NON-ISOTHERMAL KINETIC APPLIED TO THERMAL DECOMPOSITION OF COMMERCIAL ALKYD VARNISH

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Samples of commercial alkyd resin varnish were spread in a film form on slides, dried at room temperature and exposed to solar radiation from one day up to seven months.

Thermogravimetric measurements have been done. Based on the TG data, the Flynn–Wall isoconversional method was applied. The activation energy varied between 176–154 kJ mol^{-1} and log$A$ was between 15.5–12.9 min^{-1} for A, B and C samples at 95% confidence level.

Introduction

Varnish can be defined as a solution or dispersion which is the basic composition of natural and synthetic resins, vegetable oils, dryings, additives such as drying agents, UV inhibitor and dispersing agents, bactericides, pliable, volatile components and coating elements with organic origin forming, smooth, shine, transparent or colored thin layer [1].

The main constituent of the varnish is the polymer, a macromolecular material, which acts as agglutinating agent of the other components in the formulation. So far, it is responsible for the several characteristics of the film as flexibility, scratch resistance, brightness, adhesion on substrate, protection *vs.* water vapor, and weathering resistance [1].

Varnish based alkyd resin is frequently used due to its excellent physical-chemical properties e.g. durability, thermal plasticity and application facility [2].

Alkyd resins are polyesters formed by the reaction between polyols and polyacids or their anhydrides. In order to understand and predict the resistance of alkyd varnish *vs.* temperature or UV radiation, it is necessary to obtain the kinetic parameters.

Kinetic aspects

The mathematical description of the data from a single step solid-state decomposition is usually defined in term of a kinetic triplet, as activation energy, E_a, Arrhenius parameters, A and a mathematical expression of the kinetic model as a function of the fractional conversion α, $f(\alpha)$, which can be related to the experimental data as follow [3]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (1)$$

For dynamic data obtained at a constant heating rate $\beta = dT/dt$, this new term is inserted in Eq. (1) which can be simplified as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (2)$$

The activation energy from dynamic data can be obtained from the Flynn–Wall isoconversional method [4, 5] using the Doyle's approximation of $p(x)$ [6], which involves the measururement of temperature corresponding to fixed values of α obtained from experiments at different heating rates and plotting lnβ *vs.* $1/T$:

$$\ln\beta = \left[\frac{AE}{Rg(\alpha)}\right] - 5.331 - 1.052\frac{E}{RT} \qquad (3)$$

where R=gas constant (8.31432 K^{-1} J^{-1}) and $g(\alpha)$=integral of $d\alpha/f(\alpha)$ from 0 to α.

This method allows to obtain the apparent $E_a = E_a(\alpha)$ independently of the kinetic model. The preexponential factor is evaluated taking into account that the reaction is a first-order one and can be defined as [7]:

$$A = \frac{\beta E}{RT_m^2} \exp\left(\frac{E}{RT_m}\right) \qquad (4)$$

where T_m is the temperature of the sample, where the peak deflection occurs in the DTG curves.

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Kinetic model determination

A conservative estimation can be obtained through Dollimore's procedure, which is based on the 'sharpness' of the onset (T_i) and final (T_f) temperatures of the TG/DTG curve and its asymmetry [8, 9].

An accuracy procedure to predict the kinetic model described by Koga [10, 11] using data obtained from DTG curves, the activation energy and log$A$ is previously known. The selection of the kinetic model is based on the maximum value of the normalized $y(\alpha)$ and $z(\alpha)$ functions under non-isothermal conditions as follows:

$$y(\alpha) = \frac{d\alpha}{d\theta} = \frac{d\alpha}{dT}\beta\exp\left(\frac{E}{RT}\right) \qquad (5)$$

and

$$z(\alpha) = h(\alpha)g(\alpha) = \frac{d\alpha}{d\theta}\theta \qquad (6)$$

where $d\alpha/d\theta$ is the reaction rate at infinite temperature at the corresponding α, β is the heating rate, $h(\alpha)$ is the empirical kinetic model function in its differential form and $g(\alpha)$ is the integral form. θ is the generalized time introduced by Ozawa [12, 13] for Arrhenius type rate constant and given as:

$$\theta = \int_0^T \exp\left(-\frac{E}{RT}\right)\frac{1}{\beta}dT \qquad (7)$$

Experimental

Alkyd varnish samples from three different commercial sources were spread in a film form on slides, dried at room temperature and exposed to the solar radiation in a closed support from one day up to seven months in angle of 23° northward.

TG/DTG curves for the kinetic studies were performed using TA instruments, SDT 2960 module, under dynamic nitrogen atmosphere (100 mL min^{-1}), and with initial sample mass around 7 mg. The heating rates were 5, 10 and 20 K min^{-1} from 40 up to 900°C.

Results and discussion

Figure 1 shows the representative TG/DTG curves of the samples at the first month recorded at different heating rates. There was no significant mass change in the TG curves indicating similarities between the thermal behaviors. Thus, kinetic calculations will be presented only for one of the first month samples, since they may be extrapoled for the other samples and periods. Figure 1 also indicates the TG/DTG
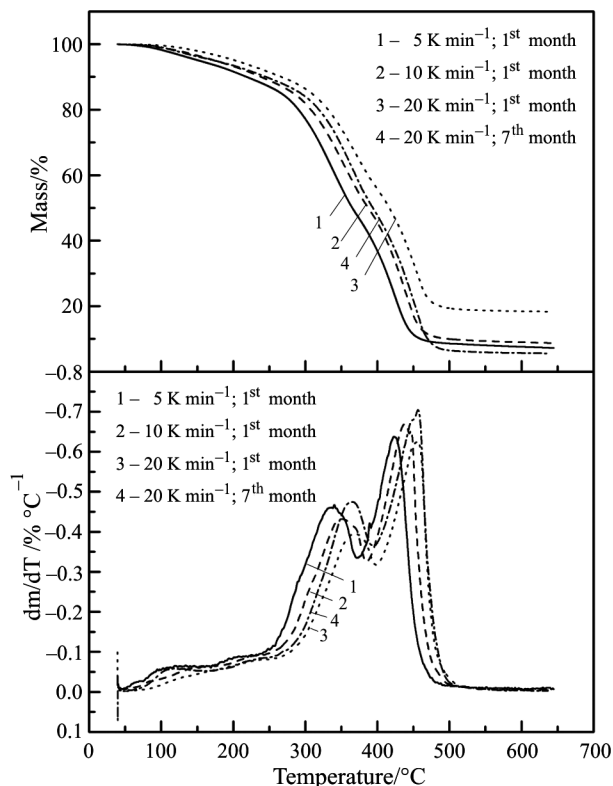
Fig. 1 TG and DTG curves of the samples of commercial varnish in nitrogen atmosphere

curves of the samples radiated for seven months (heating rate 20 K min^{-1}).

The kinetic parameters E_a and log$A$ of the thermal decomposition were obtained applying the Flynn–Wall isoconversional method [4] in the 258–391°C temperature range. For each fixed fractional conversion, α, the E_a could be calculated from the slope of lnβ *vs.* 1000/T plot, Eq. (3), and then the corresponding log$A$ through Eq. (4). The average values at 95% confidence level can be seen in Table 1.

Table 1 Average E_a and log$A$ for three different alkyd varnishes from commercial sources

Samples	Average E_a/kJ mol^{-1}	Average log$A$/min^{-1}
A	176.35±4.67	15.57±0.53
B	154.15±4.86	11.49±0.42
C	153.90±0.45	12.86±0.06

Dollimore's methods [8, 9] could be applied for the DTG curve to obtain the peak temperature, T_p=358.7°C, at $(d\alpha/dT)_{max}$, (HW=HiT-LoT which is the difference between the high-temperature and low-temperature at half-width of the DTG peak). The results led to obtain F1 (first reaction order, $f(\alpha)$=(1–α)) as the most suitable kinetic model. Knowing the average E_a and log$A$, α–T relation and $f(\alpha)$, the corresponding normalized simu-
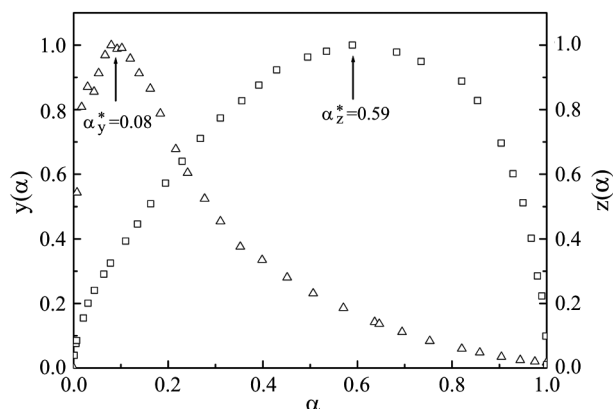
Fig. 2 The $y(\alpha)$ and $z(\alpha)$ functions calculated from first step of the thermal decomposition of the commercial varnish
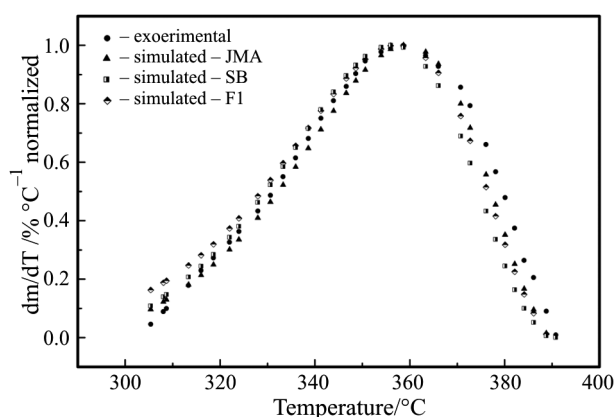
Fig. 3 Experimental and simulated DTG curves at 20 K min^{-1} to the F1, SB and JMA models

lated $d\alpha/dT$ *vs.* T plot could be obtained and compared to the normalized experimental DTG curves, (Fig. 3).

Applying Koga's procedure [10, 11] for the data taken from DTG curves (Fig. 1) the first thermal decomposition reaction, the kinetic model can be obtained through the $y(\alpha)$ and $z(\alpha)$ functions, Eqs (5) and (6), *vs.* α, Fig. 2. The maximum was found at $\alpha_z^* = 0.59$ and $\alpha_y^* = 0.08$, respectively. This behavior in which $0 < \alpha_y^* < \alpha_z^*$ and α_z^* is around 0.59 seems to be characteristic to autocatalytic SB (Šesták–Berggren) model where $f(\alpha) = \alpha^m(1-\alpha)^n$ [14]. The kinetic exponent n for the SB model could be obtained through the slope of the linear regression from the $\ln[(d\alpha/dt)\exp(E/RT)]$ *vs.* $\ln[\alpha^p(1-\alpha)]$ plot considering that α values are be-

tween 0.2 and 0.8 that yields $n=1.14$. While the kinetic exponent m could be calculated from the relation $m=pm$, where $p = \alpha_y^* / (1 - \alpha_y^*)$, thus m was 0.09. The other possibility would be the JMA model in which $m>1$. The kinetic exponent, m to the JMA model can be obtained from $m=1/(1+ \ln(1-\Box\alpha_y^*)$ which yields 1.09.

Thus, knowing that $f(\alpha)=\alpha^{0.09}(1-\alpha)^{1.14}$ and $f(\alpha)=1.09(1-\alpha)[-\ln(1-\alpha)]^{1-1/1.09}$ for SB and JMA models, respectively, besides E_a, $\log A$ and α–T relation, the corresponding normalized simulated $d\alpha/dT$ *vs.* T plots can be obtained and compared with the normalized experimental DTG curves (Fig. 3).

Conclusions

For the thermal decomposition reaction of the alkyd varnish the F1, SB and JMA model can be applied. It has to take into account that the formal mathematical descriptions are similar; so far, it is difficult to say which is the representative for the real mechanism of thermal decomposition of those samples.

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