

Vitrification and devitrification during the non-isothermal cure of a thermoset

A TOPEM study

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Abstract The processes of vitrification and devitrification that occur in an epoxy resin when it cures non-isothermally with a hardener are studied in terms of their frequency dependence and as a function of the heating rate. A novel modulated DSC technique, TOPEM, has been used which permits the evaluation of the frequency dependence for a single sample in a scan at constant underlying heating rate, thus avoiding errors arising from the composition of the sample. The effects of both frequency and heating rate on vitrification and devitrification are investigated. Some advantages of this technique are observed and discussed.

Keywords Devitrification · Non-isothermal cure · Thermoset · TMDSC · TOPEM · Vitrification

Introduction

When an epoxy resin cures with a hardener, the system changes from a viscous liquid (with an initial degree of conversion $\alpha = 0$) to a highly cross-linked network (with final $\alpha \leq 1$, depending on whether vitrification occurs or not) as the two components react. Initially, the glass transition temperature of the unreacted resin/hardener mixture, T_{g0} , is well below the actual temperature of the mixture, and hence in the early stages of the reaction the rate of cure is controlled by chemical kinetics. As the reaction proceeds and the degree of cross-linking increases, the glass transition temperature of the system, T_g , increases. In an

isothermal cure experiment, if the cure temperature T_c is sufficiently high the system will proceed to a full cure with a final degree of cure $\alpha = 1$ and a final glass transition temperature of $T_{g\infty}$. On the other hand, if $T_c < T_{g\infty}$ vitrification will occur when the glass transition temperature of the reacting system reaches the cure temperature [1, 2].

Analogous effects occur in non-isothermal cure [3, 4]. If the heating rate is sufficiently high the cure temperature will always be higher than the T_g of the system, so that the cross-linking reaction will proceed to its limit, $\alpha = 1$, and the final glass transition temperature will be that of the fully cured thermoset, $T_{g\infty}$. On the other hand, if the curing process takes place at sufficiently slow heating rates, the glass transition temperature of the reacting system can reach the cure temperature. In this case, when T_g reaches the steadily rising cure temperature, T_c , the system changes to a glassy state and vitrifies. In contrast to isothermal cure, though, for non-isothermal cure the vitrification process is followed by devitrification when the cure temperature, T_c , which is continually increasing with time, again exceeds the T_g of the vitrified system, and the cure reaction then proceeds to completion.

In the past, the non-isothermal cure of thermosets has been studied by temperature modulated DSC techniques at a single frequency [5, 6]. Nevertheless, the study of the frequency dependence of vitrification and devitrification by a calorimetric method would be interesting, for comparison with results obtained by other techniques such as dielectric relaxation [7] and torsional braid analysis [8]. This could be done by any of the temperature modulated DSC (TMDSC) techniques, such as Alternating DSC (ADSC), for which the standard mode of operation uses a sinusoidal modulation with a single frequency, but would require a series of separate experiments, together with their corresponding blank runs, at each of the frequencies to be

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investigated, which implies a considerable amount of time because the heating rates need to be very slow. More importantly, these experiments also require a fresh mixture of the resin and cross-linking agent to be made for each frequency, and the almost inevitable small variations in composition of each mixture that can occur would contribute to the experimental error.

The purpose of the present work is to extend some earlier studies related to the isothermal cure of reacting systems [9], to illustrate how the frequency dependence of the vitrification and devitrification processes in non-isothermal cure can be studied by TOPEM[®], a recently developed modulated DSC technique from Mettler-Toledo [10]. In this technique, the periodic sinusoidal modulations of 'standard' TMDSC techniques are deliberately avoided, and instead a series of stochastic temperature pulses (positive and negative, of equal amplitude) are superimposed on the underlying temperature programme. An important advantage of this technique is that only a single sample is required to study a relatively wide range of frequencies, thus avoiding the experimental error which can arise due to the composition of the samples. For the purpose of these experiments the same epoxy-diamine system previously studied in the isothermal cure [9] is used here.

Experimental

Materials

The epoxy resin used was a diglycidyl ether of bisphenol-A (DGEBA), Epon 828 (Shell Chemicals). The cross-linking agent was a polyoxypropylene diamine, Jeffamine D-230 (Huntsman Corporation). Stoichiometric mixtures of resin and diamine were prepared and samples of suitable mass, around 25 mg, were weighed into aluminium crucibles.

Methods

A Mettler-Toledo 823[°] calorimeter with an intracooler was used for the TOPEM experiments. This technique superimposes stochastic temperature pulses on the conventional non-isothermal scan, a positive pulse increasing the temperature by a fixed amount (the temperature amplitude of the pulse) and being followed later by a negative pulse of equal amplitude. The amplitude of these pulses remains constant throughout any single experiment, and the duration between pulses of opposite sign is random, between two values, minimum and maximum, and is called the 'switching time range'. All of these parameters (pulse amplitude, minimum and maximum of the switching time range) are selected by the user. The random temperature pulses result in a stochastically modulated heat flow curve,

and introduce a broad frequency spectrum in the response. The dynamic behaviour is characterised by mathematical functions, according to a 'parameter estimation method' (PEM) which is widely used in other technologies. The correlation of the stochastically modulated heating rate and heat flow curves allows the evaluation of the so-called 'quasi-static heat capacity', C_{p0} , and the separation of the reversing and non-reversing heat flow components, which are familiar quantities from other TMDSC techniques. In order to determine the frequency response, a window with a width selected by the user is shifted along the time scale to cover all the data within the transition of interest, and finally a smoothing of the data is performed. These procedures of windowing and smoothing are analogous to those used in the Fourier Transformation of the data in other TMDSC techniques, such as ADSC.

Non-isothermal scans between 25 and 100–125 °C, depending on the heating rate, were made. The heating rates selected were 0.05, 0.032, 0.025 and 0.019 K min⁻¹, which are sufficiently slow to observe vitrification and devitrification clearly separated. For comparison, a heating rate of 0.1 K min⁻¹ was also selected, this rate being sufficiently fast for no vitrification to occur. For all experiments, a temperature amplitude of the pulses of 0.1 K was selected with a switching time range with minimum and maximum values of 15 and 30 s, respectively.

Results and discussion

Figure 1 shows a typical curve for the heat flow response of the sample in a TOPEM experiment. Due to the very large number of pulses (~8,000) in the total scan, the individual pulses cannot be seen in Fig. 1, only the envelope of the response. From this envelope one can identify the heat flow due to the exothermic reaction as the rising and then falling region in which the amplitude is rather

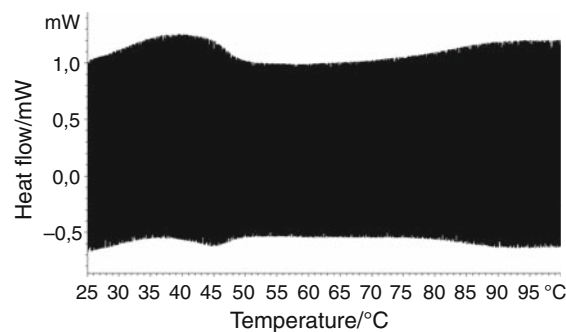


Fig. 1 Heat flow response as a function of temperature for a TOPEM experiment from 25 to 100 °C at 0.025 K min⁻¹ with a temperature amplitude of 0.1 K and switching time range of 15–30 s. The exothermic direction is upwards

constant, up to about 45 °C, followed immediately by the vitrification process, observed as a rather abrupt reduction in the amplitude, corresponding to a reduction of the specific heat capacity. At higher temperatures, there is a much more gradual increase in the amplitude, resulting from the devitrification process, where the specific heat capacity increases again.

From this response, the quasi-static specific heat capacity, c_{p0} , and the total heat flow are calculated. The frequency-dependent specific heat capacities, for various selected frequencies, can then be calculated from the c_{p0} curve. The user selects and adjusts the asymptotes of the vitrification and devitrification processes, and then chooses the frequencies required for the evaluation [10, 11]. This procedure and its results are shown in Fig. 2 for a TOPEM scan from 25 to 100 °C at an underlying rate of 0.025 K min⁻¹ and for the selected frequencies indicated, together with the quasi-static specific heat capacity and the asymptotes used for their evaluation.

The vitrification and devitrification processes are clearly identified in Fig. 2 as the sigmoidal changes in specific heat capacity, the first (negative) change being associated with vitrification and the second (positive) change being associated with devitrification. It can be seen that the change in the heat capacity is greater for vitrification than for the devitrification. This effect occurs because the system is vitrified after the first sigmoidal change in specific heat capacity, and hence is subject to diffusion controlled kinetics for which one might anticipate an essentially frozen-in structure, whereas some curing nevertheless continues to take place after vitrification. The result is that the degree of cure corresponding to the process of devitrification, α_{devit} , is greater than that corresponding to vitrification, α_{vit} . In view of the fact that there is an inverse relationship between the change in the heat capacity and the degree of cure, the implication is that the change in

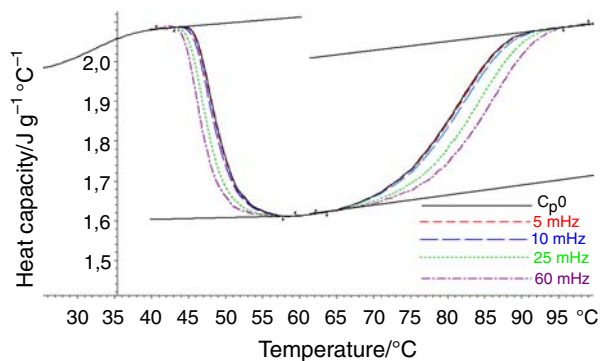


Fig. 2 Specific heat capacity as function of temperature for selected frequencies indicated: quasi-static specific heat capacity c_{p0} (full line), 5 mHz (short dashed line), 10 mHz (long dashed line), 25 mHz (dotted line) and 60 mHz (dash-dotted line)

specific heat capacity during devitrification will be smaller than that during vitrification. In fact, it has been pointed out earlier [3, 5] that the vitrification that occurs in these non-isothermal cures is incomplete.

The very small heating rates that are used here in order to ensure that (at least partial) vitrification occurs result in very long runs, 50 h in the present case. Around 240 h were needed to complete all the experiments for this study, involving four different heating rates. By comparison, with ADSC at least 2400 h would be necessary to include five frequencies and the corresponding blank runs for the same four underlying heating rates. There is also a wider frequency range available with TOPEM than with ADSC. By changing the switching time range [12], it is possible to obtain results for frequencies higher than those available with ADSC, for which the shortest modulation period available is limited by the effects of heat transfer. For example, one of the frequencies selected for the previous study of the isothermal cure [12] was 150 mHz, which corresponds to a period of only 6.7 s, well below the minimum period of about 30 s usually adopted with ADSC.

The vitrification and devitrification times and temperatures can be determined from the two changes of the specific heat capacity for each frequency, such as those shown in Fig. 2. Here, the quasi-static specific heat capacity, c_{p0} , is shown as the full line, while the selected frequency components are indicated by the various non-continuous lines. The vitrification time and temperature for each frequency are calculated from the mid-point between the two asymptotes to the first (downward) step-change in c_p , similar to the analysis of vitrification during isothermal cure [9], while the devitrification times and temperatures are determined analogously from the second (upward) step-change in c_p . Figure 3 shows the heating rate dependence

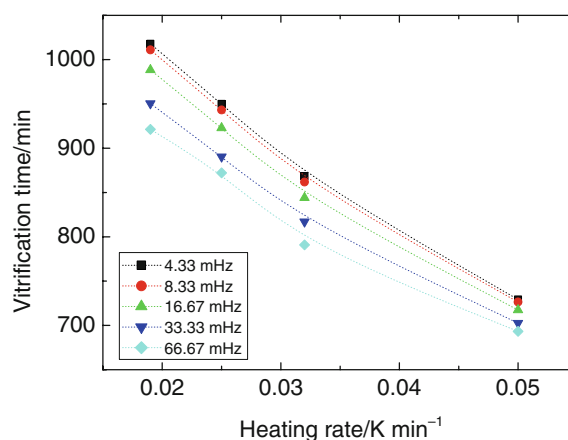


Fig. 3 Vitrification time versus heating rate for TOPEM data, with frequencies from 4.33 to 66.67 mHz, as indicated. Dotted lines are only a guide for the eye

of the vitrification time for each of the selected frequencies shown. It can be seen that the vitrification time decreases with increasing heating rate, and that simultaneously the system vitrifies earlier the higher is the frequency. There is also a non-linear relationship between the vitrification time and the heating rate, similar to the non-linear dependence of vitrification time on the logarithm of frequency observed for the isothermal cure of the same system [9, 12].

In the case of the devitrification process, as illustrated in Fig. 4, the devitrification time also decreases in a non-linear fashion with increasing heating rate, in a way similar to that for the vitrification time. On the other hand, the dependence on frequency is opposite to that for vitrification, in that the devitrification time increases with increasing frequency. The frequency and heating rate dependences of both the vitrification and devitrification times can be well modelled by a theoretical simulation, similar to the isothermal case [12], and this work has been submitted for publication.

With the results such as those presented in Figs. 3, 4 for the vitrification and devitrification times, a Continuous Heating Transformation diagram (CHT), analogous to the Time Temperature Transformation (TTT) diagram in the isothermal case, can be constructed and is shown in Fig. 5. In this figure, the vitrification and devitrification times for only two frequencies are shown, representative of low and high frequencies within the range that can be evaluated: 4.33 and 66.67 mHz. The heating rates for the non-isothermal cure and the glass transition temperature of the fully cured system, determined from a subsequent conventional DSC scan, are also included in the figure. From this figure, one can obtain information about the vitrification and devitrification regions, and how they depend on time, heating rate and frequency.

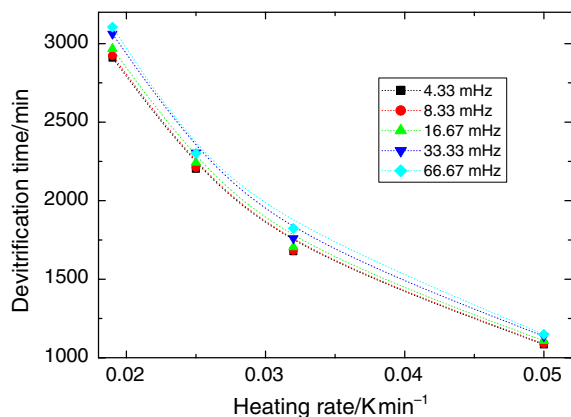


Fig. 4 Devitrification time versus heating rate for TOPEM data, with frequencies from 4.33 to 66.67 mHz, as indicated. *Dotted lines* are only a guide for the eye

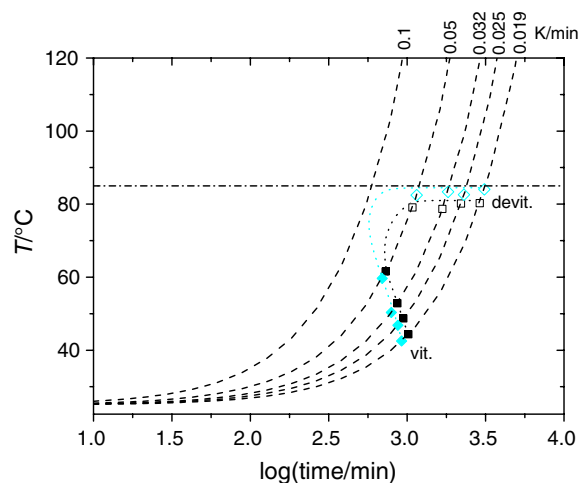


Fig. 5 Continuous heating transformation cure diagram (CHT) for the system. The experimental points indicate vitrification (*filled points*) and devitrification (*unfilled points*) times, the *dashed lines* show the underlying heating rates indicated in the figure in K min^{-1} , and the *dash-dotted line* represents the glass transition temperature of the fully cured system. *Dotted lines* are only a guide for the eye. The frequencies selected are 4.33 mHz (*squares*) and 66.67 mHz (*rhombuses*)

Conclusions

The use of TOPEM in studying the vitrification and devitrification processes during the non-isothermal cure of thermosetting resins presents a significant advantage over other temperature modulated DSC techniques, such as ADSC. A single experiment permits the evaluation of the dynamic vitrification and devitrification times for a selected range of frequencies. The dependence of the vitrification and devitrification times on frequency was studied, and a CHT diagram, useful to characterise the cure schedules of the system, was constructed using only four samples, with a single scan for each one.

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References

- Gillham JK. Formation and properties of network polymeric materials. *Polym Eng Sci.* 1979;19:676–82.
- Montserrat S. Vitrification and further structural relaxation in the isothermal curing of an epoxy resin. *J Appl Polym Sci.* 1992;44: 545–54.
- Van Assche G, Van Hemelrijck A, Rahier H, Van Mele B. Modulated temperature differential scanning calorimetry: cure,

- vitrification, and devitrification of thermosetting systems. *Thermochim Acta*. 1997;305:317–34.
4. Swier S, Van Assche G, Van Hemelrijck A, Rahier H, Verdonck E, Van Mele B. Characterization of reacting polymer systems by temperature-modulated differential scanning calorimetry. *J Therm Anal Calorim*. 1998;54:585–604.
 5. Van Assche G, Van Hemelrijck A, Rahier H, Van Mele B. Modulated differential scanning calorimetry: non-isothermal cure, vitrification, and devitrification of thermosetting systems. *Thermochim Acta*. 1996;286:209–24.
 6. Montserrat S, Martín JG. Non-isothermal curing of a diepoxide-cycloaliphatic diamine system by temperature modulated differential scanning calorimetry. *Thermochim Acta*. 2002;388:343–54.
 7. Montserrat S, Roman F, Colomer P. Vitrification, devitrification, and dielectric relaxations during the non-isothermal curing of a diepoxy-cycloaliphatic diamine. *J Appl Polym Sci*. 2006;102:558–63.
 8. Wisanrakkit G, Gillham JK. Continuous heating transformation (CHT) cure diagram of an aromatic amine/epoxy system at constant heating rates. *J Appl Polym Sci*. 1991;42:2453–63.
 9. Fraga I, Montserrat S, Hutchinson JM. Vitrification during the isothermal cure of thermosets. Part I. An investigation using TOPEM, a new temperature modulated technique. *J Therm Anal Calorim*. 2008;91:687–95.
 10. Schawe JEK, Hütter T, Heitz C, Alig I, Lellinger D. Stochastic temperature modulation: a new technique in temperature-modulated DSC. *Thermochim Acta*. 2006;446:147–55.
 11. Fraga I, Montserrat S, Hutchinson JM. TOPEM, a new modulated DSC technique: application to the glass transition of polymers. *J Therm Anal Calorim*. 2007;87:119–24.
 12. Fraga I, Montserrat S, Hutchinson JM. Vitrification during the isothermal cure of thermosets: comparison of theoretical simulations with temperature-modulated DSC and dielectric analysis. *Macromol Chem Phys*. 2008;209:2003–11.