

EFFECT OF HEAT CAPACITY CHANGES ON THE DSC BASE LINE AT THE CURING OF EPOXY RESINS

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SUMMARY

For the evaluation of DSC-curves obtained in the anhydric curing of epoxy resins, a base line which is thermochemically interpretable is to a large extent determined from the experimental data. The temperature dependency and the proportionality of conversion of the specific heat capacity of the educts and products are considered essential parameters of influence in determining the base line. The base lines obtained show a flat sigmoidal shape when the DSC-curves are derived from reactions which proceed mostly according to a uniform polyaddition mechanism. In practice, it signifies that the least errors would be made on applying the sigmoidal base lines derived from the analytical softwares used in modern thermoanalytical instruments.

INTRODUCTION

In the differential scanning calorimetric (DSC) investigation of curing epoxy resins under a linear rise of temperature with time, the base line required for the evaluation of thermograms is not accessible by the measuring technique. Thus, it leads to uncertainties and partly to considerable errors in determining the reaction enthalpies and in carrying out the kinetic analysis. The curves do not show the same heat flow before and after the enthalpic event. It changes mostly due to the dependency of heat capacity on the temperature and concentration. It in turn is composed additively of values of all educts and products involved in the reactions. Thus, a simple tracing of two base points of the curve will be arbitrary. The software of modern thermoanalytical instruments offers in general several mathematical functions as an analytical choice in establishing the base line. However, there arises a question of relevancy of such constructions.

Investigations on the nature of base lines has already been reported (refs. 1-3), which have been constructed for physical phenomena such as the change of aggregate state during melting and crystallization. However, the results cannot be transferred since

material changes also occur in addition to the phase transformations while curing epoxy resins. Therefore we have aimed to establish base lines mostly from the experimental data to improve the certainty and precision in evaluating the thermograms. At the same time, in a comparison with automatically constructed base lines only those should be chosen which best represent real conditions.

EXPERIMENTAL

The heat capacity measurements were carried out with a heat flow calorimeter DSC 910/9900 of Du Pont. A sequence of three measurements each is required for the calculation, where always the same aluminium micropans have to be used for one experiment (ref. 4).

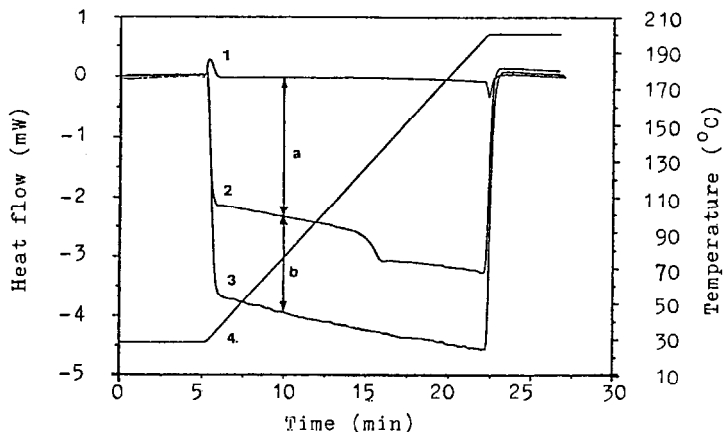


Fig. 1. DSC determination of the specific heat capacity of cured epoxy resin. (1) Base line of the instrument. (2) Measured curve with sample. (3) Measured curve with sapphire. (4) Temperature programme. (a), (b) Heat flow differences.

The curves of measurement are shown in Fig. 1. Curve 1 is recorded with the empty micropan and represents the base line of the instrument. By choosing aluminium micropans of different weights the thermal asymmetry of the cell was balanced in such a manner that the quantity of heat flow in the isothermal part and the dynamic part of the measurement was nearly the same. Curve 2 shows the sequence of measurement with a cured epoxy resin (weight 10 mg) and curve 3 that of the calibration standard with sapphire. The temperature programme for all sequences of measurements is

represented as the fourth curve in Fig. 1. The cell was initially kept isothermally at 30°C for five minutes, then heated at a heating rate of 10 K/min and subsequently maintained for five minutes at the final temperature. The beginning and end of all three curves must be brought to coincidence to keep the error low in calculating the heat capacity. The calculation of the values of heat capacity is made by using the following equation:

$$c_p = c_{ps} \cdot m_s \cdot a / [(a + b) \cdot m_p] \quad (1)$$

where c_p is the specific heat capacity in J/gK, c_{ps} the tabulated specific heat capacity of the sapphire (ref. 5), m_s the weight of the sapphire in mg, m_p the weight of the sample in mg and a , b signify the differences in heat flow in mW. The temperature calibration utilized the onset temperatures of the melting peaks of indium and tin that were attained at a heating rate of 10 K/min.

Bisphenol-A-bisglycidylether (BABGE) was used as epoxy resin. The epoxy value of 5.75 mole/kg corresponds to 98 % of the theoretical content of functional groups. The curing agent was hexahydrophthalic acid anhydride (HHPAA) with an acid content of less than 1 %. The components were mixed at a molar ratio of 1.0 and cured with 1-ethylimidazole (EI) as an accelerating agent at an amount of 1.5 % with respect to BABGE. In the thermal curing an epoxy resin molding material is obtained under exothermic reaction which proceeds mostly by a uniform polyaddition mechanism (ref. 6). The components used are commercial products which were not further purified. Therefore, in expressing heat capacity, the specific heat capacity with respect to weight, J/gK, was chosen as the unit.

RESULTS AND DISCUSSION

The measured values of specific heat capacity as dependent on temperature are listed in Table 1 for liquid state epoxy resin components and for the non-accelerated resin mixture. The upper temperature limit is due to the vapour pressure rise or it results from the incipient sublimation which falsifies the measurement. The c_p values of epoxy resin lie approximately 5 % higher than those of the acid anhydrides. The comparison between the experimentally determined and calculated c_p values of non-accelerated resin mixture shows good agreement as well as the validity of the additivity rule for heat capacity.

TABLE 1
Temperature dependency of heat capacity of epoxy resin components

Temperature (°C)	Specific heat capacity, c_p (J/gK)			
	BABGE	HHPAA	BABGE/HHPAA (1:1) exp.	cal.
60	1.93	1.81	1.88	1.87
80	1.96	1.84	1.93	1.90
100	2.00	1.89	1.97	1.95
120	2.03	1.94	2.01	1.99

The temperature dependency of heat capacity of non-accelerated resin mixture is represented by curve 1 in Fig. 2. The linear regression of the measured values yielded the following coefficients for the straight line equation:

$$c_p = A \cdot T + B \quad (2)$$

where the slope $A = 2.15 \cdot 10^{-3} \text{ J/gK}^2$ and the axis intercept $B = 1.167 \text{ J/gK}$. The linear extrapolation beyond the measured values up to 240°C is traced by the of broken line. Curve 2 shows the temperature behaviour of the heat capacity of the completely cured epoxy resin. The sudden c_p change in the range of glass transition temperature T_g is distinctly noticeable. The behaviour

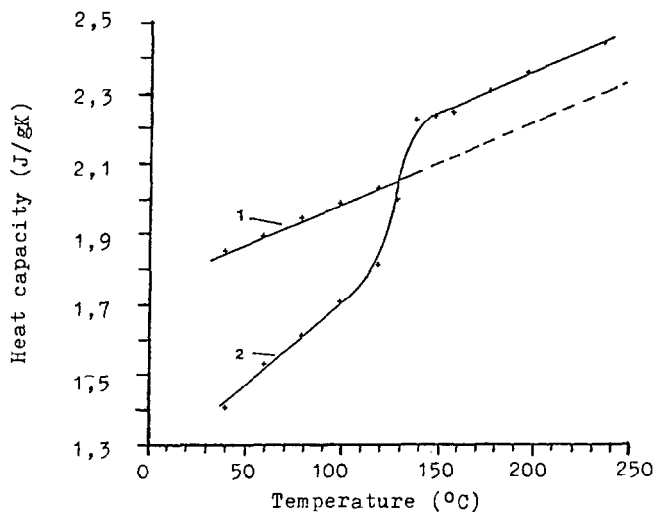


Fig. 2. Temperature dependency of the specific heat capacity c_p of epoxy resins. (1) Non-accelerated resin mixture BABGE/HHPAA, molar ratio 1,0. (2) Epoxy resin moulding material.

is characteristic of network polymers. In the glassy behaviour range, i.e. the vitreous state of the polymer, heat capacity is clearly lower than in the rubber like state. It is remarkable that the extrapolated c_p values of liquid non-accelerated resin mixture lie lower than those of the cured polymer above T_g . The coefficients obtained for Eq.(2) are: $A = 4.75 \cdot 10^{-3} \text{ J/gK}^2$ and $B = -0.067 \text{ J/gK}$ (below T_g) and $A = 2.40 \cdot 10^{-3} \text{ J/gK}^2$ and $B = 1.189 \text{ J/gK}$ (above T_g). From the difference in heat capacity values between the non-accelerated resin mixture and the cured epoxy resin, the heat flow changes result at the beginning and end of the DSC-curves for measuring epoxy resin curing. It should now be possible to calculate the DSC base line from the temperature dependent values of conversion.

However, this must be qualified by stating that the system begins to get transformed to a vitreous state at low conversions and a glass transition temperature can be assigned to it (ref. 7). Depending on the progress of reaction, the glass transition temperature rises to nearly 130°C at a complete curing. Partially cured epoxy resins react further under DSC conditions only when above the actual glass transition temperature belonging to the respective state of reaction. It is because only at this state does the system possess the necessary mobility for a further reaction. But the curing reactions of the selected epoxy resins occur so rapidly that differentiation between the heat capacity

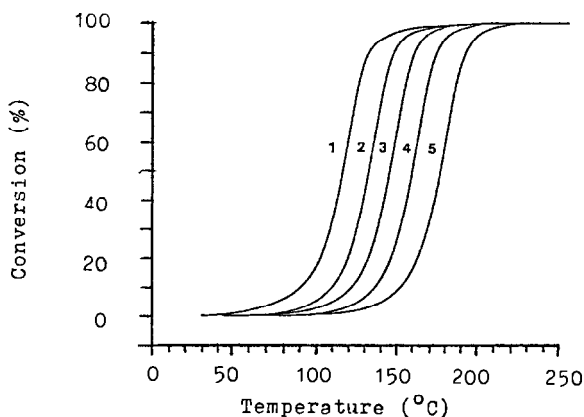


Fig. 3. Degree of conversion as dependent on the heating rate of the epoxy resin reaction (BABGE/HHPAA molar ratio 1,0, 1,5% EI). (1) 2 K/min. (2) 5 K/min. (3) 10 K/min. (4) 20 K/min. (5) 40 K/min.

and the enthalpic effect is not possible. The true c_p values of partially cured epoxy resins are not accessible in the rubber plateau. Therefore, the c_p values of the glassy behaviour state of cured polymers were taken as the basis for calculation in establishing the base line below the glass transition temperature. Hence, the base line in this temperature range displays only the largest possible effect resulting from the heat capacity change. This qualification no longer applies above the glass transition temperature, and it is more certain that an interpretable DSC base line will be achieved.

In determining the amount of conversion at the curing of epoxy resins, the integral curves in Fig. 3 show the effect of heating rates between 2 and 40 K/min. The degree of conversion is the same in all cases and yields roughly to a reaction enthalpy of 400 J/g. The glass transition temperature therefore in all cases lies between 130°C and 133°C. This was determined in a second sequence of measurement at a heating rate of 10 K/min. From the curves in Fig. 3 it can be inferred that at a heating rate of 2 K/min, the reactions had already occurred to 90 % before reaching the temperature of 130°C, whereas the reactions just begin at this temperature at a very high heating rate of 40 K/min.

A further factor of influence on the shape of the DSC base line is the change of heating rate at exothermic reactions in heat flux calorimeter. It can be well recognized from the derivative

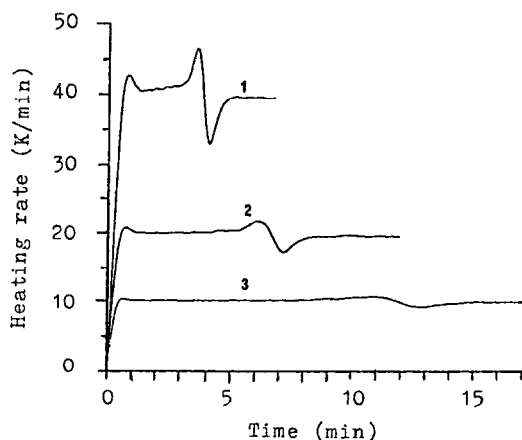


Fig. 4. Change of heating rate at exothermic reactions in heat flux calorimeter. (1) 40 K/min. (2) 20 K/min. (3) 10 K/min.

temperature curves at the curing of epoxy resins as shown in Fig. 4. At a heating rate of 40 K/min a reaction enthalpy of 400 J/g is set free within 1.5 min. In the exothermic region the heating rate changes by ± 7 K/min and it leads to a distinct change in heat flow in the cell of measurement.

Since heat production occurs over a longer period of time at lower heating rates, the deviation from the preset heating rate becomes rapidly smaller. It amounts to only ± 0.7 K/min at a heating rate of 10 K/min. The corresponding heat flow changes were determined for inert polymers by simulated temperature programmes according to Fig. 4.

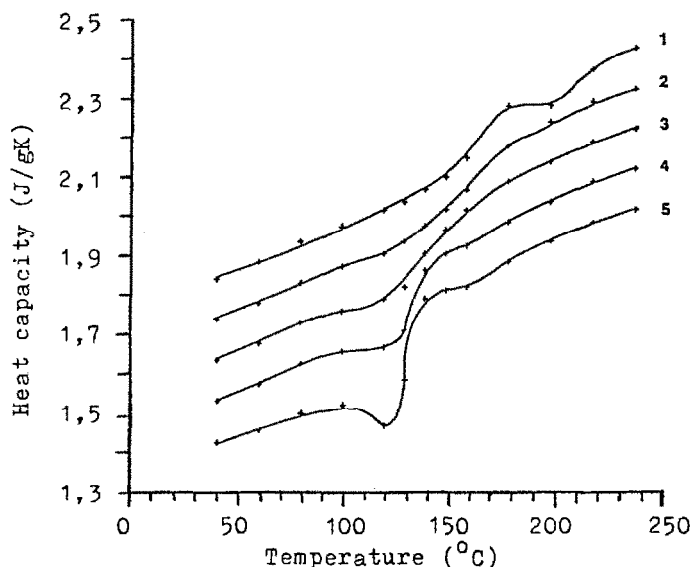


Fig. 5. Calculated base lines for sequences of DSC measurement at linear rise of temperature with time. (1) 40 K/min. (2) 20 K/min. (3) 10 K/min. (4) 5 K/min. (5) 2 K/min.

Fig. 5 represents the calculated DSC base lines at different heating rates, where the curves were plotted in terms of heat capacity vs temperature. The ordinate scale is the same for all curves. However, the ordinate values are pertinent only to curve 1. All other curves were correspondingly displaced by 0.1 J/gK for greater clarity. Curve 1 is the base line for the DSC curve of curing epoxy resin at 40 K/min. It is thoroughly interpretable and shows a flat sigmoidal shape. As a result of the thermal imbalance in the cell due to a heavy change in the heating rate, a

superimposed strongly attenuated oscillation is obtained in the temperature range between 150°C and 200°C. This effect is hardly felt in curve 2 which belongs to the DSC curve for a curing at 20 K/min. In most unfavourable cases assumed, the base lines belonging to the DSC curves with decreasing heating rates show increasing deviations from the sigmoidal shape. However, under true conditions, they will probably get equalized to a large extent.

CONCLUSION

Viewed overall, base lines are calculable for the DSC curing reactions of epoxy resins, which take place mostly under a uniform polyaddition mechanism. This is particularly true if the reactions take place largely in the rubber like temperature range of the cured polymer. The shape of the curve, however, is flatter than that of the sigmoidal one constructed as the base line by the software packet of the thermoanalytical instruments. The slight inconstancies of the base lines under the measured curves affect the results only insignificantly since they emerge in the range of higher heat flows. In heat flow calorimeters, greater deviations have to be additionally reckoned with if large quantities of heat are set free in a short time. In contrast, the DSC base line for rapid curing reactions or reactions which mostly occur below T_g can be estimated only roughly. In daily practice, it is recommendable for calculations to use the sigmoidal base line between two base points since it is most proximate to a thermoanalytically interpretable base line. Thus, errors are minimized not only in the determination of enthalpy but also in the kinetic analysis.

REFERENCES

- 1 H.M. Heuvel and K.C.J.B Lind, *Analyt. Chem.*, 42 (1970) 1044-1048.
- 2 C.M. Guttman and J.H. Flynn, *Analyt. Chem.*, 45 (1973) 408-410.
- 3 U. Bandara, *J. Thermal Anal.*, 31 (1986) 1063-1071.
- 4 M.J. O'Neill, *Analyt. Chem.*, 10 (1966) 1331-1336.
- 5 D.C. Ginnings and G.T. Furukawa, *J. Am. Chem. Soc.*, 75 (1953) 522-527.
- 6 K. Kretzschmar and K.W. Hoffmann, *Thermochimica Acta*, 94 (1985) 105-112.
- 7 G.C. Stevens and M.J. Richardson, *Polymer*, 24 (1983) 851-858.