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CURING OF ALKYDS BASED ON SEMI-DRYING OILS WITH MELAMINE RESIN

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An alkyd/melamine resin mixtures are mainly used in industrial baking enamels. The aim of this work was to study the curing behaviour of alkyds based on dehydrated castor oil and soybean oil with melamine resin by differential scanning calorimetry (DSC). The kinetic parameters obtained by the transformation of dynamic DSC results into isothermal data through Ozawa kinetic model are in good agreement with those determined by the isothermal DSC experiments. The apparent degree of curing, determined by DSC measurements and sol/gel method, has a pronounced effect on the hardness of the resultant coating film.

Keywords: *curing, DSC, melamine resin, semi-drying alkyds, sol/gel method*

Introduction

An alkyd/melamine resin mixture is the usual composition for the preparation of a coating called baking enamel and it is cured through functional groups of resins [1]. A combination of an alkyd resin with a melamine-formaldehyde resin gives a cured film with the flexibility of the alkyd constituent, while being characterized by the high chemical resistance and hardness of the melamine resin at the same time [2]. The alkyd resin plays a very important role in the coating formulation. The type of oil used in alkyd resin is responsible to a large extent for the properties of the alkyd resin [3, 4]. The melamine resin is a minor constituent and plays the role of a cross linking agent to join molecules of the alkyd resin into a cross linked network [5, 6]. The curing process proceeds via the reaction between the hydroxyl and carboxyl groups of the alkyds with the alkoxy groups of melamine resin [7, 8]. Although alkyd/melamine containing coatings have been the subject of recent reviews and search articles, the actual mechanisms of resin mixture curing are still not fully understood because of the chemical complexity of the reactions [9]. Two main reactions during the cure of alkyd/amino resins (heteropolycondensation and homopolycondensation) take place simultaneously [10]. In the paper of Gan *et al*. [9] Fourier transform infrared spectroscopy (FTIR) studies of the curing reactions of palm oil alkyd/melamine enamels are presented. The predominated reaction was identified as the formation of methylene ether linkages. However, the self-condensation reactions of the amino resin and ester linkages did not occur to any noticeable extent [9].

Literature data about the investigation of the curing of alkyd/melamine resin blends are considerably represented. The curing of a thermoreactive alkyd/amino resin systems was investigated by rheological, thermogravimetric and thermomechanical analysis, in order to construct the time-temperature-transformation diagram [10]. Cross linking kinetics and network formation in organic coatings containing melamine resin have been studied [11]. The paper of Kalenda and Kalendova [12] deals with film formation from amino resins combined with alkyd resin based on castor oil. A combination incorporating a melamine-formaldehyde resin and a castor oil modified alkyd resin was required to adapt the amino resin to alkyd resin ratio to a value of 1:1.4 [12]. The effects of non-drying alkyd/melamine resin ratio and curing temperature on the cross linking and properties of coatings were investigated [1]. Favourable coating properties could be achieved with an alkyd/melamine resin ratio 75/25, a curing temperature of 130°C and a curing time of 30 min [1]. In the paper of Haken *et al*. [13] the analysis of the alkyd components of a cross linked resin system with butylated amino resins is reported. Medium oil length glycerine alkyds based on mahua oil were modified with melamine-formaldehyde resin and cured at high temperature [14]. The suitability of these resins for high-temperature curing fly ash coating applications was established [14]. The factors which can influence the availability of functional groups in polymers are considered [15]. In particular, the importance of OH groups in the formation of film forming reactions of alkyd resins is discussed and evidence is presented to suggest that the number of OH groups available for chemical reaction is not neces-

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sarily equivalent to the theoretical value [15]. In the paper of Marshall [16] the changes in the alkyd resin during the curing process with amino resins were monitored by ^{13}C-NMR spectra. Non-isothermal kinetic was applied for the thermal decomposition of commercial alkyd varnish [17].

The characterization of the cure kinetics of thermoset materials is well established using a variety of techniques, namely spectroscopic analysis, differential thermal analysis (DTA), thermo-mechanical analysis (TMA), differential scanning calorimetry (DSC). Among these techniques, DSC is the most popular method and has been used extensively for the investigation of chemical reactions of resins. Numerous researchers have used the DSC to study the curing reactions of thermoset resins [1, 18–21]. Generally, kinetic parameters were determined from dynamic and isothermal data with the assumption that the exothermic heat evolved during cure is proportional to the extent of cure which is related to the independent variables, that is, time and temperature [22]. The nature of the curing process of an alkyd/melamine resin systems were investigated by DSC using both the dynamic method, with variation of peak exothermic temperature with heating rate and the isothermal method [23]. Curing reactions in thermosetting resins and resin-composite systems have been examined using DSC method [24]. Curing isotherms obtained from a single temperature scan have been analysed to give reaction kinetic parameters associated with the overall cure process [24]. The rates of cure of different oxidative drying oil modified alkyd resins were investigated by DSC and determined activation energy of curing process depends on the curing duration [25].

When the resin curing presents a high reaction rate, the isothermal DSC technique is not suitable to determine kinetic data. The methodology developed makes it possible to obtain the isothermal kinetic parameters for the resol resins cure using only calorimetrical data obtained by dynamic DSC runs [18]. This methodology could be extended to the curing of other thermosetting polymers. In the paper of Atarsia and Boukhili [22] a simple procedure using DSC results was developed for predicting the degree of thermosets cure *vs*. time under isothermal conditions from dynamic DSC tests and vice versa. The proposed procedure is validated with isothermal and dynamic DSC results from epoxy and polyester resin formulations [22]. Different methods for the determination of the curing kinetics of thermosetting polymers have been developed. The activation energy not only changes with the method employed but also with the conversion degree, which indicates that no single kinetics can be used for the overall curing process [18]. Among isoconversional methods, the most reliable results are obtained using the Arrhenius law and Ozawa method for isothermal and dynamic curing, respectively [18, 26].

The aim of this work was to study the curing behaviour of semi-drying oil alkyd/melamine resin mixtures when made into baking enamels and to determine the kinetic parameters from DSC measurements. The results determined by dynamic DSC were mathematically transformed for obtaining the isothermal data. These results, apparent degree of cure *vs*. time, were compared with those obtained by isothermal DSC experiments. The apparent degree of curing was also determined by measuring the sol fraction in samples after curing. The hardness of the cured film was followed in dependence on the apparent degree of curing, respectively on the ratio of reaction components and the operating conditions.

Experimental

Materials

Two kinds of alkyd resins were used: Alkyd DCO and Alkyd SO.

- Alkyd DCO, a phthalic alkyd resin containing 35 mass% of dehydrated castor oil, produced by ‘CoRes System’ (Belgrade, Serbia) was used as a 60% solution in xylene/isobutyl alcohol mixture. The characteristics of the resin were: acid number=20 mg KOH g^{-1}; dynamic viscosity at 23°C=1200 mPa s; density (20°C)=1.010 g cm^{-3}.
- Alkyd SO, a phthalic alkyd resin containing 35 mass% of soybean oil, synthesized in our laboratory, was used as a 50% solution in xylene/isobutyl alcohol mixture, with the following characteristics: acid number=12 mg KOH g^{-1}; dynamic viscosity at 23°C=1600 mPa s; density (20°C)=1.015 g cm^{-3}.
- A butylated melamine resin, produced by ‘Helios’ (Domžale, Slovenia), was used as a 56% solution in isobutyl alcohol. The characteristics of the resin were: acid number=2 mg KOH g^{-1}; dynamic viscosity at 23°C=500 mPa s; density (20°C)=1.067 g cm^{-3}.

Table 1 Designations and formulations of the prepared resin mixtures

Number of sample	Type of alkyd resin	Alkyd/melamine resin ratio
1	Alkyd DCO	70/30
2	Alkyd DCO	80/20
3	Alkyd DCO	85/15
4	Alkyd SO	70/30
5	Alkyd SO	80/20
6	Alkyd SO	85/15

Preparation of the resin mixture

A definite part by mass of the alkyd (based on dried mass) was mixed with an adequate part by mass of melamine resin and homogenizated at room temperature. The designations and the formulations of the prepared alkyd/melamine resin mixtures are presented in Table 1.

Methods

DSC studies of the curing of alkyd/melamine resin mixtures

Curing of alkyd/melamine resin mixtures were carried out in differential scanning calorimeter (DSC) using a DuPont Model 910 instrument. The sample was placed in a DSC hermetically sealed pan and freed of solvent in a vacuum oven at ambient temperature before the sample was encapsulated. The sample was then mounted in the instrument and scanned. The Ozawa isoconversional method was applied with three heating rates (2, 5 and 10°C min^{-1}) in a scanning temperature range from 25 to 200°C. Then, the results determined by dynamic DSC were mathematically transformed for obtaining isothermal data. These results, apparent degree of curing *vs.* time, were compared with data obtained by isothermal DSC measurements. The isothermal DSC runs were carried out at the temperatures of 110, 120 and 130°C. After each isothermal curing, the uncured resin mixture content was determined by heating the sample (from the temperature of isothermal curing to 220°C) in the dynamic thermal range at the heating rate of 10°C min^{-1} [1]. The apparent degree of curing from isothermal DSC curve was determined by procedure described in literature [1, 22].

Kinetic model [18, 27]

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

$$\log\beta = A' - 0.4567\frac{E_a}{RT} \qquad (1)$$

where, β is the heating rate (K min^{-1}), E_a is the activation energy (J mol^{-1}), R is the gas constant (8.31 J mol^{-1} K^{-1}), T is the temperature (K) and A' can be expressed as:

$$A' = \log\left[\frac{k_0 E_a}{Rg(\alpha)}\right] - 2.315 \qquad (2)$$

where α is the apparent degree of curing, k_0 is the pre-exponential factor of Arrhenius law and $g(\alpha)$ is a function of curing degree:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t k_0 e^{-\frac{E_a}{RT}} dt = k_0 e^{-\frac{E_a}{RT}} t \qquad (3)$$

From A' and E_a values obtained from Eq. (1) for different resins apparent curing degrees are possible to determine a new constant, A, which can be written as:

$$A = \ln\left[\frac{g(\alpha)}{k_0}\right] \qquad (4)$$

In order to determine the kinetic parameters by means of isothermal runs and to transform the dynamic data into isothermal results, the Eq. (5) is applied:

$$\ln t = A + \frac{E_a}{RT} \qquad (5)$$

The parameter 'A' of the Eq. (5) is the same of the Eq. (4), accepting 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.

Determination of the sol fraction

A thin layer of the resin mixture (a film thickness of 80 μm) was applied on a glass panel. The solvent was removed under reduced pressure in a vacuum oven at room temperature. After that the panel with solvent less enamel film was placed in drying oven set to the specified temperature for isothermal curing. The films were isothermally cured at 110, 120 and 130°C for 40 min. Then the panel with cured film was measured (m_0) and put in 200 cm^3 of acetone for 24 h, at ambient temperature, in purpose to extract the sol fraction. After that the panel with the insoluble (i.e. cross linked) film of enamel was vacuum dried and then measured (m_t). The content of sol fraction was calculated from the difference in mass of sample before (m_0) and after extraction (m_t) [28].

Determination of the hardness of cured enamel film

The hardness of the coating film was determined by the standard method JUS H.C8.055 using a Koning's bell-clapper. The bell-clapper was placed on a panel with a coating film under an angle of 6° and left to oscillate. The elapsed time (s) until the measured amplitude of the oscillation had decreased to 3° is defined as the hardness [1].

Results and discussion

DSC curves of resin mixtures curing at different heating rates are given in Figs 1 and 2.

From presented curves in Figs 1 and 2, it is seen that a single broad peak is obtained in all experiments, like it was reported in literature for some non-drying alkyd/melamine resin blends [1, 23]. The temperature of the maximum in the curing curves increases with decreasing of the ratio of melamine resin in the resin blend and with increasing of the heating rate. The type of semi-drying alkyd used in mixture with melamine resin has no significant effect on the temperature of the maximum in the DSC curves (Figs 1 and 2). In semi-drying oils, respectively in dehydrated castor and soybean oils used in alkyd resins composition, the fatty acids with one or two double bonds predominate [3, 4].

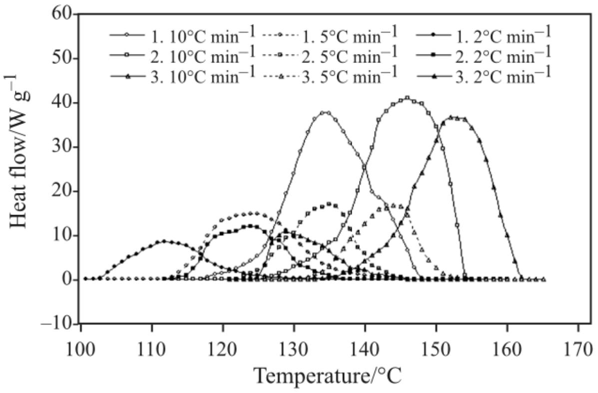

Fig. 1 Dynamic DSC curves of the curing of alkyd DCO/melamine resin mixtures

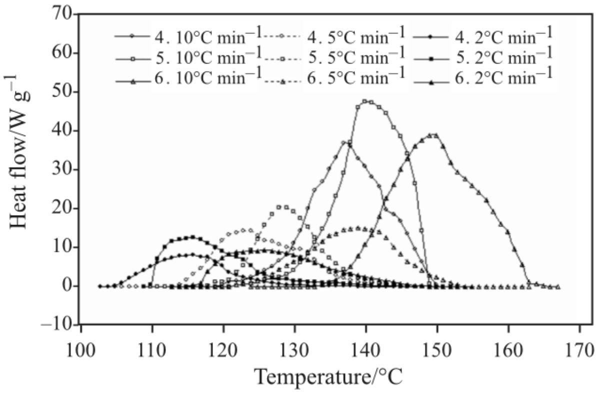

Fig. 2 Dynamic DSC curves of the curing of alkyd SO/melamine resin mixtures

The values of constant A' and activation energy E_a at different apparent curing degrees of all resin mixtures were calculated trough the Ozawa method (Eq. (1)). Activation energy values at each apparent degree of cure have been calculated from the slope of the plot of (lnβ) *vs*. (1/T), respectively. At the same time values of A' have been obtained from the intercept in each case (Eq. (1)). This data were then fitted to (Eq. (2)) to obtain parameter A. The data of A, A' and E_a for the alkyd/melamine resin blends curing at different conversion degrees are shown in Tables 2 and 3.

Activation energy significantly depends on the apparent degree of cure, increasing as conversion did, which is in agreement with literature data for other thermosetting resins [18, 19]. However, whatever the method was used (Ozawa, Kissinger, Flynn or Wall) activation energy presented strong dependence on the apparent degree of curing [19]. That is characteristic of a curing process of thermosetting resins [18, 19, 22].

From E_a and A, it can be established by the Eq. (5) isothermal fits of these starting data for resin mixtures cure. The results obtained by transformation of dynamic DSC results into isothermal data are presented in Figs 3–8, which show the conversion degree *vs*. curing time at different temperatures for all examined

Table 2 Kinetic parameters of curing of alkyd based on dehydrated castor oil/melamine resin mixtures determined by the Ozawa method

α/%	Alkyd based on dehydrated castor oil/melamine resin ratio											
	70/30				80/20				85/15			
	A'	E_a/ kJ mol^{-1}	A	R^2	A'	E_a/ kJ mol^{-1}	A	R^2	A'	E_a/ kJ mol^{-1}	A	R^2
2	14.85	99.91	–30.14	0.998	13.04	89.57	–26.07	0.995	13.52	94.86	–27.12	0.986
10	13.08	88.21	–26.18	0.997	12.96	89.73	–25.88	0.991	13.49	95.04	–27.05	0.999
20	13.09	88.67	–26.19	0.996	12.90	89.78	–25.75	0.989	13.46	95.28	–26.96	0.997
30	13.08	88.94	–26.17	0.997	12.89	89.99	–25.71	0.987	13.44	95.52	–26.93	0.996
40	13.07	89.16	–26.13	0.998	12.86	90.07	–25.64	0.985	13.42	95.66	–26.89	0.996
50	13.03	89.21	–26.06	0.995	12.82	90.09	–25.56	0.982	13.40	95.76	–26.84	0.996
60	13.01	89.39	–26.0	0.999	12.79	90.12	–25.49	0.980	13.44	96.30	–26.91	0.995
70	12.97	89.40	–25.9	0.997	12.80	90.44	–25.5	0.975	13.47	96.80	–26.98	0.993
80	12.96	89.77	–25.89	0.997	12.79	90.72	–25.49	0.971	13.49	97.25	–26.02	0.989
90	13.15	91.74	–26.3	0.997	12.99	92.58	–25.92	0.971	13.84	100.33	–27.79	0.982
100	16.54	119.52	–33.85	0.996	16.43	120.08	–33.59	0.969	17.11	127.35	–35.08	0.983

Table 3 Kinetic parameters of curing of alkyd based on soybean oil/melamine resin mixtures determined by the Ozawa method

α/%	Alkyd based on soybean oil/melamine resin ratio											
	70/30				80/20				85/15			
	A'	E_a/ kJ mol^{-1}	*A*	R^2	*A*'	E_a/ kJ mol^{-1}	*A*	R^2	*A*'	E_a/ kJ mol^{-1}	*A*	R^2
2	13.29	89.48	–26.65	0.971	12.63	85.72	–25.18	0.998	13.31	92.03	–26.67	0.976
10	13.22	89.55	–26.48	0.980	12.65	86.44	–25.22	0.999	13.22	92.14	–26.45	0.985
20	13.16	89.60	–26.34	0.979	12.65	86.73	–25.20	0.998	13.22	92.70	–26.45	0.994
30	13.13	89.79	–26.29	0.977	12.65	87.07	–25.20	0.998	13.23	93.18	–26.47	0.995
40	13.13	90.06	–26.27	0.978	12.69	87.64	–25.29	0.997	13.39	94.79	–26.82	0.995
50	13.19	90.85	–26.41	0.981	12.83	88.91	–25.60	0.996	13.55	96.36	–27.18	0.994
60	13.22	91.36	–26.46	0.985	13.03	90.64	–26.03	0..995	13.78	98.44	–27.68	0.993
70	13.19	91.51	–26.40	0.991	13.29	92.84	–26.60	0.992	13.94	100.09	–28.03	0.989
80	13.21	92.04	–26.43	0.995	13.72	96.46	–27.57	0.981	14.13	102.05	–28.45	0.981
90	13.40	94.02	–26.84	0.995	15.83	112.66	–32.28	0.991	14.83	108.07	–29.99	0.968
100	16.58	120.1	–33.93	0.996	16.89	125.49	–34.60	0.999	16.59	124.06	–33.93	0.934

samples. Transforming the dynamic data of resin mixture curing into isothermal data through Ozawa method is the possibility to obtain the curve apparent degree of curing *vs*. time at any curing temperature of interest [18]. The curing temperatures in present work are selected according to the usual range employed in making baking enamels. The data obtained from dynamic DSC using Ozawa method, which is based on the assumption that the curing process of resin mixtures comply with the isoconversional principle, were compared with those obtained by isothermal DSC experiments and the results are summarized in Figs 3–8. The results obtained by the transformation of dynamic DSC results into isothermal data through Ozawa kinetic model are in good agreement with those determined by the isothermal DSC experiments, with the exception of those at 130°C when the apparent curing degrees are higher than 90%.

From the isothermal DSC data for alkyd/melamine resin mixtures curing, the kinetic parameters of this process were calculated. The rate of chemical reaction, dα/d*t*, can be expressed as a function of the degree of conversion, α, using general formulation: dα/d*t*=*k*(*T*)*f*(α), where *t* is the time, *T* the temperature, *k* is the rate constant and *f*(α) is some function of the degree of conver-

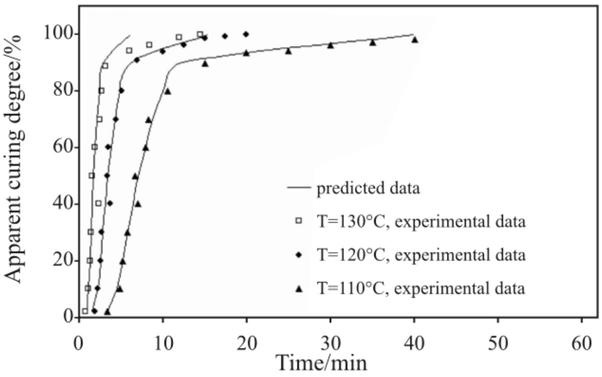

Fig. 3 Comparison between experimental and predicted curing degree of sample 1 (Alkyd DCO/melamine resin ratio 70:30)

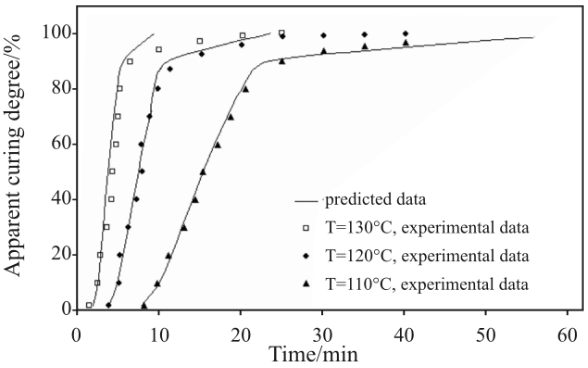

Fig. 4 Comparison between experimental and predicted curing degree of sample 2 (Alkyd DCO/melamine resin ratio 80:20)

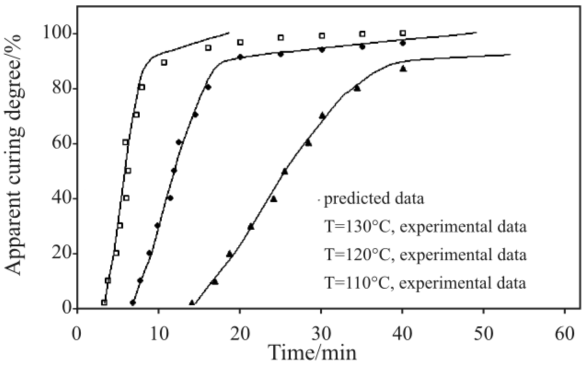

Fig. 5 Comparison between experimental and prediction curing degree of sample 3 (Alkyd DCO/melamine resin ratio 85:15)

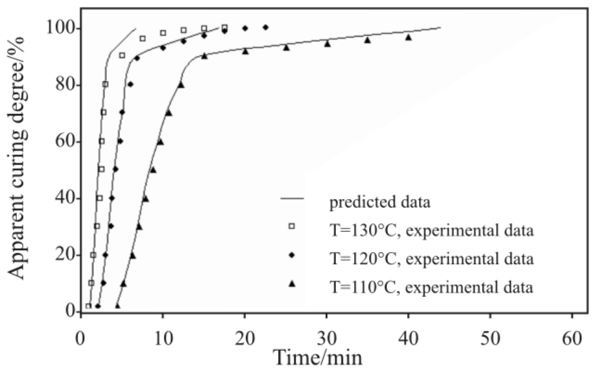

Fig. 6 Comparison between experimental and prediction curing degree of sample 4 (Alkyd SO/melamine resin ratio 70:30)

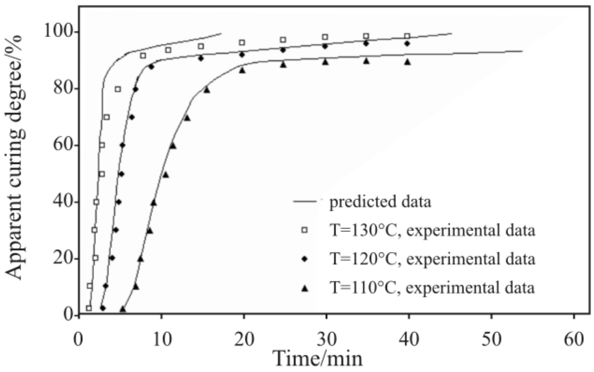

Fig. 7 Comparison between experimental and prediction curing degree of sample 5 (Alkyd SO/melamine resin ratio 80:20)

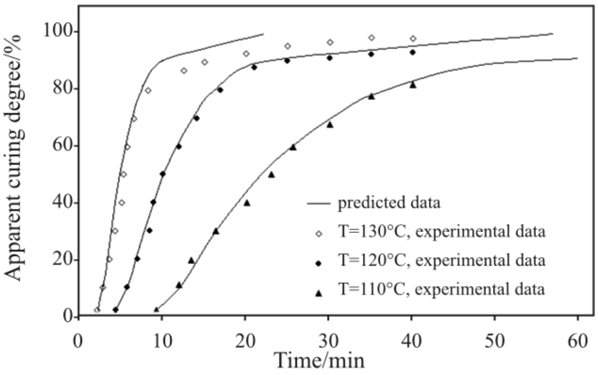

Fig. 8 Comparison between experimental and prediction curing degree of sample 6 (Alkyd SO/melamine resin ratio 85:15)

sion. Assuming that the curing reaction follows n^{th} order kinetics $f(\alpha)$ has the form [29]: $f(\alpha)=(1-\alpha)^{n}$ and the following logarithmic equation can be written: $\log(d\alpha/dt)=n\log(1-\alpha)+\log k$. Plots of $\log(d\alpha/dt)$ *vs*. $\log(1-\alpha)$ for alkyd/melamine resin mixtures cured at 120°C are shown in Fig. 9. From each slope of the straight lines in Fig. 9 the reaction order (n) has been determined. At the same time value of $\log k$ has been obtained from the intercept in each case. In all cases data fit quite well when assuming the n^{th} order reaction kinetic model, since the correlation coefficients of the regression lines are higher than 0.91. The linear fits between $\log(d\alpha/dt)$ and $\log(1-\alpha)$ are also observed for resin mixtures cured at 110 and 130°C. Determined values of the rate constants (k) and reaction order (n) are presented in Table 4. The rate constant increases with increasing the content of melamine resin in mixtures and with curing temperature. The reaction order varied from 0.85 to 1.46 for alkyd DCO/melamine resin mixtures and 1.05 to 1.53 for alkyd SO/melamine resin blends. The dependence of the rate constant $k(T)$ on the temperature follows the Arrhenius law, which allows calculating the kinetic parameters of the isothermal curing process of all resin mixtures. Depending on alkyd resin type and ratio in mixtures the values of activation energies (Table 5) are in the interval from 87.6 to 94.6 kJ mol^{-1}. The pre-exponential factors $\ln k_0$ are in range 26.0 to 27.7 (Table 5).

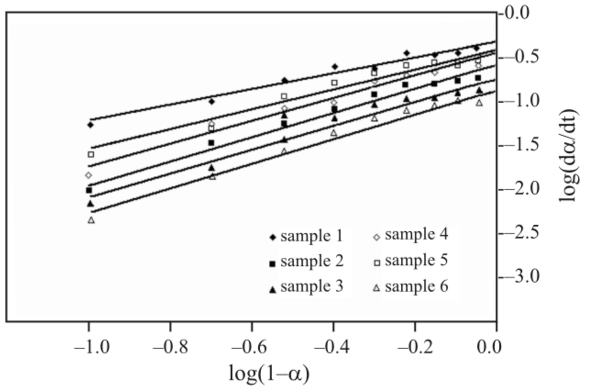

Fig. 9 Plots of $\log(d\alpha/dt)$ *vs*. $\log(1-\alpha)$ for resin mixtures cured at 120°C

There are no literature data about the activation energy of semi-drying alkyd/melamine resin blend curing. Activation energy of 60.2 kJ mol^{-1} and the reaction rate constants from 0.76 to 0.85 s^{-1} have been determined from isothermal DSC experiments for some non-drying alkyd/melamine resin blends curing [23].

The apparent degree of curing of the resin blend is an indicator of the content of reacted functional groups up to a definite time of reaction, at a certain temperature [1]. These data can be used for the estimation of the cross linking degree. The values of apparent degrees of curing after 40 min of reaction for all examined resin mixtures, determined by isothermal DSC experiments and the sol/gel method are given in Table 6. The apparent degree of curing increases with increasing ratio of melamine resin in the resin mixture and with an increase the curing temperature (Table 6). The mixtures based on dehydrated castor oil alkyd with melamine resin are characterized by slightly higher values of conversion after 40 min of reaction (from 87.1 to 100 mass%) than those based on soybean oil alkyd/melamine resin (from 81.8 to 100 mass%).

Table 4 Rate constants (k) and reaction order (n) of alkyd/melamine resin mixtures curing

Temperature/ °C	Alkyd DCO/melamine resin ratio						Alkyd SO/melamine resin ratio					
	70/30		80/20		85/15		70/30		80/20		85/15	
	k/s^{-1}	n	k/s^{-1}	n	k/s^{-1}	n	k/s^{-1}	n	k/s^{-1}	n	k/s^{-1}	n
110	0.2355	0.95	0.1418	1.33	0.0741	1.46	0.1942	1.34	0.1755	1.39	0.0629	1.53
120	0.4746	0.90	0.2607	1.37	0.1858	1.36	0.3550	1.29	0.3848	1.12	0.1348	1.40
130	0.9219	0.85	0.2592	1.12	0.31196	1.1	0.8002	1.14	0.7563	1.05	0.2752	1.38

Table 5 Activation energies and lnk_0 values of resin mixtures curing

Number of sample	Type of alkyd resin	Alkyd/melamine resin ratio	E_a/kJ mol^{-1}	lnk_0
1	Alkyd DCO	70/30	87.6	26.0
2	Alkyd DCO	80/20	92.1	26.9
3	Alkyd DCO	85/15	92.4	26.5
4	Alkyd SO	70/30	90.7	26.8
5	Alkyd SO	80/20	93.8	27.7
6	Alkyd SO	85/15	94.6	27.0

Table 6 Apparent degrees of curing of alkyd/melamine resin mixtures (t=40 min)

Number of sample	Apparent degree of curing/%					
	Determined by sol/gel method			Determined by DSC method		
	110°C	120°C	130°C	110°C	120°C	130°C
1	97.1	99.7	100	98.3	100	100
2	96.9	98.8	99.8	96.7	99.8	100
3	85.9	95.1	99.7	87.1	95.9	99.7
4	95.8	99.3	100	96.6	100	100
5	89.9	97.8	98.8	91.2	97.5	99.1
6	81.4	92.5	98.1	81.8	93.4	98.3

That can be explained by the structure of alkyd resin used. Dehydrated castor oil contains a certain amount (about 7%) of the ricinoleic acid. The hydroxyl groups in the ricinoleic acid provide good compatibility with melamine resin and also serve as sited for cross linking reactions [9]. The value of the apparent degree of curing is practically independent on the method applied for its determination (Table 6).

The hardness of the coating film increases with increasing the content of melamine resin in the mixture and with curing temperature (Table 7) in accordance with literature data for some alkyd/melamine resin blends [1, 9, 12]. That can be explained by the higher functionality of the melamine resin (containing three methylol groups) than that of the alkyd resin which results in the formation of a more cross linked coating film at higher ratio of melamine in the mixture [1, 9]. A significant increase in the hardness of the enamel film with increasing of both above-mentioned parameters was shown in this investigation so the apparent degree of curing has a pronounced effect on the hardness of obtained film. From Table 7 it is seen that the coating films based on dehydrated castor oil/melamine resin mixtures are characterized by higher values of the hardness (from 124 to 171 s) than those based on soybean oil alkyd/melamine resin mixtures (from 113 to 160 s).

Table 7 The hardness of the coating film

Number of sample	Hardness/s		
	110°C	120°C	130°C
1	140	161	171
2	132	149	167
3	124	131	153
4	140	156	160
5	123	141	155
6	113	127	143

Conclusions

Curing of alkyds based on semi-drying oils, respectively on dehydrated castor oil and soybean oil, with melamine resin when made into baking enamel were investigated. The results determined by dynamic DSC were mathematically transformed through Ozawa isoconversional method for obtaining the isothermal data. These results, apparent degree of curing vs. time, are in good agreement with those determined by the isothermal DSC experiments. By application Ozawa method it is possible to obtain the isothermal kinetic parameters for the alkyd/melamine resin mixtures curing using only calorimetrical data obtained by dynamic DSC runs. Depending on alkyd resin type and ratio in mixtures the values of activation energies of curing process of resin mixtures are from 87.6 to 94.6 kJ mol^{-1}. The rate constant of curing increases with increasing the content of melamine resin in the mixture and with curing temperature. The reaction order varied from 0.85 to 1.46 for alkyd DCO/melamine resin mixtures and 1.05 to 1.53 for alkyd SO/melamine resin blends.

The value of the apparent degree of resin mixture curing does not vary significantly with the method (DSC and sol/gel methods) applied for its determination. The conversion, i.e. the apparent degree of curing, increases with increasing the ratio of melamine resin in the blend and with curing temperature. A significant increase in the hardness of enamel film with increasing of both-mentioned parameters was shown in this investigation so the apparent degree of curing has a pronounced effect on the hardness of obtained film. The coating films based on dehydrated castor oil alkyd/melamine resin mixtures are characterized by higher hardness values than those based on soybean oil alkyd/melamine resin blends. In this paper is shown that the combinations of some semi-drying oil alkyds with melamine resin, especially those of dehydrated castor oil alkyds, could be employed as the compositions for the preparation of baking enamel.

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