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MODULATED TEMPERATURE DIFFERENTIAL SCANNING CALORIMETRY
Characterization of curing systems by TTT and CHT diagrams

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Abstract

Modulated temperature differential scanning calorimetry (MTDSC) is used to study simultaneously the evolution of heat flow and heat capacity for the isothermal and non-isothermal cure of an epoxy-anhydride thermosetting system. Modelling of the (heat flow related) chemical kinetics and the (heat capacity related) mobility factor contributes to a quantitative construction of Temperature-Time-Transformation (TTT) and Continuous-Heating-Transformation (CHT) diagrams for the thermosetting system.

Keywords: modulated temperature DSC, thermoset, TTT and CHT diagram

Introduction

Curing thermosetting materials generally involves the transformation of low molecular weight liquids to amorphous networks with infinite molecular weight by means of exothermic chemical reactions. While curing, the state of the material is governed by chemical conversion and temperature. Knowledge of the rate of cure and its dependency on temperature and conversion is important for predicting the course of reaction for a certain thermal treatment. Vitrification of a reacting thermosetting system occurs when its glass transition temperature, T_g, rises to the reaction temperature, T: the material transforms from a liquid or rubbery state to a glassy state. The vitrification process drastically influences the rate of cure. The occurrence of this phenomenon is not restricted to isothermal conditions only: for highly reactive systems, or when the applied heating rate is sufficiently small, vitrification occurs in non-isothermal conditions too. In the latter case, devitrification is observed when the reaction temperature again surpasses T_g of the vitrified system.

The chemorheological transformations while curing thermosets are depicted in Temperature-Time-Transformation (TTT) and Continuous-Heating-Transformation (CHT) diagrams, developed by Gillham and coworkers [1–5].

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Modulated temperature differential scanning calorimetry (MTDSC) allows for simultaneous measurements of the evolution of both heat flow and heat capacity [6–10]. Therefore, this recent extension of conventional DSC offers a great opportunity for studying the chemical kinetics and (de)vitrification behaviour of thermosetting systems [11, 12].

The experimental benefits of MTDSC for constructing quantitative TTT and CHT diagrams will be illustrated in this paper.

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 [11].

Modulated isothermal and non-isothermal experiments were performed on a TA Instruments 2920 DSC with MDSC^{TM} option and equipped with a refrigerated cooling system (RCS).

All details concerning the raw materials and their processing, as well as a description of the instrumentation, the experimental procedure and the calculations are given in [11, 12].

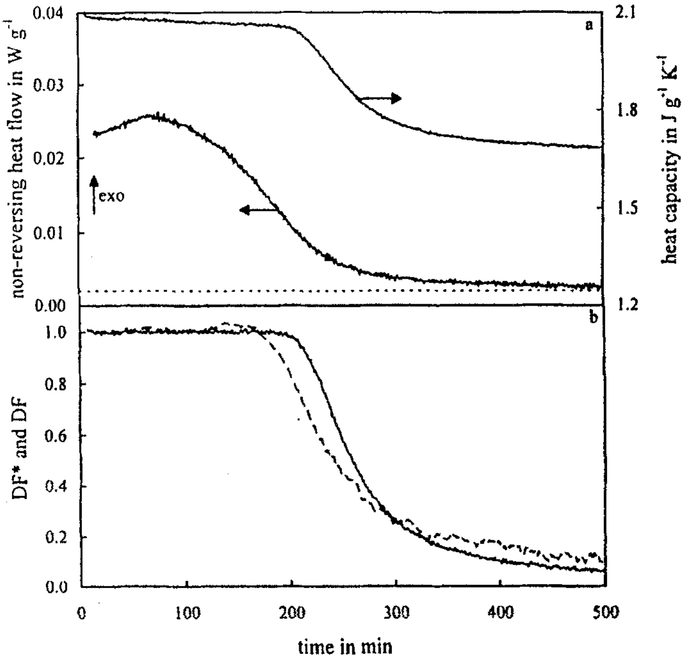

Fig. 1 Isothermal cure of the epoxy-anhydride system at 80°C: (a) non-reversing heat flow and heat capacity ; (b) comparison of the mobility factor DF^* based on heat capacity (——) and the diffusion factor DF based on heat flow (– – – –)

Results and discussion

The monitoring with MTDSC of isothermal vitrification and non-isothermal vitrification and devitrification for the anhydride-cured epoxy is illustrated in Figs 1a and 2a.

A stepwise decrease in the heat capacity is observed, which, in non-isothermal conditions (Fig. 2a), is followed by a stepwise increase at a higher temperature. The decrease and increase in heat capacity can be identified with vitrification and devitrification during cure, respectively.

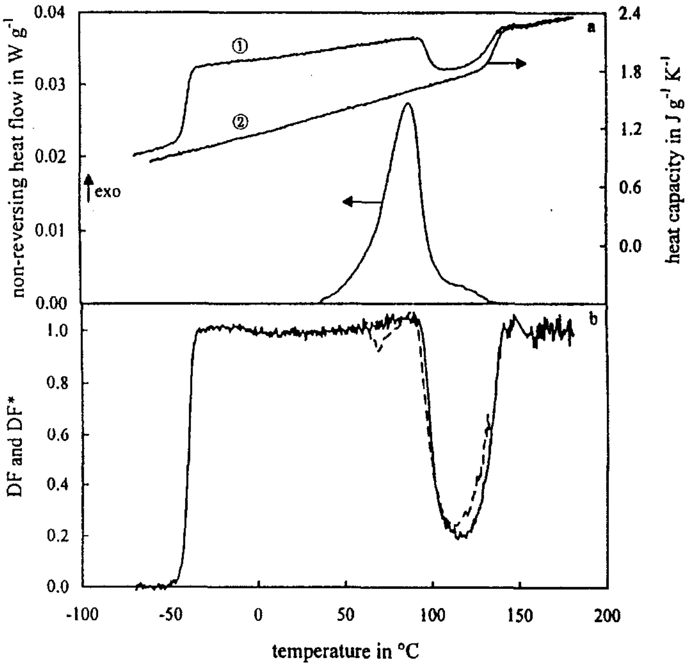

Fig. 2 Non-isothermal cure of the epoxy-anhydride system at 0.15°C min^{-1} : (a) non-reversing heat flow and heat capacity for the first heating (①), and heat capacity for the fully cured material (②); (b) comparison of the mobility factor DF^* based on heat capacity (———) and the diffusion factor DF based on heat flow (– – – –)

On transition to the glassy state, the rate of reaction drops due to the onset of mobility control. So, for accurately predicting the course of the reaction in the final stages of cure, it is necessary to correct the rate of conversion in kinetically controlled conditions, $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{kin}}$, by a 'diffusion factor', DF [11, 12]:

$$DF(x,T)=\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{\mathrm{obs}}\bigg/\left(\frac{\mathrm{d}x}{\mathrm{d}t}(x,T)\right)_{\mathrm{kin}}$$

This diffusion factor is governed by the viscoelastic state of the material and its value ranges from one in a state without mobility constraints to zero in the frozen glass. The value of $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{kin}}$ is obtained by chemical kinetics modelling (in conditions without mobility restrictions).

The decrease in rate of reaction on vitrification is due to the attendant reduction in chain segment mobility, which also causes a decrease in heat capacity C_p. Normalization of the heat capacity evolution between the values for the liquid and glassy states leads to the 'mobility factor', DF^*, proposed in [11, 12]:

$$DF^*(x,T)=\frac{C_p\,(x,T)-C_{pg}\,(x,T)}{C_{pl}\,(x,T)-C_{pg}\,(x,T)}$$

It is shown that at the instant the mobility factor equals one half, the glass transition temperature of the curing system reaches the reaction temperature [11, 12]. Therefore, the time and temperature of (de)vitrification can be determined in a single MTDSC experiment. The evolution of the mobility factor gives additional infor-

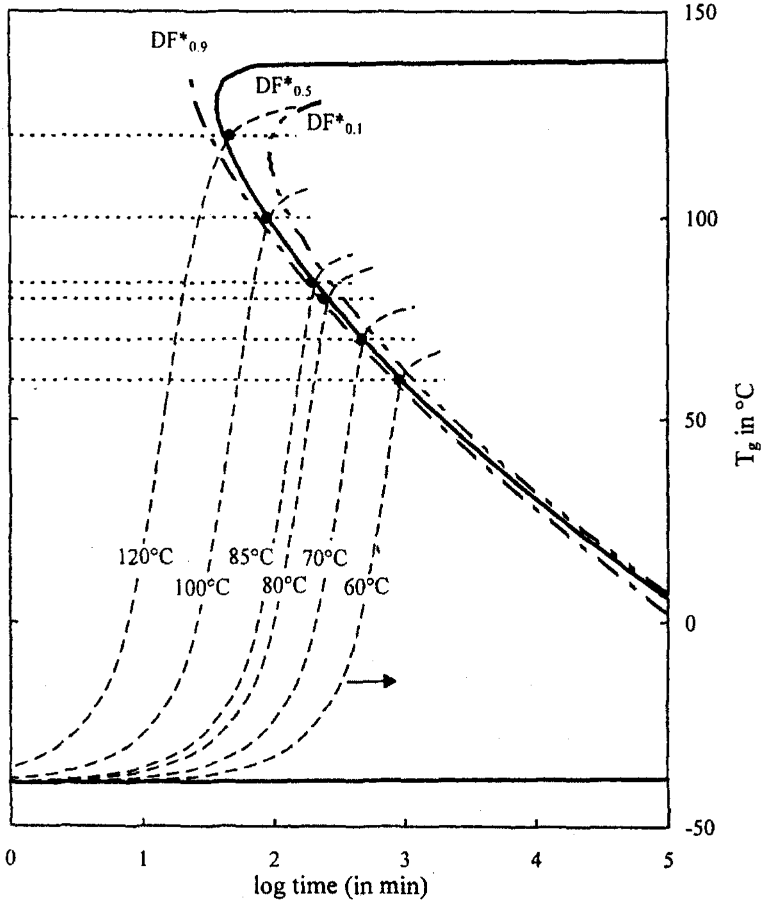

Fig. 3 Time-temperature-transformation (TTT) diagram for the isothermal cure of the epoxy-anhydride system showing the evolution of T_g (– – – –) at different cure temperatures (- - - -), and three lines of constant mobility factor. The line $DF^*_{0.5}$ is the vitrification line (———); the symbols indicate the experimental points of vitrification

mation on the degree of vitrification as the conditions evolve between unrestricted and restricted mobility.

Further, the mobility factor (obtained from the heat capacity signal) and the diffusion factor (obtained from the heat flow signal) nearly coincide for both isothermal (Fig. 1b) and non-isothermal measurements (Fig. 2b). This observation is also valid for other organic thermosetting systems, such as amine-cured epoxies [11, 12]. Therefore, the mobility factor can be used as a direct measurement of the diffusion factor over the whole range of states between the liquid or rubbery state and the frozen glass. In this way, a reliable conversion rate equation is obtained, describing the kinetics of the cure process from the early to the final stages of reaction (including diffusion effects). The model parameters are optimized by a simultaneous fitting of non-reversing heat flow and heat capacity signals of multiple isother-

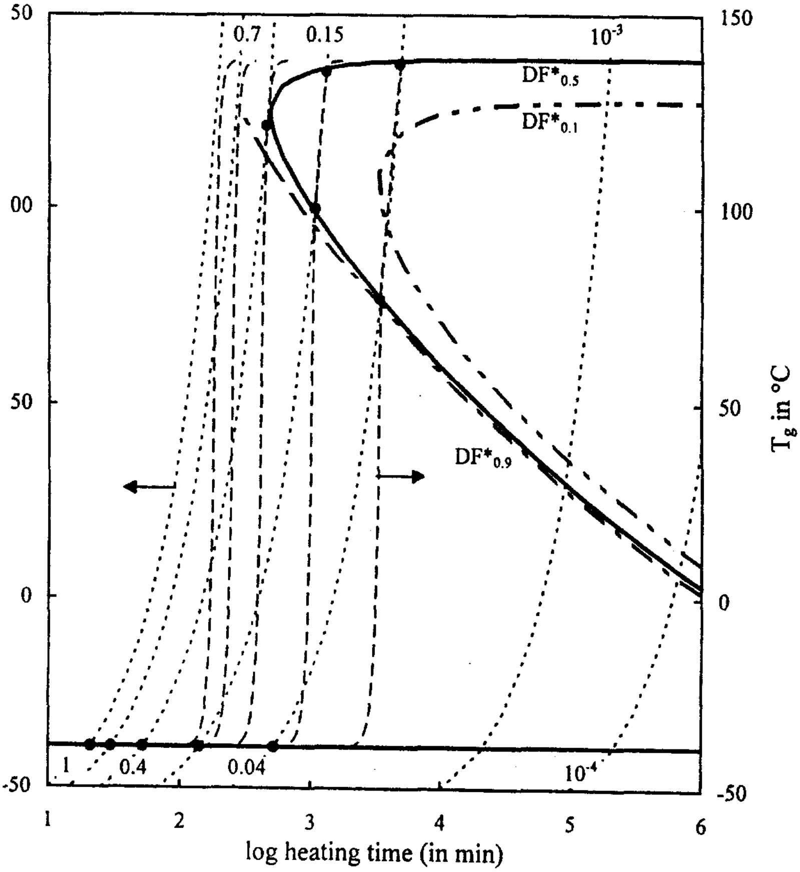

Fig. 4 Continuous-heating-transformation (CHT) diagram for the non-isothermal cure of the epoxy-anhydride system showing the evolution of T_g (– – – –) and the cure temperature (- - - -) at different heating rates (in °C min^{-1}), and three lines of constant mobility factor. The line $DF^*_{0.5}$ is the vitrification line (——); the symbols indicate the experimental points of (de)vitrification

mal and non-isothermal MTDSC experiments. More details about the model and parameter optimization will be published [13].

With this approach, the vitrification line in the Temperature-Time-Transformation (TTT) diagram (Fig. 3) and the Continuous-Heating-Transformation (CHT) diagram (Fig. 4) for the epoxy-anhydride system can be constructed. In terms of the experimental MTDSC modulation conditions, the vitrification line is almost coinciding with a DF^* value of 0.5. Contours of lower mobility ($DF_{0.1}^*$ or a rate reduction of 90%) and higher mobility ($DF_{0.9}^*$ or a rate reduction of 10%) are depicted too. The procedure of modelling and parameter optimization enables to draw continuous iso-mobility contours using a restricted number of MTDSC experiments. Both TTT and CHT diagrams show cure paths without and/or with mobility restrictions, depending on the imposed cure conditions.

Conclusions

The results obtained indicate that MTDSC is a very useful technique for studying the vitrification behaviour in thermosetting systems. Using isothermal and non-isothermal experiments, Temperature-Time-Transformation (TTT) and Continuous-Heating-Transformation (CHT) diagrams can further be developed. These quantitative diagrams can be employed for improving the processing conditions of thermosetting resins.

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