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SIMULATION OF THE CURING PROCESS OF AN UNSATURATED POLYESTER RESIN IN ADIABATIC CONDITIONS

J. M. Salla and J. L. Martin

Laboratori de Termodinàmica de la E.T.S.E.I.B., Universitat Politècnica de Catalunya,
Diagonal 647, Barcelona 08028, Spain

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Abstract

The exothermal process of curing of thermoset resins in adiabatic conditions cannot be monitored by differential thermal analysis techniques such as DSC. Starting from the specific reaction rate, heat capacity as function of the temperature and the heat of reaction at some reference temperature, it is possible to design any adiabatic operation.

In this paper we apply the energy balance to the curing process in adiabatic conditions and solve the basic rate law for the two empirical kinetic functions $f(\alpha)$ usually used: n^{th}-order kinetics [$f(\alpha)=(1-\alpha)^n$], and autocatalytic kinetics [$f(\alpha)=\alpha^m(1-\alpha)^n$], where α is the degree of conversion and n and m the reaction orders, in order to obtain the heat generation curve (dH/dt) as a function of time, as well as the change of temperature with time, the explosion time, the maximum adiabatic temperature and the rate of reaction as a function of the degree of conversion.

Keywords: adiabatic conditions, kinetics, polyester resin

Introduction

The kinetic study of an exothermic reaction like the curing of a thermoset material allows us to determine now much, how fast, and in what temperature range the heat of reaction is released. On the other hand, all chemical reactions involve a change in the energy of the system, which is revealed as a thermal interaction between the system and its surroundings. Hence, energy release or absorption provide the basis for kinetic measurements and constitute the principle of Differential Thermal Analysis for kinetic-data acquisition [1]. Thus, Differential Scanning Calorimetry (DSC) or quantitative differential thermal analysis are techniques commonly used for monitoring the process and evaluating not only the heat of reaction but also the reaction kinetics [2, 3]. Any study of reaction kinetics requires the following fundamental data: reaction rate and amount of reactant(s).

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In these thermal analysis techniques, it is common to assume that the rate of the evolution of heat exchanged with the surroundings at constant pressure is strictly proportional to the rate of the global chemical reaction(s) at any instant as follows [4]:

$$\frac{dH}{dt} = \Delta H_R \frac{d\alpha}{dt} \tag{1}$$

where dH/dt is the rate of heat evolution, ΔH_R is the heat of reaction and $d\alpha/dt$ is the rate of reaction.

It is also common to accept the following assumption in kinetic analysis of chemical reactions by thermal analysis: any chemical process of a reaction will obey a rate law of the form [5]

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{2}$$

k is the chemical rate constant which is given by an Arrhenius-type equation $k=Ae^{-E/RT}$, where A is the frequency factor and E the activation energy of the reaction. $F(\alpha)$ is some function of the degree of conversion that results from the mechanism of the process. In the curing process of thermoset resins, two empirical mechanistic models of reaction are usually assumed [6]:

- n^{th} order reaction: $f(\alpha)=(1-\alpha)^n$ and
- autocatalytic: $f(\alpha)=\alpha^m(1-\alpha)^n$.

Sometimes, in curing processes at room temperature when the curing is highly activated due to the high rate of heat generation, as well as the low thermal conductivity of the material, or in applications in which the small surface to volume ratio does not facilitate heat removal, a considerable rise of temperature occurs in the material. This can cause high shrinkage and cracks of thermosetting resins [7], at the same time modifying the properties of the material, which becomes a bad product. In this type of application, it is useful to know the maximum temperature to which the system may be heated (the adiabatic reaction temperature, T_{ad}).

As distinguished from isothermal and non-isothermal conditions of reaction (at a constant heating rate), for an exothermic reaction which occurs at adiabatic conditions, the process cannot be monitored by DSC technique and must be evaluated by other methods. For the design of any adiabatic operation, the following data are needed [8]:

1. The specific reaction rate as a function of temperature and degree of conversion, $d\alpha/dt$

2. The thermal data of the reacting system, such as the heat capacities and sensible and latent heats of all reaction partners and inert materials, as a function of temperature
3. The heat of reaction at some reference temperature.

All these data can be determined by DSC for the process.

It is known [9] that when an exothermal process such as the curing takes place at adiabatic conditions, the heat generated from the reaction at an initial temperature T_0 will result after a certain time (called the explosion time) in a temperature rise, which in turn accelerates the reaction. The rate of reaction rises too, but after reaching its maximum value at one determined temperature, it will decrease and finally diminishes to zero at the completion of the reaction at temperature T_{ad}.

Our main purpose in this paper was to determine:

– the rise of temperature of the material as a function of time, as well as the explosion time, the time point where the high rise of temperature takes place (curve: temperature *vs.* time),

– the rate of heat generation in the material as a function of time (curve: dH/dt *vs.* time), and

– the rate of reaction $d\alpha/dt$ as a function of the degree of conversion (curve $d\alpha/dt$ *vs.* α),

when the process occurs in adiabatic conditions and at constant pressure. Likewise, to study the influence on the former curves of variations in one of the kinetic parameters which characterize the process(es), while the other parameters are held constant.

Theoretical considerations

Energy balance

If a system undergoes an exothermic chemical reaction at constant pressure, the energy balance can be applied. In the absence of work, the energy released by a chemical reaction at constant pressure appears in two forms: heat loss to the surroundings and a temperature rise of the products formed and unconverted reactants and inert materials [10]. In these conditions the energy balance is [11]:

$$Q = \Delta H \tag{3}$$

where the enthalpy is the sum of the chemical and sensible and latent contribution, i.e.

$$\left\{\begin{array}{l}\textit{Heat transferred}\\ \textit{to the surroundings}\\ \textit{from the system}\end{array}\right\} = \left\{\begin{array}{l}\textit{Change in}\\ \textit{sensible}\\ \textit{heat}\end{array}\right\} + \left\{\begin{array}{l}\textit{Energy}\\ \textit{consumed}\\ \textit{by reaction}\end{array}\right\}$$

For an increment of time d*t* this expression can be written as

$$\frac{\delta Q}{\mathrm{d}t} = mc_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t} - \frac{\mathrm{d}H_{\mathrm{R}}}{\mathrm{d}t} \tag{4}$$

where m is the total mass, c_{p} the constant pressure heat capacity, δQ is the heat transferred, $\mathrm{d}T$ the temperature change which the reaction mixture undergoes and $\mathrm{d}H_{\mathrm{R}}$ the enthalpy change of the system in this increase in time. The sign (-) indicates that the system releases heat.

In adiabatic conditions the heat transferred is zero, so the equation of energy conservation is now

$$mc_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t} = \Delta H_{\mathrm{R}}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{5}$$

in which Eq. (1) is taken into account which relates the rate of heat evolution $\mathrm{d}H_{\mathrm{R}}/\mathrm{d}t$ with the rate of reaction $\mathrm{d}\alpha/\mathrm{d}t$. By eliminating the time, this expression can be reduced to a form which does not involve time.

If c_{p} is assumed to be independent of temperature and conversion, Eq. (5) can be integrated to give a relationship between temperature and conversion,

$$T = T_{\mathrm{o}} + \frac{\Delta H_{\mathrm{R}}}{mc_{\mathrm{p}}}\alpha \tag{6}$$

Note that when the completion of reaction is reached, $\alpha = 1$ and the adiabatic reaction temperature is given by

$$T_{\mathrm{ad}} = T_{\mathrm{o}} + \frac{\Delta H_{\mathrm{R}}}{mc_{\mathrm{p}}} \tag{7}$$

If one wants to obtain the change of temperature and heat generated as functions of time, as well as the rate of reaction as a function of α, the following system of equations will have to be solved [12]

$$\begin{cases} k = Ae^{-E/RT} \\ T = T_o + \dfrac{\Delta H_R}{mc_p}\alpha \\ \dfrac{d\alpha}{dt} = kf(\alpha) \end{cases} \tag{8}$$

This system can only be solved numerically, for example, by the Runge-Kutta procedure [13].

Calculation procedure

Note that the system of Eq. (8) is in fact one dependent-variable problem where the relation between time and conversion is obtained by integration of

$$t = \int_o^\alpha \frac{d\alpha}{Ae^{-E/RT}f(\alpha)} = \int_o^\alpha \frac{d\alpha}{h[T(\alpha), \alpha]} \tag{9}$$

where $T(\alpha)$ represents the expression of Eq. (6).

As has been said, only numerical integration is usually feasible. The Runge-Kutta method is such procedure. The calculation procedure is to start at $\alpha=0$, $t=0$ and calculates the necessary time at successive increments of conversion $\Delta\alpha$. If subscript n designates the number of conversion increments, the instant of time t_{n+1} is obtained from instant t_n by the formula

$$t_{n+1} = t_n + 1/6\,[k_1(n) + 2k_2(n) + 2k_3(n) + k_4(n)] \tag{10}$$

where for one dependent-variable function $H[T(\alpha),\alpha] = 1/h[T(\alpha),\alpha]$, $k_1(n)$, $k_2(n)$, $k_3(n)$ and $k_4(n)$, are given by the following working equations

$$\begin{cases} k_1(n) = \Delta\alpha\, H[T(\alpha_n), \alpha_n] \\ k_2(n) = \Delta\alpha\, H[T(\alpha_n + {}^1\!/\!_2\Delta\alpha), \alpha_n + {}^1\!/\!_2\Delta\alpha] \\ k_3(n) = \Delta\alpha\, H[T(\alpha_n + {}^1\!/\!_2\Delta\alpha), \alpha_n + {}^1\!/\!_2\Delta\alpha] \\ k_4(n) = \Delta\alpha\, H[T(\alpha_n + \Delta\alpha), \alpha_n + \Delta\alpha] \end{cases} \tag{11}$$

The accuracy of the solution obtained by this procedure will depend on the value of increment $\Delta\alpha$. The solution will be made more accurate by covering the integration interval in two steps instead of one by using $\Delta\alpha = {}^1\!/\!_2\Delta\alpha$. This procedure is continuously repeated until a good degree of accuracy is obtained. We have verified that an increment of $\Delta\alpha=0.0001$ provides a sufficiently accurate solution.

Simulated curves in adiabatic conditions: position, shape and size

n^{th}-order reaction model

The following kinetic parameters: frequency factor $A=6\cdot10^5 s^{-1}$, activation energy $E=50$ kJ/mol, reaction order $n=1$, 2, 3 and 5 were used in this study. The range of temperature for simulated curves was 10 to 40°C and we assumed a reaction heat value of 500 J/g and a specific heat capacity value of 1.67 $J\cdot g^{-1}\cdot K^{-1}$. Both values were found by the authors for the reaction of curing of an unsaturated polyester resin [14].

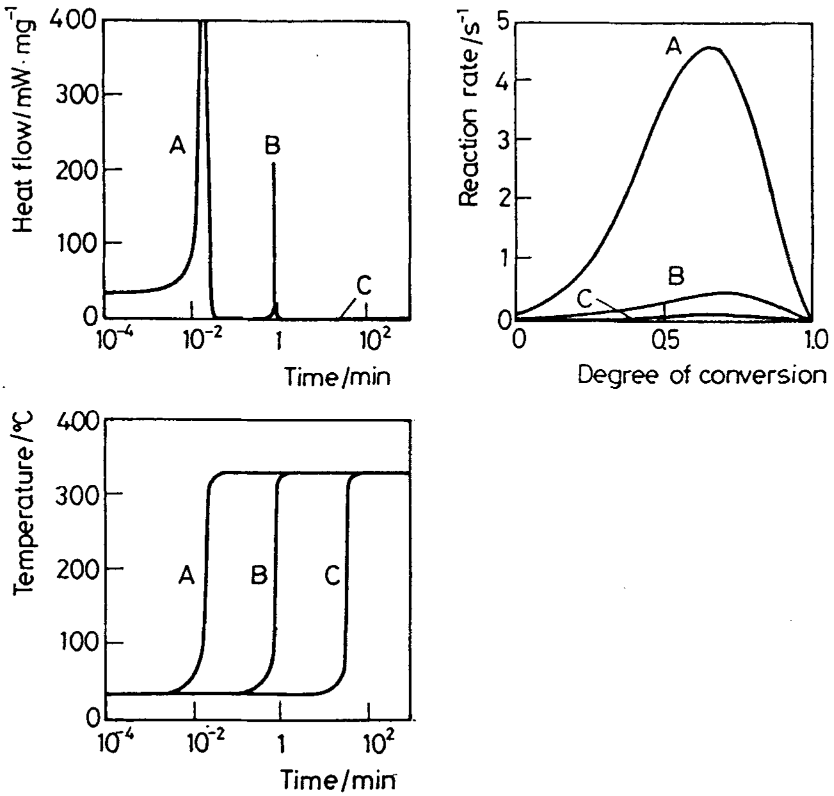

Fig. 1 Effect of the activation energy E on the shape of the theoretical dH/dt *vs.* t, T *vs.* t and dα/dt *vs.* α curves. Kinetic parameters: $T_o=30$°C; $n=2$, $A=6\cdot10^5$ s^{-1} and reaction heat: 500 J/g. (A) $E=40$ kJ/mol; (B) $E=50$ kJ/mol; (C) $E=60$ kJ/mol

In Figs 1 and 2 we show the influence of variations in the frequency factor A and activation energy E on the following plots: dH/dt *vs.* t, T *vs.* t and dα/dt *vs.* α. As can be seen, the shape of the exothermal peak does not change when the activation energy and frequency factor are varied, but the position and size of the peak do change significantly. When *E* is increased, the peak shifts to longer times, increasing the explosion time. However, the size of peak decreases and the shape is affected slightly by the increase in *E*. The effect of increasing *A* is the opposite of increasing *E*. Both variations increase or decrease the maximum reaction rate, changing its position, which is shifted to high degrees of conversion when *E* is decreased or *A* is increased.

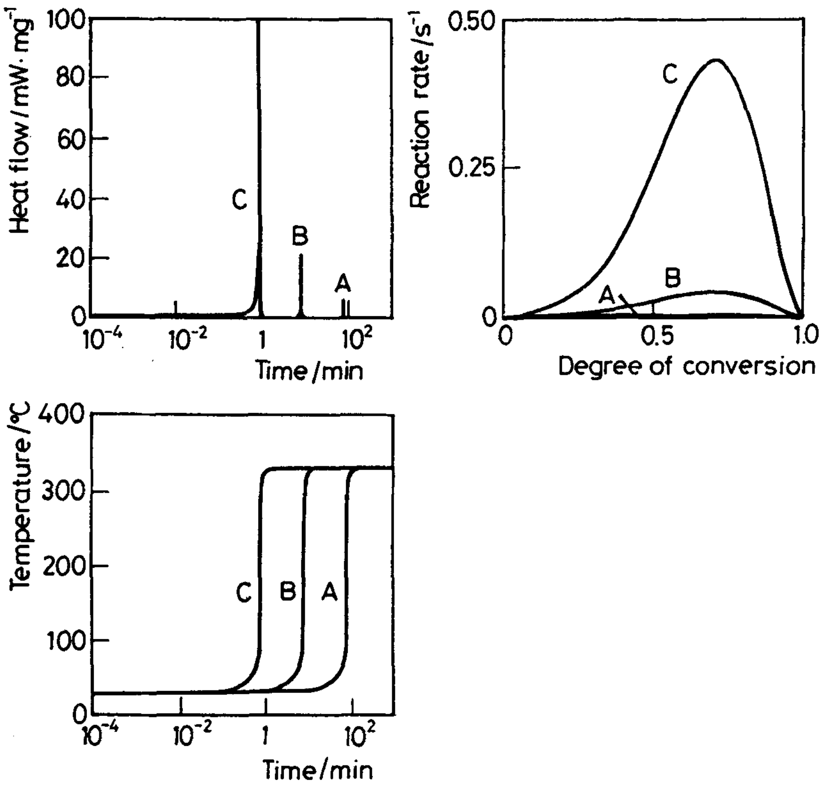

Fig. 2 Effect of the frequency factor *A* on the shape of the theoretical d*H*/d*t* vs. *t*, *T* vs. *t* and dα/d*t* vs. α curves. Kinetic parameters: T_0=30°C; n=2, E=50 kJ/mol and reaction heat: 500 J/g. (A) $A=6\cdot10^3$ s^{-1}; (B) $A=6\cdot10^4$ s^{-1}; (C) $A=6\cdot10^5$ s^{-1}

The influence of variations in the order of reaction is also represented in Fig. 3 for different values of reaction heat. The heat of reaction may decrease due to endothermal competitive reactions such as degradation processes as a consequence of the high temperatures reached. An increase in *n* causes a drastic change in the shape of heat generation curve, which becomes flatter. The peak is shifted to longer times. As can also be seen, the heat generation is different from zero for $t=0$, there being a small flux of heat. In addition, the rate of reaction is lower and more time is required to reach the adiabatic reaction temperature [T_{ad}], which is independent of the reaction order n. The size of the dα/dt *vs.* α curve decreases when n increases, its shape undergoes a drastic change and the maximum position shifts to lower degrees of conversion.

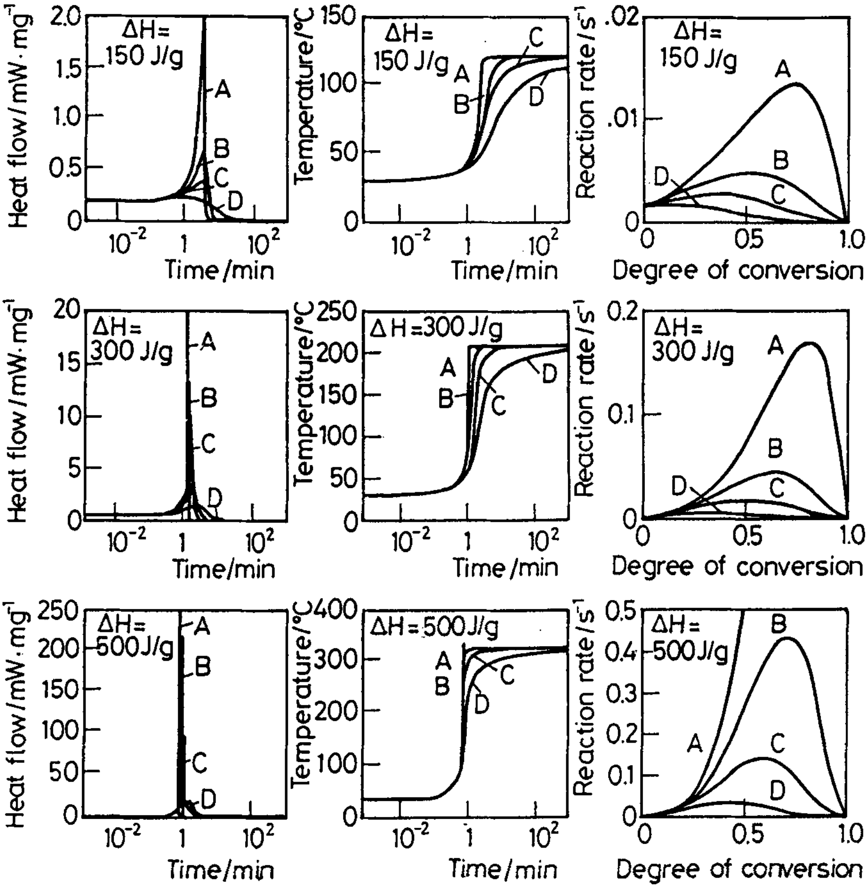

Fig. 3 Effect of the reaction order n on the shape of the theoretical dH/dt *vs.* t, T *vs.* t and dα/dt *vs.* α curves for different values of the reaction heat: $\Delta H=150$ J/g, $\Delta H=300$ J/g and $\Delta H=500$ J/g. Kinetic parameters: $T_o=30$°C; $A=6\cdot 10^5$ s^{-1}, $E=50$ kJ/mol. (A) $n=1$; (B) $n=2$; (C) $n=3$; (D) $n=5$

A decrease in the reaction heat also causes a drastic change in the shape of the heat generation curve (Fig.4), which is flatter, and the peak is shifted to longer times. The adiabatic reaction temperature decreases, too. The rate of reaction is lower, drastically changing its shape, and the maximum is shifted to

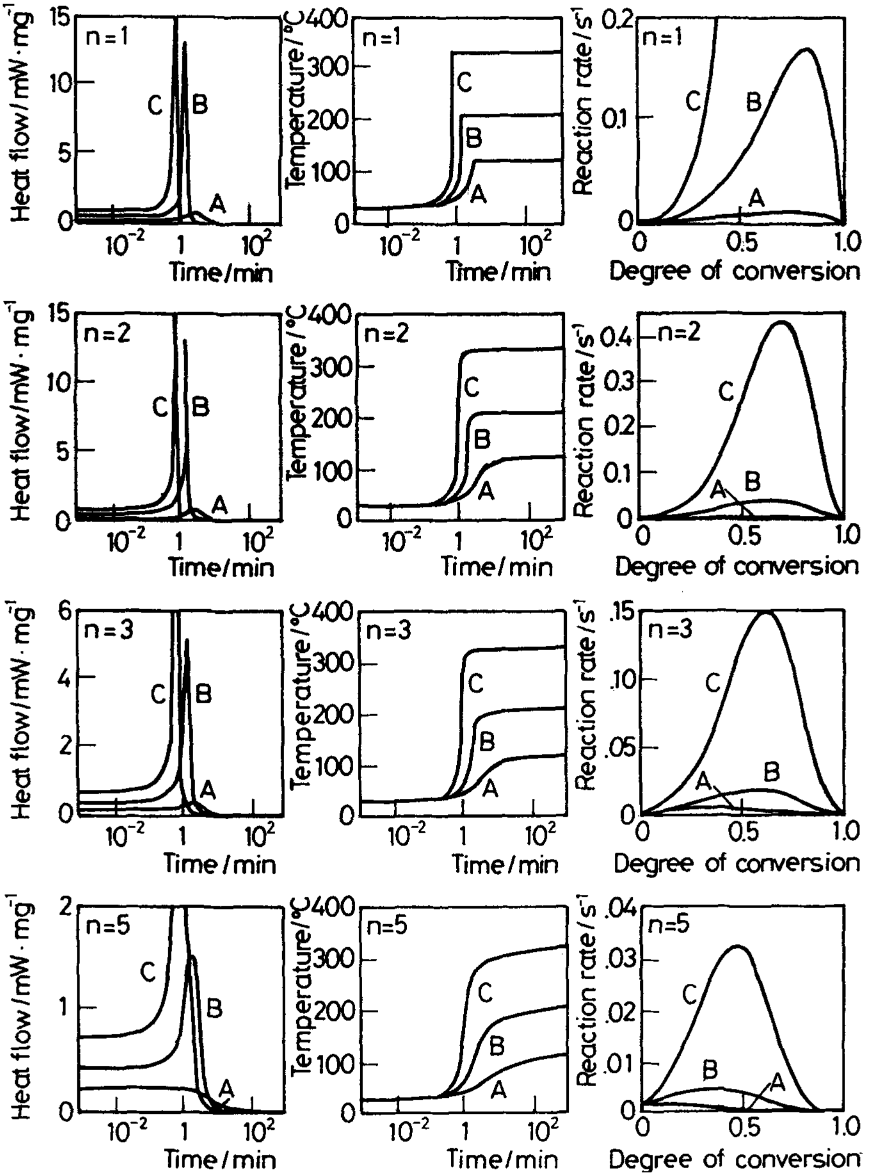

Fig. 4 Effect of the reaction heat ΔH on the shape of the theoretical dH/dt *vs.* t, T *vs.* t and $d\alpha/dt$ *vs.* α curves for different values of the reaction order: $n=1$, $n=2$, $n=3$ and $n=5$. Kinetic parameters: $T_0=30°C$; $A=6\cdot10^5\ s^{-1}$, $E=50$ kJ/mol. (A) $\Delta H=150$ J/g; (B) $\Delta H=300$ J/g; (C) $\Delta H=500$ J/g

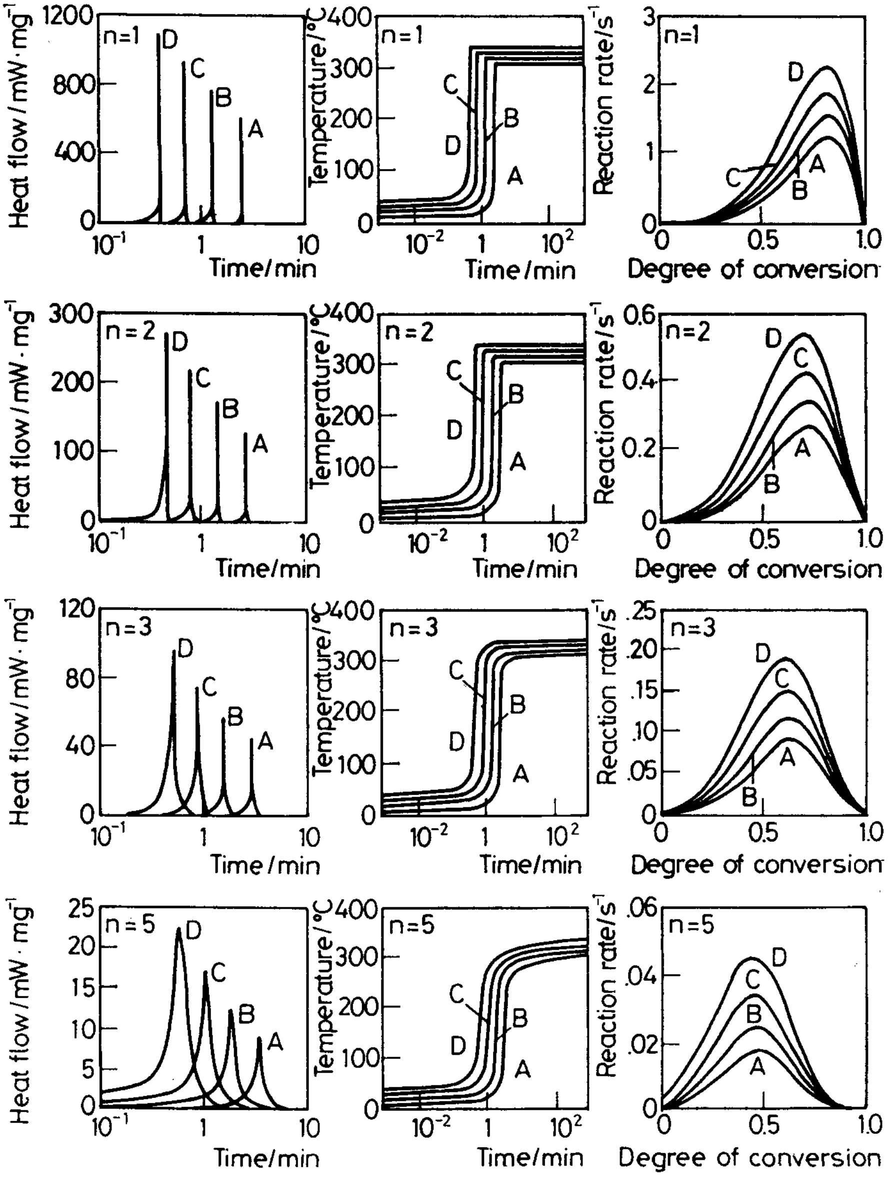

Fig. 5 Effect of the initial temperature T_o on the shape of the theoretical dH/dt *vs.* t, T *vs.* t and dα/dt *vs.* α curves for different values of the reaction order: $n=1$, $n=2$, $n=3$ and $n=5$. Kinetic parameters: $A=6{\cdot}10^5$ s^{-1}, $E=50$ kJ/mol, reaction heat: ΔH500 J/g. (A) $T_o=10$°C; (B) $T_o=20$°C; (C) $T_o=30$°C; (D) $T_o=40$°C

lower degrees of conversion. It can be seen that the maximum value is zero for $n=5$ and a reaction heat value of 150 J/g.

Figure 5 represents the effect of the initial temperature and different values of reaction order $n=1$, 2, 3 and 5 on the next set of plots: dH/dt *vs.* t, T *vs.* t and $d\alpha/dt$ *vs.* α. When the initial temperature varies, the shape of the peak on the dH/dt *vs.* t curve does not change, but its position and size do change. For high initial temperatures, the peak is higher and it is found at shorter times. Hence, the explosion time increases when the initial temperature is decreased or the reaction order is increased. Also, more time is required to reach the adiabatic reaction temperature T_{ad}. The temperature T_{ad} depends on the initial temperature T_o (Eq. (7): the higher the initial temperature, the higher is T_{ad}).

The reaction rate increases when the temperature is increased. The shape of the $d\alpha/dt$ *vs.* α curve and the position of the maximum change only slightly. Nevertheless, the maximum shifts slightly to lower degrees of conversion when the initial temperature is increased. This indicates that the reaction is faster for higher initial temperatures.

Autocatalytic model

For the simulation of the dH/dt *vs.* t, T *vs.* t and $d\alpha/dt$ *vs.* α curves in adiabatic conditions according to an autocatalytic reaction model, we used the following kinetic parameters: frequency factor $A=6\cdot10^5 s^{-1}$, activation energy $E=50$ kJ/mol, reaction order $n+m=1$, 2, 3 and 5, and exponent $m=0.2$, 0.4, 0.6 and 0.8. The range of temperature used in this study was 10 to 40°C and we also assumed a reaction heat value of 500 J/g and specific heat capacity $c_p=1.67\ J\cdot g^{-1}\cdot K^{-1}$.

The influence of the parameters A and E on the theoretical curves is the same as for the corresponding influence on simulated curves of the n^{th}-order reaction model and it will not be considered here. Figure 6 represents the influence of the heat of reaction for different values of the reaction order $n+m=1$, 2, 3 and 5 on the dH/dt *vs.* t, T *vs.* t and $d\alpha/dt$ *vs.* α curves. As seen, similar conclusions to those of Fig. 3 for the n^{th}-order reaction model can be obtained.

The only difference is that the explosion time is longer and the heat generation is zero at $t=0$ for the autocatalytic model of reaction.

In Fig. 7 we show the effect of temperature. The conclusion are also the same as those corresponding to the n^{th}-order reaction model. The effect of the exponent m on the dH/dt *vs.* t, T *vs.* t and $d\alpha/dt$ *vs.* α curves for different values of the reaction order $n+m=1$, 2, 3 and 5 is represented in Fig. 8. When the exponent m is increased, the shape of the exothermal peak does not change, but it is shifted to longer times and its size also increases. The adiabatic reaction temperature T_{ad} is not affected by variations in the exponent m. The time of explo-

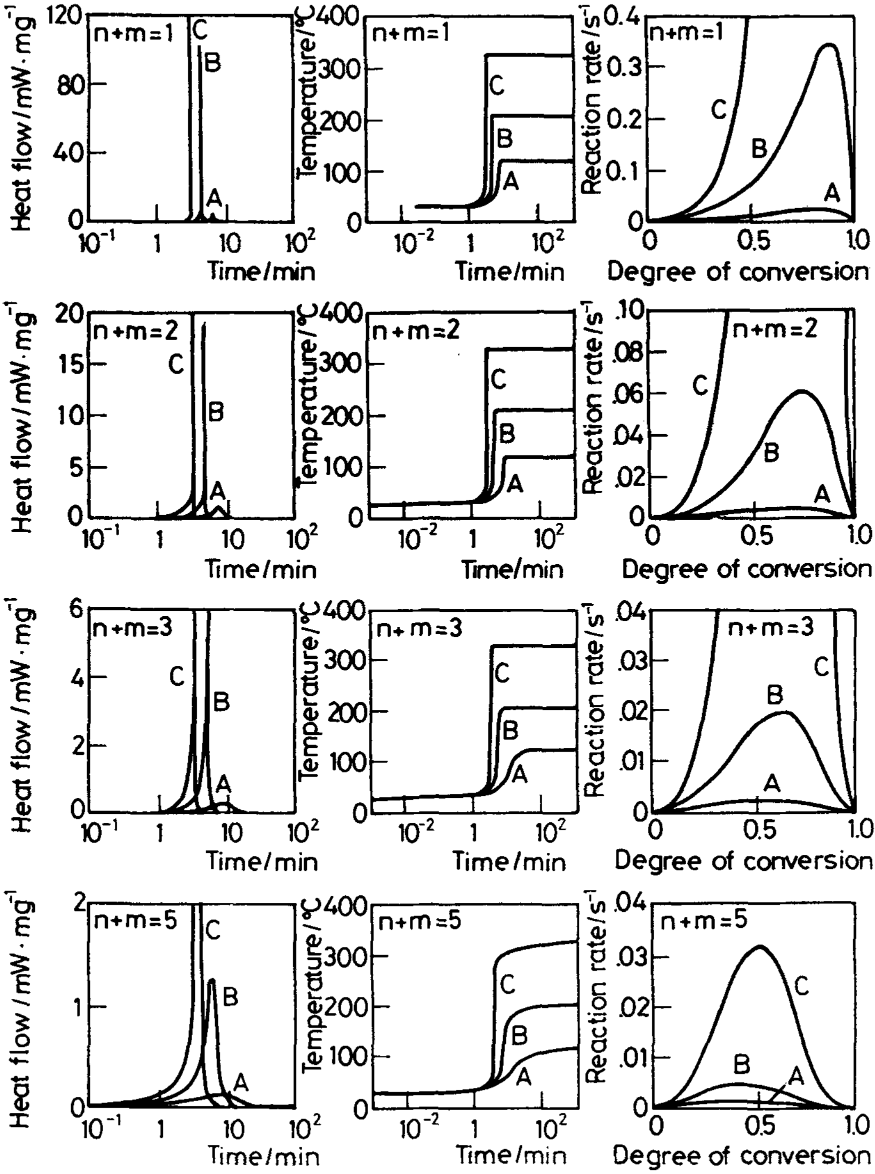

Fig. 6 Effect of the reaction heat ΔH on the shape of the theoretical curves: dH/dt vs. t, T vs. t and $d\alpha/dt$ vs. α curves for different values of the reaction order: $n+m=1$, $n+m=2$, $n+m=3$ and $n+m=5$. Kinetic parameters: $T_0=30°C$, $A=6{\cdot}10^5\ s^{-1}$, $E=50$ kJ/mol, exponent $m=0.4$. (A) $\Delta H=150$ J/g; (B) $\Delta H=300$ J/g; (C) $\Delta H=500$ J/g

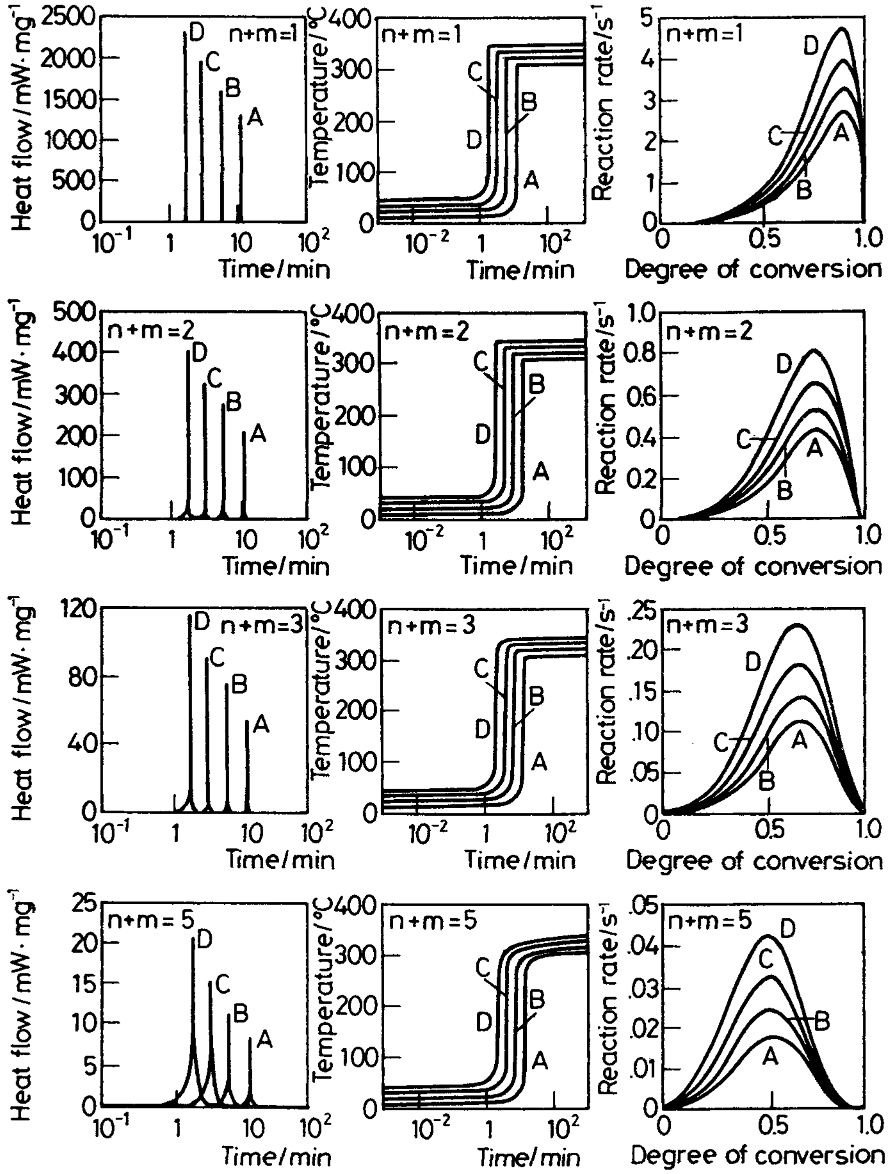

Fig. 7 Effect of the initial temperature T_0 on the shape of the theoretical dH/dt *vs*. t, T *vs*. t and dα/dt *vs*. α curves for different values of the reaction order: $n+m=1$, $n+m=2$, $n+m=3$ and $n+m=5$. Kinetic parameters: $A=6\cdot10^5$ s^{-1}, $E=50$ kJ/mol, exponent $m=0.4$ and reaction heat: $\Delta H=500$ J/g. (A) $T_0=10$°C; (B) $T_0=20$°C; (C) $T_0=30$°C; (D) $T_0=40$°C

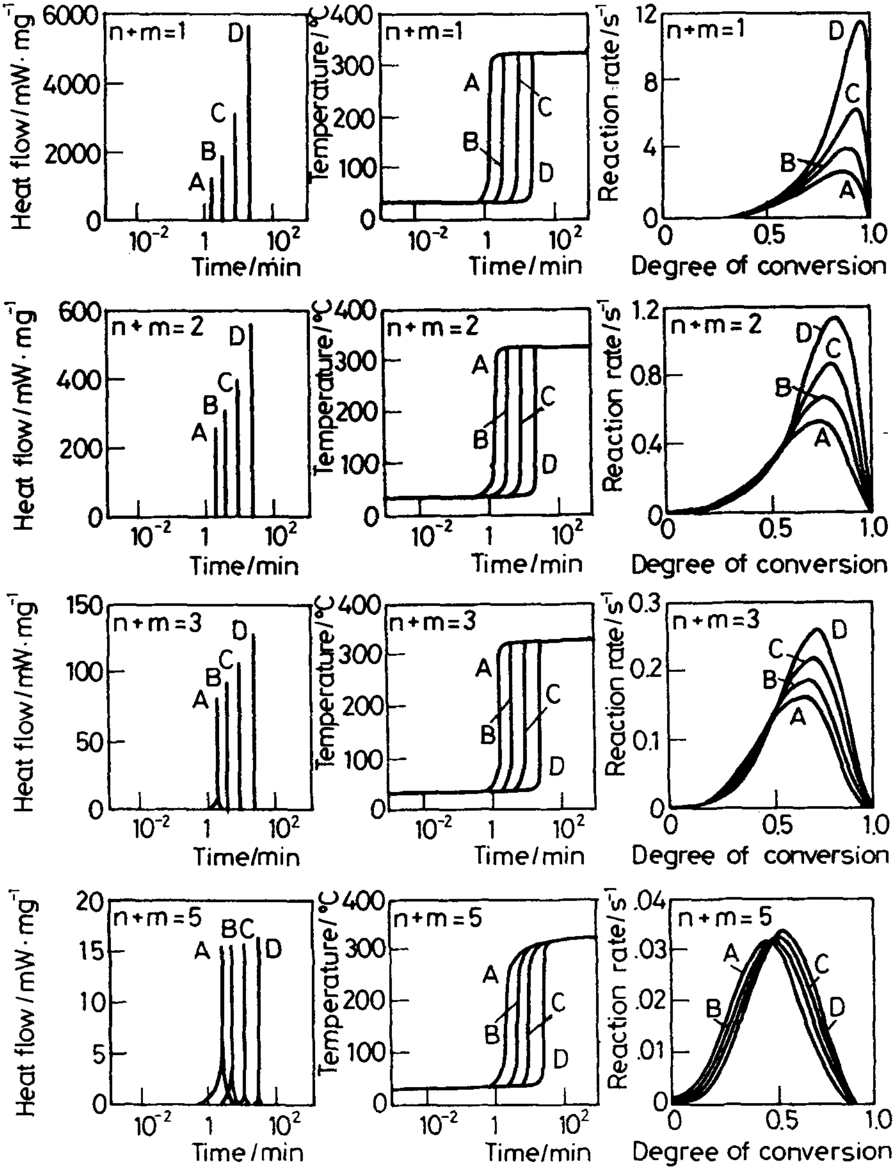

Fig. 8 Effect of the exponent m on the shape of the theoretical dH/dt *vs.* t, T *vs.* t and dα/dt *vs.* α curves for different values of the reaction order: $n+m=1$, $n+m=2$, $n+m=3$ and $n+m=5$. Kinetic parameters: $A=6\cdot10^5$ s^{-1}, $E=50$ kJ/mol, $T_o=30$°C and reaction heat: $\Delta H=500$ J/g. (A) $m=0.2$; (B) $m=0.4$; (C) $m=0.6$; (D) $m=0.8$

sion increases with m, but after that, a shorter time is required to reach the value of T_{ad}.

The shape of the reaction rate *vs.* α curve changes drastically (the curves are overlapped) when m is increased. Its size also increases and the maximum is shifted to higher degrees of conversion.

Conclusions

The theoretical simulation of the curing process of unsaturated polyesters based on the application of energy balance and basic rate law, as well as a numerical calculation procedure such as the Runge-Kutta method, allows us to obtain the heat generation curve as a function of time, the change of temperature and reaction rate as a function of the degree of conversion. This would not be feasible experimentally by differential thermal analysis such as the DSC technique.

The simulated curves that correspond to an autocatalytic reaction model show a longer explosion time than those corresponding to an n^{th}-order reaction model. This is due to the existence of an induction period in order for the reaction to start up. On the other hand, as distinguished from an n^{th}-order reaction model, the heat generation for the autocatalytic model is different from zero at $t=0$.

Variations in the kinetic parameters (A, E and reaction order) produce in turn variations in the position, size and shape of the simulated curves, and allows us to construct a set of reference curves that can be used to simulate the real kinetic process when it occurs in adiabatic conditions.

Similar effects are produced by variations in the initial temperature and heat of reaction. The variations in the heat of reaction may be important, since due to the high temperatures reached in the material, the process in adiabatic conditions may be affected by endothermic processes such as degradation, which can cause shrinkage and cracks in the material.

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References

1 K. H. Lin, H. C. Van Ness and M. M. Abbots, Perry's Chemical Engineers's Handbook, 6th Ed., section 4. McGraw-Hill 1984.
2 A. A. Duswalt, Thermochim. Acta, 8 (1974) 57.
3 M. E. Brown, Introduction to Thermal Analysis, Chapman and Hall, London 1988.
4 W. Hemminger and G. Höhne, Calorimetry: Fundamentals and Practice, Verlage Chemie, Weinheim 1984.

5 J. Sesták, Thermal Analysis, Vol. XII. Wilson and Wilson's Comprehensive Analytical Chemistry, G. Svehla (Ed.), Elsevier, Amsterdam 1984, Chapter 9.

6 R. B. Prime, Thermal Characterization of Polymeric Materials, E. Turi (Ed.), Academic Press, New York 1981, Chapter 5.

7 H. J. Peschke, Third International Congress on Polymers in Concrete, Koriyama, Japan 1981, p. 477.

8 S. M. Waks, Reaction Kinetics for Chemical Engineers, McGraw-Hill, New York 1959, Chapter 2.

9 D. I. Townsed and J. C. Tou, Thermochim. Acta, 37 (1980) 1.

10 K. Wark, Thermodynamics, 4th Ed., McGraw-Hill, New York 1983, Chapter 14.

11 J. M. Smith and H. C. Van Ness, Introduction to Chemical Engineering Thermodynamics, 4th edition. McGraw-Hill, New York 1988.

12 J. M. Smith, Reaction Kinetics for Chemical Engineers, 3rd Ed. McGraw-Hill, New York 1985.

13 V. G. Jenson and G. V. Jeffreys, Mathematical Methods in Chemical Engineering, Academic Press, London 1977.

14 J. M. Salla and J. L. Martin, Thermochim. Acta, 126 (1988) 339.

Zusammenfassung — Der exotherme Vorgang des Erhärtens von Duroplasten unter adiabatischen Bedingungen kann mittels differentialer Thermoanalyse wie z.B. DSC nicht verfolgt werden. Ausgehend von der spezifischen Reaktionsgeschwindigkeit und der Wärmekapazität als Funktionen der Temperatur sowie der Reaktionswärme bei einigen Referenztemperaturen ist es möglich, ein adiabatisches Vorgehen zu konstruieren.

Vorliegend wird die Energiebilanz beim Erhärtungsvorgang unter adiabatischen Bedingungen angewendet und das Geschwindigkeitsgesetz für zwei empirische kinetische Funktionen $f(\alpha)$ gelöst: Kinetik n-ter Ordnung $[f(\alpha)=(1-\alpha)]$ und Autokatalysekinetik $[f(\alpha)=\alpha^m(1-\alpha)^n]$, wobei α der Konversionsgrad und n und m die Reaktionsordnungen sind, um die Wärmefreisetzungskurve (dH/dt) als eine Funktion der Zeit, den Temperaturverlauf in Abhängigkeit der Zeit und die Explosionszeit, die maximale adiabatische Temperatur und die Reaktionsgeschwindigkeit als Funktion des Konversionsgrades zu erhalten.