Characterization of thermal reaction by peak temperature and height of DTG curves

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Abstract

A relationship between the peak temperature and height in derivative thermogravimetry (DTG) curves was explored to seek their specific combination for addressing the uniqueness of a thermal reaction. The functional relationship between the peak temperature and height was closely related to the activation energy and reaction order, but rarely affected by the pre-exponential factor and heating rate. Determining peak temperature and height at a heating rate was enough to characterize a thermal reaction of first-order kinetics or known reaction order, but was insufficient to specify a reaction without knowing the shifting pattern of either peak temperature or peak height with heating rate. The peak temperature and height varied with the heating rate according to the kinetic parameters. The shifting pattern of the peak temperature with the heating rate was related to the activation energy, while that of the peak height was confined by the reaction order together with the activation energy.

Keywords: DTG, Kinetic parameters, Peak height, Peak temperature

A	pre-exponential factor
c	defined as $1/e$
E	activation energy
H_m	peak height
n	reaction order
$P(u_m)$	defined in Eq. (9)
R	gas constant

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T	absolute temperature
T_m	peak temperature
u	defined as E/RT
u_m	defined as E/RT_m
x	weight conversion
x_m	weight conversion at peak temperature

Greek letters

α_1, α_2	constants of Eq. (50)
β	linear heating rate
ζ	$\ln(AE/R\beta) + \ln(n/\phi_a - n + 1) - 5.3305$
ξ	$\ln(AE/R\beta) - 5.3305$
ϕ_a	average value of ϕ_m
ϕ_m	conversion factor at peak temperature
$\Lambda(u)$	defined in Eq. (11)

1. Introduction

Derivative thermogravimetry (DTG) is a powerful tool for characterizing the kinetic parameters of thermal reactions by applying various analytical techniques, due to its uniqueness with respect to the kinetic parameters [1, 2]. This uniqueness may also derive from the peak temperature and height of a DTG curve because of their proven relationships with activation energy [1, 3, 4].

Many investigators have noted that the shifting pattern of the peak temperature with heating rate is related to the activation energy of a reaction [1, 5–7]. Since the peak temperatures for reactions of low activation energies shift more distinctly than those of high activation energies, it may be possible to separate reaction peaks of different activation energies, in the case of independent reactions, by varying the heating rates [8, 9].

However, less attention has been paid to the peak height (rate) as a potential tool for characterizing a reaction. Murray and White [3] formulated the peak height as a function of the activation energy and peak temperature. It was demonstrated that the peak height could be used to estimate the activation energy along with the peak temperature [1, 3, 4]. The peak height increases linearly with increasing activation energy [1, 9] and pre-exponential factor [2]. Although there is a variety of circumstantial evidence that the peak height may be a critical property reflecting the characteristics of a single reaction, little effort has been made to investigate its role in characterizing a specific reaction.

Flynn [9] noted that the peak temperature increases but the peak height decreases with increasing heating rate. Since a relationship is likely to exist between the peak temperature and height, it is necessary to investigate the peak temperature and height in an integrating manner.

The objective of this research was to explore the role of peak temperature and height in characterizing a specific reaction. A relationship between the peak temperature and

height was implemented to seek their specific combination for addressing the uniqueness of a reaction. Since the kinetic parameters are unique with respect to a reaction, it was crucial to link the relationship with the kinetic parameters. Also, the role of the heating rate was investigated in characterizing the variation patterns of the peak properties in terms of representing a specific reaction.

2. Theoretical

For a single kinetic reaction, a DTG curve is mathematically represented by

$$\frac{\mathrm{d}x}{\mathrm{d}T} = \frac{A}{\beta} \exp\left(-\frac{E}{RT} \right)(1-x)^n \tag{1}$$

where x is the weight conversion fraction of a compound at an absolute temperature T(K), A is the pre-exponential factor (min^{-1}), E is the activation energy (J mol^{-1}), n is the reaction order, R is the gas constant (J mol^{-1} K^{-1}), and β is the linear heating rate (°C min^{-1}). Throughout this paper, the heating rate refers to the linear heating rate.

At a peak temperature, differentiating Eq. (1) with respect to temperature yields zero

$$\frac{E}{nRT_m^2(1-x_m)^{n-1}} = \frac{A}{\beta} \exp\left(-\frac{E}{RT_m} \right) \tag{2}$$

where subscript m refers to the maximum rate of weight conversion. The above equation depicts a necessary and sufficient condition for confining peak properties.

3. Kinetic parameters

The peak temperature and height can be utilized to estimate the activation energy and pre-exponential factor of a reaction. Substituting Eq. (2) into Eq. (1) yields the expression for the activation energy [1, 4]

$$E = \frac{nRT_m^2 H_m}{(1-x_m)} \tag{3}$$

where H_m denotes the peak height. Subsequently, the pre-exponential factor is given by

$$A = \frac{H_m \beta \exp\left(\dfrac{E}{RT_m} \right)}{(1-x_m)^n}. \tag{4}$$

Also, the activation energy can be calculated from two peak temperatures at different heating rates as follows

$$E = R\left(\frac{T_{m1} T_{m2}}{T_{m1} - T_{m2}} \right) \ln\left\{ \left(\frac{\beta_1}{\beta_2} \right)\left(\frac{1-x_{m2}}{1-x_{m1}} \right)^{n-1}\left(\frac{T_{m2}}{T_{m1}} \right)^2 \right\} \tag{5}$$

$$\approx R\left(\frac{T_{m1} T_{m2}}{T_{m1} - T_{m2}} \right) \ln\left\{ \left(\frac{\beta_1}{\beta_2} \right)\left(\frac{T_{m2}}{T_{m1}} \right)^2 \right\} \tag{6}$$

where subscripts 1 and 2 refer to different heating rates. The above equation is conceptually equal to the differential method proposed by Flynn and Wall [1] who indicated that x_m would rarely vary with heating rate; thus it is considered to be a constant. Thus, the pre-exponential factor may be derived at either heating rate as follows

$$A = \left(\frac{E\beta}{nR}\right)\frac{(1-x_m)^{1-n}}{T_m^2\exp(-E/RT_m)} \tag{7}$$

4. Conversion factor

The conversion factor at a peak temperature can be mathematically defined as [10]

$$\phi_m = \frac{P(u_m)}{\{\exp(-u_m)/u_m^2\}} \tag{8}$$

where ϕ_m is the conversion factor at a peak temperature, u_m is E/RT_m, and

$$P(u_m) = -\int_\infty^{u_m}\frac{\exp(-u)}{u^2}\,\mathrm{d}u \tag{9}$$

Since there is no exact solution for $P(u)$, many approximate expressions have been developed [1, 10–14]. According to our preliminary tests, the expression below seemed to be one of the most reliable approximations and, thus, was adopted [7]

$$P(u) = \left\{\frac{\exp(-u)}{u}\right\}\Lambda(u): \quad u \geqslant 15 \tag{10}$$

where

$$\Lambda(u) = \frac{1}{u+1} - \frac{1}{(u+1)(u+2)} + \frac{2}{(u+1)(u+2)(u+3)}$$

$$- \frac{4}{(u+1)(u+2)(u+3)(u+4)}$$

$$+ \frac{14}{(u+1)(u+2)(u+3)(u+4)(u+5)}$$

$$- \frac{38}{(u+1)(u+2)(u+3)(u+4)(u+5)(u+6)}$$

$$+ \frac{216}{(u+1)(u+2)(u+3)(u+4)(u+5)(u+6)(u+7)}$$

$$- \frac{600}{(u+1)(u+2)(u+3)(u+4)(u+5)(u+6)(u+7)(u+8)}. \tag{11}$$

Although Eq. (8) depicts the functional relationship between ϕ_m and u_m, it is not easy to develop a tangible relationship between u_m (or peak temperature) and ϕ_m due to the

complicated expression for $P(u_m)$. Instead, an empirical relationship between ϕ_m and u_m was developed below by plotting ϕ_m versus u_m

$$\phi_m \approx -\frac{1.6658}{u_m} + 0.9951 = -\left(\frac{1.6658\,R}{E}\right)T_m + 0.9951: \quad r^2 = 0.9996 \qquad (12)$$

where u_m ranges from 20 to 50, which may be responsible for general cases, and correspondingly, ϕ_m ranges from 0.9163 to 0.9622. The average value of ϕ_m within a confidence interval of 99% was 0.9440 ± 0.0065; r is a correlation coefficient.

From the empirical equation, the partial derivative of ϕ_m with respect to the peak temperature can be expressed as

$$\frac{\partial \phi_m}{\partial T_m} = -\left(\frac{1.6658\,R}{E}\right) \approx 0 \qquad (13)$$

In most cases $(E > 1\ \text{kJ mol}^{-1})$, the derivative may be close to zero suggesting that ϕ_m may vary little with the peak temperature.

In addition, ϕ_m can coalesce various parameters related to x_m which can be derived from Eqs. (1) and (9) as follows

$$n = 1; \quad x_m = 1 - \exp\left\{-\left(\frac{AE}{R\beta}\right)P(u_m)\right\} \qquad (14)$$

$$n \neq 1; \quad x_m = 1 - \left\{1 + (n-1)\left(\frac{AE}{R\beta}\right)P(u_m)\right\}^{1/(1-n)} \qquad (15)$$

The above equations reflect the intricate relationships of x_m with various parameters. However, Eqs. (2) and (8) yield, respectively

$$\frac{AE}{\beta R} = \frac{u_m^2}{n(1 - x_m)^{n-1}\exp(-u_m)} \qquad (16)$$

$$P(u_m) = \phi_m\left\{\frac{\exp(-u_m)}{u_m^2}\right\}. \qquad (17)$$

Substituting Eqs. (16) and (17) into Eqs.(14) and (15) leads to

$$n = 1; \quad x_m = 1 - \exp(-\phi_m) \qquad (18)$$

$$\approx 1 - \exp(-\phi_a) \qquad (19)$$

$$n \neq 1; \quad x_m = 1 - \left\{1 - \left(\frac{n-1}{n}\right)\phi_m\right\}^{1/(n-1)} \qquad (20)$$

$$\approx 1 - \left\{1 - \left(\frac{n-1}{n}\right)\phi_a\right\}^{1/(n-1)} \qquad (21)$$

where ϕ_a is the average value of ϕ_m and was previously determined to be 0.9440. As already noted, x_m can be accounted for by a constant which is only dependent on reaction order, since ϕ_m varies little with peak temperature.

5. Peak temperature

According to Eq. (2), the functional relationships between the heating rate and peak temperature are described as

$$n=1; \quad \beta = \left(\frac{AR}{E}\right) T_m^2 \exp\left(-\frac{E}{RT_m}\right) \tag{22}$$

$$n \neq 1; \quad \beta = \left(\frac{nAR}{E}\right)(1-x_m)^{n-1} T_m^2 \exp\left(-\frac{E}{RT_m}\right) \tag{23}$$

In the case of first-order kinetics, the relationship is also expressed by relating Eq. (17) to Eq. (22)

$$\beta = \left(\frac{AE}{R}\right)\frac{P(u_m)}{\phi_m}, \tag{24}$$

whilst Eq. (23) is modified by relating Eqs. (17) and (20)

$$\beta = \left(\frac{AE}{R}\right)\left(\frac{n}{\phi_m}-n-1\right)P(u_m). \tag{25}$$

It is not likely that an exact expression for peak temperature can be derived from the above equations. By trial-and-error calculation, peak temperatures at other heating rates can be extrapolated, once the kinetic parameters are determined. The equation may be expressed by

$$T_m = 2\sqrt{\left(\frac{\beta R}{AE}\right)\frac{\exp(E/RT_m)}{n(1-x_m)^{n-1}}}. \tag{26}$$

The approximation calculation may be repeated until a target tolerance is met. However, taking natural logarithms of Eqs. (24) and (25) may yield

$$n=1; \quad \ln\beta = \ln\left(\frac{AE}{R}\right) - \ln\phi_m + \ln P(u_m) \tag{27}$$

$$n \neq 1; \quad \ln\beta = \ln\left(\frac{AE}{R}\right) + \ln\left(\frac{n}{\phi_m}-n+1\right) + \ln P(u_m). \tag{28}$$

Ozawa [7] approximated the above relationships by introducing two approximation schemes: (1) Doyle's approximation [14] where $\ln P(u) \simeq -5.3305 - 1.0516 (E/RT)$, and (2) Kissinger's approximation [5,15] where $x_m = 1 - 1/e$ at $n=1$ and $x_m = 1 - n^{1/(1-n)}$ at $n \neq 1$. Thus, the peak temperature is expressed as a function of heating rate as follows

$$T_m = \left(\frac{1.0516}{R}\right)\left(\frac{E}{\xi}\right) \tag{29}$$

where

$$\xi = \ln\left(\frac{AE}{R\beta}\right) - 5.3305.$$

Partial derivatives of the above equation were taken with respect to the heating rate and kinetic parameters, in order to investigate their effects on the peak temperature. The derivatives are summarized as

$$\frac{\partial T_m}{\partial \beta} = \left(\frac{1.0516}{R\beta}\right)\left(\frac{E}{\xi^2}\right) > 0; \tag{30}$$

$$\frac{\partial T_m}{\partial E} = \left(\frac{1.0516}{R}\right)\left(\frac{1}{\xi} - \frac{1}{\xi^2}\right) > 0; \tag{31}$$

$$\frac{\partial T_m}{\partial A} = -\left(\frac{1.0516}{R\beta}\right)\left(\frac{E}{A\xi^2}\right) < 0 \approx 0 \tag{32}$$

where ξ may be greater than unity except for cases of extremely high heating rates ($\xi > 1$ at $\beta = 1$; $AE > 0.562$ kJ mol^{-1} min^{-1}). Thus, Eq. (31) may be greater than zero for most cases. However, peak temperature may vary little with pre-exponential factor (Eq. (32)), since the pre-exponential factor in a general case is usually much greater than the activation energy. In order to investigate the effect of the reaction order, Eq. (28) was used instead of Eq. (29) after adopting Doyle's approximation. Also, ϕ_m was considered to be independent of the peak temperature (Eq. (13)). After incorporating Doyle's approximation and ϕ_a into Eq. (28), its partial differentiation with respect to the reaction order gives

$$\frac{\partial T_m}{\partial n} = -\left(\frac{1.0516}{R}\right)\left(\frac{E}{\zeta^2}\right)\left\{\frac{1 - \phi_a}{n(1 - \phi_a) + \phi_a}\right\} < 0 \tag{33}$$

where

$$\zeta = \ln\left(\frac{AE}{R\beta}\right) + \ln\left(\frac{n}{\phi_a} - n + 1\right) - 5.3305.$$

In summary, the peak temperature increases with increasing heating rate and activation energy, but decreases with increasing reaction order. In addition, the peak temperature varies little with the pre-exponential factor.

6. Peak height

According to Eqs. (3), (18) and (20), the peak height can be defined as

$$n = 1; \quad H_m = \frac{E \exp(-\phi_m)}{RT_m^2}; \tag{34}$$

$$n \neq 1; \quad H_m = \frac{E\left\{1 - \left(\frac{n-1}{n}\right)\phi_m\right\}^{1/(n-1)}}{nRT_m^2}. \tag{35}$$

It may be justifiable to use ϕ_a for ϕ_m, as already mentioned. The properness of using the ϕ_a will be discussed in the following section. Thus, the peak height can be

approximated to be

$$n = 1; \quad H_m \approx \frac{E\exp(-\phi_a)}{RT_m^2}; \tag{36}$$

$$n \neq 1; \quad H_m \approx \frac{E\left\{1 - \left(\dfrac{n-1}{n}\right)\phi_a\right\}^{1/(n-1)}}{nRT_m^2}. \tag{37}$$

If Kissinger's approximation, however, is used, the peak height might be described by

$$n = 1; \quad H_m \approx \frac{E}{eRT_m^2}; \tag{38}$$

$$n \neq 1; \quad H_m \approx \frac{En^{n/(1-n)}}{RT_m^2}. \tag{39}$$

According to Eqs. (38) and (39), partial differentiations of the peak height with the heating rate and kinetic parameters are given by

$$\frac{\partial H_m}{\partial \beta} = -\left(\frac{1.8085cR}{\beta}\right)\left(\frac{\xi}{E}\right) < 0; \tag{40}$$

$$\frac{\partial H_m}{\partial E} = cR\left\{1.8085\left(\frac{\xi}{E^2}\right) - 0.9043\left(\frac{\xi}{E}\right)^2\right\} < 0; \tag{41}$$

$$\frac{\partial H_m}{\partial A} = (1.8085cR)\left(\frac{\xi}{AE}\right) > 0 \approx 0 \tag{42}$$

where $c = 1/e$ at $n = 1$, and $c = n^{n/(1-n)}$ at $n \neq 1$. However, the partial derivative with the reaction order is given by

$$\frac{\partial H_m}{\partial n} = -\left(\frac{n^{n/(1-n)}}{R}\right)\left(\frac{E}{T_m^2}\right)\left\{\frac{1-n+\ln n}{(1-n)^2} - \left(\frac{2}{T_m}\right)\left(\frac{\partial T_m}{\partial n}\right)\right\}. \tag{43}$$

Substituting the expression for T_m (Eq. (29)) and $\partial T_m/\partial n$ (Eq. (33)) into the above equation yields

$$\frac{\partial H_m}{\partial n} = \left(\frac{n^{n/(-n)}R}{1.1059}\right)\left(\frac{\zeta^2}{E}\right)\left[\left(\frac{2}{\zeta}\right)\left\{\frac{1-\phi_m}{n(1-\phi_m)+\phi_m}\right\} + \frac{1-n+\ln n}{(1-n)^2}\right] < 0 \tag{44}$$

where

$$\frac{2}{\zeta}\left\{\frac{1-\phi_m}{n(1-\phi_m)+\phi_m}\right\} \approx \frac{2}{\zeta}\left(\frac{1-\phi_a}{n(1-\phi_a)+\phi_a}\right) = \frac{2}{\zeta(n+16.9)} \approx 0;$$

$$-3.6 < \frac{1-n+\ln n}{(1-n)^2} < -0.00960: \quad 0.01 < n < 100.$$

In summary, the peak height decreases with increasing heating rate, activation energy and reaction order, but varies little with pre-exponential factor.

7. Discussion

It is first necessary to investigate whether or not a specific DTG curve can be represented by a unique combination of the peak temperature and height. Eqs. (3) and (4) depict the functional relationships of the peak temperature and height with the kinetic parameters. There are two equations with three independent variables: the activation energy, pre-exponential factor, and reaction order. Thus, a combination of the peak temperature and height at a single heating rate may not specify a unique reaction except for cases of first-order kinetics or known reaction orders. The variation pattern of the peak properties with heating rate may provide, however, the third equation. The dynamic features of the peak properties, hence, should be considered to investigate their relationships with the kinetic parameters.

In addition to the peak temperature and height, x_m seems to be another property necessary to derive the kinetic parameters from Eqs. (3)–(7). However, x_m is a dependent variable of the activation energy, pre-exponential factor, and peak temperature (Eqs. (14) and (15)). Thus, the peak temperature and height are only required theoretically. The intricate expression for x_m (Eqs. (14) and (15)), however, may make it impossible to derive the activation energy and pre-exponential factor analytically, thereby necessitating a TGA curve for obtaining x_m. It is worth noting that x_m is relatively constant against heating rate, activation energy and pre-exponential factor [1, 5, 7, 15]. Here, ϕ_a ($= 0.9440$) was used for ϕ_m in Eqs. (18) and (20), although other researchers [1, 5, 7, 15] have made ϕ_m unity.

As example cases, three elastomers, natural rubber (NR), polybutadiene rubber (BR), and styrene–butadiene rubber (SBR), were considered. The thermal decompositions may be accounted for by first-order kinetics, except for NR, and their kinetic parameters are listed in Table 1. Theoretical DTG curves of three binary elastomers (NR/SBR, SBR/BR, and NR/BR) of equal weight ratios are simulated at three linear heating rates (Figs. 1, 2, and 3), based on the assumption of first-order kinetics and independent reactions. Although Yang et al. [16] reported a second-order decomposition reaction for NR, first-order kinetics were adopted to address the effect of activation energy and pre-exponential factor on the geometric features of a DTG curve in a consistent manner.

The kinetic parameters of these elastomers were calculated by the two methods described in the Section 2. The first method (Eqs. (3) and (4)) required the peak

Table 1
Activation energies and pre-exponential factors of three elastomers [16]

Elastomer	Activation energy (kJ mol^{-1})	Pre-exponential factor (min^{-1})
NR[a]	207.0	3.13×10^{16}
BR[b]	215.0	6.32×10^{14}
SBR[c]	147.7	3.49×10^{10}

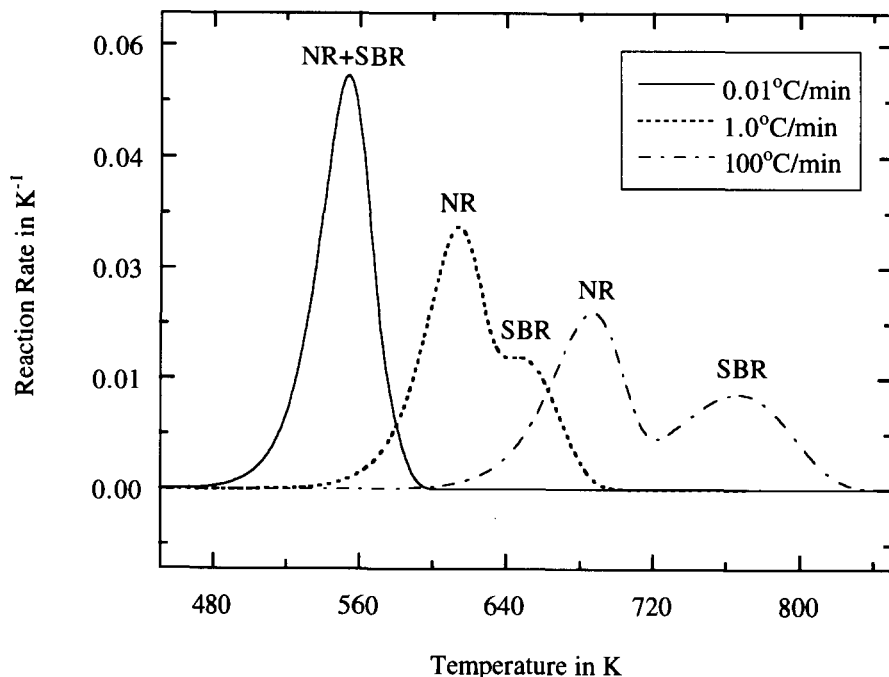[a] Natural rubber.
[b] Polybutadiene rubber.
[c] Styrene-Butadiene rubber.

Fig. 1. DTG curves for the binary elastomer of natural rubber and styrenen-butadiene rubber at three heating rates of 0.01, 1.0 and 100°C min^{-1}.

temperature, peak height and x_m at a certain heating rate, but the overlapping peaks made it difficult to estimate separately the peak heights of individual elastomers. Hence, the second method (Eqs. (5) and (7)) using two peak temperatures was adopted instead; however, applying this method should be carefully considered for some cases of complex reactions because the disturbance of peak temperatures arising from significant overlapping is problematic [9]. The NR/SBR elastomer may demonstrate no disturbance of peak temperatures at heating rates greater than 100°C min^{-1}, whereas the SBR/BR elastomer demonstrates no disturbance at heating rates lower than 0.002°C min^{-1}. No disturbance was observed for the peak temperatures of NR/BR elastomer at any heating rates. Neither method, however, can be highly recommended to estimate the kinetic parameters in the complex reactions because in both there are difficulties in identifying visually the extent of disturbance of peak temperature or height without understanding the reaction kinetics. Recently, Kim et al. [17] developed a separation technique for overlapping peaks. After appropriate separation practices, these methods may be applicable for cases of complex reactions.

Although both methods mentioned above may provide exact kinetic parameters in cases of single reactions, the methods may be easily subject to experimental errors during the course of determining the peak properties. Many investigators have pointed out that peak temperature is known to be one of the major experimental problems for
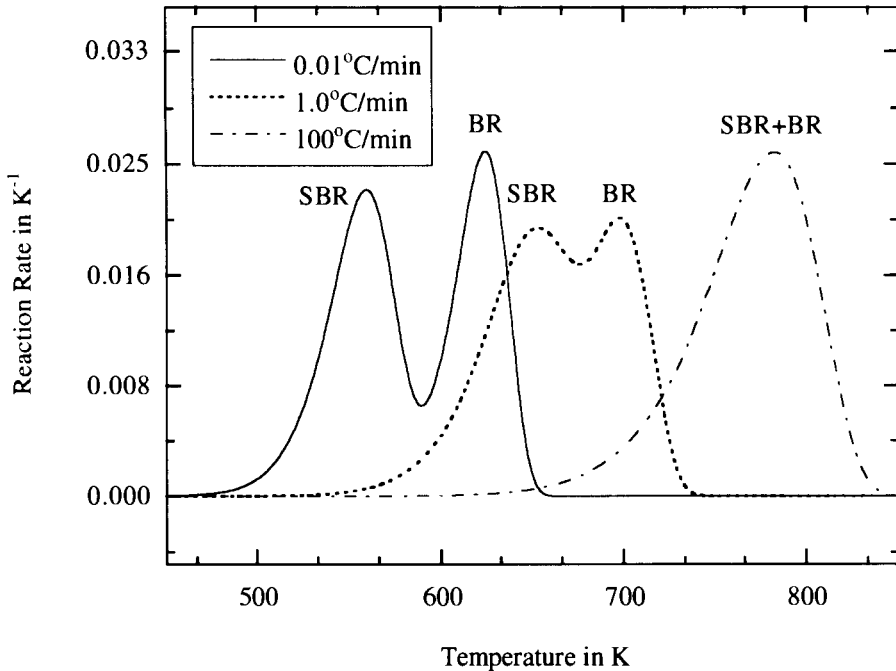
Fig. 2. DTG curves for the binary elastomer of polybutadiene rubber and styrenen-butadiene rubber at three heating rates of 0.01, 1.0 and 100°C min^{-1}.

TGA and DTG [2, 18, 19, 20]. In addition, application of the methods is limited to cases of known reaction orders.

As already noted, a unique combination of the peak temperature and height may characterize a specific reaction of first-order kinetics or known reaction order, but it is uncertain what combination can represent a specific reaction. Thus, it is critical to develop a relationship between the peak temperature and height via the kinetic parameters. Fig. 4 depicts a linear relationship between the peak height and $1/T_m^2$ ($r^2 = 1.0000$) from Eq. (34). The linearity was expected because ϕ_m varies little with peak temperature (Eq. (13)). Two equations were proposed to represent the linear relationship, as shown in Eqs. (36) and (38). The two equations were compared to determine which one provides better accuracy in the case of estimating the activation energy. Eq. (36) gave much better accuracy in determining the activation energies of the elastomers. The deviations from the real activation energies when adopting Kissinger's approximation (Eq. (38)) were 4.8, 5.2, and 7.0% for NR, BR, and SBR, respectively, whereas the deviations when using ϕ_a (Eq. (36)) were 0.9, 0.5, and 1.2%, respectively.

The linear relationships suggest that the ratios of the peak heights to the inverse squares of peak temperature, which are accounted for by the slopes of the linear lines, may be constant regardless of the heating rate and pre-exponential factor (Eqs. (36) and (37)). The ratio is linearly proportional to the activation energy, but inversely propor-
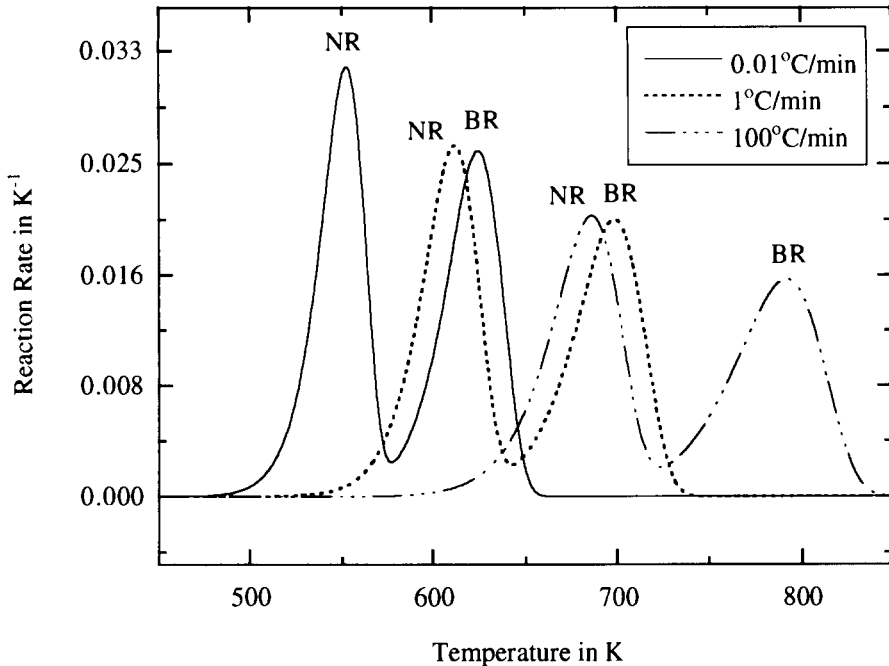
Fig. 3. DTG curves for the binary elastomer of natural rubber and polybutadiene rubber at three heating rates of 0.01, 1.0 and 100°C min^{-1}.

tional to the reaction order. Thus, reactions of high activation energies might exhibit higher peak heights than those of low activation energies, provided that their peak temperatures are identical [2]; whereas, if their pre-exponential factors are equivalent, the opposite pattern may be observed because the peak temperature increases with increasing activation energies (Eq. (31)).

The activation energy may characterize the functional relationship between the peak temperature and height, but the peak properties cannot be finalized without knowing the pre-exponential factor. A high pre-exponential factor may accompany a low peak temperature (Eq. (32)) with a high peak height (Eq. (42)), in accordance with the functional relationship between the peak temperature and height.

Together with the activation energy, the reaction order plays an important role in determining the relationship between the peak temperature and height; however, the activation energy and reaction order counteract each other (Eq. (37)).

Although the peak temperature and height are specific properties representing the characteristics of a reaction, their quantities can be varied with the heating rate, unlike the kinetic parameters. This interesting feature leads to the following speculations: (1) the shifting patterns may be unique with respect to the heating rate and (2) it may be possible to separate overlapping peaks in complex reactions by varying heating rates.
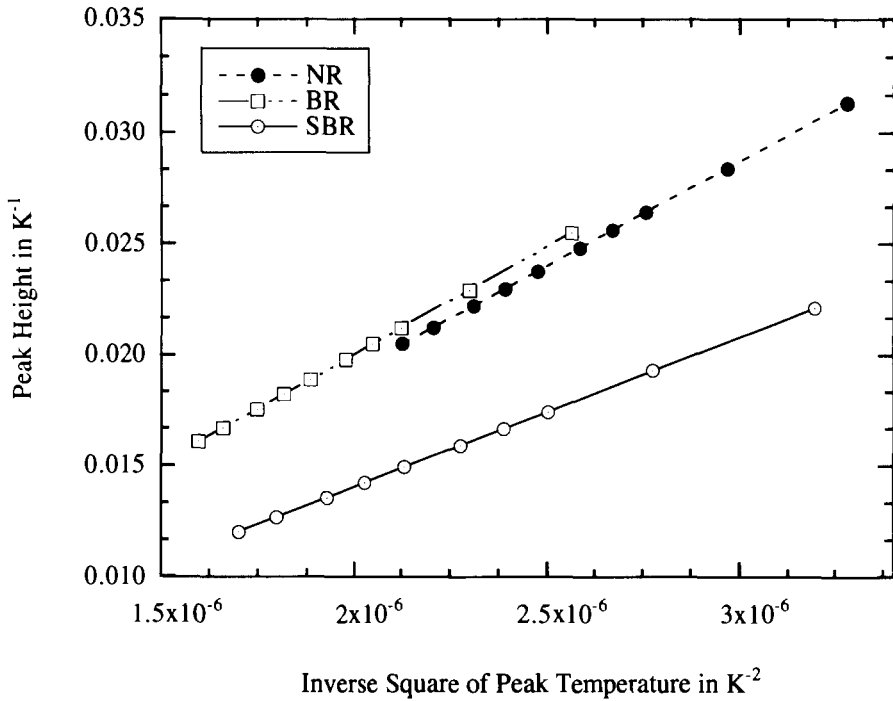
Fig. 4. Functional relationships between peak temperature and peak height for three elastomers.

First, it is necessary to extrapolate the peak temperature and heights accurately to other heating rates. The trial-and-error method may yield accurate peak temperatures with respect to a target tolerance. In practice, the equation used for the trial-and-error calculation (Eq. (26)) was modified as follows

$$n = 1; \quad u_m = \ln\left(\frac{AE}{\beta R u_m^2}\right) \tag{45}$$

$$n \neq 1; \quad u_m = \ln\left[\frac{AEn\{1 - ((n-1)/n)\phi_m\}}{\beta R u_m^2}\right]. \tag{46}$$

The above equations were repeated to meet a tolerance of 10^{-7} for u_m and their convergence was generally accomplished in 8 or 9 iterations. Then, the corresponding peak temperatures were calculated. Subsequently, the peak height can be derived from the relationships with the peak temperature (Eqs. (34) and (35)).

The trial-and-error calculation, however, may rarely suggest any tangible relationship between peak temperature and heating rate. Fig. 5 indicates a linear relationship between the natural logarithm of the heating rate and the inverse peak temperature ($r^2 = 1.0000$), which was approximated by the Ozawa plot [6, 7]. The relationship was also used to extrapolate the peak temperature at other heating rates, but deviations increase as the reaction order increases (Fig. 6).
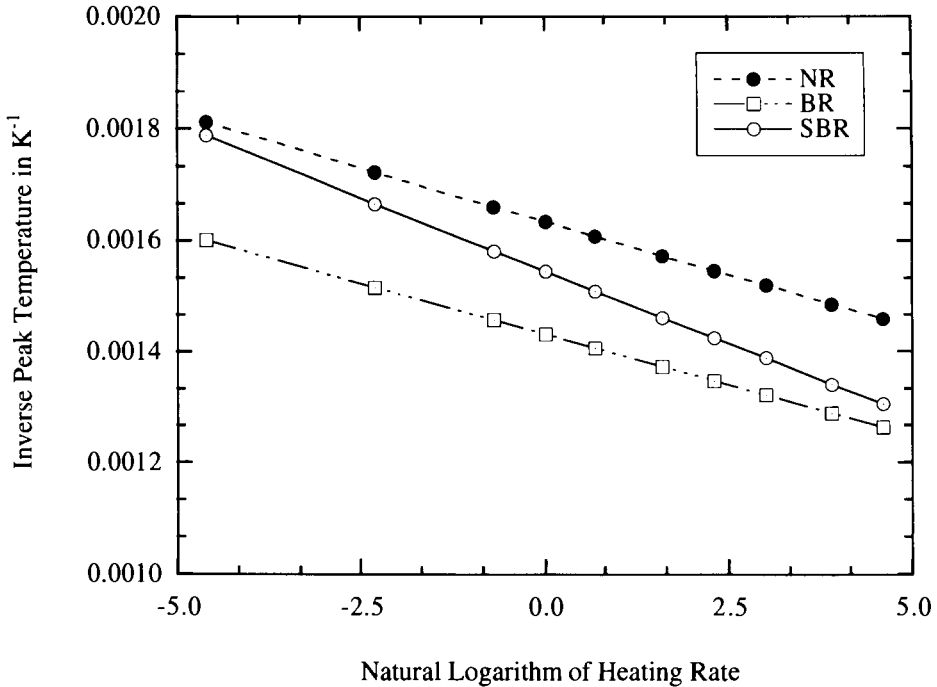
Fig. 5. Functional relationships between heating rate and peak temperature for three elastomers.

The Ozawa method was revised to take into account the role of the reaction order by eliminating Kissinger's approximation. The revised equations are described by:

$$n = 1; \quad \ln \beta = \ln\left(\frac{AE}{R}\right) - \ln \phi_a - 5.3305 - 1.0516\left(\frac{E}{RT_m}\right) \tag{47}$$

$$n \neq 1; \quad \ln \beta = \ln\left(\frac{AE}{R}\right) + \ln\left(\frac{n}{\phi_a} - n + 1\right) - 5.3305 - 1.0516\left(\frac{E}{RT_m}\right) \tag{48}$$

where ϕ_a (0.9440) was used for ϕ_m in Eqs. (27) and (28). As shown in Fig. 5, the linear relationships between the natural logarithms of the heating rates and the inverse peak temperatures may justify the use of ϕ_a. Although the revised method improved the accuracies considerably in predicting the peak temperature at a certain heating rate (Fig. 7), the trial-and-error method may still be preferred because of better accuracies.

Although the Ozawa and revised methods only represent the approximated express-ions, they were of great use in understanding the effect of the heating rate on the peak temperature and height. It was found that the peak temperature increased with increasing heating rate (Eq. (30)), but the peak height decreased (Eq. (40)).

In order to clarify the role of the kinetic parameters, the partial derivative of the inverse peak temperature with respect to $\ln \beta$ was introduced by

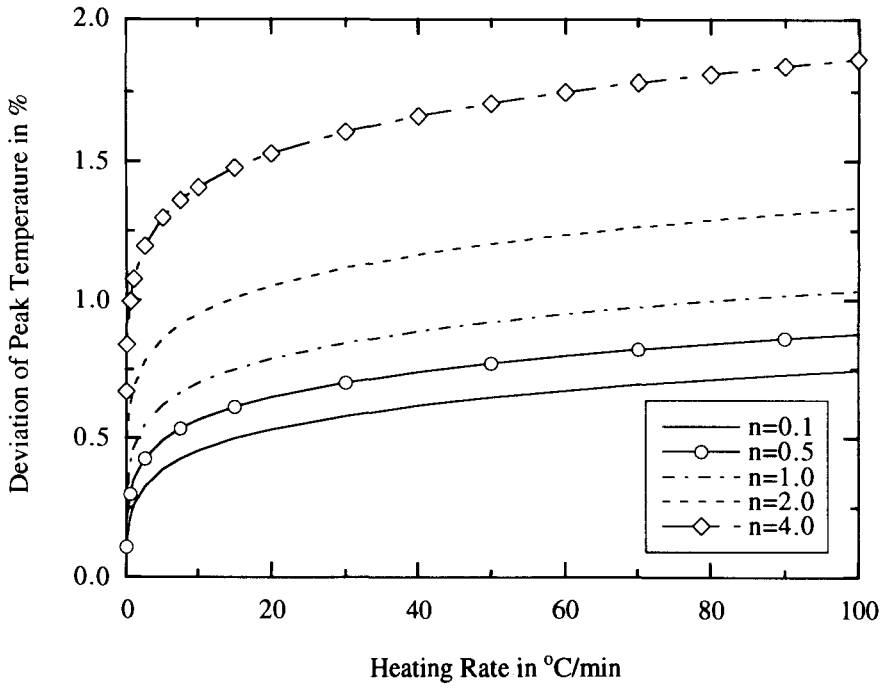$$\frac{\partial(1/T_m)}{\partial \ln \beta} = -\left(\frac{R}{1.0516E}\right). \tag{49}$$

Fig. 6. Deviations of peak temperature of SBR at various reaction orders calculated by Ozawa approximation.
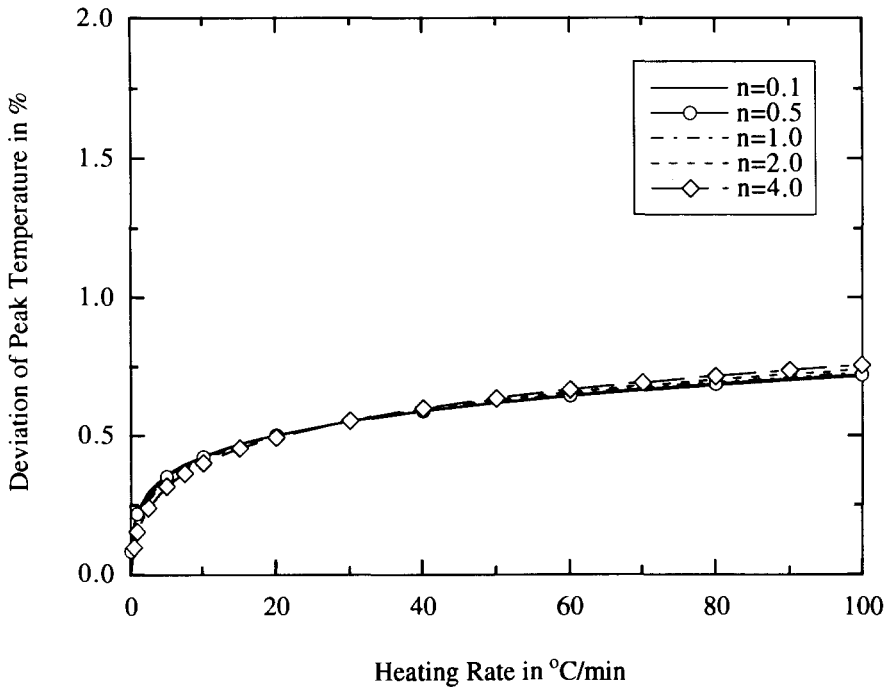

Fig. 7. Deviations of peak temperature of SBR at various reaction orders calculated by the revised equations.

The above derivative indicates that reactions of lower activation energies may yield larger shifts of peak temperatures with the heating rate [9], whereas pre-exponential factors may rarely have an effect. Thus, varying the heating rate may separate overlapping peaks ascribed to compounds having distinctly different activation energies (Figs. 1 and 2). However, peak temperatures may shift evenly by varying the heating rate for compounds having different pre-exponential factors but similar activation energies (Fig. 3). It was manifest, hence, that the peaks of the NR/SBR elastomer could be separated at high heating rates, whereas those of the BR/SBR elastomer could be separated at low heating rates. The NR/BR elastomer exhibited no overlapping at any heating rates.

As shown in Eq. (40), the peak height may decrease with increasing heating rate, in harmony with the variation of the peak temperature. The relationship between the peak height and heating rate can be developed via the peak temperature. Substituting the revised equations (Eqs. (47) and (48)) into Eqs. (36) and (37), respectively, yields

$$H_m^{1/2} = -\alpha_1 \ln \beta + \alpha_2 \tag{50}$$

where, for $n = 1$

$$\alpha_1 = 0.9506 \sqrt{\frac{R \exp(-\phi_a)}{E}}$$

$$\alpha_2 = 0.9752 \left\{ \ln\left(\frac{AE}{R}\right) - \ln \phi_a - 5.3305 \right\} \sqrt{\frac{R}{E}}$$

and for $n \neq 1$;

$$\alpha_1 = 0.9506 \left\{ 1 - \left(\frac{n-1}{n}\right) \phi_a \right\}^{1/2(n-1)} + \sqrt{\frac{R}{nE}}$$

$$\alpha_2 = 0.9752 \left\{ \ln\left(\frac{AE}{R}\right) - \left\{ 1 - \left(\frac{n-1}{n}\right) \phi_a \right\}^{1/(n-1)} - 5.3305 \right\} \sqrt{\frac{R}{E}}.$$

Fig. 8 supports the linear relationships between the square root of the peak height and the natural logarithm of the heating rate for the example cases ($r^2 = 1.0000$). The slopes of the linear lines are inversely proportional to the activation energy, suggesting that the peak heights of reactions of low activation energies decrease more distinctly with increasing heating rate. Also, the peak height is proportional to the pre-exponential factor of a reaction, provided that other conditions are constant.

The peak temperature may rarely be varied with the reaction order (Fig. 9). In addition, the partial differentiation of the inverse peak temperature with the reaction order is expressed by

$$\frac{\partial(1/T_m)}{\partial n} = \left\{ \frac{1 - \phi_m}{n(1 - \phi_m) + \phi_m} \right\} \left(\frac{R}{1.0516E}\right) \tag{51}$$

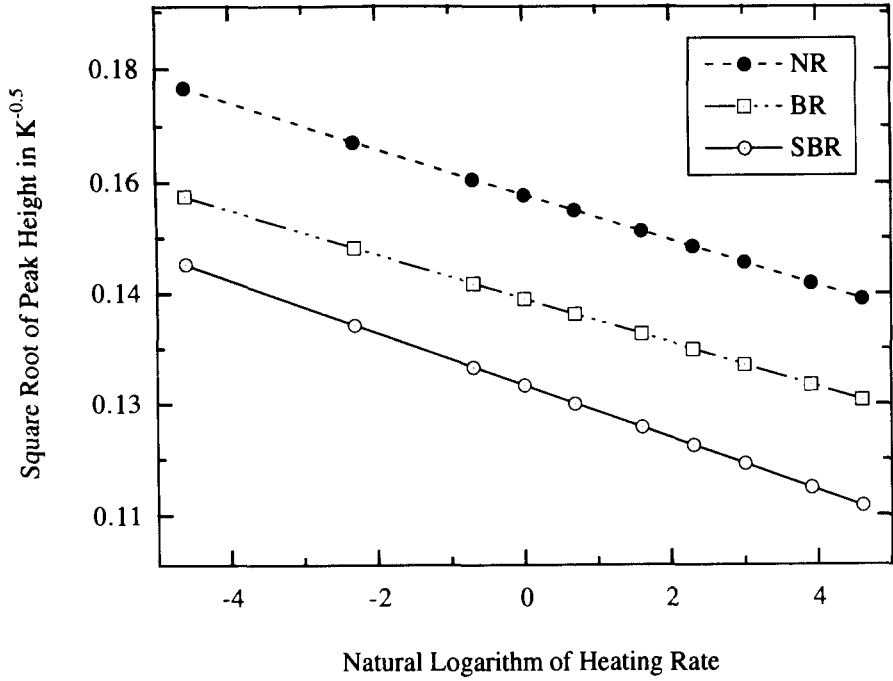$$\approx \left(\frac{1}{n + 16.8571}\right) \left(\frac{R}{1.0516E}\right) \approx 0. \tag{52}$$

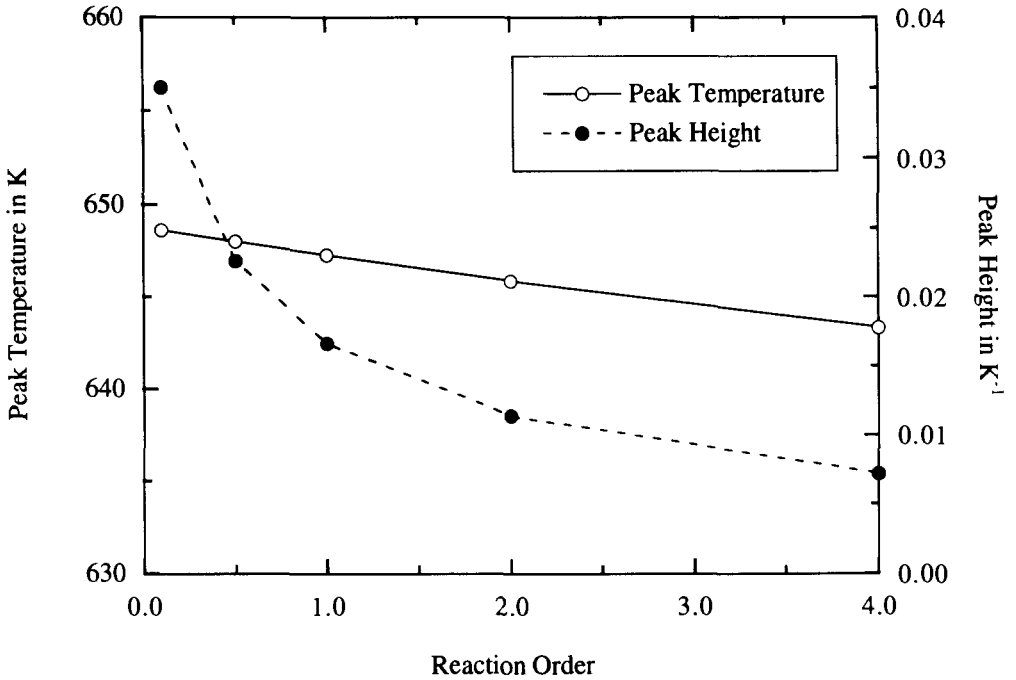Fig. 8. Functional relationships between heating rate and peak height for three elastomers.

Fig. 9. Variation of peak temperature and peak height with reaction order at a heating rate of $1°C\,min^{-1}$ for SBR.

Since the above derivative may be close to zero for most cases ($E > 5 \, \mathrm{kJ \, mol^{-1}}$), it can be said that the peak temperature varies little with the reaction order. Thus, it was expected that the shifting pattern of the peak temperature with the heating rate is rarely affected by the reaction order [21].

However, the peak heights decrease with increasing reaction order [8, 21], provided that the activation energy and pre-exponential factor are constant, because the term including the reaction order, $n^{n/(1-n)}$, in Eq. (39) decreases exponentially from unity as the reaction order increases. Also, α_3, the slope of the straight line representing $\ln\beta$ versus $H_m^{1/2}$ (Eq. (50)), decreases with increasing reaction order, suggesting that the peak heights for reactions with high reaction orders may decrease less distinctly. This feature implies that the variation pattern of the peak height with the heating rate may be a distinguishable characteristic for identifying a reaction order.

In the case of nth order kinetics, it is necessary to obtain the shifting pattern of either peak temperature or peak height, or both, with heating rate so as to estimate reaction order, together with activation energy and pre-exponential factor. There may be various ways to determine the kinetic parameters by means of utilizing the shifting pattern of peak properties. In this study, the revised equation was used to estimate the activation energies from the slope of the straight line plotting $\ln\beta$ versus $1/T_m$. After estimating the activation energies, the reaction orders may be derived from Eq. (20) by using trial-and-error calculations [22], or substituting the values of activation energy into Eq. (3) may provide the reaction orders directly. Subsequently, the pre-exponential factor may be obtained from Eq. (4).

The above scheme, however, carries potential errors arising from using ϕ_a rather than ϕ_m, as shown in Eq. (48). In order to check its reliability, theoretical DTG curves of three elastomers were first simulated at six heating rates (0.1, 1, 5, 10, 20, and 50°C min^{-1}) for each presumed reaction order ($n = 0.1, 0.5, 2$ and 4). The peak properties (T_m, H_m and x_m) at the six heating rates were obtained from the theoretical DTG curves and were used to estimate the kinetic parameters using Eqs. (3), (4), and (48). Table 2 summarizes the calculated activation energies and reaction orders of the example cases, which duplicate well the originally assigned values (Table 1) except those of SBR. The high deviations of SBR seem to be attributed to relatively low u_m values which may be close to the limit for reliable regions for Doyle's approximation [23].

Table 2
Calculated activation energies and reaction orders of three elastomers

Reaction order	NR		BR		SBR	
	E (kJ mol^{-1})	Reaction order [a]	E (kJ mol^{-1})	Reaction order [a]	E (kJ mol^{-1})	Reaction order [a]
0.1	206.4	0.1	215.4	0.10	150.6	0.07
0.5	206.5	0.5	215.5	0.52	150.7	0.36
2.0	206.8	2.0	215.8	2.09	151.1	1.46
4.0	207.1	4.0	216.3	4.18	151.6	2.93

[a] Calculated reaction order.

8. Conclusions

Evaluating the peak temperature and height at a single heating rate is likely to be insufficient for specifying a reaction except for cases of first-order kinetics or known reaction orders. It is necessary, thus, to explore the shifting pattern of either peak temperature or peak height with the heating rate for the purpose of characterizing a specific reaction.

The peak temperature and height at a certain heating rate are interrelated via the activation energy and reaction order of a reaction, but their relationships are rarely affected by the pre-exponential factor and heating rate. A linear relationship exists between the peak height and the inverse square of the peak temperature, and the slope of the straight line is confined by the activation energy and reaction order. A reaction with high activation energy might demonstrate a high peak height with respect to the peak temperature, but the opposite pattern was observed for that with high reaction order.

The peak temperature increased with increasing heating rate. Reactions of low activation energy shifted more distinctly with respect to the heating rate, but the pre-exponential factor rarely influenced the shift pattern of the peak temperature. In addition, the peak temperature remained relatively constant regardless of the reaction order. There is a linear relationship between the inverse peak temperature and the natural logarithm of the heating rate, and the slope was accounted for by the activation energy.

The peak height decreased with increasing heating rate, in accordance with the functional relationship with the peak temperature. The square root of the peak height exhibited a linearity with the natural logarithm of the heating rate. The slope was inversely proportional to the activation energy and reaction order, suggesting that reactions of high activation energy and reaction order might decrease less distinctly with increasing heating rate. Unlike the peak temperature, the peak height may evidently decrease with increasing reaction order. The variation pattern of the peak height with the heating rate might offer an insight into characterizing the order of a reaction.

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