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Note

Quantitative isothermal DTA-studies

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Isothermal experiments offer some advantages compared to dynamic scans:

(1) no problems caused by changes in heat capacity in the course of the reaction;

(2) no secondary reactions at the end of the peak due to unrealistic high temperatures;

(3) the isothermal DTA curve shows directly the reaction rate during the reaction.

On the other hand, Fava[1] found out that isothermal studies are not quantitative, at least not during the initial stage of reaction.

This paper shows the procedure to obtain quantitative results from isothermal DTA-experiments. Analyses were performed on a Mettler TA2000 system.

EXPERIMENTAL

(1) A crucible containing an inert sample with a heat capacity, C_s, is placed in the DTA cell which is kept isothermal at the desired temperature T_p. An empty crucible of the temperature $T_r = T_p$ acts as reference. The sample temperature, T_s, will reach the cell temperature T_p, following an exponential law:

$$T_s = T_p - (T_p - T_0) \exp -(t/R_t(C_s + C_{SH}))$$

T_0 = initial temperature of sample cup = room temperature; t = time after inserting the cup; R_t = thermal resistance between furnace and sample cup = 0.6 °C mcal^{-1} sec^{-1}; C_{SH} = heat capacity of sample cup; and ΔT-sensor in sample area = 18 mcal °C^{-1}.

The time constant $\tau = R_t(C_s + C_{SH})$ equals 12 sec for usual sample size and it follows herewith for $T_p = 160$ °C and $T_0 = 20$ °C:

$$T_s = 160\,°C - 140\,°C \exp -(t/12\ \text{sec})$$

This is exactly in agreement with curve 1 in Fig. 1.

(2) Now let us run the same experiment with an epoxy premix (mixture of 100 parts Araldit F (Ciba–Geigy), 90 parts methyl tetrahydrophthalic anhydride and 0.5 parts benzyl dimethylamine as catalyst): curve 2 in Fig. 1. Owing to the beginning of curing, this curve deviates from the inert one. The hatched area, shaped like a

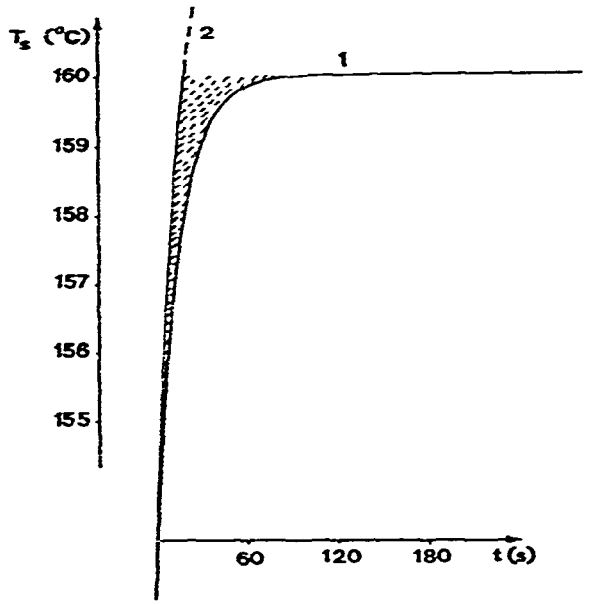

Fig. 1. Curve (1), The DTA-signal of an inert sample (15 mg Al_2O_3) follows Newton's exponential law. Curve (2), The DTA-signal of epoxy premix (10 mg) already deviates some degrees below furnace temperature from curve 1, due to the onset of the exothermal curing reaction. The hatched area amounts to 84 mcal which is more than 10% of the complete reaction enthalpy! Furnace temperature 160°C.

wedge, was lost in the past. It is important to start the recorder the second time at exactly the same place on the paper and also at the same signal level ($T_s = T_p - 10$°C proved to be sufficient), so that the time base for both curves coincides. The size of the hatched area increases with the initial reaction rate of the sample and, for this epoxy system, amounts to 5% of the total peak area at 150°C and to 20% at 170°C.

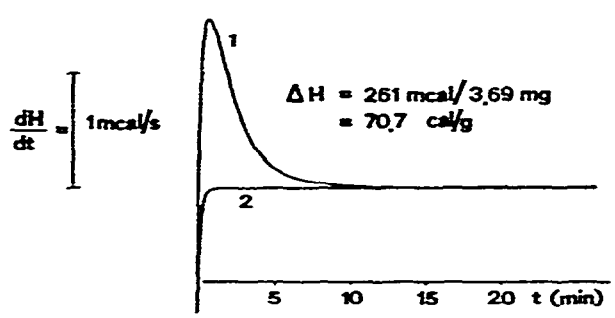

Fig. 2. Curve (1), DTA-curve of 3.69 mg epoxy premix (first run). Curve (2), DTA-curve of the cured sample (second run, the sample now acts as an inert material of the same heat capacity). Furnace temperature 160°C.

Figure 2 shows the complete curing exotherm of the same epoxy premix (curve 1). The reaction rate increases rapidly to a maximum and then decreases

exponentially due to the decreasing amount of reactive groups. The completely cured epoxy was then used as inert sample (second run, curve 2). The area between the two curves represents the heat of reaction and amounts to 261 mcal ($\hat{=}$ 70.7 cal g^{-1}).

The new isothermal method is also applicable to endothermal reactions, such as the well known fusion of indium (Fig. 3). Here, the furnace is kept slightly above melting point, namely at 158°C. Curve 1 is the blank curve with inert material of

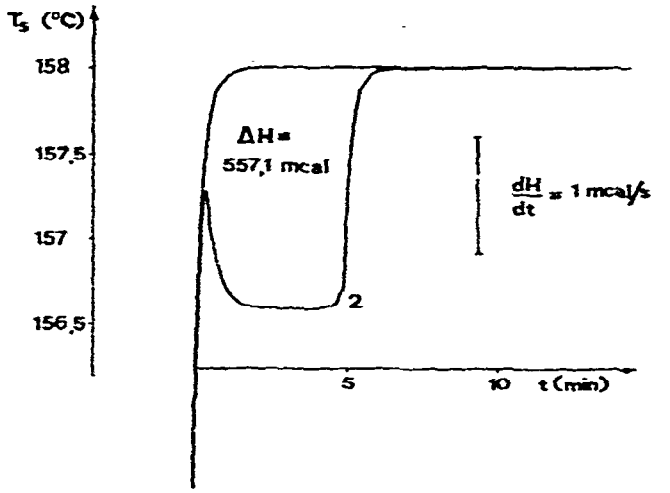

Fig. 3. Curve (1), DTA-curve of inert sample (18 mg Al_2O_3). Curve (2), Fusion curve of 81.5 mg indium. The sample temperature during fusion remains constant at 156.6°C, due to the very high purity of the sample. Furnace temperature 158°C.

the same heat capacity (18 mg Al_2O_3). The small peak at the beginning of the fusion curve 2 is due to the fact that a temperature gradient exists between the ΔT-sensor and the sample during the rapid temperature increase. The constant signal which lasts for minutes is caused by a constant melting rate of the sample, showing a constant temperature of fusion of this extremely pure material. The area between the two curves corresponds to 557.1 mcal or 6.84 cal g^{-1}.

REFERENCE

1 R. A. Fava, *Polymer*, 9 (1968) 137.