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ISOCONVERSIONAL KINETIC ANALYSIS OF THE ALKYD/MELAMINE RESINS CURING

The curing reaction for the mixtures of alkyd resins based on ricinoleic acid, phthalic anhydride and three polyols (glycerin, trimethylolpropane or ethoxylated pentaerythritol) with two different commercial melamine resins was investigated by differential scanning calorimetry (DSC). The curing kinetics analysis was performed using the isoconversional methods (Ozawa-Flynn-Wall, Kissinger-Akahira-Sunose and Friedman). Isoconversional methods were carried out with three heating rates (5, 10 and 20 °C/min) in a scanning temperature range from 40 to 250°C. It was found that the curing activation energy of resin mixtures is influenced by alkyd and melamine resin type due to the catalytic effect of hydroxyl group on the reactions. The dependence of apparent curing degree on time, which was obtained by mathematical transformations of dynamic DSC data using Ozawa-Flynn-Wall method, describes well the isothermal DSC experiments.

Keywords: coating, thermosetting resins, curing, DSC, isoconversional methods.

Alkyd resins are used as conventional binders in coatings. They are products of polycondensation reaction between polyhydric alcohols (*e.g.*, glycerin, pentaerythritol), polybasic acids or its anhydrides (mostly phthalic anhydride) modified with fatty acids or oils. The popularity of alkyd resins for coatings is large due to their unique properties such as film hardness, durability gloss and gloss retention, resistance to abrasion, etc., impacted on them through the modification with oils [1]. Oils that are mostly employed for alkyd resin synthesis are linseed, soybean, castor and tall oils [2].

Alkyd resins have been widely used in the surface coating systems normally in the combination with other resins, mainly with amino ones. Melamine-formaldehyde resins are used together with alkyd resins for the coatings which cure rapidly and give hard films. The alkylated melamine-formaldehyde resins (mainly butyl) form a film by the reaction between adjacent molecules and between hydroxyl groups of the alkyd resins [3-5]. Alkyd with amino resins are used for oven-drying industrial and automotive finishes.

Gloss, solids content and adhesion are determined by the alkyd resin, whereas the amino resin component permits rapid drying at elevated temperatures and improves the mechanical properties of the coating [6]. In purely oven-drying alkyd resin coating materials, the resins normally employed are short-oil alkyd in the combination with amino resins. In such system, drying involves not only physical evaporation of the solvent, but also, and predominantly, chemical curing, while oxidative drying is relegated to a very minor rule [6]. Mixtures of melamine resins with suitable alkyd resin in the surface coatings yield to better hardness and chemical resistance, and also reduce the time of thermal curing [7]. When the types of alkyd and melamine resin are defined, the optimization takes place by varying and testing different mixing ratios of both resins. The optimum mixing ratio is influenced by the quantity of functional groups on both resins [8].

In the synthesis of thermosets, curing is the most important stage because this reaction sets the final properties of the polymer [9]. It is necessary to study the extent of the curing and kinetic parameters, in order to obtain high performance resins. The characterization of the cure kinetics of thermoset materials is well established using a variety of techniques, namely spectroscopic analysis, differential thermal analysis and differential scanning calorimetry (DSC).

DSC technique has the advantage of being based on the relationship between the heat flow and reaction rate of the resin curing process [10,11]. The curing behaviour of the alkyds was studied using DSC in numerous researches [12-17]. Filipović *et al.* [13] investigated the curing process of the alkyd/melamine resin mixture, in order to evaluate the kinetic parameters from DSC data. In all dynamic DSC curves, a single broad peak was observed after 350 K. Using the dynamic DSC measurements at four different heating rates the activation energy was calculated (around 79 kJ mol^{-1}) [13]. The curing kinetics of alkyd resins based on dehydrated castor oil with melamine resin was also studied [15]. The attention was focused on the influence of the mixture ratio on the activation energy, the values of which were determined in the range from 51 to 114 kJ mol^{-1} [15]. The alkyd/hexamethoxymethyl melamine nanocomposites have also been a subject of interest, where the influence of alkyd resin ratio on the curing reaction of coatings was followed by DSC analysis [17].

Curing kinetic parameters of thermoset polymers can be obtained from isothermal or dynamic data using this thermal analysis by applying several different methodologies [11,18]. Alkyd/melamine mixtures are very complex systems and the change in their activation energies depends on the conversion degree during the curing process. Isconversional methods reveal changes in the curing kinetics throughout the process and have been applied to the curing of epoxy, epoxy-amine, unsaturated polyester and resol resins using the dynamic DSC regime [9].

The aim of this work was to study the influence of resin type on curing kinetics of conventional alkyds based on ricinoleic acid, phthalic anhydride and three polyols (glycerin, trimethylolpropane or ethoxylated pentaerythritol). The curing of alkyd resins with two commercial melamine resins was followed by DSC measurements by applying three conventional isoconversional methods: two integral (Ozawa-Flynn-Wall [19] and Kissinger-Akahira-Sunose [20,21]) methods and one differential (Friedman [22]) method. The dependence of apparent activation energy on the curing degree for all prepared alkyd/melamine systems

was estimated. The results determined from the dynamic DSC curves were mathematically transformed in order to obtain the isothermal data. Good agreement of the dependence of apparent curing degree on time in comparison with those obtained from isothermal DSC experiments was achieved.

EXPERIMENTAL

Materials

Alkyd resins formulated to have ricinoleic acid content of 30 wt.% were synthesized with the following raw materials: glycerine (produced by Merck); trimethylolpropane and ethoxylated pentaerythritol (purchased from Perstorp Specialty Chemicals AB); phthalic anhydride (provided by Henkel) and ricinoleic acid (99% purity) from Sigma Aldrich. Detailed information about the synthesis and properties of these alkyd resins can be found in our previous work [23]. Three alkyds were synthesized differing in values of acid and hydroxyl number: alkyd AG based on glycerine with acid number = 2.1 mg KOH/g and hydroxyl number = 218.9 mg KOH/g; alkyd ATMP based on trimethylolpropane with acid number = 9.2 mg KOH/g and hydroxyl number = 241.8 mg KOH/g; alkyd AEP based on ethoxylated pentaerythritol with acid number = 4.5 mg KOH/g and hydroxyl number = 252.7 mg KOH/g. Two types of commercial melamine resins were used: Maprenal MF 580 (produced by INEOS Melamines) and Cymel 303 (produced by Cytec Industries Inc.).

Maprenal MF 580. Imino type, isobutylated melamine-formaldehyde resin, dynamic viscosity at 23 °C, 1500 mPa s; density at 20 °C, 0.98 g/cm^3; iodine colour number < 1.

Cymel 303. Hexamethoxymethylmelamine, supplied in the liquid form at > 98% non-volatile, dynamic viscosity at 23 °C, 2600-5000 mPa s; density at 20 °C, 1.2 g/cm^3; iodine colour number: 1, maximum.

The alkyd/melamine resins were prepared using a weight ratio of 70:30 based on dried mass. The mixtures were homogenized at the room temperature. The codes and descriptions of the samples are presented in Table 1.

Table 1. Sample codes and descriptions of the prepared resin mixtures

Sample code	Type of alkyd	Melamine resin
AG/MF 580	Alkyd AG based on glycerine	Maprenal MF 580
AG/Cymel 303	Alkyd AG based on glycerine	Cymel 303
ATMP/MF580	Alkyd ATMP based on trimethylolpropane	Maprenal MF 580
ATMP/Cymel 303	Alkyd ATMP based on trimethylolpropane	Cymel 303
AEP/MF 580	Alkyd AEP based on ethoxylated pentaerythritol	Maprenal MF 580
AEP/Cymel 303	Alkyd AEP based on ethoxylated pentaerythritol	Cymel 303

DSC Analysis

Isothermal and non-isothermal curing kinetics were carried out by a model DSC Q20, TA Instruments. The DSC instrument was calibrated using indium. The samples of mass between 3 and 5 mg were put into an aluminium pan and, in order to get free of solvent, placed in a vacuum oven at the ambient temperature, after which the pan was hermetically sealed. An empty pan was used as the reference. The measurements were performed at three different heating rates (5, 10 and 20 °C/min). In order to apply the isoconversional analysis, the original DSC data of exothermic peaks were transformed into curves of curing conversion (α) vs. temperature, at various heating rates. The values of α were obtained by the exothermic peak integration based on the following equation:

$$\alpha = \frac{H_\alpha}{H_{\text{total}}} \tag{1}$$

where H_α is the fractional enthalpy and H_{total} is the total enthalpy of the cure reaction.

The isothermal DSC runs were carried out at the temperature of 120 °C. After each isothermal curing, the uncured resin mixture content was determined by additional heating the sample (from 120 to 250 °C), in the dynamic thermal regime at the heating rate of 10 °C/min [24]. Apparent degree of curing from isothermal DSC curve was determined by the procedure described in the literature [24,25].

Curing kinetics methods

The most commonly used equation to describe the reaction rate in the non-isothermal curing is present below:

$$\beta \frac{d\alpha}{dT} = k_0 e^{-Ea/RT} f(\alpha) \tag{2}$$

where β is the heating rate ($\beta = dT/dt$ (K/s)), α is the curing degree, k_0 is the pre-exponential factor, Ea is the activation energy (J/mol), R is the universal gas constant (8.314 J/(mol K)), t is the reaction time (s) and T is the reaction temperature (K). The function $f(\alpha)$ represents the mathematical expression of the kinetic model.

Ozawa-Flynn-Wall and Kissinger-Akahira-Sunose isoconversional methods were applied to calculate kinetic parameters of resin mixtures curing from dynamic DSC curves.

The Ozawa-Flynn-Wall method is based on the following expression:

$$\log\beta = A' - 0.4567\frac{Ea}{RT} \tag{3}$$

and A' can be calculated as:

$$A' = \log\left[\frac{k_0 Ea}{Rg(\alpha)}\right] - 2.315 \tag{4}$$

where $g(\alpha)$ is the integral form of $f(\alpha)$:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{5}$$

From A' and Ea values obtained from Eq. (3) for different apparent curing degrees, it is possible to determine a new constant, A, which can be written as:

$$A = \ln\left[\frac{g(\alpha)}{k_0}\right] \tag{6}$$

The isoconversional Ozawa-Flynn-Wall 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 $\log\beta$ *vs.* $1/T$, and the activation energy (Ea) is obtained as the slope of the straight line. In this case, the conversion-dependence function ($f(\alpha)$ or $g(\alpha)$) are not required. Another expression similar to a proposal by Ozawa-Flynn-Wall is the Kissinger-Akahira-Sunose model (KAS) based on the Coats-Redfern approximation [26], which is described by Eq. (7):

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

Therefore, if Kissinger's assumptions based on the Coats-Redfern approximation [26] are correct, a plot of $\ln(\beta/T^2)$ vs. $1/T$ (Eq. (7)) should be linear and the activation energy might be obtained from the slope ($-Ea/R$).

The differential isoconversional method suggested by Friedman [22] (FR) is based on Eq. (8):

$$\ln\beta\frac{d\alpha}{dT} = \ln A + \ln f(\alpha) - \frac{Ea}{RT} \tag{8}$$

For α = const., the plot $\ln(\beta d\alpha/dT)$ *vs.* $(1/T)$, obtained from thermograms recorded at several heating rates should be a straight line whose slope allows the evaluation of the activation energy.

The experimentally determined kinetic parameters are appropriate to call "apparent", or "effective", or "global", in order to stress the fact that they can derivate from the intrinsic parameters of a certain individual step [27]. In this work, the term "apparent" was

used to describe the kinetic parameters (apparent degree of curing and apparent activation energy). It was assumed that no other process that might contribute in kinetic calculations appears during the resin curing process. This assumption was confirmed with no registered peaks in the second DSC run [23].

RESULTS AND DISCUSSION

DSC Thermograms of resin mixtures curing at different heating rates are given in Figure 1. From the presented curves, it can be seen that a single broad peak is obtained in all experiments, like it was reported in the literature for the some alkyd/melamine resin blends [13-15,23]. The heating rate shows a great influence on the curing process. At the lower heating rate, the exothermal peaks appear first, while at

higher heating rate, the peak areas are greater and the exothermic peaks and conversion curves are shifted to the higher temperatures. After the curing in hermetically sealed DSC pans, the samples were cooled down and scanned again. During the second heating, there were no observed exotherms indicating that the curing reactions were completed after the first scan.

The original DSC data of exothermic peaks were transformed and plotted as curing conversion (α) *versus* temperature at various heating rates (Figure 2). The values were obtained by the integration of exothermic peak based on Eq. (1). The mixtures containing alkyd prepared from ethoxylated pentaerythritol (samples AEP/MF 580 and AEP/Cymel 303) became cured at lower temperatures than those obtained from alkyd based on glycerin (AG/MF 580
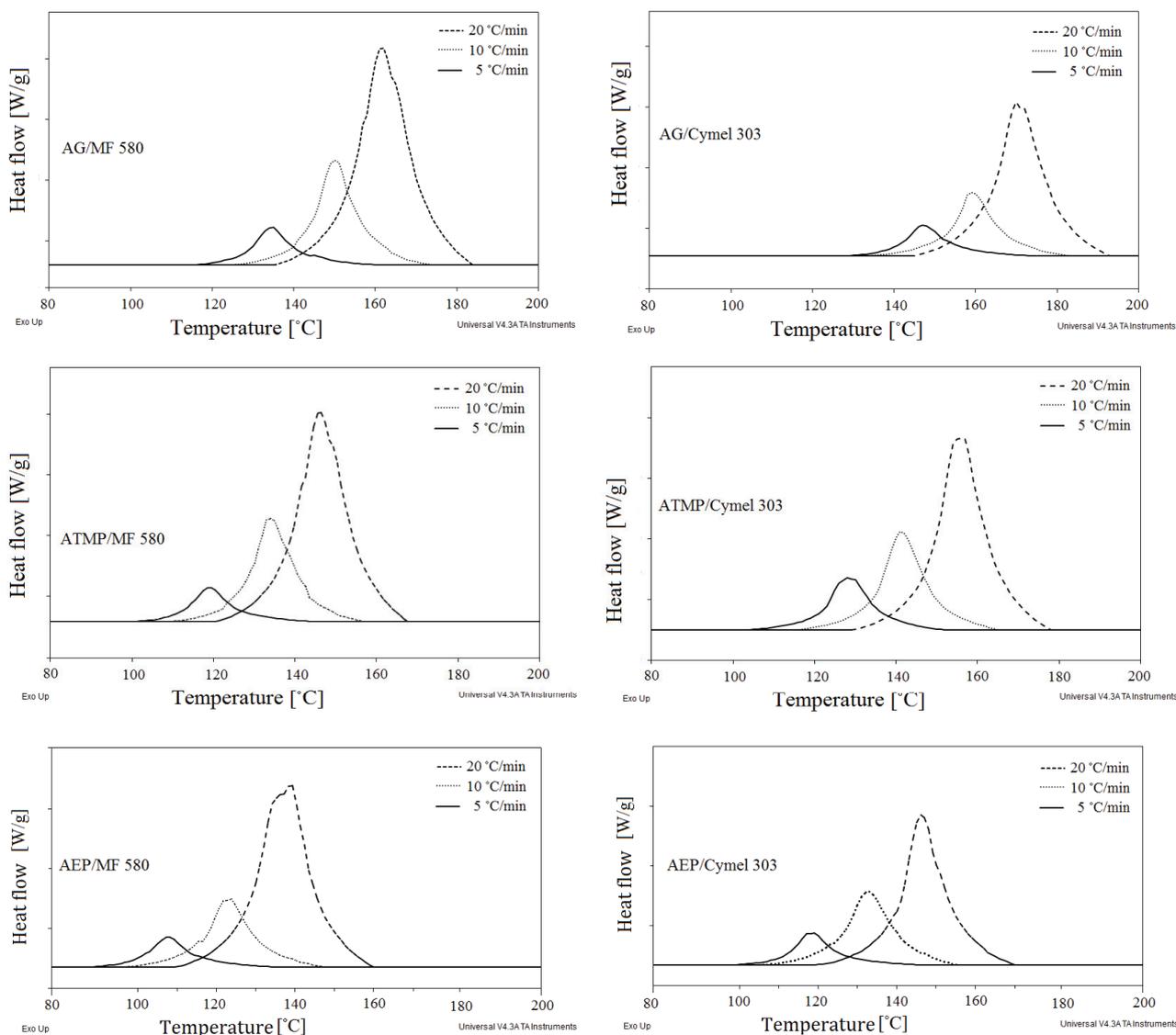

Figure 1. DSC Thermograms for all mixture resins recorded at different heating rates (5, 10 and 20 °C/min).
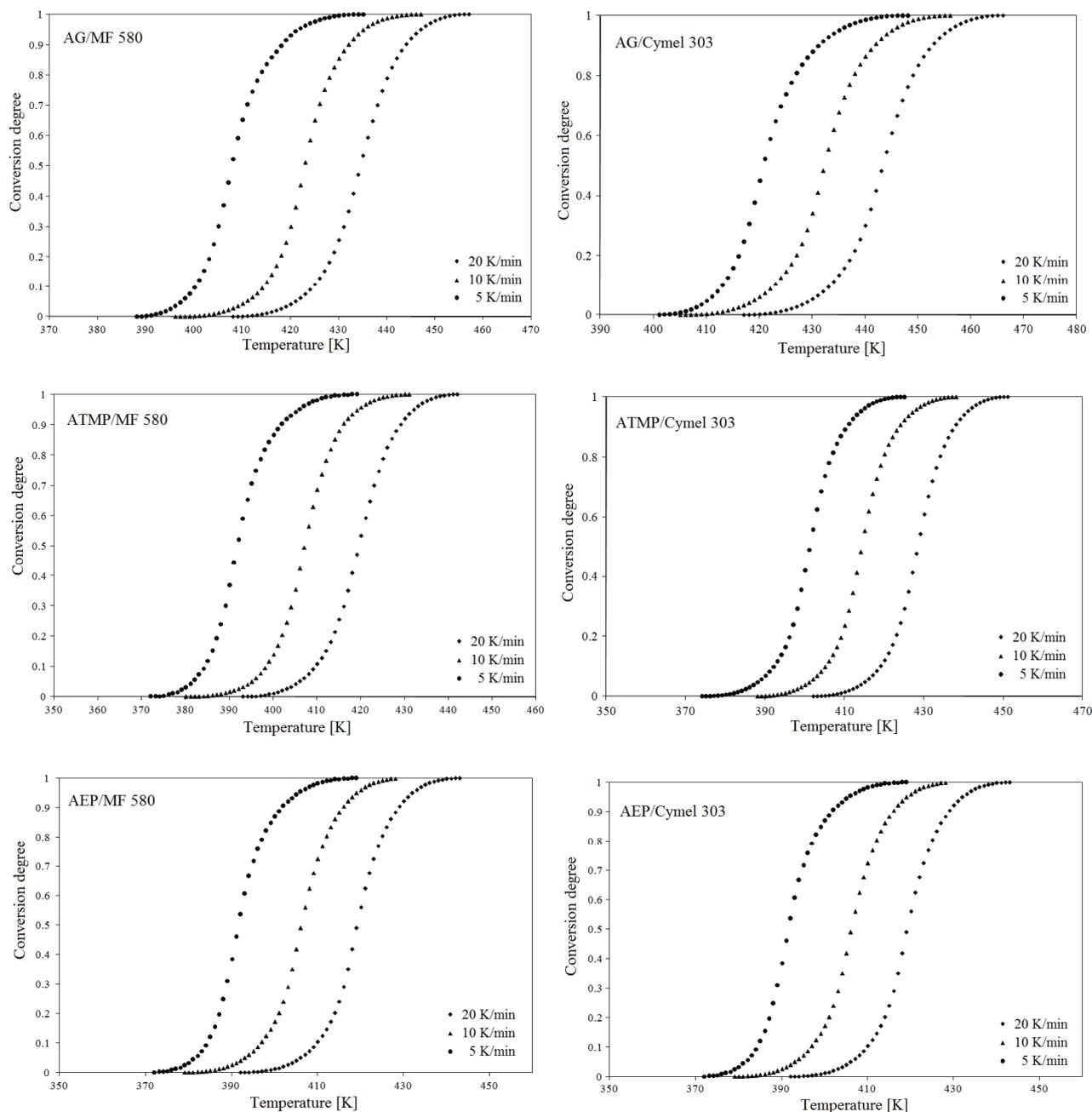
Figure 2. The temperature dependent conversion degree for all mixture resins recorded at different heating rates (5, 10 and 20 °C/min).

and AG/Cymel 303 samples) or trimethylolpropane (ATMP/MF 580 and ATMP/Cymel 303).

The obtained dependence of curing temperature on the content of hydroxyl groups (–OH) in alkyd resins might be explained by crosslinking reactions of –OH with functional groups of melamine resin [23,28,29]. The curing reaction of alkyd/melamine mixtures is also influenced by the type of melamine resin. In Figure 1 it can be seen that isobutylated melamine-formaldehyde resin (Maprenal MF 580) is more reactive with synthesized alkyds than with hexa-

methoxymethyl melamine resin (Cymel 303). These results were expected since Maprenal MF 580 consists of highly reactive imino-groups, and, on the other hand, Cymel 303 is a fully methylated melamine resin due to possible presence of steric hindrance.

The application of the isoconversional methods requires the determination of the absolute temperature at which a fixed extent of reaction from the several DSC curves is recorded at different heating rates. The obtained data were applied to isoconversional methods (Ozawa-Flynn-Wall and Kissinger-Akahira-

-Sunose) in order to determine the kinetic parameters of the resins curing process. The conversion range between 0.05 and 0.95 was investigated.

For the constant curing degree, the plot of log β *vs.* 1/T, (Ozawa-Flynn-Wall method (OFW), Eq. (3)) shows straight lines with slopes that give Ea/R values. The activation energy at each apparent curing degree has been calculated from the slope and value of A' has been obtained from the intercept (Eq. (3)). The activation energy is obtained based on the conversion extent that consequently allows the determination of the parameter A (Eq. (6)). The coefficient of determination (R^2) was between 0.97 and 0.99 for all mixture resins. The change of activation energy with the curing degree is observed. Results from the application of the isoconversional method in the conversion range between 5 and 95% are shown in Figure 3 for all investigated samples.

For constant α, the plot of ln(β/T^2) *vs.* 1/T, according to the Kissinger-Akahira-Sunose analysis (KAS), should be a straight line with a slope value representing the activation energy. For all sets of α values (5-95% conversion range) in the isoconversional plots, the coefficient of determination was higher than 0.97. Figure 4 shows the results for apparent activation energy obtained after fitting the data to the Kissinger-Akahira-Sunose model (Eq. (7)).

Results from applied the differential isoconversional Friedman method (Eq. (8)) in the conversion range between 5 and 95% are shown in Figure 5, for

all investigated samples. The coefficient of determination ranged between 0.97 and 0.99.

From data obtained applying three different isoconversional methods, it is shown that the Ozawa-Flynn-Wall (OFW) and Friedman (FR) models describe similar evolution of the activation energy with the curing degree (Figures 3-5). For all alkyd/melamine resin mixtures, slightly smaller Ea values obtained with Kissinger-Akahira-Sunose (KAS) than those determined by OFW and FR methods were estimated (Table 2). The activation energy values are insignificantly influenced by apparent curing degree α, especially in the range from 20 to 70% (Figures 3-5). By increasing the apparent curing degree to more than 70%, the activation energy showed dependence on α values [30], which is also noticed for the curing process of other thermoset resins [11,30,31] and ascribed to the slower diffusion. From the obtained results, it can be seen that the apparent activation energy is higher for the resin mixtures with Cymel 303 (AG/Cymel 303, ATMP/Cymel 303 and AEP/Cymel 303) than those containing Maprenal MF 580 (AG/MF 580, ATMP/MF 580 and AEP/MF 580) with the same alkyd resin, which could be explained by the different reactivity of melamine resin. The apparent activation energy is higher for the resin mixtures with Cymel 303 than for those containing Maprenal MF 580 with the same alkyd resin due to possible steric hindrance in fully methylated Cymel 303 melamine resin, while Maprenal MF 580 having highly reactive imino-groups
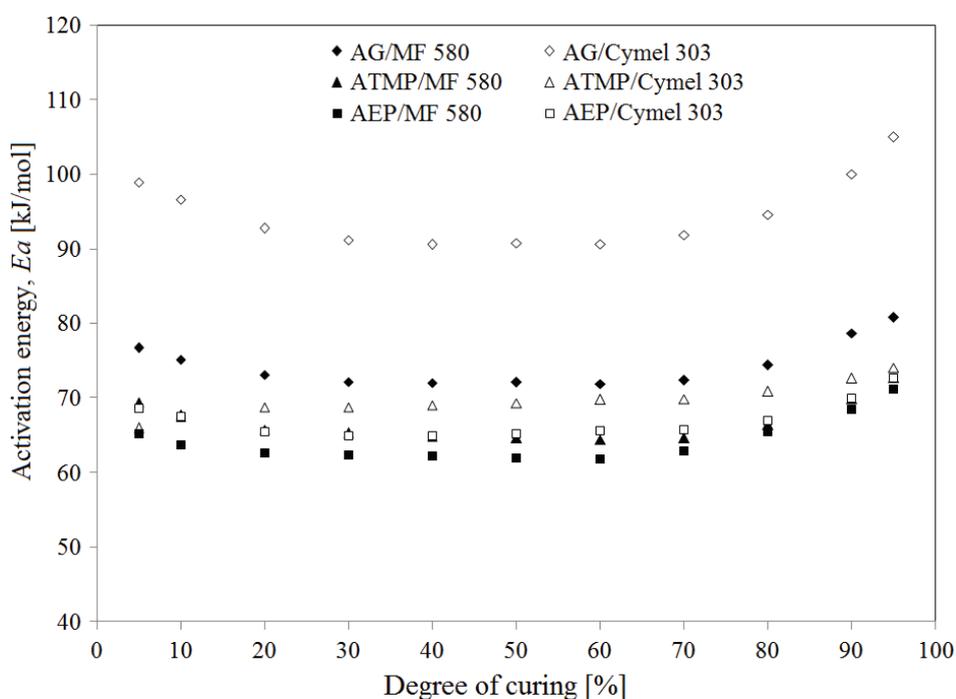

Figure 3. The activation energy dependence on curing degree, obtained by applying Ozawa-Flynn-Wall isoconversional model.
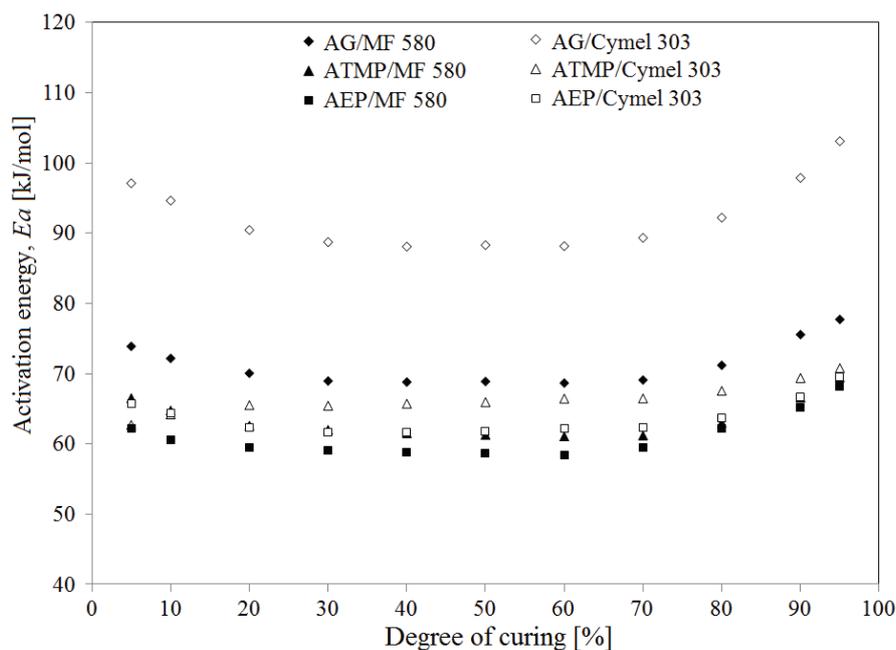
Figure 4. Activation energy dependence on degree of cure by applying Kissinger-Akahira-Sunose isoconversional model.
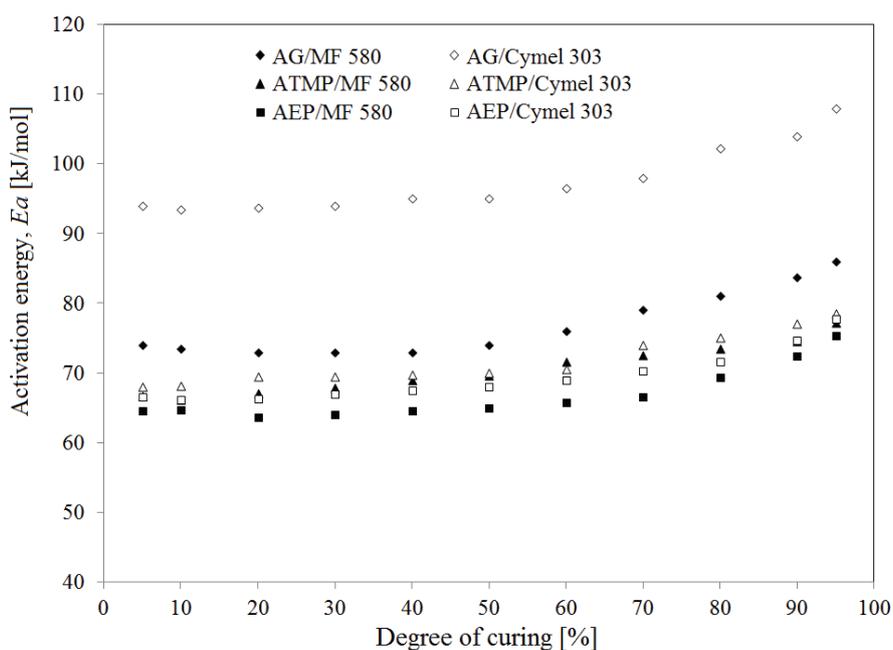

Figure 5. Activation energy dependence on degree of cure by applying Friedman method.

causes the lower apparent activation energy of the resin mixtures. Due to the highest hydroxyl number of alkyd based on ethoxylated pentaerythritol (AEP), which can have a catalytic effect on the curing reaction, the AEP/MF 580 and AEP/Cymel 303 resin mixtures have lower values of *Ea* than those obtained from alkyd AG (AG/MF 580 and AG/Cymel 303) and alkyd ATMP (ATMP/MF 580 and ATMP/Cymel 303).

Transformation of dynamic DSC results into isothermal data

The data from dynamic DSC curves (*A′*, *Ea* and *A*) were mathematically transformed using Ozawa-Flynn-Wall isoconversional method to obtain the isothermal data. In order to determine the kinetic parameters by means of isothermal runs and to transform the dynamic data into isothermal results, Eq. (9) is applied:

Table 2. The average values of activation energy obtained by isoconversional methods: two integral (Ozawa-Flynn-Wall and Kissinger-Akahira-Sunose) methods and one differential (Friedman) method

Sample code	Ozawa-Flynn-Wall Ea / kJ mol^{-1}	Kissinger-Akahira-Sunose Ea / kJ mol^{-1}	Friedman Ea / kJ mol^{-1}
AG/MF 580	74.5±6.3	71.4±6.4	76.9±9.0
AG/Cymel 303	94.9±10.2	92.6±10.5	97.6 ±10.4
ATMP/MF580	66.9±5.8	63.6±5.9	70.5±6.7
ATMP/Cymel 303	69.7±4.4	66.4±4.4	71.8±6.6
AEP/MF 580	64.4±6.9	61.1±7.0	66.9±8.4
AEP/Cymel 303	67.1±5.7	63.1±4.7	69.5±8.2

$$\ln t = A + \frac{Ea}{RT} \qquad (9)$$

The parameter A in the Eq. (9) is the same as in Eq. (6), accepting the equal kinetics in dynamical and isothermal experiments. In both equations, A is a function of $g(\alpha)$ and k_0 and consequently, only a function of resin apparent curing degree.

The main advantage of transforming the dynamic data for alkyd/melamine mixture resins into the isothermal ones is the possibility to obtain the curves of apparent curing degrees versus time (Figure 6) at any curing temperature of interest [11,16]. The data obtained from dynamic DSC using Ozawa-Flynn-Wall method were compared with those obtained by isothermal DSC experiments (at 120 °C) and the results are summarized in Figure 6 for all samples. Dependence of apparent curing degrees on time at 90, 100,

110 and 120 °C for AEP/Cymel 303 resin mixture are shown in Figure 7.

The results obtained after the transformation of dynamic DSC results into the isothermal data through Ozawa-Flynn-Wall model are in good agreement with those determined by the isothermal DSC experiments. The resin mixtures consisting of alkyd AEP cure faster than those obtained from alkyd AG or alkyd ATMP, Figure 6. The reason for that observation might be due to the highest content of hydroxyl groups in alkyd AEP which serve as sites for cross-linking reactions with the melamine resin [28-30]. The type of melamine resin also affects the curing time in the DSC curves (Figure 6). Isobutylated melamine-formaldehyde resin (MF 580) is more reactive with synthesized alkyds than hexamethoxymethyl melamine resin (Cymel 303). That finding was expected because MF 580 contains highly reactive imino-
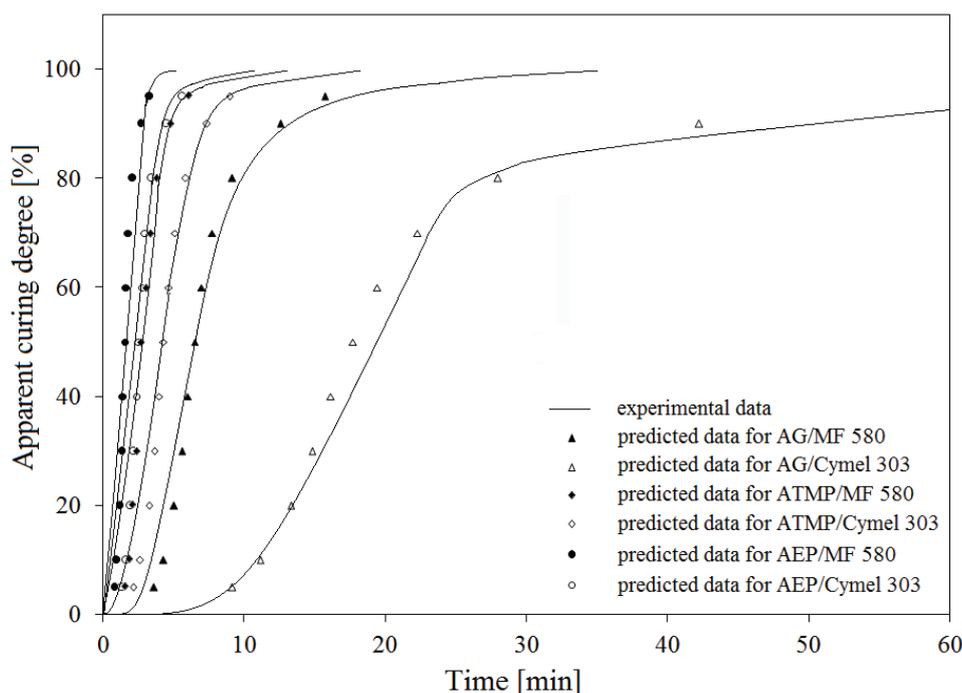

Figure 6. Dependence of apparent curing degrees on time at 120 °C for all resin mixtures.
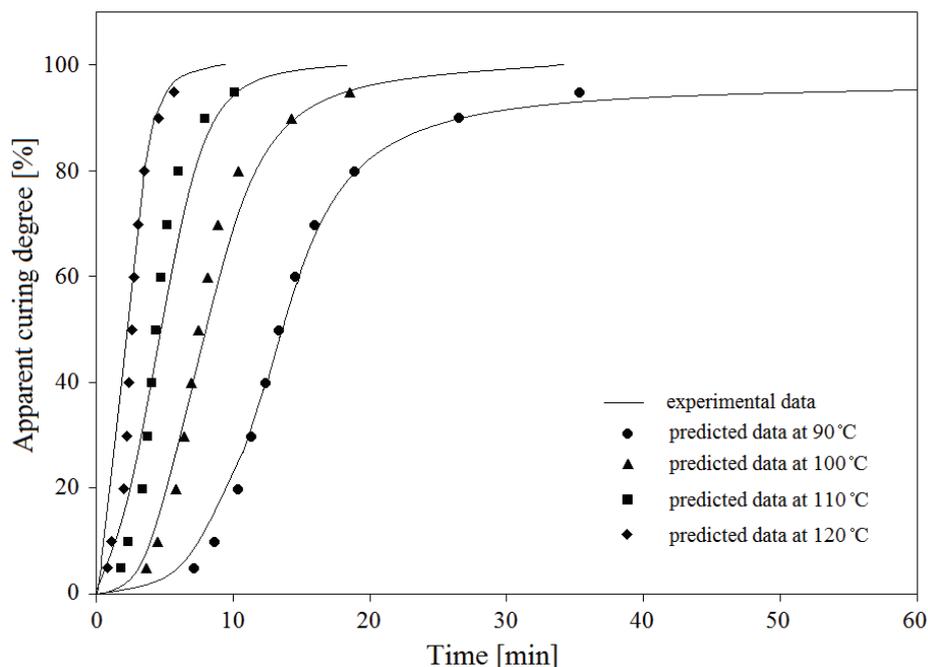
Figure 7. Dependence of apparent curing degrees on time at 90, 100, 110 and 120 °C for AEP/ Cymel 303 resin.

groups and, at the other hand in Cymel 303 the steric hindrance is possibly present because it is fully methylated melamine resin [23].

CONCLUSION

In this work, three different alkyd resins with high hydroxyl number were synthesized, and the influence of alkyd type on the curing of alkyd/melamine mixture was investigated. Kinetic analysis of dynamic DSC data on the alkyd/melamine systems was performed applying three conventional isoconversional methods: Ozawa-Flynn-Wall, Kissinger-Akahira-Sunose and Friedman method. For all alkyd/melamine resin mixtures, slightly smaller apparent activation energy (*Ea*) values obtained with KAS than those determined by OFW and FR methods were estimated. In the range of apparent degree of curing (α) from 20 to 70%, the activation energy was not significantly dependent on α value. In all the applied methods, for the apparent curing degree higher than 70%, the influence of α on the apparent activation energy was more pronounced, which is assigned to the slower diffusion. The mixtures consisting of alkyd resin prepared from ethoxylated pentaerythritol show lower values of *Ea* than those obtained from alkyd based resins with glycerin or trimethylolpropane due to the catalytic effect of higher hydroxyl number of alkyd AEP. The type of melamine resin also affects the curing reaction of alkyd/melamine mixtures. The apparent activation energy is higher for resin mixtures

with Cymel 303 than for those containing Maprenal MF 580 with the same alkyd resin, which might be explained by the steric hindrance in fully methylated Cymel 303 melamine resin. The resin mixtures with Maprenal MF 580 have the lower apparent activation energy due to its highly reactive imino-groups. The dependence of the apparent curing degree on time, which was obtained by mathematical transformations of dynamic DSC data using OFW method, was in good agreement with those determined by the isothermal DSC experiments.

Acknowledgements

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NAUČNI RAD

IZUČAVANJE KINETIKE UMREŽAVANJA ALKID/MELMINSKIH SMOLA MODELIMA IZOKONVERZIJE

Reakcije umrežavanja smeše alkidnih smola na osnovu ricinolne kiseline, anhidrida ftalne kiseline i tri poliola (glicerin, trimetilolpropan ili etoksilovan pentaeritritol) sa dve različite komercijalne melaminske smole su praćene metodom diferencijalne skenirajuće kalorimetrije (DSC). Kinetika umrežavanja je određena pomoću tri modela izokonverzije: Ozawa-Flynn-Wall, Kissinger-Akahira-Sunose i Friedman. Umrežavanje je vršeno sa tri različite brzine zagrevanja (5, 10 i 20 °C/min) u temperaturnom opsegu od 40 do 250 °C. Utvrđeno je da energija aktivacije reakcije umrežavanja smeša smola zavisi od vrste alkidne i melaminske smole što je posledica katalitičkog efekta hidroksilne grupe na reakciju. Na osnovu dinamičkih DSC podataka uz pomoć Ozawa-Flynn-Wall modela dobijena je zavisnost prividnog stepena umreženosti od vremena. Izračunate vrednosti se dobro poklapaju sa izotermnim DSC eksperimentima.

Ključne reči: premaz, termoreaktivne smole, umrežavnje, DSC, modeli izokonverzije.