



Full Length Article

The insulating effect of the low thermal conductivity of epoxy on the resolution of the heat of reaction during polymerization by differential scanning calorimetry



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ABSTRACT

It is demonstrated that the heat of epoxy cure as measured by isothermal differential scanning calorimetry (DSC), as commonly calibrated by the heat of fusion of an indium standard, is consistently low as compared to methods “directly” calibrated by Joule heating [i.e., isothermal microcalorimetry (IMC)]. The discrepancy between measurement techniques is shown to be on the order of 15% for low thermal conductivity epoxy thermosets. In addition to direct comparisons between DSC and IMC measurements during epoxy polymerization, indium samples embedded in cured epoxy were studied to determine if the DSC was able to accurately capture the total heat of fusion through the polymeric insulating layer. It is found that the indium heat of fusion measured by DSC is lower when the indium is embedded in epoxy than when the indium is in direct contact with a steel sample pan. The fraction of the indium heat of fusion detected through the epoxy insulation by the DSC cell is comparable to the fraction of the heat of reaction detected by DSC during epoxy cure, as determined from the DSC-IMC comparison. It is concluded that the heat flow detected by DSC during epoxy cure must be scaled by a factor of 1.18 in order to accurately portray the full heat of reaction under the conditions used in this work. It is argued that the difference found between DSC and IMC is in reasonable agreement with qualitative heat transfer calculations and with previous thermal conductivity measurement of polymers via DSC. The specific scaling factor is anticipated to depend on the material studied, on the pan type, on the sample geometry, on the purge gas details, and on the instrumentation. Instruments used in this work include a Q2000 DSC and a TAM Air IMC (both TA instruments). The epoxy was diglycidyl ether of bisphenol A (DGEBA) cured with diethanolamine (DEA).

1. Introduction

Differential Scanning Calorimetry (DSC) is commonly used in isothermal mode during the study of the curing kinetics of epoxies [1–5]. The bulk of the heat generated during cure results from the epoxide ring opening and, consequently, the instantaneous heat flow measured is proportional to the rate of epoxide consumption, or the reaction rate. Typically, the DSC thermogram is integrated to find the cumulative heat of reaction as a function of time, $H(t)$. The extent of reaction, $\alpha(t)$, is found by dividing $H(t)$ by the total heat of reaction, H_0 , defined as the long-time limit of $H(t)$ when the reaction is performed under conditions that allow it to reach completion.

In order for the calorimetric analysis to be a viable approach, it is necessary that the reaction be rapid enough that the heat flow signal

measured by the DSC is resolvable above the background noise. When the signal-to-noise ratio is insufficient, it can be improved by either reducing the baseline noise or by increasing the heat flow signal. In many cases, the reaction kinetics are sufficiently simple that the cure temperature of the epoxy can be increased until the signal-to-noise ratio is optimized. However, such an adjustment is not always possible. For instance, the reaction in question may be one that progresses slowly under standard processing conditions but whose mechanism(s) change with temperature. Consequently, increasing temperature not only changes the rate of reaction but also changes the nature of the reaction itself. In this case, if temperature is increased, reactions which previously played a minor role may come to dominate the heat signal. In other cases, the reaction time may be so short at the elevated temperature which provides sufficient signal-to-noise ratio that the initial

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portion of the reaction is missed during the start-up of the measurement.

Alternatively, the sample mass may be increased to raise the heat flow signal (“raw” heat flow versus the heat flow per sample mass) and potentially boost the signal-to-noise ratio of the DSC. However, pan volume limits associated with the size of the DSC detection cell and the efficiency of transferring the heat produced within the pan to the detection cell are eventually reached. When these types of modifications to the DSC experimental protocol are unsuccessful in obtaining a sufficient signal-to-noise ratio for the heat flow, alternate characterization techniques, such as isothermal micro-calorimetry (IMC), are useful supplemental methods.

An epoxy reaction that challenges the resolution of DSC is the cure of diglycidyl ether of bisphenol A (DGEBA) with diethanolamine (DEA). This reaction has recently been investigated in considerable detail [6]. The primary reaction at low temperature ($< 90\text{ }^{\circ}\text{C}$) and, in particular, under standard cure conditions (isothermal at $70\text{ }^{\circ}\text{C}$) is an anionic chain growth polymerization. This polymerization process has a slow reaction rate, with typical cure times of 24 h. or more. An increase in temperature to above $90\text{ }^{\circ}\text{C}$ disrupts the anionic growth mechanism and the reaction rate slows down. Thus, the reaction occurs most rapidly at about $70\text{ }^{\circ}\text{C}$. Below $70\text{ }^{\circ}\text{C}$ the reaction slows in an Arrhenius manner while above $70\text{ }^{\circ}\text{C}$ the polymerization reaction mechanism-change causes the slowdown.

For the DGEBA/DEA reaction, isothermal DSC heat flow signals were no longer distinguishable from the baseline noise after approximately 2 days at $70\text{ }^{\circ}\text{C}$. This was partly associated with thermal fluctuations in the external environment (the laboratory that the DSC resided in) during multiday experiments that perturbed the baseline heat flow signal. However, even when the temperature of the external environment and apparatus was controlled to within one degree Celsius or tighter, the uncertainty in the determination of the baseline in the (above mentioned) integration scheme for the DSC heat flow signal resulted in total heat of reaction calculations that varied as much as 10%. These difficulties increase at lower temperatures as the reaction slows even further but the baseline noise remains constant.

In an effort to achieve a better signal-to-noise ratio in the long-time limit of the DGEBA/DEA reaction, an isothermal microcalorimetric (IMC) instrument was employed. This technique provided an exceptionally precise baseline and permitted an accurate integration of the heat of reaction for time periods over a month. In what follows, it will be shown that comparisons of the IMC and DSC results permit the resolution of whether discrepancies between the measurements are solely associated with the absolute heat flow value or whether the time dependence of the heat flow signal differs between the instruments. Moreover, differences between absolute heat flow measurements from the two instruments can be compared to the ability to quantitatively determine the thermal conductivity of polymers by DSC. Specifically, it has been observed [7,8] that “*For very low thermal conductivity samples, such as polystyrene [$\kappa = 0.14\text{ W/(Km)}$], the thermal conductivity of the nitrogen purge gas surrounding the test specimen [$\kappa = 0.026\text{ W/(Km)}$] is an appreciable fraction (about one quarter) of the specimen conductivity. Hence, under flowing purge gas conditions, the assumption of no heat flow through the sides of the sample is not strictly true.*” Since the thermal conductivity [9] of our epoxy [$\kappa = 0.216\text{ W/(Km)}$] is similar to that of polystyrene, it is reasonable to anticipate similar discrepancies. This knowledge prompted us to design a simple experiment to examine the insulation effect of low thermal conductivity polymer on the heat of fusion for indium that is measured by DSC. We find that (1) the simple experiment on epoxy-housed indium, (2) comparisons of both peak heat flow and total heat flow resolved by IMC to those resolved by DSC during DGEBA/DEA polymerization, and (3) qualitative heat transport calculations related to the amount of heat lost to the DSC purge gas all provide a consistent picture of the magnitude of the heat generated during epoxy cure that is not resolved by DSC.

The remainder of the paper is organized as follows. In Section 2, the

specifics of the epoxy and experimental methods are reported. In Section 3, results and discussion of the experiments and calculations mentioned above are presented in detail. In Section 4, our results are summarized and conclusions are drawn. Finally, in Appendix A, our qualitative heat transport calculations are presented.

2. Materials and experimental techniques

The epoxy resin used in this study was EPON 828 (Momentive), a diglycidyl ether of bisphenol A (DGEBA). It has a mass per epoxide of 185–192 g/eq and a mass density of 1.16 g/ml at $25\text{ }^{\circ}\text{C}$. Its viscosity is 110–150 Poise at room temperature and, consequently, requires heating to $70\text{ }^{\circ}\text{C}$ (which reduces the viscosity to a few Poise) before mixing with the hardener.

The curing agent, or hardener, employed was diethanolamine (DEA), whose chemical formula is $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$. It has a molecular weight of 105.14 g/mole. The mix ratio of DGEBA:DEA was 1:0.12 parts by weight (pbw). Reagents are heated to $70\text{ }^{\circ}\text{C}$ before mixing and held at $70\text{ }^{\circ}\text{C}$ for about 10–30 min after mixing, while the initial adduct is formed by reaction of the secondary amine with epoxide. The adduct then slowly continues to react through various reaction paths over the course of multiple days to form a network. Measurements are restricted to the post-adduct reaction (the “gelation” reaction) in the present study. Additional processing and reaction details are provided elsewhere [6].

Isothermal DSC runs were performed on a Q2000 calorimeter (TA instruments). The instrument was housed in a thermally controlled environmental chamber and the sample chamber was preheated to the test temperature for four hours before inserting the preheated (to the test temperature) sample. Typical isothermal runs on the DSC were carried out for 3 days. Steel high volume (100 μL) pans (TA Instruments) were used without lids to minimize sample dewetting of the bottom of the pan that reduces efficiency of heat transport to the DSC cell. The typical sample mass was 70 mg. Additional experimental details were previously reported [6]. A few runs were performed on standard hermetically sealed pans to check for consistency.

Isothermal microcalorimetric experiments were performed on an air cooled, thermal activity monitor (TAM Air) calorimeter (TA instruments). Standard 20 mL glass ampoules were used with sample masses of 5 g to 15 g. Multiple samples were run concurrently and excellent reproducibility was found. Typical runs were 1 month in length. As in the DSC experiments, the instrument was preheated to the test temperature (in this case for 2 days) before inserting the preheated (to the test temperature) samples. Experimental procedure was as recommended by TA Instruments, with dry sand used as references to balance heat capacity effects. Although isothermal microcalorimetry is commonly used for the study of reaction kinetics (e.g. [10] and references therein), previous measurements of epoxy cure are rare [11,12].

Calibration of the IMC was performed through the internal electronic heat source supplied with the instrument. Our IMC results were cross-checked at $70\text{ }^{\circ}\text{C}$ by validating that the DGEBA/DEA reaction exotherm data was equivalent between an experiment performed on a TAM Air at TA instruments’ lab [13] and with a second TAM Air instrument at our institution. Various chemical reactions are also available for the verification of IMC calibration. These include the imidazole catalyzed hydrolysis of triacetin [14–17] and the base-catalyzed hydrolysis of methyl paraben [18,19]. For the purposes of this work, such additional calibration checks were deemed unnecessary due to the observed consistency across TAM Air instruments and due to the consistency found in the comparison of TAM AIR results to DSC results over a range of temperatures.

To investigate the insulation effects of an epoxy on the heat flow resolved by DSC, indium samples were embedded in epoxy. This was done by drilling a small cavity (using a lathe) in a previously cured DGEBA/DEA epoxy sample (in a TA Instruments high volume pan) and filling the cavity with indium (54.4 mg). The diameter of the cavity was

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