

CHARACTERIZATION OF ALKYD BASED THERMOSETTING RESINS

Calorimetric investigations

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Abstract

The rate of cure of different oxidative drying oil modified alkyd resins are investigated by DSC, when the cure is made under UV light or not. We determine, from the Kissinger equation, the apparent activation energy at different stages of the curing process. This activation energy depends on the curing conditions (temperature, illumination or not). These variations lead to the determination of a time constant, characteristic of the curing kinetics. Two particular values of the apparent activation energy are also defined. The first one called ΔE_0 is a characteristic of the varnish at the liquid state, the second one called ΔE_{inf} characterizes the stability of the structural state of the final film.

Keywords: alkyd based resins, curing kinetics, DSC, Kissinger method

Introduction

Oxidative oil modified alkyd resins are mainly used as varnishes and stains in the field of the wood protection in exterior use. A commercial varnish is the result of a mixture of different compounds. The base is an alkyd resin generally modified by an oil (Soya ...) also called siccative oil and playing the role of the curing agent. The cure is obtained by oxidative reactions [1] and can be enhanced by introducing different catalysts as cobalt, zirconium, ... The protection durability is improved by introducing anti-oxidizer and UV absorber compounds. Finally, the appearance of the varnish can be modified by introducing coloured pigments. Characterizing the properties of these varnishes requires the determination of physical quantities representative of their behaviours at short and at long duration. At short duration, the curing reactions are preponderant, whereas the aging phenomena appear at long duration. On the other hand, it is well known that calorimetric investigations (as DSC) performed on a thermosetting resin reveal different thermal transitions: the glass transition when the rate of cure is high and the exothermal reaction of curing when this last reaction is in progress. In a previous work, we have shown that the glass

transition temperature measurement, performed by DSC, was an interesting method to follow finish products aging [2]. An other work, concerning the rate of cure of different oil modified alkyd resins [3], has shown that the variations of the temperature of the exothermic curing peak with the heating rate follow the Kissinger equation. From the Kissinger plot, an apparent activation energy is determined at each stage of the curing process. This activation energy depends on the curing duration and the following relationship was proposed

$$\Delta E = \Delta E_{\text{inf}} + (\Delta E_o - \Delta E_{\text{inf}})e^{-t/\tau} \quad (1)$$

where ΔE_{inf} and ΔE_o are the apparent activation energies after an infinite curing duration and at the origin respectively and τ a characteristic time constant.

This work deals with the roles that played an UV irradiation on the curing kinetics of alkyd based resins. We will give one's mind to the physical meaning of ΔE_{inf} and of ΔE_o .

Experimental details

Oil modified alkyd resins used in this study are commercial ones. The first one R_1 is an oil modified alkyd resin without any other compounds. The second and the third ones called R_2 and R_3 are R_1 plus different Hindered Amine Light Stabilizer and UV absorbers.

To obtain a film, a controlled thickness (30 μm) of liquid is laid on an inert polymer substract. The first set of experiments consists in holding the samples at different constant temperatures into a furnace with an ambient air and without illumination. The second set of experiments is made following the same protocol as before, but samples are illuminated during all the curing duration. The illumination is performed with UV lamps (black-light type source, following the NFT 51 195 recommendations). Their intensities are 2100 W/cm^2 . The sample source distance is 20 cm and remains constant during all the experiments. The optical beams are perpendicular to the sample area. The optical source emits energies between 300 and 500 nm with a maximum at 365 nm. The absorption coefficients of our resins are different in the same range of energy.

Thermal measurements are performed on a DSC (Perkin Elmer system 7). Calibration of the calorimeter is achieved from the determination of the temperature and the energy of fusion of indium. Calorimetric experiments are made under nitrogen ambience.

Results and discussion

The enthalpic curves displayed on the Fig. 1 show the variations with the heating rate of the exothermic curing peak observed on R_i . From the Kissinger

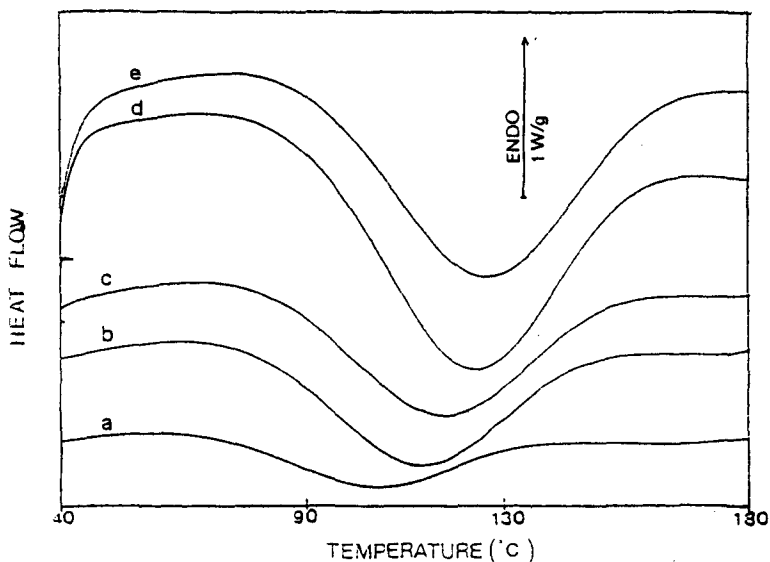


Fig. 1 Example of DSC traces obtained on R_1 after an isothermal curing period of 12 h performed at 30°C; curve a, 10 deg·min⁻¹; curve b, 20 deg·min⁻¹; curve c, 30 deg·min⁻¹ and curve d, 50 deg·min⁻¹

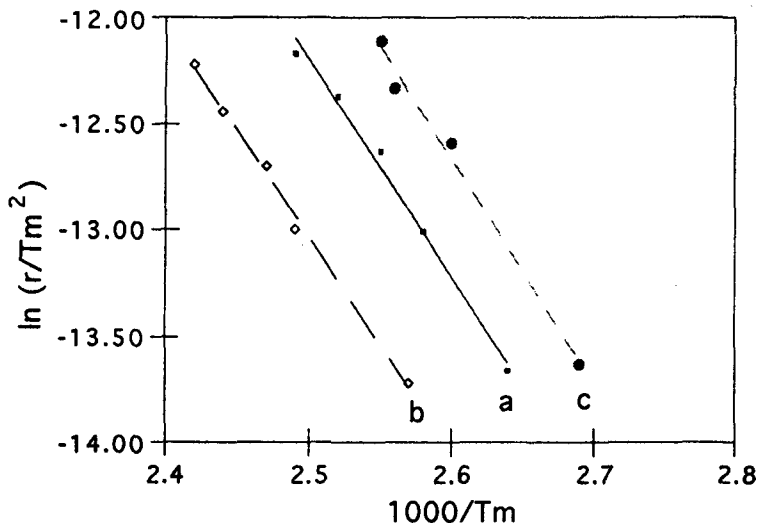


Fig. 2 Kissinger plot obtained on R_1 after an isothermal curing period performed during 25 h at: curve a, 20°C; curve b, 40°C; curve c, 20°C and under UV irradiation

plot (Fig. 2 shows an example obtained on R_1) we determine, for each curing temperature and for different curing durations, the apparent activation energy obtained from:

$$\Delta E = R \frac{d(\ln r/T_m^2)}{d(1/T_m)} \quad (2)$$

where r is the heating rate, T_m is the extremum of the exothermic peak.

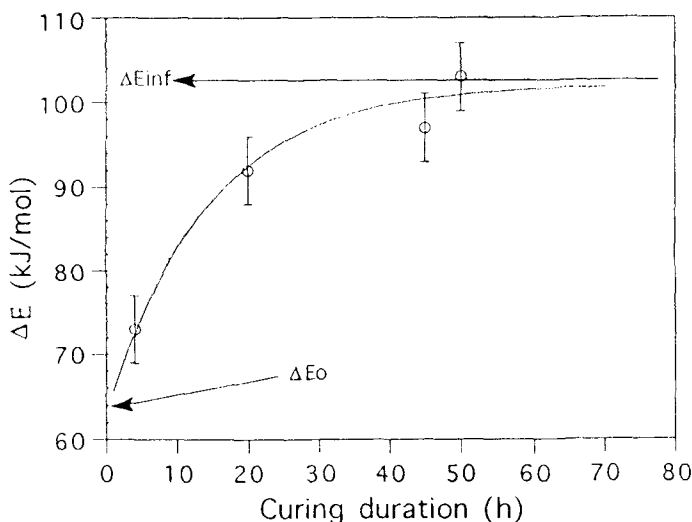


Fig. 3 Variations of the apparent activation energy with the curing duration observed on R_3 maintained at $T_c = 20^\circ\text{C}$ and under UV irradiation

Then, the variations of this apparent activation energy with the curing duration are plotted (Fig. 3 shows an example obtained on R_3). The fit of the experimental data using Eq. (1) allows the determination of ΔE_o and τ . The value of ΔE_{inf} can be estimated directly from the experimental curve shown on the Fig. 3 while ΔE_o cannot. Concerning ΔE_o , this impossibility is due to preliminary reactions, called inhibition and initiation, which are precursors of the curing reaction [4]. In Table 1, the results concerning the three resins are presented.

Table 1 Values of ΔE_{inf} , ΔE_o and τ obtained on the three varnishes, for different curing conditions and from Eq. 1

	R_1			R_2			R_3		
	$\Delta E_{inf} /$	$\Delta E_o /$	$\tau /$	$\Delta E_{inf} /$	$\Delta E_o /$	$\tau /$	$\Delta E_{inf} /$	$\Delta E_o /$	$\tau /$
	$\text{kJ}\cdot\text{mol}^{-1}$		h	$\text{kJ}\cdot\text{mol}^{-1}$		h	$\text{kJ}\cdot\text{mol}^{-1}$		h
$T_r = 20^\circ\text{C}$	91	56	15	106	40	9	102	50	10
$T_r = 40^\circ\text{C}$	85	56	9	100	40	6	100	63	2
UV	88	56	4	100	40	4	102	63	14

The analysis of these data shows that the value of ΔE_0 changes from one resin composition to another one. The values of ΔE_{inf} reached by R_2 and R_3 are nearly the same and are higher than those obtained on R_1 . For R_1 , R_2 and R_3 , higher is the curing temperature, lower is the value of τ and so higher is the rate of liquid to solid transformation. This result is consistent with what is generally observed for the curing reaction of thermosetting resins. For R_1 and R_2 , UV irradiation leads to an increase of the curing kinetics, while for R_3 the opposite behaviour is observed.

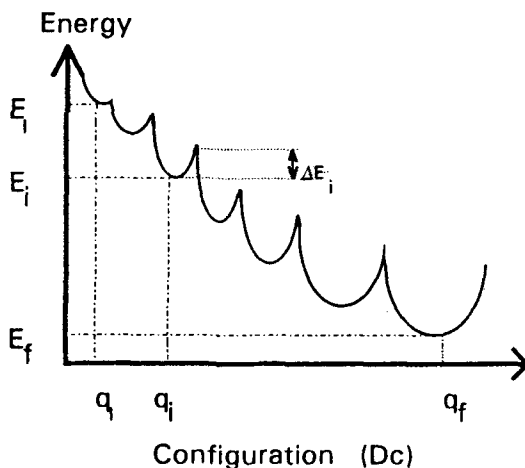


Fig. 4 Energy-Configuration diagram characterizing the isothermal curing period

To determine the physical meaning of these parameters, two stages inherent in the experimental method used must be distinguished. The first one concerns the isothermal curing reactions in progress before the DSC scan, the second one concerns the curing reactions induced by the heating during the DSC analysis.

The first stage can be schematically explained from the Energy-Configuration diagram displayed on the Fig. 4. The X axis called configuration (q) can be replaced by the curing duration (D_c). On this diagram, the liquid state is characterized by the configuration q_1 and the energy E_1 , (q_1, E_1). When the cure is in progress at a constant temperature T_{ci} , the resin changes from the liquid state to the solid one and reaches theoretically after an infinite duration the state characterized by (q_f, E_f) $_{T_{ci}}$. The passage of one state (q_i, E_i) $_{T_{ci}}$ to the following one (q_{i+1}, E_{i+1}) $_{T_{ci}}$, requires the jump of a potential barrier (ΔE_i). As the curing reaction is progressing, as the potential barrier is growing ($\Delta E_i < \Delta E_{i+1}$). For each curing temperature (T_{ci}) and after a given curing duration (D_{ci}), the resin reaches the state defined by (q_i, E_i) $_{T_{ci}, D_{ci}}$.

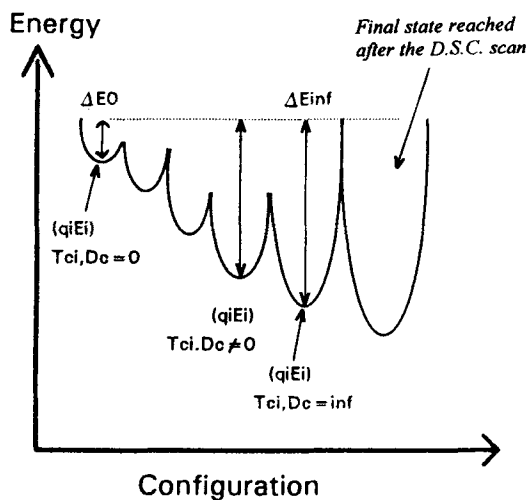


Fig. 5 Energy-Configuration diagram characterizing the non-isothermal curing period occurring during the DSC analysis

The same Energy-Configuration diagram (Fig. 5) can explain the results obtained during the DSC analysis. The X axis still called configuration could be now replaced by the temperature scanned during the DSC analysis. In this stage, the initial state before the DSC analysis corresponds to the final state reached during the isothermal curing state $(q_i, E_i)_{T_{ci}, D_{ci}}$. Heating a sample consists in jumping the potential barrier which separates the $(q_i, E_i)_{T_{ci}, D_{ci}}$ state from the final state corresponding to the maximum and accessible rate of transformation. So for a small isothermal curing duration, this last potential barrier appears lower than those observed after a long isothermal curing duration. The apparent activation energy determined from the Kissinger method follows the same variations as these last potential barriers. It is tempting to associate these both energies, nevertheless they are not equal, but for the best proportional. So ΔE_0 characterizes the varnish at the liquid state and ΔE_{inf} characterizes the thin film state reached after an isothermal curing duration. From the values of ΔE_{inf} we are able to conclude that the thermal stability of R_2 and R_3 will be similar but better than those obtained for R_1 and that the curing rate reached after the isothermal curing duration for each varnish follows the same way.

Conclusion

In this work, we have shown that the Energy-Configuration diagrams can explain the physical meanings of the parameters (ΔE_{inf} , ΔE_0 and τ) determined from the behaviour equation proposed to describe the variations of the apparent

activation energy with the curing conditions. So ΔE_o characterizes the varnish at the liquid state, ΔE_{inf} characterizes the thermal stability of the thin solid film and τ the kinetics of the film formation.

References

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Zusammenfassung — Vorliegend wurde mittels DSC-Messungen die Aushärtungsgeschwindigkeit von mit oxidativen trocknenden Ölen modifizierten Alkydharzen untersucht, sowohl mit als auch ohne Einwirkung von UV-Licht. Auf der Grundlage der Kissinger-Gleichung ermittelten wir die scheinbare Aktivierungsenergie für verschiedene Schritte des Aushärtungsprozesses. Diese Aktivierungsenergie ist eine Funktion der Aushärtungsbedingungen (Temperatur, Belichtung oder nicht). Diese Varianten führten zur Bestimmung der für die Aushärtungskinetik charakteristischen Zeitkonstante. Weiterhin wurden zwei spezielle Werte der scheinbaren Aktivierungsenergie definiert. Der erste, genannt ΔE_o , charakterisiert den Lack im flüssigen Zustand, der zweite, genannt ΔE_{inf} , charakterisiert die Stabilität des Strukturzustandes des endgültigen Filmes.