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Frequency dependent heat capacity in the cure of epoxy resins

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Abstract

Different *temperature modulated differential scanning calorimetry* (*TMDSC*) approaches were explored for studying the frequency dependence of the vitrification phenomenon during the cure of a thermosetting epoxy resin. All approaches show the expected decrease in vitrification time with increasing frequency. *Light* (*heating*) (*temperature*) *modulated DSC* (*LMDSC*), developed by Saruyama, offers the advantage that the frequency range for direct measurements is extended (from 0.01 to 1 Hz). However, at frequencies above 0.1 Hz, the results contain information about the changing thermal diffusivity (for samples above 100 μm thick). A *complex saw-tooth modulation method*, developed by Wunderlich, allows multiple frequencies (over almost one decade) to be measured in a single experiment, thus eliminating effects of sample reproducibility. For studying the frequency dependence during (chemical) transformations, such as cure, the desired invariance of the sample during at least one modulation period and thermal diffusivity effects (even for films of only 100 μm thick) limit a further extension of the frequency domain to lower and higher frequencies, respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Temperature modulated differential scanning calorimetry; Thermosetting polymer; Frequency

1. Introduction

The network formation of thermosetting polymer systems often depends on both chemical reactivity and mobility of the reactive units. This mobility is influenced by the visco-elastic state of the changing material. The *vitrification* of the developing polymer network is a transformation from a *mobile* liquid or rubbery state to a *frozen* glassy state. This transition occurs when the glass transition T_g of the reacting network reaches the cure temperature due the increase in molecular weight or crosslink density. Due to the attendant decrease of the chain segment mobility the reaction becomes *diffusion-controlled*, which eventually leads to a complete halt of the reaction, with residual reactive units and reduced properties as a consequence.

In previous work, temperature modulated differential scanning calorimetry (TMDSC) proved to be very advantageous for studying the cure and vitrification of thermosetting systems [1–4]. The reaction exotherm is observed in the heat flow while vitrification is simultaneously seen as a decrease in heat capacity and a minimum in heat flow phase (Fig. 1). This decrease in heat capacity, attributed to the loss of the co-operative mobility involved in the glass transition, occurs when the characteristic time-scale of the co-operative movements becomes longer than the modulation period (or the characteristic time-scale of the experiment) [5]. If the modulation frequency is increased, the corresponding T_g of the (curing) material will be higher (for the same conversion), and thus vitrification

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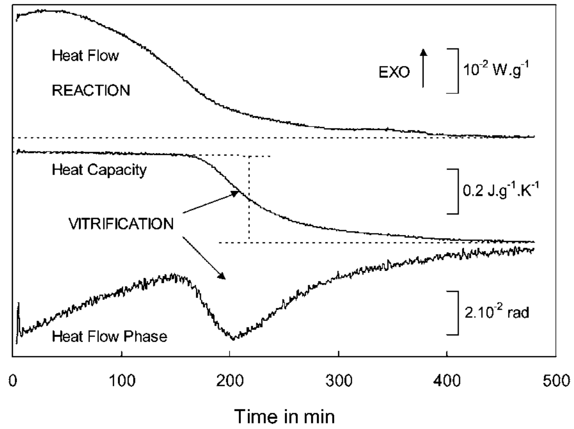

Fig. 1. Quasi-isothermal cure and vitrification of an epoxy-anhydride resin at 80°C by MDSC™ at a frequency of 1/60 Hz.

will be observed at a lower degree of conversion (Fig. 2). Note that the reaction rate itself depends on the average temperature and remains largely unaffected by the modulation.

The reaction process (r) can be considered as a consecution of diffusion (d) and chemical reaction (cr), each with its respective characteristic time τ [6].

$$\tau_r = \tau_d + \tau_{cr} \tag{1}$$

The reaction will remain chemically controlled as long as τ_d is much smaller than τ_{cr}. As the reaction conversion increases, the diffusion process is slowing down (τ_d increases) due to the increase in viscosity. When τ_d becomes comparable to τ_{cr} the reaction becomes diffusion-controlled.

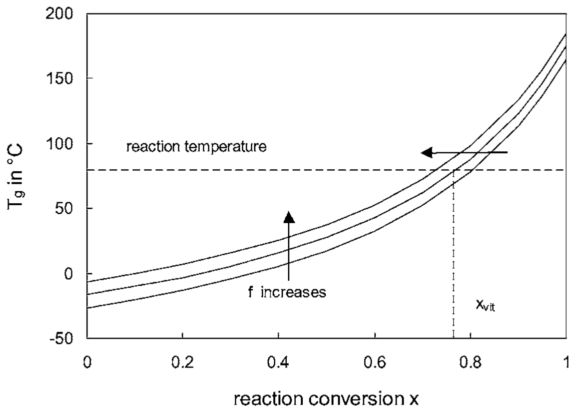

Fig. 2. Illustration of the influence of frequency *f* on the evolution of glass transition T_g with conversion x; x_{vit} is the conversion at vitrification.

For the step-growth amine-cured epoxy resins and for the anionic polymerization of anhydride-cured epoxy systems, the diffusion control is non-specific (or overall) [6]. This means that the diffusion control is determined by a single (or average) mobility, the chain segment mobility and the mobility of the anhydride monomer, respectively. Results for amine and anhydride-cured epoxy systems showed that the decrease in heat capacity at vitrification, measured at 1/60 Hz, can be used as a quantitative model for the description of the decrease in the rate of reaction [1,2], and it results in quantitative CHT and TTT-diagrams for the systems studied [7]. The model describing the interrelation between τ_d and τ_{cr} and its effect on the global reaction kinetics (Eq. (1)) are elaborated in [8] and quantitative results are shown. Thus, for these amine and anhydride–cured epoxy systems, the characteristic times for the (co-operative) chain segment mobility involved in the glass transition (region) measured at a frequency of about 1/60 Hz, are comparable to those of the (reaction) rate-determining mobility upon transition to diffusion-controlled reaction conditions. Since, only a limited frequency domain is available for TMDSC and since a quantitative correspondence was found for 1/60 Hz, no attempt was made to fine-tune the frequency for each of the epoxy–hardener systems. However, for other systems with a different reaction mechanism and rate-controlling mobilities the frequency of correspondence might be totally different. Examples include unsaturated polyesters, in which molecules with largely different mobilities are involved in the free radical polymerisation [4], and the low-temperature synthesis of inorganic polymer glasses for which the reaction is unaffected by the main (glass) transition [9]. Therefor, a study of the effect of frequency on the vitrification of resin systems related to their chemical structure and reaction mechanism might offer new insights concerning reaction kinetics, vitrification, and diffusion control effects. In this paper, an exploration of the technical feasibility to study the frequency dependence of the vitrification phenomenon during cure using TMDSC and LMDSC techniques is discussed.

2. Experimental

2.1. Materials

A DGEBA-type epoxy resin (Epikote 828 VLEL, Shell) was cured using an amine hardener (4,4′-methylenedianiline, MDA, Aldrich) in a stoichiometric ratio, or using an anhydride hardener (methyltetrahydrophthalic anhydride, HY917, Ciba-Geigy) and an accelerator (1-methyl imidazole, DY070, Ciba-Geigy) in a 100/90/1 ratio by weight.

2.2. Instruments

Quasi-isothermal cure experiments at different frequencies were made in three instruments using different approaches.

Light heating temperature modulated DSC (LMDSC, [10–12]) measurements were performed using a modified Rigaku Thermo Plus 8230 DSC operated at selected frequencies ranging from 0.01 to 1 Hz. More details concerning the technique are given below and in [10–12].

A TA Instruments 2920 DSC with MDSC^{TM} option and RCS was operated (1) in MDSC^{TM} mode at a frequency of 1/60 Hz, and (2) using a multi-frequency approach [13]. The latter approach was also used on a Perkin-Elmer Pyris 1 DSC.

All instruments were calibrated for temperature and enthalpy, and if appropriate, for heat capacity.

2.3. Sample preparation

Reactive mixtures were prepared in the correct weight ratios. Prior to use, they were stored for up to 1 month in small, sealed recipients at a temperature below −18°C. For measurements by TMDSC and using the multi-frequency approach, a drop of 8–15 mg was brought into an aluminium sample pan, which was hermetically sealed.

For LMDSC measurements, a drop of ca. 2 mg was brought into a non-hermetic aluminium pan, a close-fitting aluminium lid was dropped onto the liquid resin, and subsequently a carbon coating was applied to the lid. This carbon coating absorbs the irradiation and heats up the sample. Since, the sealing is not hermetic, a weight loss was observed for experiments with the more volatile anhydride. Therefor, this system was not studied elaborately using LMDSC.

3. Results and discussion

3.1. Light heating temperature modulated DSC (LMDSC)

A schematic representation of an LMDSC, developed by Saruyama [10], is shown in Fig. 3. The instrument is based on a commercial heat flux DSC. Light-beams of modulated intensity irradiate the carbon-coated sample and reference pan. This leads to a small temperature modulation for sample and reference pans, superimposed on the average temperature that is controlled by the furnace. Note that the modulated heat flow to the sample is controlled (by way of the amplitude of the modulated light intensity) and the amplitude and phase of the resulting temperature modulation is measured.

Using different approaches, the sample heat capacity can be derived from the amplitude and phase of the modulated temperature difference, which is measured below the sample and reference pans [10,12]. The main advantage of the LMDSC approach over the other approaches used is that the modulation is applied directly to the pans, instead of to the furnace. Hence, the frequency can be increased up to 1 Hz, or one order of magnitude higher. Since, the instrument's response depends on the frequency, a frequency dependent heat capacity calibration is needed (if absolute values are desired).

Quasi-isothermal cure experiments at 80°C were made at frequencies from 0.01 to 1 Hz. The heat flow

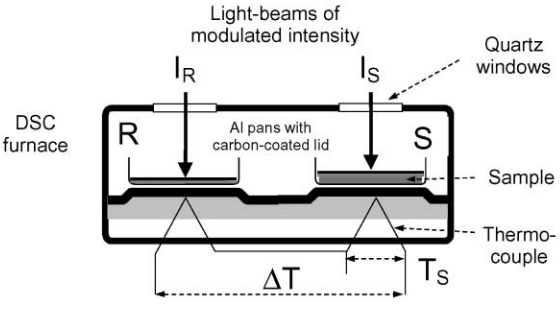

Fig. 3. Schematic illustration of the light heating temperature modulated DSC (LMDSC), developed by Saruyama [8–10].

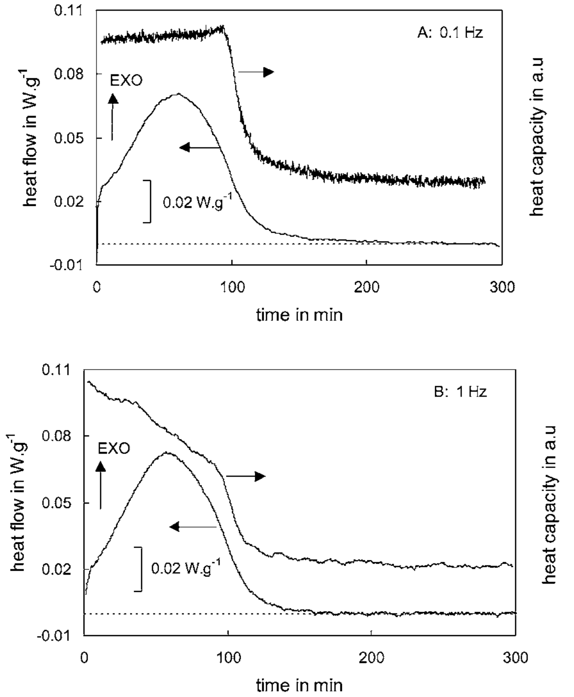

Fig. 4. Quasi-isothermal cure and vitrification of an epoxy–amine resin at 80°C by LMDSC, heat flow and heat capacity at a frequency of (A) 0.10 and (B) 1 Hz.

and heat capacity for 0.1 and 1 Hz are shown in Fig. 4. The reaction kinetics (averaged heat flow) are not markedly influenced by the small temperature modulation. In the (uncalibrated) heat capacity signal vitrification is observed as a step-wise decrease. Model calculations indicate that for frequencies larger than 0.1 Hz the sample is not uniformly following the temperature modulation, the amplitude of the temperature modulation decays slightly as the wave propagates through the 100 μm thick sample. This results in a higher (apparent) heat capacity before reaction. As the thermal diffusivity increases due to the increasing molecular weight and crosslink density, the (apparent) heat capacity gradually decreases, as observed before vitrification at higher frequencies (Fig. 4, 1 Hz). The vitrification time is defined as the time to reach half of the step-wise decrease in heat capacity [1]. It decreases gradually with increasing frequency (Fig. 5). The considerable scatter on the results is attributed to small differences in sample composition and average cure temperature (every point is an individual experiment).

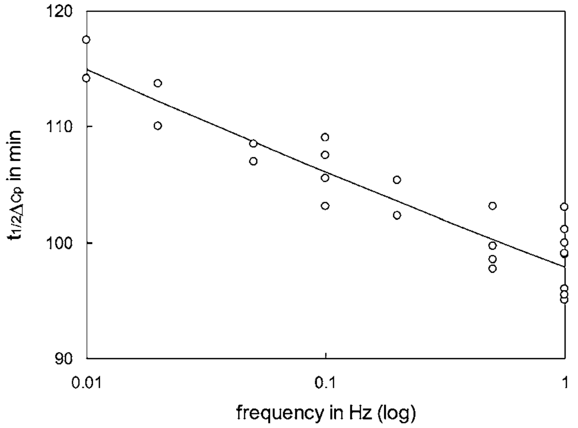

Fig. 5. Vitrification times $t_{1/2\,\Delta C_p}$ as a function of frequency for quasi-isothermal cure of an epoxy–amine system at 80°C for modulation frequencies of 0.01 to 1 Hz (LMDSC).

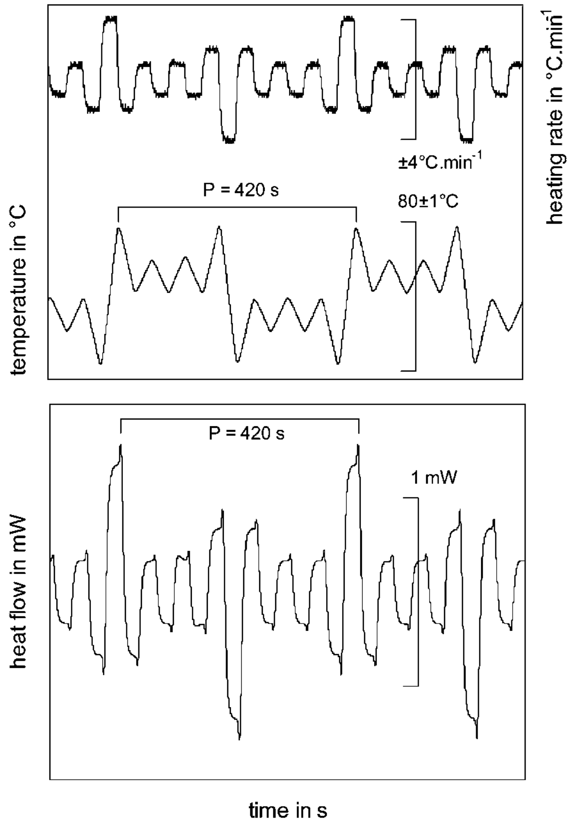

Fig. 6. Sample temperature, heating rate and resulting heat flow for a complex saw-tooth modulation experiment with a period P of 420 s.

3.2. Multi-frequency saw-tooth modulation

Recently, multi-frequency modulation methods for measuring the heat capacity with higher precision were developed by Wunderlich et al. [13] and Schick et al. [14,15]. The *complex saw-tooth modulation approach* [13] was applied to the epoxy–anhydride system to study the frequency-dependence of heat capacity during cure. By appropriately designing the complex modulation, similar modulation amplitudes result for the first, third, fifth and seventh harmonics [13], corresponding to frequencies of 1/420, 1/140, 1/84, and 1/60 Hz.

Results for the cure of the epoxy–anhydride system (same as in Fig. 1) are shown in Figs. 6 and 7. The temperature, heating rate, the resulting heat flow output for a complex modulation with a period of 420 s are shown in Fig. 6. Fig. 7 shows the data for frequencies corresponding to the first, third and ninth harmonics of a Fourier series of the results of Fig. 6. The decrease in vitrification time with increasing frequency is again observed. Using this method, the frequency dependence can be studied over almost one decade in a single experiment.

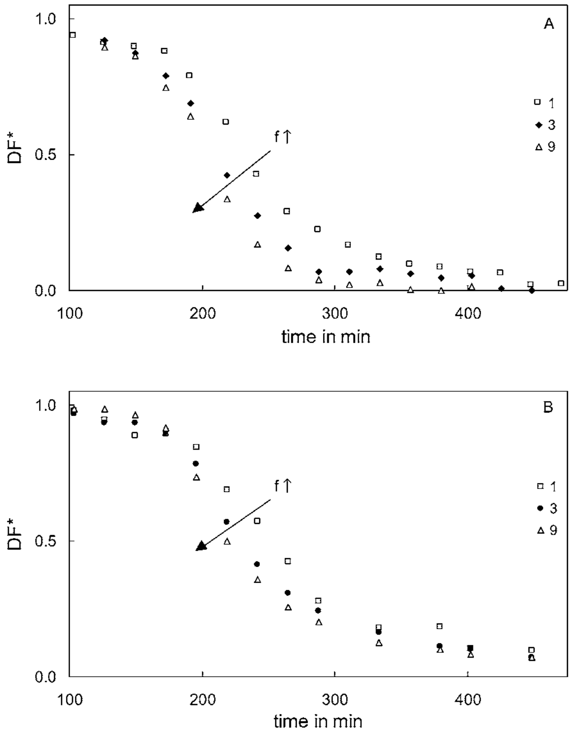

Fig. 7. Normalised heat capacity DF^* for the quasi-isothermal cure of an epoxy–anhydride system at 80°C for the basic, third and ninth harmonics of a complex saw-tooth modulation experiment with a 420 s period: (A) on a TA Instruments 2920 DSC; (B) on a Perkin-Elmer Pyris 1 DSC .

4. Final remarks

Different approaches were explored to study the frequency dependence of the vitrification phenomenon during the cure of a thermosetting epoxy resin using *TMDSC* and *LMDSC*. All approaches show the expected decrease in vitrification time with increasing frequency. *LMDSC*, developed by Saruyama, offers the advantage that the frequency range is extended up to 1 Hz. At frequencies above 0.1 Hz, the results contain information about the changing thermal diffusivity (for samples of 100 μm thick). The main advantage of the *complex saw-tooth modulation method* developed by Wunderlich is that multiple frequencies are measured in a single experiment, thus eliminating effects of sample reproducibility.

Even with this extended frequency range (ca. 1 decade for the multi-frequency approach and ca. 2 decades for LMDSC) the simultaneously measured heat flow is not accurate enough to correlate a specific frequency with the reaction kinetics of the different epoxy thermosetting systems. Indeed, there is a considerable experimental error (scatter in Fig. 5) and the variation of the conversion at vitrification associated with 2 decades in frequency is about 6%, which is below the accuracy of the reaction enthalpy determination (LMDSC).

The use of lower frequencies (<0.01 Hz) is often limited by the desired invariance of the sample during at least one modulation. Especially if the heat flow of the (chemical) transformations needs to be simultaneously and quantitatively measured, this invariance is often restricting the lowest usable frequency. On the higher frequency end, at frequencies above 0.1 Hz, thermal diffusivity effects become important for a film thickness above 100 μm. In this case, the amount of sample necessary for quantitative measurements restricts further extension.

Depending on the reaction chemistry and the rate-controlling mobility (or mobilities), the frequency at which vitrification coincides with the mobility control of the reaction (or individual reaction steps) is expected to be totally different. As mentioned above, some ionic reactions involving smaller scale mobilities might remain unaffected by the main (glass) transition [9], while in free radical polymerisations molecules with very different sizes and mobilities (e.g. monomers and growing polymer chains) are involved in the different reaction steps [4]. Thus, even a further extension of the frequency domain would be desirable in order to distinguish different kinds of (mobility-controlled) reaction mechanisms, but this would require further developments in the measuring devices.

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