

DSC DETERMINATION OF TEMPERATURE-TIME PROFILES FOR THE COMPLETE CONVERSION OF THERMALLY CURABLE EPOXY RESINS

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SUMMARY

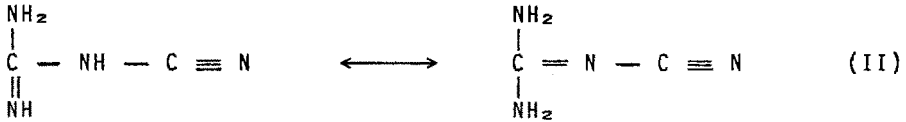
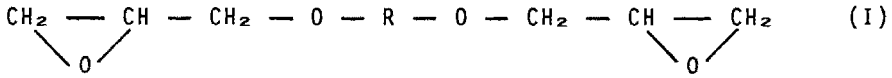
The initiating reactions of the epoxy resin curing have already taken place in the thermally prereacted epoxy resins to oligomerisates (B-state) which are used to bond the laminates. The kinetics of overall reaction lead to the conclusion that a uniform reaction mechanism is mostly involved till curing is completed. Therefore, the DSC curves of measurement of such resins are particularly suited in time-conversion calculations for the computer supported optimization of quality. With a computer program it can be shown that the bulk quantities, such as order of reaction (n), activation energy (E_A) and collision factor (A), calculated from a single sequence of DSC measurement are sufficient for mathematical simulation of the curve over its entire range. The temperature-conversion-time nomograms so derived permit the reaction conditions for the complete curing of the resins to be ascertained without involving a tedious series of experiments. At the same time, technical restrictions such as mass dependent heating times, for instance, watt density of mold tools, can be drawn into account.

INTRODUCTION

In the electrical industry, thermally curable reactive resins are processed to high grade molding materials which are electrically, thermally and mechanically durable. A prerequisite to such process is the controlled and complete curing, since the characteristic features can otherwise change to a critical extent. In practice, the thermal curing conditions are determined by tests and control of the degree of curing (ref. 1). These investigations are very elaborate and tedious depending on the particular application.

The curves of measurement of dynamic differential calorimetry implicitly contain all pieces of information which are necessary in ascertaining the temperature-time profiles for the complete thermal curing of modified epoxy resins. For calculation, the parameters of reaction at discrete temperatures must be deduced from the experiment under dynamic conduction of temperature.

Epoxy resins (I) curable with dicyandiamide (II) are used in the form of prepregs as adhesive films for the preparation of high grade multilayer printed circuit boards in electrical technology. The epoxy resins are prereacted to oligomerisates (B-state) to improve the storage properties of the films.



Thus, the initiating reactions of epoxy resin curing have already been completed so that from the kinetics of overall reaction a uniform reaction mechanism can be deduced to operate to a large extent till completion of curing.

The DSC curves of measurements of these resins are therefore particularly suited for time-conversion calculations. The method is suitable for the determination of isothermal conversions in the case of dynamically pursued exothermic chemical reactions. In this manner, the required conduction of temperature for curing under practical conditions can also be predicted for technical processes with finite heating times.

EXPERIMENTAL

The samples used were prepregs based on bisphenol-A-epoxy resins cured with dicyandiamide, in prereacted state (B-state) on fibre glass cloth.

The differential scanning calorimetric (DSC) investigations were carried out with the thermal analyzer system 1090/910 of DuPont. The measurements were made with 15mg-20mg of prepreg in a cold welded aluminium micropan. A small quartz plate was used as a reference to compensate for the changes in heat capacity caused by the fibre glass cloth.

The samples were conditioned to give faultless measurements. This was done by heating the samples to about 5 K above the glass-

transition temperature T_g , followed by slow cooling and immediate measurement. This process makes it possible to eliminate the enthalpy relaxation occurring in the T_g range (ref. 2).

In the measurements where the temperature rise is linear with time, the heating rate must be chosen in such a manner that the heat flow of the exothermic curing reactions at the end is nearly the same as at the beginning. A value of 2 K/min has proved to be the most favourable heating rate. Indium and tin were used for temperature calibration and indium for enthalpy calibration (see Fig. 1).

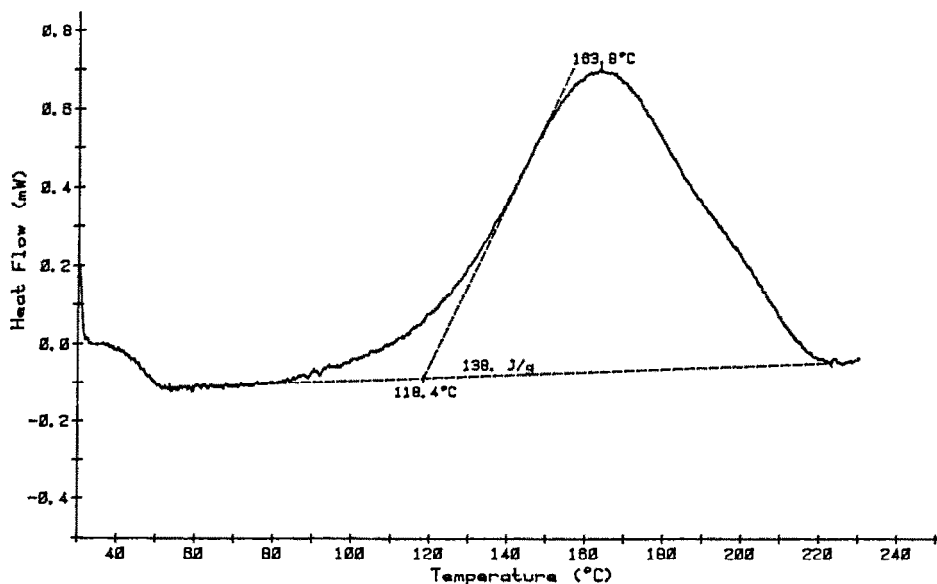


Fig. 1. DSC curve for dicyandiamide curing of epoxy resin

The straight base line in Fig. 1 is drawn automatically by the thermal analyzer system. For following calculations the curve at the beginning and end of the reaction are joined by a sigmoidal base line (ref. 3).

CALCULATION

According to a method basically known and using a Desk-top computer (PC), the kinetic data of reaction are calculated from the temperature dependency of the heat flow at linear rise of temperature; data which are actually necessary (ref. 4) for the determination of rate constants and degree of conversion at

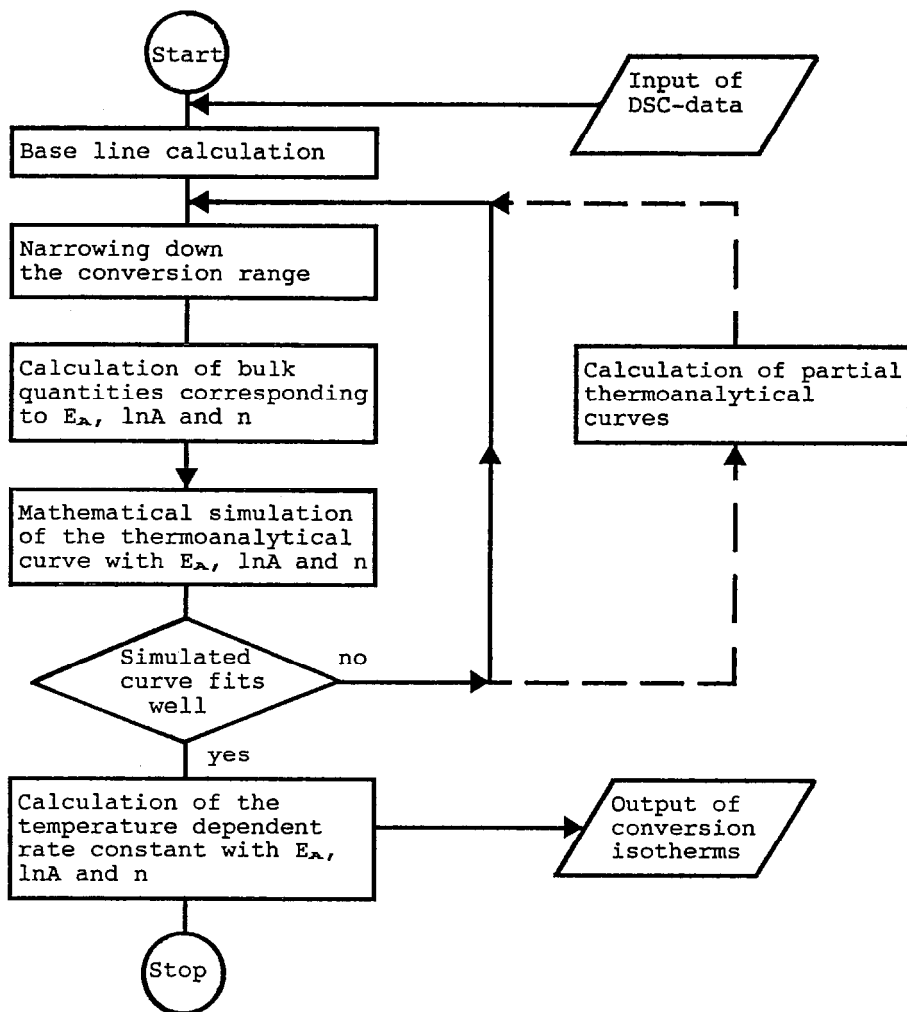


Fig. 2. Program for the kinetic evaluation of thermoanalytical curves

discrete temperatures. However, for each step of calculation, a self-developed computer program permits the relevancy of parameters determined by means of an interactive mode to be controlled (see Fig. 2). By conversion, these data are processed as numerically comparable with those of thermoanalytical measurement. Thus, it is ensured that the computed values remain valid throughout the entire temperature-time range of interest. That part of the thermogram, which lies within a minimum

conversion range of 5 % to 25 % and a maximum on of 65 % to 80 %, is taken into account for the evaluation. In this range, the errors of measurement are sufficiently small due to high heat flow. The calculated parameters of reaction, E_A , n and $\ln A$, which

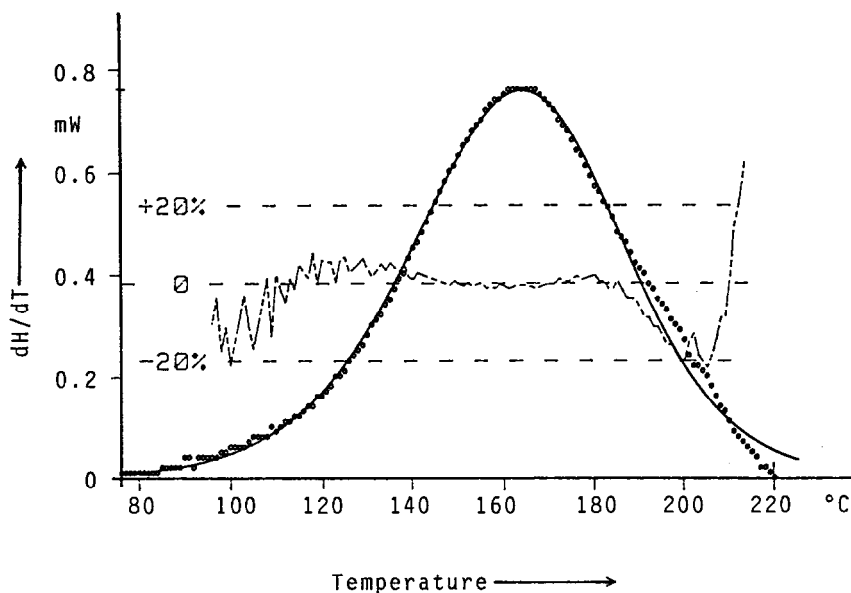


Fig. 3: Comparison of experimental and calculated variation of heat flow dH/dT with temperature for dicyandiamide curing of epoxy resin.

Method of evaluation according to Ellerstein (ref. 5);

Conversion range: 25 % to 80 %;

Simulation with: $E_A = 81.5$ kJ/mol, $n = 1.50$, $\ln A = 16.0$;

oooo measured curve, ——— simulated curve and

--- Difference.

formally correspond to the activation energy, to the order of reaction and to the natural logarithm of the collision factor, are adequate for a mathematical simulation of the measured curve over the entire range (see Fig. 3).

The recalculated thermogram is compared with the measured values of an individual sequence of DSC measurement or by taking the mean of several standardized thermograms. The differential curve shows the deviations that result from the calculated

parameter in each region of the measured curve. On good approximation of the calculated curve to the measured one, a high degree of certainty is obtained for the relevancy of parameters.

If both curves deviate systematically from each other over a considerable range other limits must be chosen for the temperature range to be evaluated and the evaluation repeated. If satisfactory matching is still not achieved, it may then be attributed to the reactions which have a different mechanism and take place in only part of the investigated temperature range. This can, for instance, be the case with initiating reactions. Such data ranges must be mathematically separated before being evaluated separately.

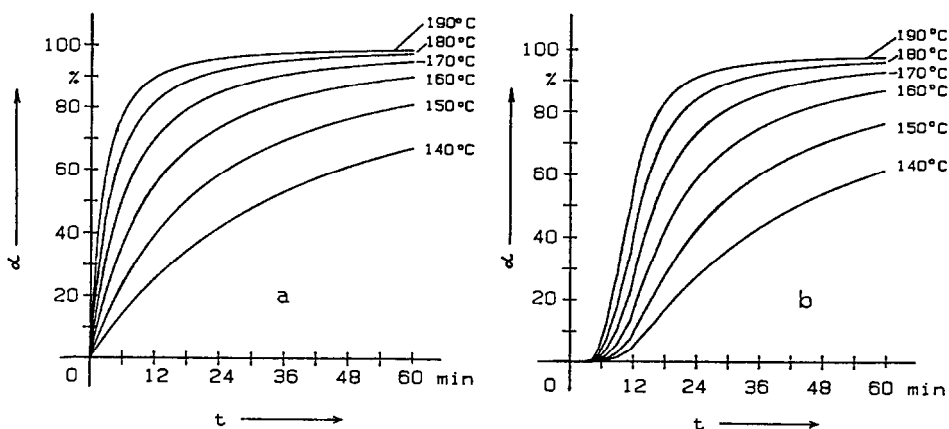


Fig. 4: Degree of conversion α during dicyandiamide curing of epoxy resin. a: direct exposure to the temperature of reaction; b: exposure to reaction temperature after a heating phase of 15 min.

The isotherms of the conversion rates are calculated from the temperature dependent reaction rates according to Grentzer et al. (ref. 6). The degree of conversion against time can be plotted at constant temperature as a parameter (see Fig. 4a) or it can be obtained from a temperature-time programme which is derived by calculation and lining up of partial conversions at different temperatures (see Fig. 4b).

The straight lines shown in Fig. 5 are obtained by changing the parameters and redrawing as nomograms based on Gaussian normal

distribution. The nomogram b in Fig.5 yields the degree of conversion during a certain period of time at an arbitrarily chosen temperature and considers a heating phase of 15 min from room temperature. The nomogram a in Fig. 5 shows the degree of conversion without or with a negligibly small heating phase.

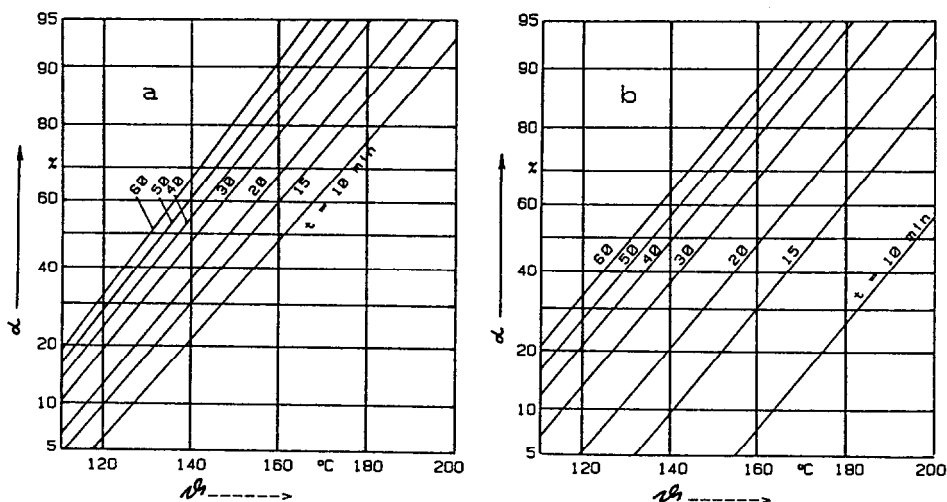


Fig. 5: Nomograms for the evaluation of technical curing conditions for dicyandiamide curing of epoxy resin.
 a: direct exposure to reaction temperature;
 b: exposure to reaction temperature after a heating phase of 15 min

DISCUSSION

The basis of calculation for the degree of conversion from the rate constants, like the one for simulation of the DSC measured curve, is derived from the general law of homogeneous kinetics and the Arrhenius equation. Hence, the set of time-conversion curves using temperature as a parameter correspond to the thermoanalytical curve in as similar a manner as the simulated curve. Technical factors such as heating times at actual masses are taken into account by linear lining up of several isothermal curves of conversion.

In actual practice, temperatures are preset which allow for the thermal loading capacities of the material and the molding tool as well as the resin flow and the molding time in processing epoxy

resins to molding materials. In determining the corresponding reaction times, nomograms based on normal distribution are specially suitable, which depict the degree of conversion with respect to reaction temperature and time as parameters. The heating time during which the resin is exposed to a constantly rising temperature, can also be deduced from the set of time-conversion curves in Fig. 4b.

The amounts of conversion determined by means of these temperature-conversion-time nomograms are in very good agreement with the experimental data. Thus, it is possible without a series of tedious experiments to establish temperature-time profiles for complete curing, by DSC measurements which are simple to carry out.

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