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DIFFERENTIAL SCANNING CALORIMETRY APPLIED TO CROSS-LINKING OF A FILLED EPOXY RESIN: ACCURACY OF THE BORCHARDT AND DANIELS EQUATION FOR DESCRIBING THE CURING PROCESS KINETICS

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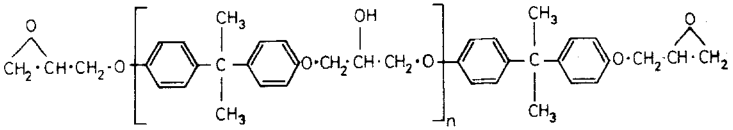
From the point of view of the chemical reactions describing the curing process of a mixture epoxy resin–dicarboxylic acid anhydride–tertiary amine–polyol and silica filler, it is difficult to understand the network formation: several different reactions are involved, so that the interaction between the epoxy resin and the other components of the mixture is unquestionably complex. However, a linear plot is obtained when Kissinger's method is applied to dynamic DSC results (four different scanning rates), which confirms the calculation assumptions. In particular, the Borchardt and Daniels equation, where the specific rate constant is assumed to be of Arrhenius form appears to be a good mathematical model for describing the curing process under dynamic DSC conditions. The apparent activation energy determined by means of this analytical method is in good agreement with those obtained by other methods in the literature.

Epoxy resins comprise a major class of polymeric materials used in the electrotechnical industry as castings for power transformers ("dry transformers"). Such insulation materials seem to provide a solution to toxic problems occurring in the event of fire: it is now known that most liquid dielectrics, the "pyralene" dielectrics, undergo thermal decomposition with dioxin emission, whereas epoxy resins offer high safety against toxic combustion products [1, 2].

The epoxy resins used in the electrotechnical industry are generally diglycidyl ethers of bisphenol A (DGEBA):



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DGEBA is crosslinked with dicarboxylic acid anhydrides, in the temperature range 80–150°. A tertiary amine is used as a catalyst ("accelerator" of the curing process) and the presence of a polyol means that the mixture will not be too viscous ("flexibilizator"). In the case of electrical applications, epoxy resins are generally filled with silica flour, quartz flour, aluminium hydroxide, etc.

The curing process therefore involves a chemical system including at least five different components and a full description of the various chemical reactions leading to the network constitution will obviously be highly complex. Investigations in the field of epoxy curing process chemistry can be found in the literature [3, 7]: these extensive studies show that several different chemical reactions are involved and point to the presence of co-catalysts, such as water, which seems to be one of the main factors influencing the extension of the curing process [7].

The purpose of the present work is not to propose new reaction mechanisms permitting a better knowledge of the epoxy resin-anhydride polymerization, but to show that the Borchardt and Daniels (BD) equation [8] is enough to describe such a complex process as epoxy resin crosslinking with anhydride. This process is examined by means of DSC in its dynamic mode in the presence of an accelerator, a flexibilizator and silica filler. The accuracy of the BD model has been established by applying an analytical method proposed by Kissinger [9].

Principle of method

The crosslinking of epoxy resin and additives occurs during a dynamic DSC experiment, at a scanning rate β (deg s^{-1}). Kissinger's method is supported by the following assumptions:

a) The BD equation is used to describe the kinetics:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \qquad (1)$$

$\frac{d\alpha}{dt}$ = reaction rate, s^{-1}
k = specific rate constant, s^{-1}
α = extent of cure (growing from 0 to 1)
n = reaction order
t = time, s

b) The reaction mechanism is not specified, but it is assumed not to change with conversion and with scanning rate. Thus, it is assumed that the reaction mechanism is the same throughout the dynamic scan, whatever the scanning rate β may be. This mechanism follows the Arrhenius equation:

$$k = k_0 e^{-Ea/RT} \tag{2}$$

k_0 = preexponential factor, s^{-1}
Ea = activation energy, $J \cdot mol^{-1}$, for the studied mechanism
R = gas constant (8.31 $J \cdot mol^{-1}\ deg^{-1}$)
T = absolute temperature, K

c) It is assumed that the extent of cure is proportional to the amount of heat during a DSC experiment. Thus, the extent of cure is expressed by the following equation:

$$\alpha = \frac{Hp}{Ht} \tag{3}$$

where Hp is the partial heat of the reaction and Ht is the total heat of the reaction, i.e. the total area under the exotherm.

Although this assumption is reasonable for simple reactions, it may not be so obvious in the case of crosslinking when epoxy resin polymerization takes place. The purpose of this work is to assess the reliability of the results obtained through simple assumptions.

d) Whatever β may be, it is assumed that the extent of cure is always the same at the maximum point of the DSC curves, for the peak temperature (Tp). This assumption is generally accepted in the literature [13, 14].

With these four assumptions, Eqs (1), (2) and (3), applied to the exotherm peak, lead to the following equation, established by Kissinger [9]:

$$\frac{d \ln (\beta/Tp^2)}{d(1/Tp)} = \frac{-Ea}{R} \tag{9}$$

Therefore, if our assumptions are correct, a plot of $\ln (\beta/Tp^2)$ versus $(1/Tp)$ should be linear and the activation energy might be obtained from the slope (Ea/R).

Experimental

Materials

The organic materials considered in this study were commercial products from CIBA–GEIGY. The epoxy resin was Araldite F: this prepolymer is a DGEBA. The crosslinking agent, HY 905, is a mixture of dicarboxylic acid anhydrides. DY 061 was used as a catalyst: this tertiary amine is 2,4,6-tris(dimethylaminomethyl)phenol. The flexibilizator was DY 040, the main compound of which is polypropylene glycol.

The silica flour used as filler was provided by SIFRACO. Its composition is 99.5% SiO_2, with traces of Al_2O_3 and Fe_2O_3.

Instrumental procedure

A system Araldite F–HY 905–DY 061 and DY 040, filled with 60% of silica flour, was mixed at 80° for 4 hours.

Samples (the usual weight was about 30 mg) were taken from this mixture and cooled down to 0°.

Finally, the samples were polymerized by dynamic DSC, at several scanning rates, on a SETARAM DSC 111. The calorimeter was coupled with an HP 86 microcomputer, so that the total heat of reaction Ht (proportional to the total area under the exothermic peak in the DSC curve) and the temperature Tp at the maximum point were automatically computed (after calibration of the apparatus at several scanning rates).

An empty aluminium pan was used as reference, and four heating rates (1, 2, 5 and 10 deg min^{-1}) were tested. The sensitivity was 0.250 mV (0.100 mV if necessary).

Results and discussion

Figure 1 presents four dynamic DSC curves: of these curves, Ht (on line ENTHALPY) and Tp (referred to as TOP OF PEAK TEMPERATURE) were automatically computed. For instance, the printed experimental data and results for $\beta = 1$ deg min^{-1} were as follows:

Resine reticulee par balayage a	1 K/mn
Initial temperature	330.2 K
Final temperature	480.2 K
Scanning rate	1.00 C/mn
Amplification range	.100 mV
Sample mass	32.500 mg
Sampling rate	1.92 s
Storage	4687 points
Integration with a linear base line	
Peak start	98.2 C
Peak end	159.4 C
Enthalpy	12.847E+002 mJ or 94.579E−001 cal/g
Exothermic peak top of peak temperature	129.1 C

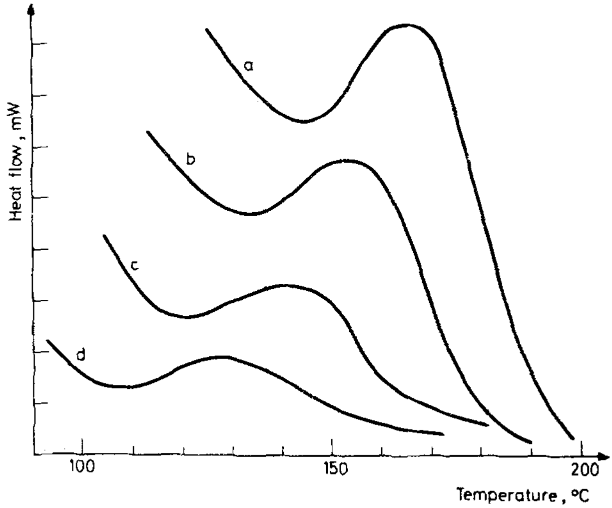

Fig. 1 (a) 10 deg/min; (b) 5 deg/min; (c) 2 deg/min; (d) 1 deg/min

The results of these dynamic cure experiments are listed in Table 1, with the calculated values of $\ln(\beta/Tp^2)$ and $(1/Tp)$.

Table 1 Thermochemical values from dynamic DSC experiments

β, deg s^{-1}	Ht, J·g^{-1} mixture	Ht, J·g^{-1} organic compds.	Tp, K	$\ln(\beta/Tp^2)$	$(1/Tp)\cdot 10^3$, deg^{-1}
10/60	25.50	63.75	440.0	−13.97	2.273
5/60	32.59	81.47	429.2	−14.61	2.330
2/60	34.98	87.45	415.5	−15.46	2.407
1/60	39.54	98.85	402.3	−16.09	2.486

It can be observed in Table 1 that:

a) The greater the peak area in Fig. 1, the lower the Ht value. Such an observation may seem surprising. However, it must be borne in mind that the areas in Fig. 1 cannot be compared, because the x-axis is not a time axis. Consequently, as Ht is computed after integration of the heat flow $P(t)$ with respect to time t:

$$Ht = \int P(t)\,\mathrm{d}t \tag{5}$$

it is obvious that a comparison between the peak areas will be possible only when the thermal curves provide a curve of the heat flow versus time, or when all the exotherms are obtained at the same scanning rate.

b) Since silica flour is not involved in the chemical reactions permitting the constitution of the crosslinked network, two measurement units can be suggested for the total heats of reaction *Ht*. In column 2 of Table 1, *Ht* is expressed in joules per gram of the mixture, including silica in the total mass. In column 3, *Ht* is given per unit of mass of the reactive compounds, without taking silica flour into account, since it is not involved in the heat released during epoxy resin crosslinking. The total heats of reaction *Ht* are low in comparison with those found in other studies [10, 14]. This seems to suggest that polymerization begins with the mixing at 80°. Accordingly, the *Ht* measured during dynamic DSC is lower than the *Ho* computed for polymerization of the hypothesized mixture of monomers and additives, which is conceptually the most adequate reference quantity [11]. However, as the polymer is filled, it might be suggested that silica prevents the formation of many crosslinks, inserting itself between the reactive groups. This will be checked in further studies.

c) *Ht* depends on the scanning rate β, which is well known [10]. However, these variations in *Ht* may not be due to a change in cure mechanism only; other factors too may influence the *Ht* values (initial polymerization when DSC scan begins, shape of the sample, etc.).

From Table 1, we can plot ln (β/Tp^2) versus $(1/Tp)$, as shown in Fig. 2. The plot obtained is linear with a slope of $-10.027 \cdot 10^3$ deg (in Fig. 2, the points are experimental and the line is from a linear regression).

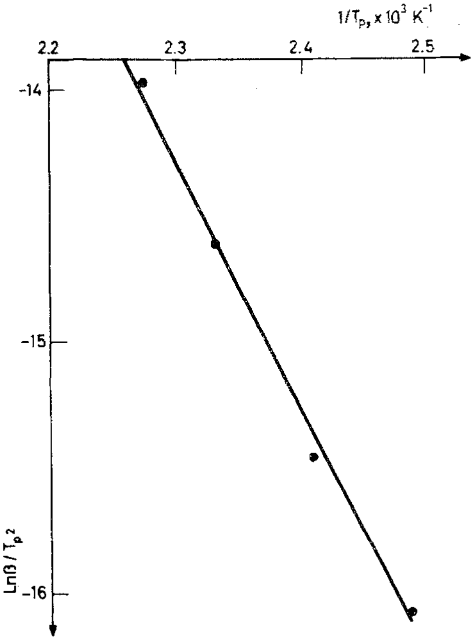

Fig. 2 Kissinger's plot

The assumptions made in the theoretical considerations can therefore be used with good accuracy in the description of the curing process taking place when a sample (Araldite F–HY 905–DY 040–DY 061 and silica flour) is subjected to a dynamic DSC experiment.

From the slope *Ea*/*R*, the activation energy was found to be 19.85 kcal/mol, which is in good agreement with those obtained by other analytical methods [13, 14].

Conclusion

To assess whether Eqs (1) and (2) are valid, Kissinger's method has been applied. The linear plot proves that the BD equation (where the specific rate constant is assumed to be of Arrhenius form) is an accurate mathematical model when it comes to describing the kinetics of complex polymerization which is widely used in electrotechnical industry.

Electrotechnical firms are interested in possible energy saving during the curing process of insulation material. Accordingly, investigations of this kind of polymers require determination of the time-temperature dependence of the degree of cure, to optimize the process conditions. From dynamic DSC experiments, using Eqs (1) and (2) given in this work, the literature describes some methods for predicting isothermal conversion time curves over a wide temperature range [12, 15], with non-isothermal DSC data.

It is also necessary to reflect about the correlation between the non-isothermal process occurring in a dynamic DSC experiment and the isothermal curing process, which is generally the process used in electrotechnical industries. Last but not least, a clear relationship must be established between the extent of cure measured on a dynamic DSC curve and the degree of polymerization well defined by Schiraldi and Baldini [11].

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Zusammenfassung — Die bei der Härtung eines Epoxidharz, Dicarboxylsäure-Anhydrid, tertiäres Amin, Polyol und einen SiO_2-Füllstoff enthaltenden Gemisches vor sich gehende Vernetzung ist schwer zu überblicken; es verlaufen mehrere unterschiedliche Reaktionen, so daß die Wechselwirkung zwischen dem Epoxidharz und den anderen Komponenten außerordentlich komplex ist. Eine lineare Abhängigkeit wird jedoch erhalten, wenn dynamische DSC-Ergebnisse erhalten bei 4 verschiedenen Scanning-Geschwindigkeiten nach der Kissinger-Methode aufgearbeitet werden, was die Richtigkeit der für die Berechnung gemachten Annahmen bestätigt. Besonders die Gleichung von Borchardt und Daniel, bei deren Ableitung für die spezifische Geschwindigkeitskonstante eine Arrhenius-Form angenommen wird, scheint ein gutes mathematisches Modell zur Beschreibung des Härteprozesses unter DSC-Bedingungen zu sein. Die nach dieser Methode bestimmte scheinbare Aktivierungsenergie stimmt gut mit den nach anderen in der Literatur beschriebenen Methoden bestimmten Werten überein.

Резюме — Химические реакции, используемые для описания процесса отверждения смеси эпокси смола — ангидрид дикарбоновой кислоты — третичный амин — наполнитель (полиспирт или силикагель), очень сложные и не дают ясного представления о процессе сшивания. Одновременно протекает несколько реакций и поютому взаимодействие между эпокси смолой и другими компонентами смеси остается невыясненным. Применяя же метод Киссинджера к данным ДСК измерений (четыре различные скорости сканирования), получают линейный график, который подтверждает вычисленные предположения. Установлено, что в условиях динамической ДСК, уравнение Борхарда и Даниюля, где специфическая константа скорости должна быть аррениусовского типа, является хорошей математической моделью для описания процесса сшивания. Кажущаяся энергия активации, найденная по этому уравнению, хорошо согласуется с данными, полученными другими методами.