

KINETIC RESPONSE OF AN EPOXY THERMOSETTING SYSTEM OBSERVED BY TMDSC

A. Toda^{}, T. Arita and M. Hikosaka*

Faculty of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama
Higashi-Hiroshima 739-8521, Japan

Abstract

The response of a chemical reaction to temperature modulation has been examined experimentally in an epoxy thermosetting system. The kinetic response appears in the imaginary part of the complex heat capacity determined by TMDSC. From the imaginary part and the ‘non-reversing’ heat flow of reaction, the activation energy has been determined. The value of the activation energy obtained is in good agreement with the value determined from Kissinger’s plot utilizing the peak temperatures of the exothermic reaction with different heating rates.

Keywords: activation energy, epoxy thermosetting system, TMDSC

Introduction

Temperature modulation introduces a modulation in a transformation process, the rate of which is dependent on temperature. When the time scale of transformation is long enough in comparison with the modulation period, we can think of the steady response of transformation to the modulation in temperature. For transformation processes satisfying the condition of steady response, we have proposed the following expression for apparent heat capacity, $\tilde{\Delta}C e^{-i\alpha}$, obtained with temperature-modulated differential scanning calorimetry (TMDSC) [1–3],

$$\tilde{\Delta}C e^{-i\alpha} \equiv \tilde{\Delta}C' - i\tilde{\Delta}C'' = C_s + \frac{i}{\omega} F_T' \quad (1)$$

where C_s represents the true heat capacity, ω the angular frequency of modulation and F_T' the temperature coefficient of the exo- or endothermic heat flow of transformation [4–7]. In the case of a slow transformation, F_T' becomes independent of the modulation frequency and is determined by the temperature dependence of the transformation rate. If this is the case, the temperature coefficient, F_T' , can be obtained from the imaginary part of the apparent heat capacity as $F_T' = -\omega \tilde{\Delta}C''$.

* Corresponding author, Tel: +81-(0)824-24-6558, Fax: +81-(0)824-24-0757,
E-mail: atoda@hiroshima-u.ac.jp

If we choose small supercooling for crystallization, polymer crystallization can be a slow transformation process [4–7]. Since the driving force of crystallization is the supercooling from the melting point, the growth rate of crystals is modulated by the temperature modulation and hence the temperature coefficient F'_T is determined by the temperature dependence of the growth rate. From the experimental data of TMDSC, i.e. the temperature coefficient, F'_T , determined from $\Delta C''$ and the underlying heat flow of crystallization, \bar{F} , it has been shown that the temperature dependence of the growth rate, G , is obtainable as $d\ln(G/G_0)/dT = F'_T/\bar{F}$, where G_0 represents a reference growth rate.

The subject of the present paper is the application of this argument to the chemical reaction of epoxy cure which occurs in a wide temperature range on heating and can also attain the steady response to temperature modulation. The major application of TMDSC on an epoxy thermosetting system has been the capability of separation of exothermic heat flow due to chemical reaction and the change in heat capacity due to vitrification, which appear in the ‘non-reversing’ and ‘reversing’ heat flows respectively [8]. This application utilizes the relatively weak dependence on temperature of the reaction kinetics, which brings only a small F'_T in the imaginary part of the apparent heat capacity, compared to the true heat capacity in the real part. The contribution is therefore negligible in the ‘reversing’ heat flow and enables the separation. In the following discussion of our approach, we utilize the small change in the imaginary part which represents the modulation of reaction rate caused by temperature modulation.

A general expression for the reaction rate will be given as,

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x) \quad (2)$$

where x represents the degree of conversion, A the frequency factor, E the activation energy, R the gas constant, T the absolute temperature and $f(x)$ accounts for the type of kinetics of conversion [9]. Then, the exo- or endothermic heat flow of conversion, F , and its temperature coefficient, F'_T is given as,

$$F = \Delta H A \exp\left(-\frac{E}{RT}\right) f(x) \quad (3)$$

$$F'_T = \Delta H \frac{E}{RT^2} A \exp\left(-\frac{E}{RT}\right) f(x) \quad (4)$$

where ΔH represents the change in enthalpy on conversion. Therefore, by taking the ratio of F'_T and \bar{F} we will be able to obtain the activation energy from a single TMDSC run without detailed information on the conversion kinetics;

$$E = RT^2 \frac{F'_T}{\bar{F}} = -RT^2 \frac{\omega \tilde{\Delta} C \sin \alpha}{\bar{F}} \quad (5)$$

It is noted that the information on the conversion kinetics is retained in $f(x)$ and is canceled out by taking the ratio. Therefore, this method is not dependent on the

choice of reaction kinetics. In the following, the applicability of this analysis is examined experimentally.

Experimental

A DSC 2920 Module controlled with a Thermal Analyst 2200 (TA Instruments) was used for all measurements. Helium gas with a flow rate of 40 ml min^{-1} was purged through the cell. The reference pan was removed to avoid introducing an uncontrollable parameter of the thermal contact between the reference pan and base plate [10].

The epoxy-amine sample was a bisphenol A-epichlorohydrin resin (Epikote 828, Yuka Shell Epoxy Co., Ltd., CAS No. 25068-38-6) with a stoichiometric amount of aliphatic amine hardener of triethylenetetramine (TETA, Katayama Chemical Industries Co., Ltd.). The total mass of the sample was in the range of 6–13 mg.

The sample in an aluminum pan was initially cooled to -60°C and then heated to 250°C with a heating rate of $0.5\text{--}8 \text{ K min}^{-1}$ in the DSC. The modulation period examined was in the range of 20–80 s with a modulation amplitude of 0.5 K (or 0.2 K for 20 s modulation). Temperature control in these experiments was checked by plotting Lissajous diagrams of the modulated heat flow and the temperature.

Results and discussion

Figure 1 shows the raw data of the ‘total’ and ‘reversing’ heat flow in (a) and the change in the phase angle between the modulation components of temperature and of heat flow in (b). On heating, the exothermic reaction in the range of $20\text{--}170^\circ\text{C}$ can be seen in the heat flow and phase angle.

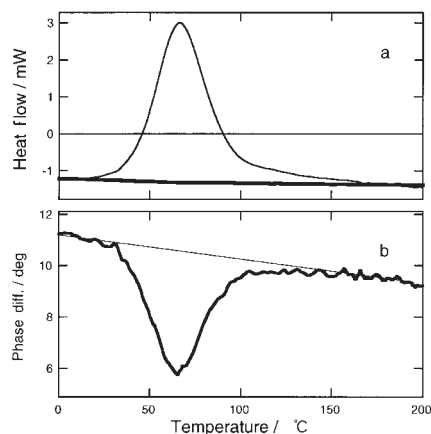


Fig. 1 a – ‘Reversing’ (thick line) and ‘total’ heat flow (thin line) and b – the difference in phase angle between the modulation components of temperature and heat flow plotted vs. temperature for the reaction processes of the epoxy-amine system. The underlying heating rate was 2.0 K min^{-1} and the applied modulation period was 80 s. The sample mass was 12.38 mg

For the application of the present method, the reaction exotherm should not be overlapped with vitrification on cures, because vitrification/devitrification introduces a peak in the phase angle and in the imaginary part of the apparent heat capacity. In Fig. 1a, it is seen that (re-)vitrification does not follow the reaction on heating with the present epoxy-amine system. It has been confirmed experimentally that the vitrification temperature of partially reacted samples was well below the reaction temperature, while the vitrification of the original and the fully-cured samples occurred at around -22 and 119°C , respectively.

In Fig. 1a, the contribution of reaction kinetics to the ‘reversing’ heat flow is negligibly small compared to the contribution of heat capacity, as is frequently the case for chemical reactions because of the weak temperature dependence of chemical reaction compared to the case of e.g. melting of polymer crystals. In this case, we can assume that ‘non-reversing’ heat flow corresponds to the underlying exothermic heat flow of reaction.

In Fig. 1b, the phase angle shows a small negative peak ($\leq 5^{\circ}$) on conversion, owing to the positive temperature dependence of the reaction kinetics. It is known that the phase angle also depends on the heat capacity of sample and the thermal conductivity between the sample pan and the base plate [10], and hence on temperature. Since the change in heat capacity (‘reversing’ heat flow) during the conversion is negligibly small, we can assume a linear baseline for the change in the phase angle as shown in Fig. 1b [11]. Then, we can determine the imaginary part of complex heat capacity from the data shown in Fig. 1. The proposed method expressed in Eq. (5) is based on the assumption that F_T' is independent of modulation frequency. This assumption must be justified by examining the frequency dependence of the imaginary part of the complex heat capacity, $\Delta C''$. Figure 2 is a plot of $\Delta C''$ at the main peak on conversion against modulation period. As shown in Fig. 2, $\Delta C''$ is inversely proportional to the frequency, and hence we can confirm that F_T' in the expression of Eq. (1) must be a constant and is determined from the imaginary part.

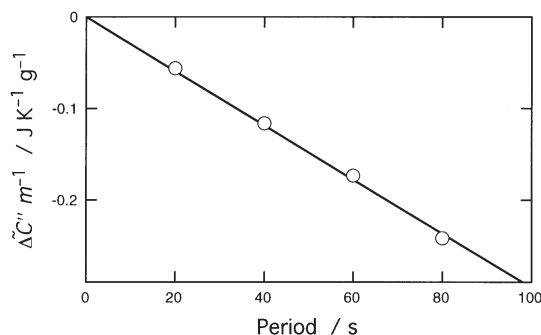


Fig. 2 Frequency dependence of the imaginary part of the apparent heat capacity taken at the main peak of the reaction process in a plot such as shown in Fig. 1. The imaginary part was normalized by sample mass. The underlying heating rate was 2.0 K min^{-1}

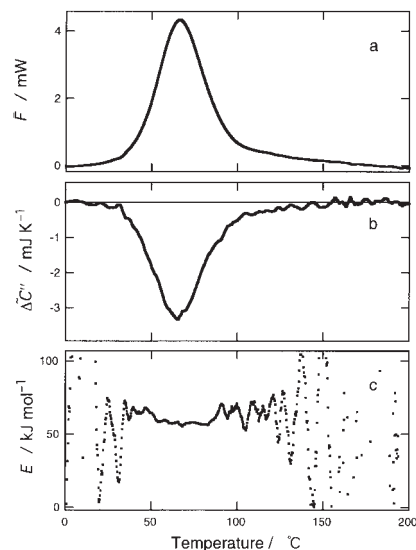


Fig. 3 Plots of a – the ‘non-reversing’ heat flow; b – the imaginary part of the apparent heat capacity and; c – the activation energy determined from Eq. (5) during the conversion process of epoxy-amine. The experimental conditions are the same as given in Fig. 1

With the imaginary part and the exothermic heat flow of conversion corresponding to the ‘non-reversing’ heat flow, we are able to obtain the activation energy from Eq. (5), as shown in Fig. 3. It is seen that the activation energy has a constant value in the temperature range of conversion. The average value of the activation energy was 59 kJ mol^{-1} .

Here it should be noted that there can be several different chemical reactions occurring simultaneously, as in the case of epoxy thermosetting system. In such a case, because the rate constants can be different for different reactions, the activation energy can also be different, and hence the expression of Eq. (5) should be regarded as the apparent activation energy of the overall reaction. On the other hand, the reactions, with different rate constants appear as peaks in separate temperature ranges on heating, and hence the overall activation energy in each temperature range can be a good approximation of the true activation energy of the respective reaction. It is also noted that, in most cases, the reactions of a primary amine and a secondary amine with epoxide occur simultaneously and are manifested by a single DSC peak [9]; this fact justifies the application of the present method to the epoxy-amine thermosetting system.

The most common method for determining the activation energy with DSC is the method [12] utilizing the relationship between the peak temperature of heat flow, T_p , and heating rate, β . The approximate formula is expressed as,

$$\ln(\beta T_p^{-2}) = C_1 - \frac{E}{RT_p} \quad (6)$$

where C_1 is a constant. It is noted that, for the method to be valid, the peak temperature must be isoconversional for different heating rates; the relationship is known to hold empirically for thermosetting systems [9]. From the slope of the plots shown in Fig. 4, the activation energy has been evaluated as 57 kJ mol^{-1} with Eq. (6). The agreement of the values determined from this method and from TMDSC is quite satisfactory.

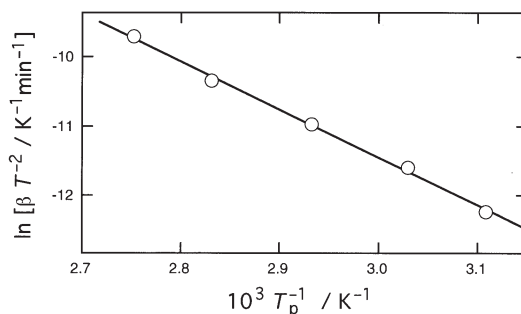


Fig. 4 Plots of the heating rate, β , vs. the peak temperatures of heat flow, T_p , determined by DSC. The plots correspond to the formula of Eq. (6). The heating rate was $0.5\text{--}8 \text{ K min}^{-1}$

Conclusions

We have experimentally confirmed that chemical reaction can be analyzed by TMDSC if the process is slow enough compared to the modulation period. The kinetic response to temperature modulation is determined by the activation energy of reaction, and hence the activation energy can be determined from the kinetic response appearing in the imaginary part of the complex heat capacity and the underlying heat flow of conversion. The results agreed well with the analysis of Kissinger's plot and proved the applicability of TMDSC based on the present analysis method. The method is not dependent on the details of reaction kinetics and will have a wider application in this field.

* * *

The authors are grateful to Mr. Hirai (Murata Manufacturing Co., Ltd.) and Prof. N. Koga (Hiroshima University) for their valuable discussions.

References

- 1 P. S. Gill, S. R. Sauerbrunn and M. Reading, *J. Thermal Anal.*, 40 (1993) 931.
- 2 M. Reading, D. Elliott and V. L. Hill, *J. Thermal Anal.*, 40 (1993) 949.
- 3 M. Reading, A. Luget and R. Wilson, *Thermochim. Acta*, 238 (1994) 295.
- 4 A. Toda, T. Oda, M. Hikosaka and Y. Saruyama, *Polymer*, 38 (1997) 231.
- 5 A. Toda, T. Oda, M. Hikosaka and Y. Saruyama, *Thermochim. Acta*, 293 (1997) 47.
- 6 A. Toda, C. Tomita, M. Hikosaka and Y. Saruyama, *Polymer*, 38 (1997) 2849.

- 7 A. Toda, C. Tomita, M. Hikosaka and Y. Saruyama, *Polymer*, 39 (1998) 1439.
- 8 G. Van Assche, A. Van Hemelrijck, H. Rahier and B. Van Mele, *Thermochim. Acta*, 268 (1995) 121.
- 9 R. B. Prime, in 'Thermal Characterization of Polymeric Materials', E. A. Turi eds, Academic Press, San Diego, 2nd Ed., 1997, Ch. 6.
- 10 I. Hatta and S. Muramatsu, *Jpn. J. Appl. Phys.*, 35 (1996) L858.
- 11 A. Toda, T. Arita, C. Tomita and M. Hikosaka, *Polymer*, in press.
- 12 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.