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TEMPERATURE GRADIENT IN DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

A temperature gradient is required for any type of heat flow process. In a dynamic calorimeter, temperature gradients exist in the entire calorimetric system during the measurement of temperature differences or heat flow. Most organic materials are of relatively low thermal conductivity in comparison to metallic and inorganic materials. Therefore large temperature gradients are expected to exist in organic materials during the measurement. The magnitude of the temperature gradient can be estimated through a simple modeling procedure. The results of experimentally determined temperature gradients during the cure of an epoxy resin in a differential scanning calorimeter are presented to confirm the expected magnitude of temperature non-uniformity.

INTRODUCTION

All heat transport processes depend on temperature differences. As long as there is a heat flow, there exists a temperature gradient. This occurs regardless of the type of dynamic calorimetry being used, whether it is a differential thermal analyzer (DTA), quantitative DTA, heat flux type differential scanning-calorimeter (DSC) or power-compensated type DSC. The thermal conductivities of organic materials are about three orders of magnitude less than those of most metals. Therefore, in studying organic materials by dynamic calorimetry, the majority of the temperature non-uniformity lies within the sample of concern.

Although the influence of the sample thermal conductivity on the shape of DSC curves is well known, in most data treatments the temperature of the sample is generally considered to be uniform and its average deviation from the temperature of the thermometer is considered to be correctable through calibration procedures. A complete analysis of the temperature profile throughout the calorimeter requires the knowledge of all heat flow paths and their interactions, and is therefore highly complex and difficult to solve. Armand and Vergnaud have published a series of papers, e.g. refs. 1,2,

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modeling the temperature profile of a 150 mg cylindrical sample in a heat flux type DSC. The center temperature lags behind that of the face during a programmed heating, but can exceed that of the face by 50 K or more during certain conditions of curing of unsaturated polyester or epoxy resins.

Direct measurement of the temperature gradient in a DSC is difficult, because not only are the dimensions small (typically less than 1 cm), but any invasive insertion of a temperature measuring device would completely change the characteristics of the heat flow paths of the calorimeter. We have, however, demonstrated experimentally the magnitude of the temperature non-uniformity of a disc-shaped sample in a power-compensated DSC, by placing a small piece of a thin (5 μm) indium sheet on the top of a gelled but not fully cured epoxy sample during cure. For the particular sample size and experimental set-up investigated, the temperature gradient as a function of heat flow was found to be approximately 0.1 K mm^{-1} mW^{-1} and temperature differences greater than 10 K were observed. This magnitude of the temperature non-uniformity and the temperature excursions in dynamic calorimetry are large enough, especially at high heating rates and with large exothermic heats of reaction, that care must be exercised in the interpretation of the DSC curves for the detailed analysis of kinetic parameters of the reaction being studied.

EXPERIMENTAL

A commercial power-compensated calorimeter, Perkin-Elmer DSC-7 *, was used in this experiment. Other dynamic calorimeters, regardless of the operational principle, should show similar behavior. The major part of the calorimeter is the sample container holder, which is made of platinum (Pt) a somewhat low thermal conductivity metal. A heater and a resistance thermometer are embedded inside the Pt holder with electrical insulation. The thermal lag between the thermometer and the Pt surface, together with the time constant of the electronic control circuit, forms the overall instrument response time. Slight temperature non-uniformity of the holder was found as a result of a radial heat flow [3]. A Pt cover sits loosely on a ledge inside the holder. The cover temperature lags further from the temperature of the holder.

Using similar techniques as in ref. 3, we have found that around the melting point (T_m) of In (156.6°C), even at a low heating rate of 0.1 K

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* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply necessarily the best available for the purpose.

$\min^{-1}$, the temperature at the center of the holder is approximately 0.5 K higher than that near the edge and that the cover temperature is about 6 K lower than the holder, with the center of the cover lagging a further 0.5 K. The indication of the large differences between the cover and the holder temperatures may be somewhat exaggerated, as the small piece of In on the top of the cover may exchange heat with the surroundings faster than the cover itself. Thus this magnitude of temperature non-uniformity may largely be the result of an unrecorded steady background heat flow required to counterbalance the heat loss to the surroundings.

In the following studies, a liquid type of aluminum (Al) sample container with a bottom diameter of 4 mm was used. The nominal weight of the sample was around 10 mg, or the thickness of the sample was approximately 1 mm. An Al cover provided a relatively vapor-tight seal, which did not touch the top of the sample. The high thermal conductivity of Al provided a relatively uniform temperature surface to conduct heat in and out of the sample through contact, despite any temperature difference that existed between the sample container and the Pt holder. An empty sample container was used as the reference.

The resin system used as a tool for this experiment consisted of diglycidyl ether of bisphenol-A (DGEBA) with 3 parts per hundred resin (phr) of 2-ethyl-4-methyl imidazole (EMI). The ultimate glass transition temperature for this resin is around 170°C. The resin sample in the sample container was left at room temperature for a few days to gel. A small piece (< 1 mg) of thin sheet (5 μm) of pure In (99.99%) was placed on the top of the gelled epoxy sample, so that it would remain on the top even going through a high temperature cure cycle. The remainder (approximately 60%) of the heat of reaction provided enough heat, which produced a temperature rise of the sample above the programmed thermometric temperature. This was observed as if the In melted at an apparently lower programmed temperature reading during a scan cure of the resin. A subsequent observation on the cured sample with the same heating rate yielded normal melting point readings of In similar to the calibration runs.

RESULTS

Scan

In the scanning mode, aside from the control instability at the beginning of the scan, there is a smooth steady state background of heat flow, upon which heat releases from reaction are superimposed. Therefore the comparison of when the In melts, during and after the cure of the resin, yields an indication of the temperature non-uniformity of the resin during a cure reaction over that of a normal run. By choosing appropriate scan rates, the

TABLE 1

Excess temperature during cure reaction

Heating rate ($K\ min^{-1}$)	$T_{cured} - T_{curing}$ (K)	dQ/dt (mW)
20	0.3	2
40	1.6	30
40	1.5	15
80	5.6	50
200	> 9.2	140

maximum rate of the exothermic curing reaction for the DGEBA/EMI resin system can occur near the T_m of In.

Table 1 lists the results of the observation of the programmed temperature readings for the onset of the melting of a small piece of thin In sheet on the top of the resin. The difference of the lowered apparent onset temperature during cure (T_{curing}) from that after cured (T_{cured}) is listed against the scan rate. The magnitude of the exothermic heat release (dQ/dt) where the onset during cure occurred, is also listed. It appears the temperature gradient produced by the sample self-heating is about 0.1 K mW^{-1} for the nominal 1 mm thick epoxy resin, as shown by filled circles in Fig. 1. The apparent lowering of the melting point during the cure is a measure of the temperature rise of the top of the sample during the cure, in comparison to a normal temperature gradient that existed in the cured sample during a similar scan.

The onset of the melting during cure at a scan rate of 200 K min^{-1} occurred just around the peak of the reaction exotherm. It was believed the

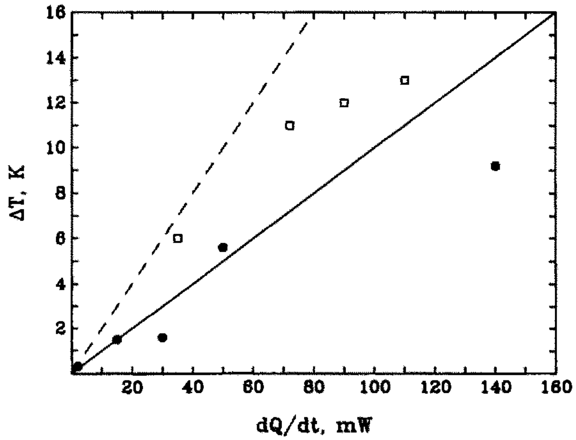

Fig. 1. Temperature gradient and rate of heat flow: □, at beginning of isothermal; ●, scan.

temperature gradient was greater than 9.2 K. Scan rates greater than 200 K min^{-1} were not used for this resin system.

Isothermal

It is difficult to observe the temperature gradient in the sample during an isothermal cure. If the isothermal curing temperature (T_{iso}) was assigned as the initial temperature, the results having In on the top of gelled epoxy samples were almost identical to those of cured samples, and were all similar to the results with a heating rate of 500 K min^{-1} to the isothermal temperature. It was found that the instrument, despite software parameter changes, used its maximum rate of 500 K min^{-1}, to reach the initial temperature to start a programmed run. With a loaded sample container, the rate of heat flow for heating the holder and its contents could easily reach 100 mW or higher. This magnitude of heat flow due to instrumental heating produced an overwhelming effect in addition to the exothermic heat output from the curing reaction. There was a small oscillation in the temperature control within 5 s after reaching the isothermal temperature. Any melting of In was difficult to resolve from the oscillation. At isothermal temperatures between 145 and 155°C, a small exothermic peak was observed superimposed on the major exothermic peak of reaction. The magnitude of the small peak corresponded to the heat of crystallization of the amount of In used. The freezing generally occurred within 1 min after the isothermal temperature was reached. Because a certain amount of undercooling below the T_{m} of In was needed for nucleation and growth, longer times were needed for the crystallization process when the isothermal temperature was closer to the T_{m} of In. The observation became quite difficult at above 155°C. At much lower isothermal temperatures, the freezing again became difficult to observe. If the isothermal temperature was set too low, the overshoot might not be high enough to melt the In. Even if the In sample was melted, a large undercooling below the T_{m}, and the freezing, occurred immediately after the isothermal temperature was in control.

By assigning a heating rate from an initial temperature to a second temperature as T_{iso}, it was possible to find out the minimum heating rate or the rate of heat flow required to produce a required overshoot. The freezing of In on top of a cured resin was observed at T_{iso} values of 143, 144, 145, and 150°C, with a corresponding minimum heating rate of 500, 400, 300, and 150 K min^{-1}, respectively. The ending heat flow rate during the scan to T_{iso} and the corresponding minimum overshoot of T_{iso} (the difference between the T_{m} of In of 156.6°C and the T_{iso}) are shown as squares in Fig. 1. The influence of the background heat flow due to heat losses to the surroundings was neglected. The additional influence from the heat of reaction combined with the influence of high heating rates to T_{iso} was not tested. If the heating rates were too slow, the resin would have cured and released most of its heat before reaching T_{iso}.

This overshoot was mainly an instrumental factor (including its software control algorithm) and was a function of the rate of heat flow, which depended on the heating rate to the isothermal temperature, and also somewhat on the adjustment of the instrument. Without knowing the complete control circuitry and the algorithm of the control software, the exact relationship between the magnitude of the overshoot in temperature or in energy with the heating rate or the rate of heat flow cannot be determined.

DISCUSSION

In the following analysis, only the heat flow through conduction from the contacts between the sample container and the holder is considered. Gaseous heat transfer and radiation heat transfer between the container and the holder are neglected. The temperature of the Al container is considered to be uniform, in comparison to the much lower conductive sample.

The temperature gradient in an infinite parallel sheet with the heat flow normal to the surfaces may be estimated as

$$\mathrm{d}T/\mathrm{d}l = (\mathrm{d}Q/\mathrm{d}t)/(A\lambda)$$

where T is the temperature, l the distance in thickness, $\mathrm{d}Q/\mathrm{d}t$ the rate of heat flow, A the area and λ the thermal conductivity. The thermal conductivity of unfilled epoxy resins were quoted as 3–6 mW cm^{-1} K^{-1}, by commercial sources, and a value around 4 mW cm^{-1} K^{-1} was used in most of Armand and Vergnaud's papers [1,2]. Thus by assuming a disc, where $l = 0.1$ cm, $A = 0.04\pi$ cm^2 ($D = 0.4$ cm) and $\lambda = 4$ mW cm^{-1} K^{-1}, the temperature difference (ΔT) in kelvin between the two surfaces will be $0.2(\mathrm{d}Q/\mathrm{d}t)$, where the rate of heat flow is in milliwatts. The result of this simple estimation is shown as the dashed line in Fig. 1.

However, there is an additional heat flow, from the edge of the disc-shaped sample in contact with the high conductivity container. This flow is assumed to be far away from the center and does not affect materially the temperature profile in the center of the disc. The additional edge area of 0.04π cm^2 doubled the total area for the heat flow. Thus $\mathrm{d}Q/\mathrm{d}t$ observed will also be doubled for the same ΔT, or ΔT in K is approximately $0.1(\mathrm{d}Q/\mathrm{d}t)$ where $\mathrm{d}Q/\mathrm{d}t$ is in milliwatts. The latter result is in fact very close to what was observed during the scan cure. Considering the simplicity in the estimation, the agreement between the experimental observation and the estimation is good, especially as no detailed adjustments are applied to the variation in the sample thickness and its geometry, such as the meniscus formation on the wall.

For a large sample container of 0.6 cm diameter, 2 mm height and with a top cover in contact with the sample, the area of contact is increased to $2 \times 0.09\pi$ cm^2 for the disc faces and 0.12π cm^2 for the edge. Assuming the top cover has a good thermal contact with the rest of the sample container, then the largest thermal gradient which exists between the middle of the sample to the surfaces will be reduced by a factor of almost 4 from the above observations and estimation.

The temperature of a sample cannot be assumed to be uniform, especially when high rates of heat flow occur with large heats of reaction and at high rates of scan. The temperature gradient becomes greater for a thicker sample or in a loosely packed powder where thermal contacts are poor. As the magnitude of the temperature non-uniformity in a DSC experiment can become quite large, caution must be exercised when the thermogram is used to generate kinetic parameters of a reaction. The kinetic parameters are in turn applied in modeling to generate profiles of temperature gradients during specific manufacturing processes, e.g. ref. 4.

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