*Journal of Thermal Analysis, Vol. 49 (1997) 443-447*

# MODULATED TEMPERATURE DIFFERENTIAL SCANNING CALORIMETRY

## Considerations for a quantitative study of thermosetting systems

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## Abstract

The influence of temperature modulation and signal treatment (deconvolution procedure) of modulated temperature differential scanning calorimetry is discussed with respect to the investigation of cure kinetics of thermosetting systems. The use of a 'dynamic' heat capacity calibration is not important for this purpose due to normalization of the heat capacity signal in all cure experiments. The heat flow phase during isothermal and non-isothermal cure is always small, giving rise to negligible corrections on the heat capacity and reversing heat flow signals in-phase with the modulated heating rate. The evolution of the heat flow phase contains information on relaxation phenomena in the course of the chemical reactions.

**Keywords:** modulated temperature DSC, thermoset, heat capacity, phase angle

## Introduction

Modulated temperature differential scanning calorimetry (MTDSC) allows for simultaneous measurement of both heat capacity and heat flow [1–5]. Therefore, this extension of conventional DSC offers an excellent opportunity for studying the chemical kinetics and (de)vitrification behaviour of thermosetting systems [6, 7].

In this paper, the influence of the signal treatment (deconvolution procedure) will be discussed with respect to investigations of thermosetting systems. The importance of (i) a 'dynamic' heat capacity calibration (over the entire temperature range) instead of a 'single point' calibration (at one temperature), and (ii) the evolution of the heat flow phase during cure, will be discussed in terms of the quantitative interpretation of cure kinetics using heat capacity and heat flow signals.

## Experimental

A bifunctional epoxy (LY 556) cured with an anhydride hardener (HY 917), using an accelerator (DY 070), was studied. All components are from Ciba-Geigy. This epoxy system is the same as in [6].

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*0368–4466/97/ $ 5.00*

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Modulated isothermal and non-isothermal experiments were performed on a TA Instruments 2920 DSC with MDSC$^{TM}$ option. The experiments of [8] were used as isothermal and non-isothermal reference experiments.

All details concerning the raw materials, the instrumentation, the experimental procedure and the calculations are given in [6, 7].

## Results and discussion

### *Dynamic heat capacity calibration*

In all previous cure experiments [6, 7], and in the reference results of [8], the heat capacity signal was calibrated at a single temperature. The experimental error on the heat capacity can further be reduced by a dynamic calibration over the entire temperature range. The effect of this dynamic calibration can be checked by measuring the heat capacity of a 23 mg sapphire standard (TA Instruments) over the temperature range of interest (e.g. from –150°C to 300 at 2.5°C min$^{-1}$ with a 0.5°C per 60 s modulation). A gradual evolution of the heat capacity calibration constant, $K_{C_p}$, with a total variation of 5% between –50°C and 300°C is observed.

Below –50°C the variation on $K_{C_p}$ increases, and the dynamic calibration must be applied for accurate heat capacity studies in that low-temperature region. For the application of MTDSC on the thermosetting systems studied, this correction is not so important: when calculating the mobility factor, $DF^*$, the heat capacity is normalized to reference heat capacities determined at the same temperature [6–8]. Thus, changes in $K_{C_p}$ have almost no effect on the final results and their interpretation.

Besides, the non-reversing heat flow obtained in isothermal MTDSC experiments agrees very well with the heat flow evolution obtained in a conventional DSC experiment, performed under the same conditions with exception of the modulation. Neither changing the modulation amplitude nor the period has an effect on the reaction exotherm seen in the non-reversing heat flow. These results indicate that the temperature modulation does not affect (or to a negligible extent) the reaction kinetics.

In non-isothermal conditions too, the chemical rate of reaction can be obtained quantitatively from the non-reversing heat flow. Note that 'heating only' conditions are not necessary for a correct and quantitative interpretation of the results. However, to calculate the non-reversing heat flow in non-isothermal experiments, attention has to be paid to the values of the heat capacity and heating rate used, in order to correctly subtract the heat capacity contribution (reversing heat flow) from the total heat flow. So, for more accurate results, one should use (i) the dynamic heat capacity calibration in order to correct for the temperature dependency of $K_{C_p}$, and (ii) the measured underlying heating rate instead of the programmed heating rate, as currently implemented in the commercial software (TA Instruments). The deviation of the measured heating rate from the programmed heating rate (amounting up to 10% in some conditions) can play an important role. However, in the cure experiments shown in [6–8], the effect of both the dynamic heat capacity calibration and the heating rate correction is always small because the contribution of the change in reversing heat flow is small compared to the non-reversing heat flow. The corrections on the non-reversing heat flow are generally much smaller than the experimental error which is due to small differences in the mixing ratios (a new epoxy-hardener mixture is prepared for each experiment) and the influence of small (irreproducible) amounts of moisture on the reaction kinetics. Nevertheless, when modelling the kinetics, and comparing conventional and modulated DSC experiments, the measured temperature (and hence the measured heating rate) should be used.

### *Heat flow phase*

In many thermal analysis techniques that use an oscillating excitation of the material, for example dynamic mechanical analysis, torsional braid analysis, dielectric thermal analysis, and dynamic rheometry, a phase angle is defined between the 'modulated' input and the resulting output signal. A similar approach can be used for MTDSC [1, 9, 10]: the heat flow phase is defined as the phase angle of the modulated heat flow output (with the convention of a negative heat flow for exothermic events) with respect to the modulated heating rate input. A contribution of the instrument to the heat flow phase has to be taken into account. The correction for the instrument (MDSC TA Instruments) can be performed by shifting the heat flow phase curve to the zero level for reference points where no material transition occurs [1, 3, 10, 11].

The influence of the heat flow phase on the quantitative nature of MTDSC cure experiments was investigated for the epoxy-anhydride cured at 80°C. The heat flow phase measured isothermally at 80°C for the fully cured resin after residual non-isothermal curing, was used as a reference point. The corrected heat flow phase, $\varphi$, initially amounts to –2.0° (Fig. 1). As the reaction proceeds, $\varphi$ slowly evolves toward zero. A (downward) local extreme is observed at 247 min; this relaxation phenomenon corresponds to the vitrification transition. At the end of the isothermal experiment, $\varphi$ equals –0.6°.

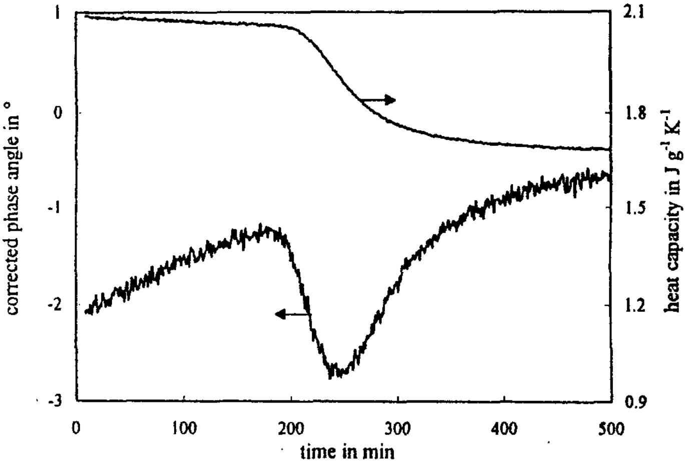

**Fig. 1** Corrected heat flow phase and heat capacity for the isothermal cure of the epoxy-anhydride system at 80°C

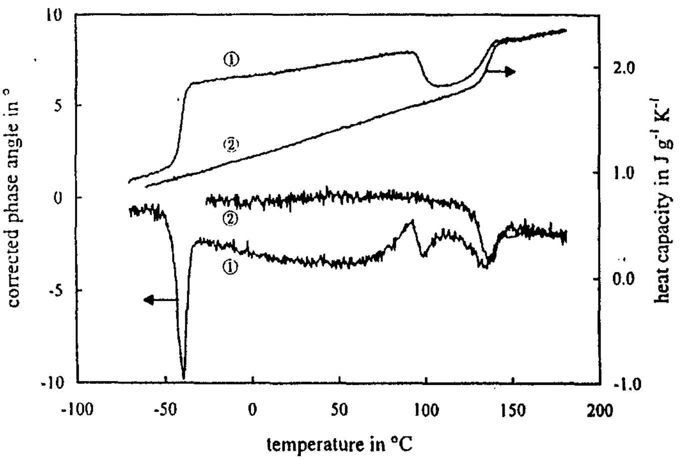

**Fig 2** Corrected heat flow phase and heat capacity for the non-isothermal cure of the epoxy-anhydride system (①) and for the fully cured material (②) at 0.15°C min$^{-1}$

The evolution of the corrected heat flow phase for the first and second heating of the epoxy-anhydride system at 0.15°C min$^{-1}$ is depicted in Fig. 2. The points at –25 and 70°C for the fully cured resin (second heating) were chosen as reference points for the instrument phase correction, and thus were shifted to zero. In the first heating, three (downward) local extremes can be observed at –40, 99 and 133°C. These relaxation phenomena coincide with, respectively, initial devitrification, vitrification, and devitrification, as observed from the heat capacity evolution. The corrected heat flow phase $\varphi$ slowly evolves toward zero as the reaction proceeds. In the second heating $\varphi$ stays close to zero with only one relaxation at 137°C corresponding to the glass transition of the fully cured system.

Using the corrected phase angle and the modulus of the complex heat capacity, $|C|$, which is the ratio of the amplitudes of heat flow output over heating rate input, the components in-phase ($C' = |C|\cdot\cos\varphi$) and out-of-phase ($C'' = -|C|\cdot\sin\varphi$) with the modulated heating rate can be calculated (for more detailed approaches see [1, 9–11]). The in-phase component $C'$ corresponds to the thermodynamic heat capacity [9, 10]. The out-of-phase component $C''$ is linked to kinetic events [10].

For the epoxy systems and conditions studied, the heat flow phase always remains small over the course of the reaction: the maximum difference with respect to the reference state is –5° (–10° at $T_{g0}$). $C'$ and $|C|$ thus coincide within 0.4%, and $C''$ is always close to zero. This implies that the reversing and non-reversing heat flows calculated using $C'$ (approach called 'complete deconvolution') or $|C|$ (approach called 'simple deconvolution') are virtually identical. Hence, the use of the phase angle is not necessary for the quantitative interpretation of all cure results of [6–8].

It should be noted that, when the 'complete deconvolution' is used, the modulated DSC approach (TA Instruments MDSC), based on Fourier deconvolution, is completely equivalent to the dynamic DSC approach (Perkin Elmer DDSC), based on linear response theory [9], giving rise to analogous in-phase and out-of-phase components. Results for non-isothermal epoxy curing confirm the equivalency of both techniques. However, in order to be able to obtain quantitative results with the DDSC device for isothermal curing conditions, the current software implementation of DDSC, based on an *internal* heat capacity and phase angle calibration, has to be adapted.

## Conclusions

In general, the use of a 'dynamic' heat capacity calibration is important below –50°C. For studies at temperatures between –50 and 300°C, only small corrections (less than 5%) on the 'single point' calibration constant $K_{C_p}$ are needed. With respect to the current investigations of thermosetting systems, even the latter are not important since all heat capacity values are normalized against reference values.

The corrected heat flow phase $\varphi$ during cure is always small, so that its influence on the quantitative nature of the results is negligible. However, the evolution of $\varphi$ seems to contain additional information on thermoset cure. $\varphi$ is increasing while chemical reactions are proceeding. Local extremes in $\varphi$ are observed caused by relaxation phenomena during cure. This information will also enable interpretations on the heat capacity evolution due to chemical reactions *before* vitrification. At this instant, more results are needed for a thorough discussion of heat flow phase information during the cure of thermosetting systems.

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