KINETICS OF THE CURING PROCESS OF ALKYD–MELAMINE RESIN SYSTEMS

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ABSTRACT

The aim of this work was to investigate the nature of the curing process of an alkyd–melamine resin mixture, and to determine the kinetic parameters from DSC measurements (Perkin–Elmer 2). The experiments were performed using both the dynamic method, with variation of peak exotherm temperature with heating rate, and the isothermal method. A single broad peak was observed in all experiments. Practically no reaction was observed below 350 K. From the dynamic experiments at four heating rates an activation energy of 78.7 kJ mol^{-1} was obtained. More precise results were obtained from isothermal experiments by scanning the temperature range 415–430 K: a reaction order very close to one, reaction rate constants from 0.76 to 0.85 s^{-1} and an activation energy of 60.2.

INTRODUCTION

The nature of the curing process of alkyd–melamine resin systems has been under investigation for about three decades. Wohnsiedler [1] produced the first detailed study on this subject, concluding that reactions between hydroxyl groups in the alkyd and alkoxymethyl and hydroxymethyl groups in the melamine resin are the most important in co-condensation, but several other possibilities are also indicated. The self-condensation of melamine resin leads to the formation of methylene linkages between the aminotriazine structures with a simultaneous loss of alcohol and formaldehyde. Wohnsiedler pointed out that transesterification is the predominant curing reaction with hydroxyl/carboxyl-containing polymers. This view has been supported by other authors [2,3].

The reaction of self-curing is favoured in cases where there is a high concentration of =NH and =NCH$_2$OH groups [3–5] and represents the main reaction even in the presence of alkyds with high–OH numbers. Highly

alkylated melamine resins have been used to favour the curing between the alkyd and melamine components. The curing reaction is accomplished in the presence of acid catalyst. Free carboxyl groups of the alkyd resin are efficient in this respect but in order to increase the reaction rate, external catalysts such as *p*-toluene-sulfonic acid are usually employed.

The curing mechanism has been investigated by Holmberg [6], who concluded from numerous experimental data from the work of various authors that the curing process of alkyd–melamine resin systems goes by a conventional S_N2 type mechanism. The rate expression in such cases is

Rate: $k[=N-CH_2-O-R][HO-R']$

i.e. the rate of reaction is dependent on the concentration of the amino and alkyd components.

Other authors have suggested that the process goes by an S_N1 type mechanism [7–9], where the rate expression is dependent only on the concentration of amino resin

Rate: $k[=N-CH_2-O-R]$

Gauler and Mohler [10] have investigated samples of various alkyd and melamine resins by the DSC method, performing isothermal measurements at very high temperatures, and have obtained data on some kinetic parameters.

This present work investigates the curing process in alkyd–melamine systems where the two components are mixed in the ratio which is used in the automobile industry. The DSC method was used, and the reaction mechanism deduced from the results of isothermal and dynamic measurements. This method could provide a quick way of determining the optimum temperature for the process in the coating industry.

EXPERIMENTAL

The alkyd resin used was a commercial product with 33% dehydrated castor oil fatty acids with acid number 25 and hydroxyl number in the range 50–100, as a 60% solution in a mixture of aromatic solvents with high boiling points. The melamine resin was a highly butylated commercial product dissolved in a 9:1 isobutanol–xylene mixture.

All the measurements were made using a Perkin–Elmer DSC-2 thermo-analyser, with a maximum sensitivity of 0.1 mcal s^{-1} full scale. The samples were prepared by mixing the two resin components in the desired ratio (70 parts per weight of alkyd and 30 parts of melamine) and evaporating the solvent in a rotatory evaporator. The sample was then dried on a glass plate in vacuo at 40° C and the dry ground film transferred to aluminium pans for volatile samples, to prevent the evaporation of volatile products of the curing reaction. A series of DSC measurements were taken by the dynamic

method in the temperature interval 323–523 K. A second set of measurements were taken isothermally at several characteristic temperatures.

RESULTS AND DISCUSSION

The Dynamic Method: Variation of the Peak Exotherm Temperature with Heating Rate

The peak exotherm temperature T_p varies in a predictable manner with heating rate ϕ, and several methods are known for the calculation of the activation energy E and the pre-exponential factor A. Kinetic parameters obtained in this way have been very satisfactory with respect to known material properties. The approach has been described by Duswalt [11] and is identical with the ASTM method E 698-79 for determining the Arrhenius kinetic constants for thermally unstable materials. It is valuable as a precursor to isothermal studies and is a convenient way of analysing the curing kinetics of systems with multiple exotherms [12], solvent effects [13] or unreliable baselines [14]. The following relationship between activation energy, heating rate and peak exotherm temperature is based upon the work of Ozawa [15]

$$E = \frac{-R \, \Delta \lg \phi}{0.456 \, \Delta(1/T_p)} = \frac{-R \, \Delta \ln \phi}{1.052 \, \Delta(1/T_p)}$$

From the peak reaction temperature as a function of heating rate, the activation energy can be obtained with a precision of $\pm 3\%$ [11].

Kissinger [16] has derived an expression for the frequency factor of the nth order reaction

$$A = \frac{E \, e^{E/RT_p}\phi}{RT_p^2\left[n(1 - \alpha_p)^{n-1}\right]} = \frac{E \, e^{E/RT_p}\phi}{RT_p^2}$$

Measurements were taken by the dynamic method at three different heating rates: 5, 10 and 20°C min^{-1} (Fig. 1). The results obtained for T_p and corresponding values of ϕ are listed in Table 1.

The values from Table 1 were used to make a plot of $\lg \phi$ vs. $1000/T_p$, and to calculate E and A, using

$$E = -2.19 \times 8.32(-4462) = 81311 \text{ J mol}^{-1}$$

where -4462 represents the value of the slope of the plot of $\lg \phi$ vs. $1000/T_p$ (Fig. 2).

According to Duswalt, the value of E can be more precisely calculated if correction for D is introduced, from the table of dependence between x (E/RT) and D $(D = -d \ln(x)/dx$, assuming that $(x) = (x + 2)^{-1}$
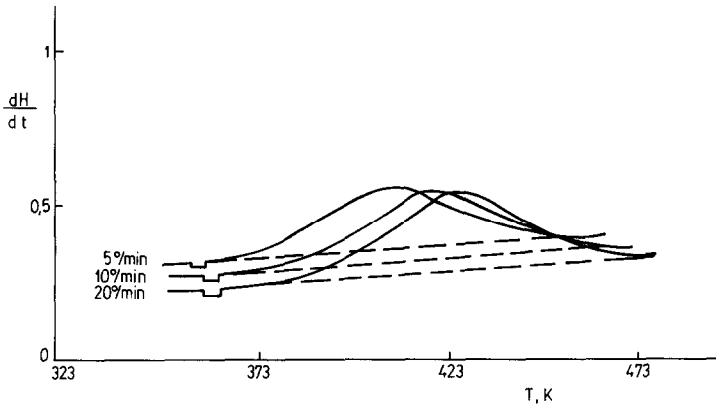
Fig. 1. Variation of the peak exotherm temperature T_p with heating rate ϕ.

$x^{-1} e^{-x}$): for $E'/RT = 81311/8.32(0.00238) = 23.33$, D is 1.086, so the more exact value for $E = -2.303 \ (-4462/1.086) = 78750$ J mol^{-1}. The pre-exponential factor is

$$A = 10 \times 78750 \left(\frac{e^{78750/8.32 \times 415^2}}{8.32 \times 419^2} \right) \left(\frac{1}{60} \right) = 5.8 \times 10^7 \text{ s}^{-1}$$

The peak temperature is for a heating rate near the middle of the range.

The isothermal method

This method is based on the capacity of the DSC instrument to measure simultaneously the reaction rate $(d\alpha/dt)$ and the degree of the reaction α, which allows the use of the rate expression in the derivative form. The sample is placed in the instrument at room temperature and heated with a maximum rate to the desired temperature. After the measurement has been completed, the same procedure is repeated with the same sample in order to determine the heat quantity which was not recorded, as a difference between the first and second measurements. The rate of heat evolution is measured as a function of time (Fig. 3).

TABLE 1

Values of peak exotherm temperature and heating rate for alkyd–melamine resin mixture

Heating rate, ϕ ($^\circ$C min^{-1})	Corrected heating rate, ϕ_{corr} [a] ($^\circ$C min^{-1})	T_p (K)	$1/T_p \times 10^3$ (K^{-1})
5	5.0	406.3	2.461
10	10.0	419.0	2.387
20	18.3	423.9	2.359

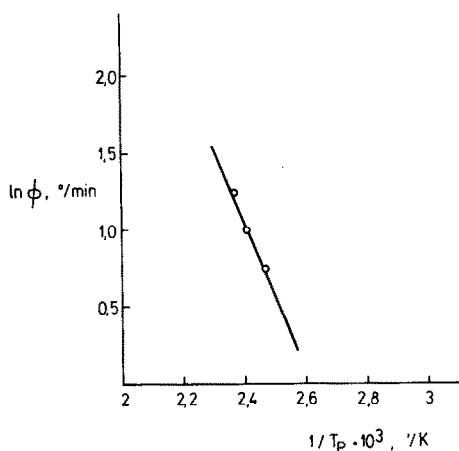[a] ϕ_{corr} as according to ref. 11.

Fig. 2. Plot of the logarithm of heating rate lg ϕ vs. reciprocal peak exotherm temperature $1000/T_{\mathrm{p}}$.

To calculate the degree of conversion, the following equation can be used

$$\alpha = \Delta H_1 / \Delta H_{\mathrm{RXN}}$$

where ΔH_1 is the heat quantity evolved with time t, ΔH_{RXN} is the exothermal heat per mole of reacting groups.

The results for measurements in the interval 415–421 K were treated, and values for the order of the reaction x and reaction rate constants were obtained from the plot of $d\alpha/dt$ vs. $\ln(1 - \alpha)$. These plots are straight lines (Fig. 4), and the results are listed in Table 2.
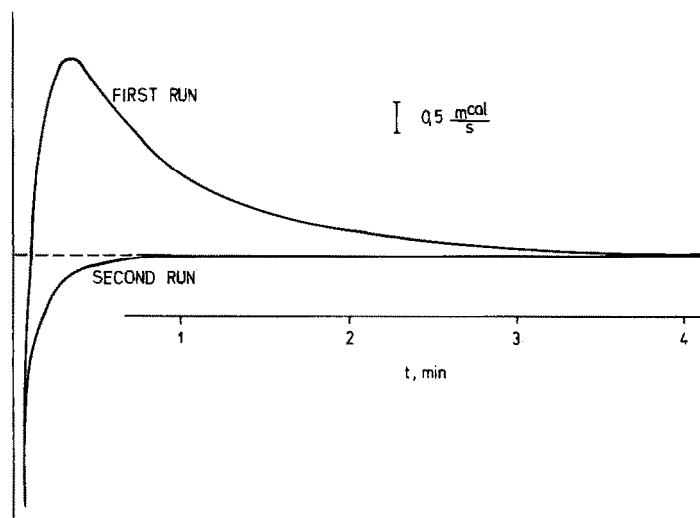

Fig. 3. Dependence of the rate of heat evolution dH/dt vs. time t for the alkyd–melamine mixture at 420 K.
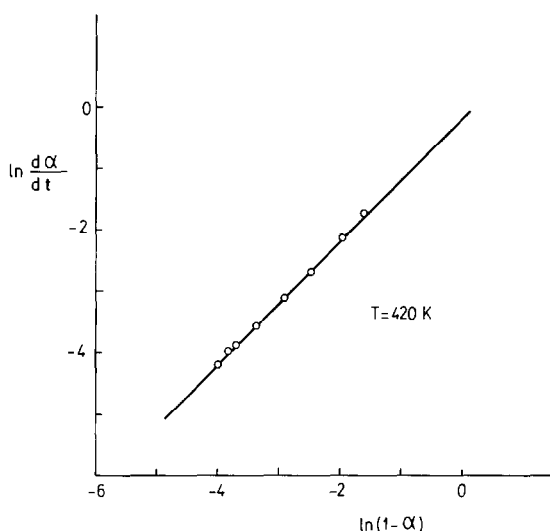
Fig. 4. Variation of the rate of conversion at constant temperature $d\alpha/dt$ with $\ln(1-\alpha)$.

Using these results, the relation $\ln k$ vs. $1/RT \times 10^4$ can be plotted (Fig. 5), and the straight lines obtained have intercept A and slope E. Values for E and A obtained from the graph are

$$E = 61200 \text{ J mol}^{-1} \qquad A = 2.5 \times 10^7 \text{ s}^{-1}$$

The values obtained for the order of the reaction are all very close to 1 (Table 2) indicating an S_N1 type reaction mechanism for the polycondensation of the alkyd–melamine resin mixture. The process of that reaction can be represented as
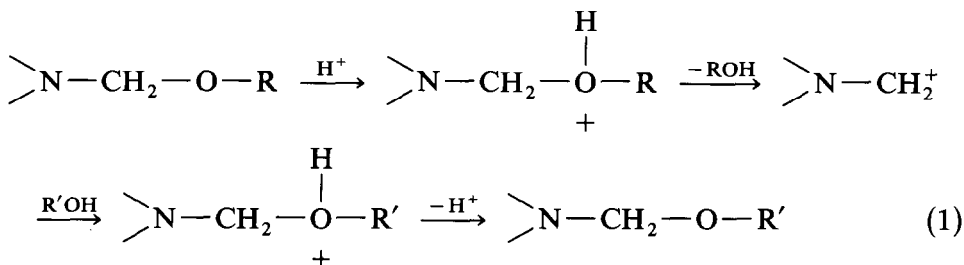
$$\geq N-CH_2-O-R \xrightarrow{H^+} \geq N-CH_2-\overset{\overset{\displaystyle H}{\displaystyle |}}{O}-R \xrightarrow{-ROH} \geq N-CH_2^+$$

$$\xrightarrow{R'OH} \geq N-CH_2-\overset{\overset{\displaystyle H}{\displaystyle |}}{O}-R' \xrightarrow{-H^+} \geq N-CH_2-O-R' \qquad (1)$$

TABLE 2

Values of the order of reaction x and rate constant k for alkyd–melamine resin mixture

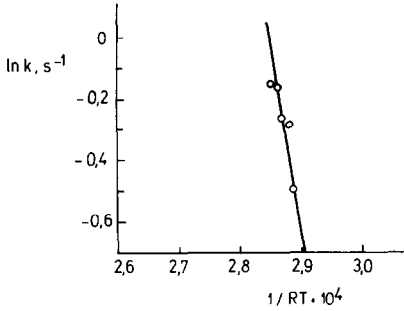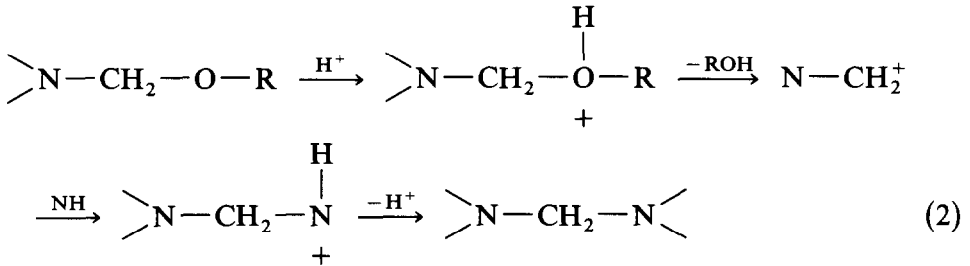| T (K)	x	$\ln k$ (s^{-1})	k (s^{-1})	$1/RT \times 10^4$ (mol J^{-1})	H (mol g^{-1})
415	1.00	-0.280	0.756	2.986	20.14
416	0.98	-0.503	0.605	2.889	20.76
418	1.03	-0.272	0.762	2.875	21.90
420	1.01	-0.149	0.861	2.862	23.32
421	1.01	-0.159	0.853	2.855	20.81

Fig. 5. Plot of ln k vs. $1/RT \times 10^4$, from values in Table 2.

An analogous mechanism is suggested for the polycondensation of the pure resin.

$$\textstyle{>}N-CH_2-O-R \xrightarrow{H^+} {>}N-CH_2-\overset{\overset{\displaystyle H}{\displaystyle |}}{\underset{+}{O}}-R \xrightarrow{-ROH} N-CH_2^+$$

$$\xrightarrow{NH} {>}N-CH_2-\overset{\overset{\displaystyle H}{\displaystyle |}}{\underset{+}{N}} \xrightarrow{-H^+} {>}N-CH_2-N{<} \tag{2}$$

It is assumed that reaction (1) is predominant during the curing of alkyd–melamine resin, and the reaction of self-condensation is minimized by the butylated melamine component. The rate expression is dependent on the concentration of the amino resin only and can be represented as

$$\text{Rate: } k\left[{>}N-CH_2-O-R \right]$$

SUMMARY AND CONCLUSIONS

The results obtained by the dynamic and isothermal DSC methods were compared. The isothermal method gives more accurate results, but the dynamic method can be used for quick determinations for industrial purposes. From the results given in Table 1 it is deduced that the process of curing for the alkyd–melamine resin is of the first order, i.e. the reaction rate depends upon the concentration of amino resin only, in the samples we investigated. The same mechanism is valid for the reaction of self-condensation of amino resin, but that reaction is suppressed in the butylated product where the concentration of $>$NH and $>$NCH$_2$OH groups is greatly diminished. For this particular system, according to the results given in Tables 1 and 2, the optimal curing temperature is close to 420 K.

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