of the adhesive samples, which is usual for this adhesive system.

- Temperature maximums of the curing reactions, at the applied heating rates, were the lowest for the UF adhesive control sample (without the addition of extracts), which also resulted in the lowest activation energy (73.6kJ/mol) and the highest enthalpy of the curing reaction (158.63). Contrary, the highest peak temperatures were recorded for the UF adhesive mixed with poplar extracts. The same adhesive mix has influenced in the highest activation energy (83.0kJ/mol) and the lowest enthalpy of the curing reaction (84.18J/g).

- The obtained kinetic results suggest that some extraneous compounds, especially in the poplar wood, might react with the catalyst or with free formaldehyde or methyl groups in the adhesive and thus interfering in the main curing reactions.

- The influence of the extracts from selected wood species on the kinetic parameters of the UF adhesive cure correlates well with their acidic buffer capacity. The increase in the acid buffer capacity of the wood extracts has increased the activation energy, but decreased the enthalpy of reaction. In the same aspect, the pH value of extracts has showed lesser effects.

- The application of the Ozawa-Flynn-Wall and the Kissinger-Akahira-Sunose isoconversional methods has further explained the wood extracts influence on the curing mechanics of UF adhesive.

- The results of the apparent activation energy for different conversion degrees have showed almost negligible effect of the fir extracts on the UF adhesive behaviour during cure.

- The addition of poplar extracts, however, has the most retarding effect. The relevant adhesive sample showed constant increase in the activation energy, which became steeper at the conversion degree of 75%, thus suggesting that poplar extracts might have caused the diffusive control reaction, especially at the end of the cure.

- The transformation of data obtained by dynamic DSC scans into isothermal data have showed the significantly slowest curing rate of the UF adhesive mixed with poplar extracts.

- Such findings correlate well with the results of pH and acid buffer capacity measurements of wood extracts.

The results of this study underline the poplar wood as the critical wood species with high inhibitory potential in the acidic conditions of UF adhesive cure. Accordingly, the high acid buffer capacity of the poplar extracts implicates its retarding effects during UF curing in the real processing conditions.

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