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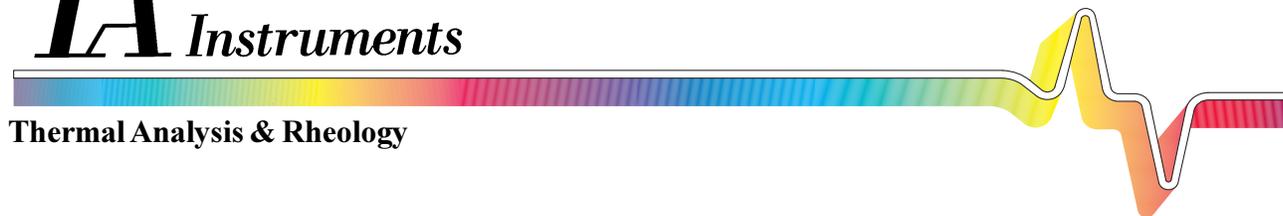
Thermal Analysis & Rheology

MODULATED DSC™ EVALUATION OF ISOTHERMAL CURE & VITRIFICATION FOR THERMOSETTING SYSTEMS †

by Bruno Van Mele, et al

Summary

Conventional differential scanning calorimetry (DSC) is a technique which has been extensively used to characterize the curing of thermosetting materials based on shifts in the glass transition temperature (Tg), as well as the heat flow and kinetics associated with the curing exotherm. Modulated DSC™ is a new thermal analysis technique which provides the same information as conventional DSC, but in addition provides the unique ability to measure heat capacity continuously even during the exothermic curing process. This new information aids in the generation of temperature-time transformation cure diagrams. Furthermore, for the organic systems studied here, a heat capacity mobility factor can be calculated which agrees well with the widely used diffusion factor, where the latter is defined as the ratio of the observed rate of reaction to the rate of reaction in the absence of diffusion control (i.e., the reaction rate predicted by kinetic modeling).

Introduction

Curing thermosetting materials involves the transformation of low molecular weight liquids into amorphous networks with infinite molecular weight by means of exothermic chemical reactions. The state of the material at any time is dependent on the temperature (T) and the amount of chemical conversion which has occurred (x), and can be monitored by properties such as the glass transition temperature. For example, when the material is cured at a temperature substantially below the glass transition temperature of the fully cured network (Tg_∞), the glass transition temperature of the growing network (Tg) gradually rises with time to the cure temperature. The attendant transition of the liquid or rubbery state to the glassy state at that Tg is called vitrification. Furthermore, the decrease in heat capacity (Cp) upon vitrification is comparable to that observed when cooling unreacted material to a temperature below its Tg.

Near vitrification, the kinetics of curing are often complicated by diffusion and/or mobility control, leading to a decrease in the rate of reaction as well as a final conversion lower than unity. Hence, accurate prediction of the course of the reaction during the final stages of cure requires the kinetic rate equation to be corrected with a diffusion factor (DF). This diffusion factor (see equation [1]) describes the effects of the decrease in mobility on the rate of reaction and ranges from unity in the absence of mobility constraints to zero in the frozen glassy state.

$$\left(\frac{dx}{dt}\right)_{obs.} = \left(\frac{dx}{dt}\right)_{kin.} \bullet DF \qquad\qquad [1]$$

$\left(\frac{dx}{dt}\right)_{obs.}$ is the experimentally observed rate of conversion. $\left(\frac{dx}{dt}\right)_{kin.}$ is the fictive rate of conversion in the absence of mobility restrictions (i.e., the chemical rate). For autocatalytic reactions, this latter kinetic term can be described by:

$$\left(\frac{dx}{dt}\right)_{kin.} = \left(k_1 + k_2\, x^m\right)\left(1 - x\right)^n \qquad\qquad [2]$$

Since the decrease in the rate of reaction at vitrification is coupled to a restriction in segment mobility and the associated decrease in heat capacity, a new "mobility factor" DF*, which is based on the change in Cp at vitrification, should provide similar information about the kinetics during the final stages of cure.

$$DF^* = \frac{Cp - Cp_g}{Cp_1 - Cp_g} \qquad\qquad [3]$$

where: Cp = heat capacity at a specific reaction time and temperature
Cp_g = heat capacity in the glassy state (fully cured)
Cp_1 = heat capacity in the liquid or rubbery state (before curing)

This latter approach of evaluating cure based on the change in Cp is attractive compared to the conventional diffusion factor approach because it does not require a kinetic model. Unfortunately, the continuous measurement of Cp during cure is not feasible with conventional DSC.

Modulated DSC^{TM}, on the other hand, measures both heat flow and heat capacity in a single experiment by superimposing a modulated heating rate (changing heating rate) on top of a linear average heating rate. The linear change in temperature permits the measurement of heat flow, while the modulated change permits the calculation of heat capacity. This same principle can also be applied to an isothermal situation where the material remains at a constant average temperature while modulation occurs. Hence, the continuous measurement of Cp during isothermal cure is feasible with modulated DSC.
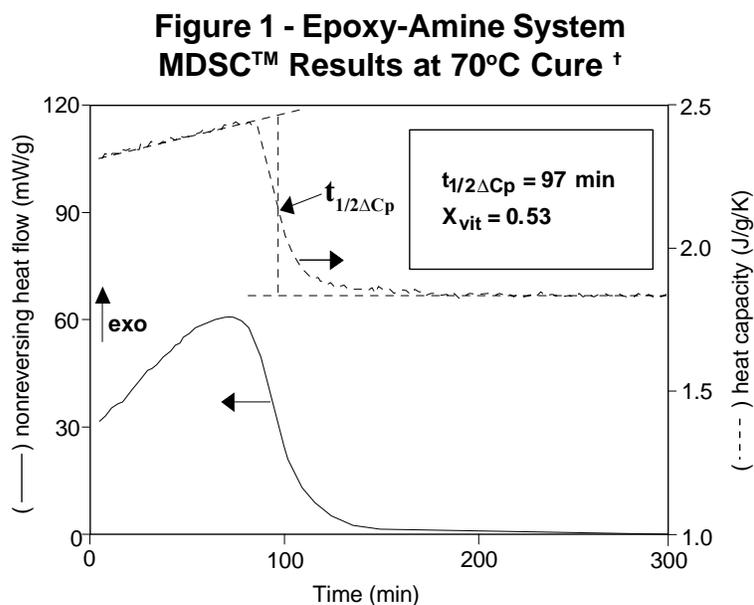
Experimental

Two organic thermosetting systems were studied: an amine-cured epoxy and an accelerated anhydride-cured epoxy. Stoichiometric amounts of epoxy and hardener were used. Modulated DSC measurements were performed on a TA Instruments Modulated DSC 2920 using a refrigerated cooling system (RCS) and a helium DSC cell purge (at 25 ml/min). Hermetic aluminum pans were used. The instrument was calibrated for temperature using cyclohexane and indium, and for enthalpy using indium. The heat capacity signal was calibrated with linear polyethylene (NIST SRM 1475) at 150°C (Cp = 2.57 J/g/K) using the same period (60 seconds) as in the corresponding sample experiments.

Isothermal sample experiments were performed for times up to 2500 minutes. The baseline stability over these long experiments is better than 20μW. For partial cure reactions, the isothermal experiment was halted at a predetermined time. The residual reaction enthalpy (ΔH_{res}) and the glass transition temperature (Tg) were measured by first cooling the partially reacted sample to -50°C and then heating to 275°C at 2.5°C/min with a ±0.3°C modulation amplitude and a 60 second period. ΔH_{res} was used to determine conversion by comparison to the exothermic ΔH for an untreated sample.

Results and Discussion

Figure 1 shows the modulated DSC heat capacity and nonreversing heat flow results for the epoxy-amine system as a function of time at 70°C. The nonreversing heat flow exotherm (shape) indicates that the curing process is autocatalytic. The heat capacity shows a stepwise decrease during the latter stages of the curing exotherm. Figure 2 shows the related changes in the amount of conversion [x] and the glass transition [Tg] as cure progresses. These curves were generated from a series of conventional DSC experiments on samples pretreated for various times at 70°C, and indicate that the material's initial Tg is -23°C but with time, the Tg surpasses the reaction temperature T_{iso} (t_{vit}) and eventually levels off at 103°C. Comparison of the heat capacity change in Figure 1 and the Tg change with cure time in

Figure 1 - Epoxy-Amine System
MDSC^{TM} Results at 70°C Cure [†]

$t_{1/2\Delta Cp}$

$t_{1/2\Delta Cp}$ = 97 min

X_{vit} = 0.53

exo

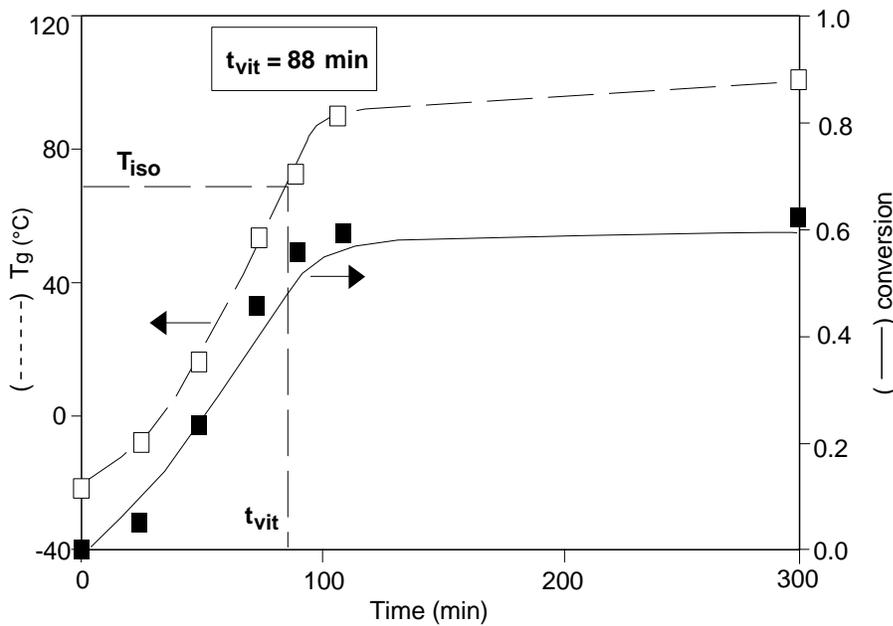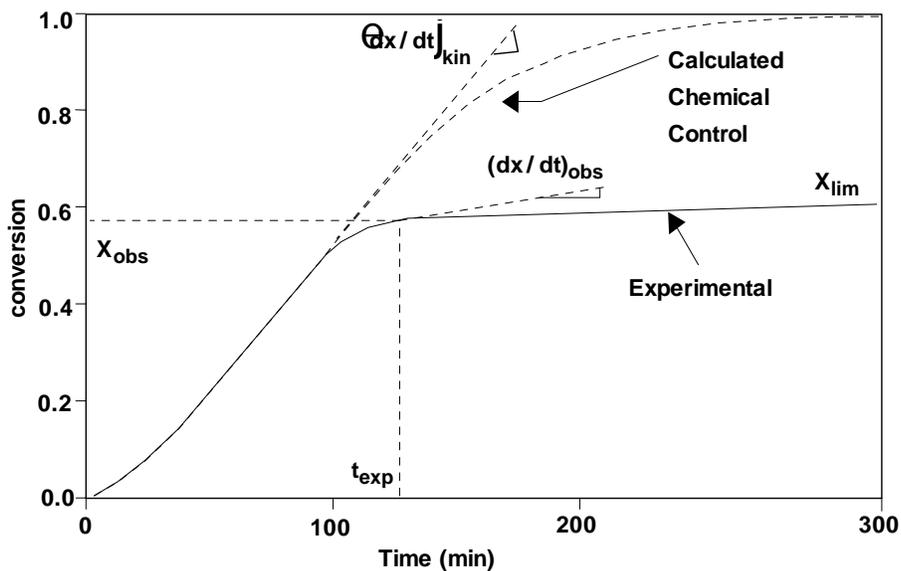## Figure 2 - Epoxy-Amine System
Conversion & Tg From 70°C Cure [†]

Figure 2 indicates that the time $t_{1/2\Delta Cp}$ corresponds well with time of vitrification (t_{vit}). Thus, the $t_{1/2\Delta Cp}$ obtained from modulated DSC[TM] can be used to rapidly determine the time of vitrification.

Figure 3 compares the experimental conversion results from Figure 2 with the conversion expected based on theory (i.e., based on the autocatalytic rate equation [2]). Up to the onset of vitrification, both curves coincide. After vitrification, however, the experimental rate of conversion decreases and approaches a limiting conversion (x_{limit}). This deviation of the experimental conversion from the theoretical conversion is the result of mobility restricting effects within the cured material. The experimental and theoretical conversion rates can be determined from the slopes of the respective curves in Figure 3 (for the same conversion x_{obs}). These rates are shown in Figure 4, and the resultant

Figure 3 - Epoxy-Amine System
## Conversion vs. Reaction Time for 70°C Cure [†]

**Figure 4 - Epoxy-Amine System
Conversion Rate vs. Reaction Time for 70°C Cure †**

**Ideal (No Mobility
Restrictions)**

Experimental

y-axis: **dx/dt (10^{-5}s^{-1})**
x-axis: **Time (min)**
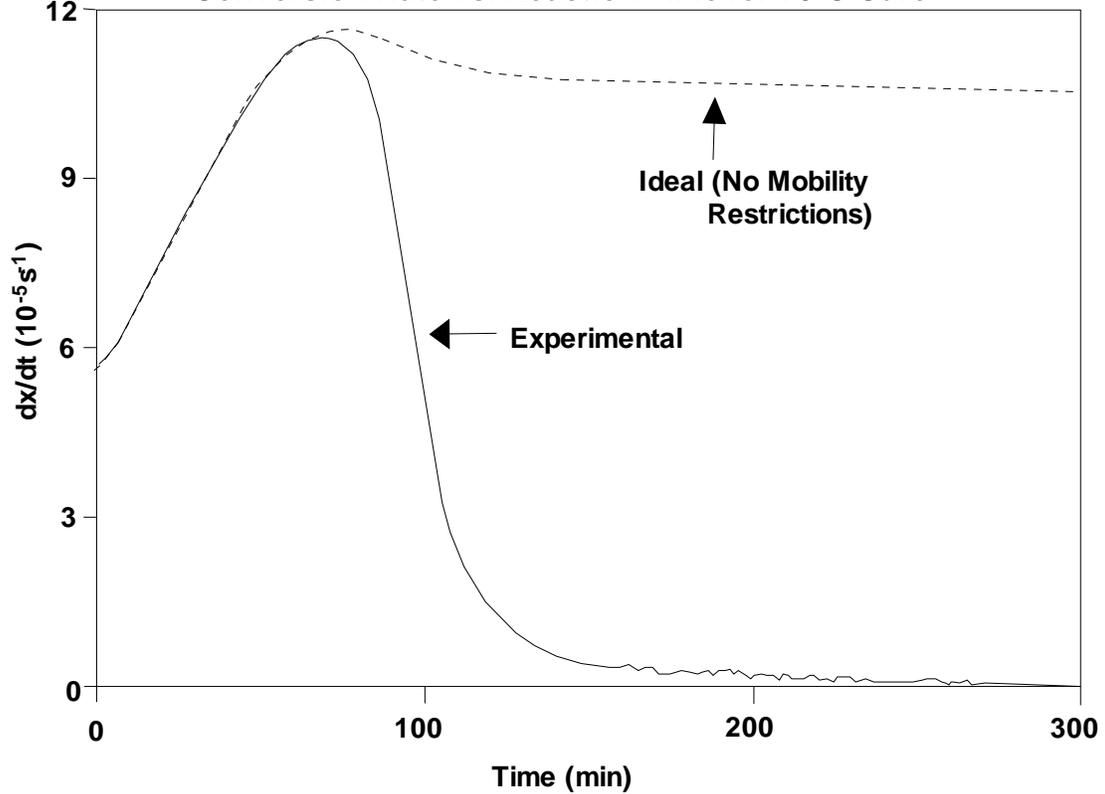
diffusion factor DF calculated using equation [1] is shown in Figure 5 (dashed line). The diffusion factor determined using the heat capacity curve in Figure 1 and equation [3] is represented by the solid line in Figure 5. The excellent agreement verifies the MDSC^{TM} heat capacity approach.

**Figure 5 - Epoxy-Amine System
DF and DF* Comparison for 70°C Cure †**

**DF* (MDSC
Heat Capacity
Basis)**

**DF (DSC Heat
Flow Basis)**

y-axis: **DF and DF***
x-axis: **Time (min)**
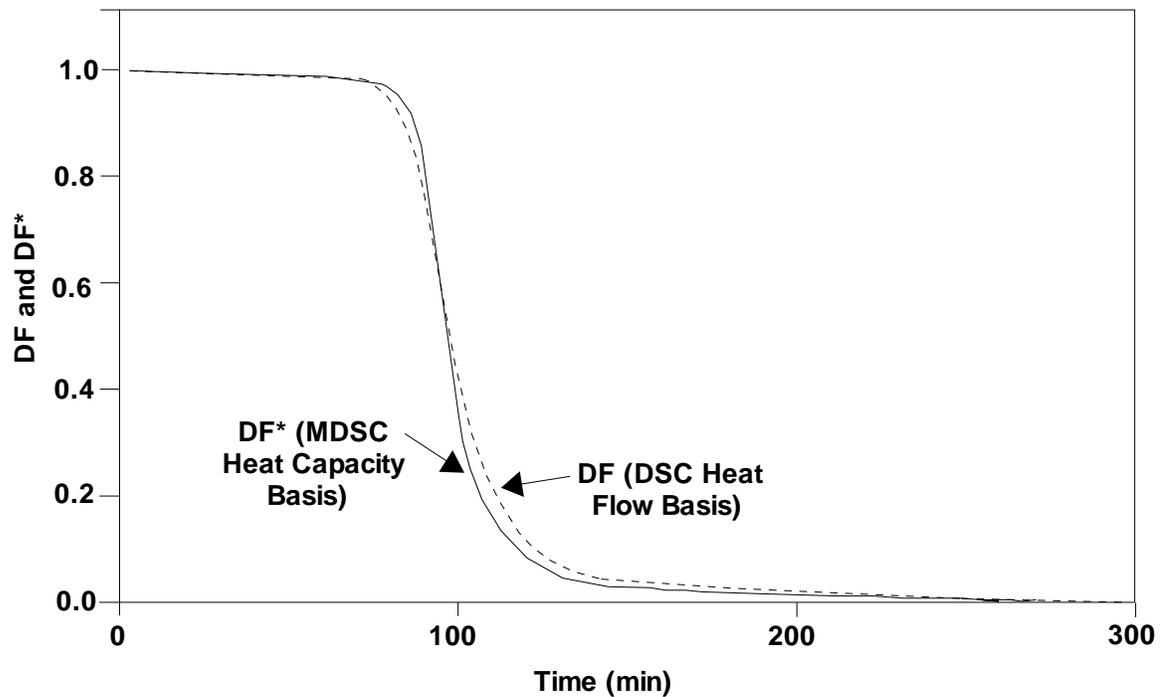
The modulated DSC nonreversing heat flow and heat capacity results for the anhydride-cured epoxy resin cured isothermally at 85°C are shown in Figure 6. The reaction is again autocatalytic. The final isothermal conversion and Tg determined by a subsequent heating experiment are 86% and 105°C respectively. No sharp decrease in heat flow is observed at $t_{1/2\Delta Cp}$ as in the epoxy-amine system, but the reaction rate at $t_{1/2\Delta Cp}$ is already substantially lower than at the maximum of the cure exotherm.

Figure 6 - Epoxy-Amine System
MDSC™ Results at 85°C Cure †
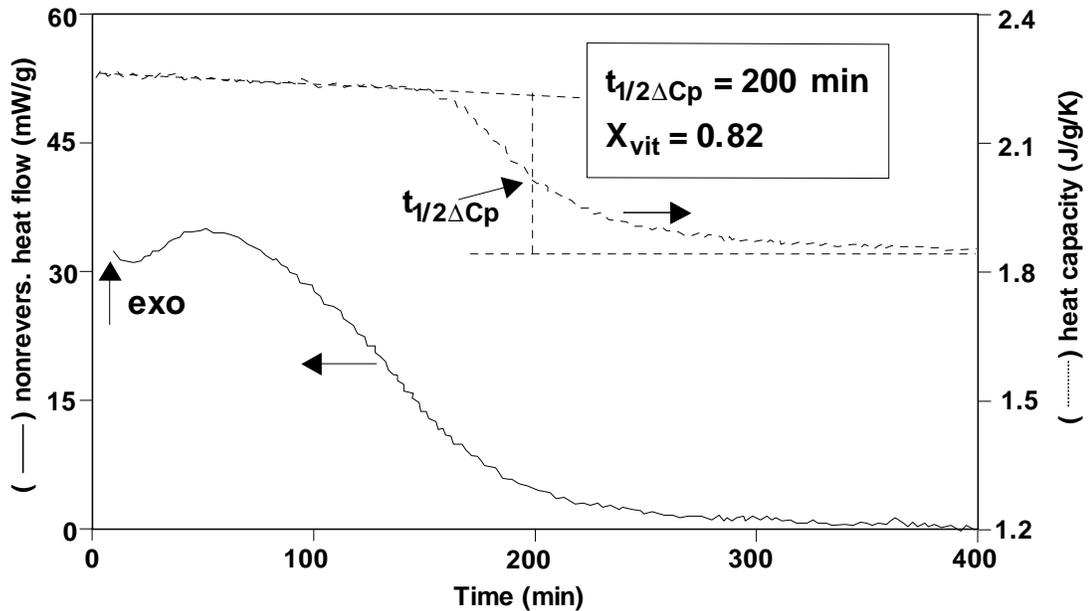
The ability of $t_{1/2\Delta Cp}$ to predict t_{vit} is again verified by treating a sample at 85°C for 200 minutes before scanning (heating) to detect Tg. As expected, the Tg is essentially T_{iso} (83°C versus 85°C). Figure 7 shows the DF and DF* curves for the epoxy-anhydride which also illustrate good agreement as in the epoxy-amine system. The mobility

Figure 7 - Epoxy-Anhydride System
DF & DF* Comparison For 85°C Cure †
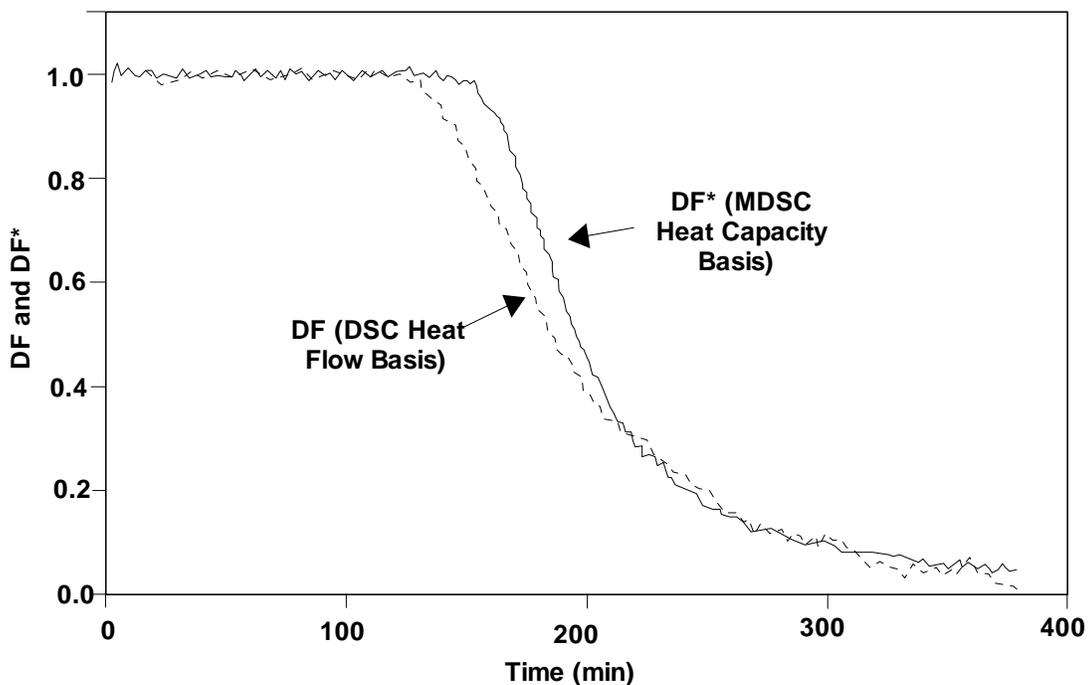
factor DF* for the epoxy-anhydride at several different isothermal reaction temperatures (Figure 8) indicates that vitrification occurs at shorter reaction times as the reaction temperature increases. The ability to determine DF* at 60°C is particularly significant because the amount and rate of conversion (and hence DF) cannot be accurately measured at this reaction temperature due to the very slow reaction.

Figure 8 - Epoxy-Anhydride System
Mobility Factor vs. Cure Temperature [†]
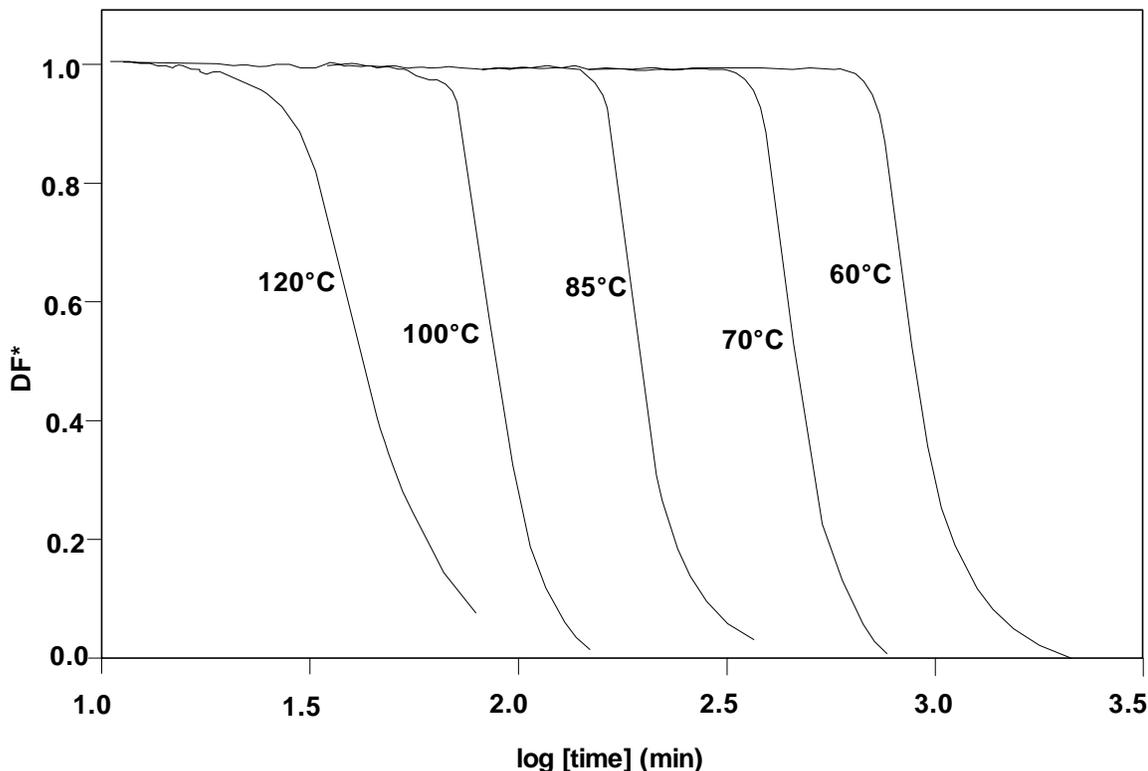
Comparison of the two systems also shows clear differences in vitrification behavior. At 70°C, e.g., the conversion attained at vitrification (x_{vit}) for the epoxy-anhydride is more than 20% greater than for the amine-cured epoxy. In addition, a higher crosslink density and Tg are achieved for the same level of conversion. As a result, the epoxy-anhydride reaction is more hindered by the occurrence of vitrification. This is confirmed by comparison of the DF curves at 70°C (Figures 5 and 8).