

ANALYTICAL TECHNIQUES ESTIMATING KINETIC PARAMETERS FOR PYROLYSIS REACTION OF SCRAP TIRE RUBBERS

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Abstract—Analytical techniques using derivative thermogravimetry (DTG) and thermogravimetry analysis (TGA) were developed to estimate kinetic parameters for complex decomposition reactions of a heterogeneous substance like scrap tire rubbers. Two methods using non-isothermal techniques were proposed: (1) subtraction method and (2) method utilizing peak properties in a DTG curve. The former method is a reliable tool to determine the kinetic parameters of decomposition reaction of each compositional component, but it may run into a difficulty provided that tire components demonstrate similar thermal stability, thus leading to a complete superposition of peaks in a DTG curve. The subtraction method, however, can be applied after manipulating heating rate, since overlapped peaks can be separated by increasing or decreasing heating rate. Although the peak temperature and height (rate) in a DTG curve in the latter method were closely related to kinetic parameters of a single reaction, they can be rarely utilized to estimate the kinetic parameters of complex reactions because of disturbance arising from peak superposition.

Key words: Peak Properties, Pyrolysis, Scrap Tire Rubbers, Subtraction Method

INTRODUCTION

Scrap tire causes environmental, health, aesthetic, handling and disposal problems. These problems are listed below:

- Stockpiles of scrap tires have potential fire hazards. Burning tires have usually lasted for months and generated acrid smoke and oily residues. The U. S. Environmental Protection Agency (EPA) reported 87 tire pile fires in 1989, 65 in 1988, and 46 in 1987 [Clark et al., 1991].

- Tire provides breeding sites for mosquitoes which can be a major nuisance due to bites as well as the spread of serious diseases.

- The disposal cost of scrap tires to landfill is on the rise, because landfill spaces has become limited and most of them have been established only for shredded tires, which impose processing fees. Many countries ban tires from landfills and the rest countries will follow in the near future.

About 0.9 million scrap tires are annually generated in Korea. In addition, over 20 million scrap tires are accumulated in nationwide stockpiles or uncontrolled dumps. In the United States, approximately one tire per person is discarded annually [Scrap Tire Management, 1990; EPA, 1991] and two to three billion tires are stockpiled across the nation [Scrap Tire Management, 1990; Clark et al., 1991; EPA, 1991]. It is estimated in the United States that 7% of the discarded tires are currently being recycled into new products, 11% are converted to energy, and nearly 78% are land-filled, stockpiled or illegally dumped [EPA, 1991; EPA, 1993].

Scrap tire problems have received much attention in recent years because public recognition of the health and fire hazards associated with large tire stockpiles has increased as a result of tire fires near major metropolitan area in Virginia, Florida, Washi-

ngton, and Texas.

The necessity for the cleanup of tire piles has been strongly voiced, but landfills cannot handle the huge stockpiles by themselves. Alternative disposal, recycling, and recovery techniques should be sought to effectively remove the piles nationwide. Scrap tire management is full of alternatives, compromises, legislation, and conflicting reports on technological success. Desirable methods should at least include three facets: (1) minimum environmental impact, (2) maximum reutilization of potential resources, and (3) economic feasibility.

According to the extent of processing, the recycling and recovery methods are divided into three groups: (1) no processing (tire-derived fuel, artificial reefs, crash barrier, etc.), (2) low processing (tire splitting and crumbling), and (3) high processing (pyrolysis, microwave devulcanization, and biological degradation).

Pyrolysis, among the various alternatives, is one of the most promising techniques because of its proven applicability and marketable by-products [Beckman et al., 1973; Bush, 1980; Bracker, 1981; Dodds et al., 1983; Roy et al., 1990]. In addition, the pyrolysis of scrap tire has little adverse effect on the environment and contributes to resource and energy conservation [Collins et al., 1974].

Full-scale operations of tire pyrolysis, however, have not been attempted widely despite the advantages of generating valuable by-products, because of the insufficiently justifiable high capital and operational costs. A high capital outlay and long payback period have discouraged the investment of private ventures without government subsidy, which has taken place in Europe and Japan.

Most research efforts in tire pyrolysis, so far, have concentrated on producing valuable products and seeking engineering alternatives rather than exploring the pyrolysis kinetics and mechanisms of scrap tires systematically. The basic research may be essential to optimizing the pyrolysis process, eventually leading to economically viable designs; however, this may have been rarely accom-

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plished because complicated reactions arising from a variety of unknown tire components have impeded systematic approaches. A few studies have been conducted for the purpose of characterizing the thermal decomposition patterns of each elastomer and furthermore identifying the compositional components of tire rubbers [Brazier and Nickel, 1975; Sircar and Lamond, 1975].

The objective of this research was to develop analytical techniques using DTG and TGA to separately estimate the kinetic parameters of each compositional component in heterogeneous substances like scrap tire. Two analytical techniques were proposed: (1) subtraction method and (2) method utilizing peak properties in a DTG curve.

THEORETICAL

Yang et al. [1993] fitted DTG data to estimate the kinetic parameters for individual decomposition reactions of known rubber compounds in tire. It is, however, difficult to generalize the fitting practice, since compositional information on a specific tire is rarely available. Kim et al. [1995a] first developed analytical technique named as the subtraction method. Also, Kim and Park [1995b] attempted to estimate the kinetic parameters from peak temperature and height of each compositional compound in a DTG curve. In this section, the above techniques were reviewed critically.

SUBTRACTION METHOD

The subtraction method is based principally on one of the differential methods implemented by Kofstad [1957] and Flynn and Wall [1966]. The main idea of the subtraction method is that there may be undisturbed temperature regions of each elastomer, unless the peaks in the DTG curve are superimposed completely. Thus, the kinetic parameters of a compound which is decomposed at the highest temperatures can first be estimated using the differential method within the undisturbed temperature regions. The contribution due to the compound which is decomposed at the highest temperature regions is subtracted from the original TGA and DTG result and subsequently, the kinetic parameters for the compound which decomposes at the next highest temperature region are derived from the newly-formed TGA and DTG results. Since the present authors introduced the subtraction method in a former paper [Kim et al., 1995a], its concept was summarized briefly in this section.

If the complex reaction is accounted for by independent decomposition reactions of two compositional components which exhibit different decomposition rates with respect to temperature, the pyrolysis pattern in the DTG curve may be characterized by high, medium, and low temperature regions. The high temperature region is defined as the region where a more thermally stable compound is only decomposed, while the other is decomposed solely at the low temperature region. The medium temperature region is accounted for by concurrent decomposition of both compounds. The DTG curve corresponding to each temperature region was described mathematically as:

• high temperature region:

$$\beta \frac{dW}{dT} \approx -A_1 \exp\left(-\frac{E_1}{RT}\right) W_1; \quad (1)$$

• medium temperature region:

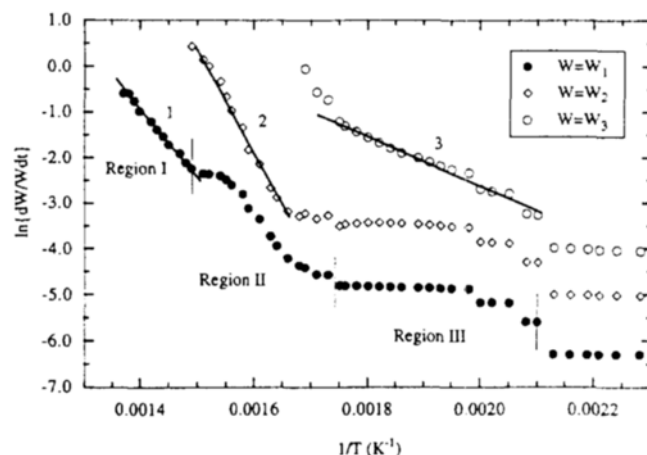


Fig. 1. Graphical expression of the subtraction method to estimate the kinetic parameters of compositional compounds of the tread rubber at a heating rate of 7.5°C/min.

Region I=high temperature region; Region II=medium temperature region; and Region III=low temperature region. Straight lines 1, 2, and 3, respectively, reflect the characteristics of pyrolysis reactions of compound 1, 2, and 3 [Kim et al., 1995a].

$$\beta \frac{dW}{dT} = -A_1 \exp\left(-\frac{E_1}{RT}\right) W_1 - A_2 \exp\left(-\frac{E_2}{RT}\right) W_2; \quad (2)$$

• low temperature region:

$$\beta \frac{dW}{dT} \approx \beta \frac{dW_2}{dT} = -A_2 \exp\left(-\frac{E_2}{RT}\right) W_2 \quad (3)$$

where β =linear heating rate (°C/min); W =weight of tire compound at a time t (kg); A =frequency factor (min^{-1}); E =activation energy (J/mol); subscript 1=more thermally stable component; subscript 2=less thermally stable component; R =gas constant (J/mol·K); and T =absolute temperature (K).

Owing to the differential method [Kofstad 1957; Flynn and Wall 1966], the kinetic parameters for the decomposition reaction of more stable compound were obtained from Eq. (1). Also, the initial weight of the more stable compound ($W_{1,0}$) could be determined as follows:

$$W_{1,0} = W_a \exp\left[\frac{A_1 RT_h^2}{\beta E_1} \left\{1 - \frac{2RT_h}{E_1} + 4\left(\frac{RT_h}{E_1}\right)^2\right\} \exp\left(-\frac{E_1}{RT_h}\right)\right] \quad (4)$$

where $W_a = W - W_x$ =degradable portion of tire weight at a time t (kg); W_x =residual weight of tire (kg); and T_h =temperature at the high temperature regions (K).

A DTG curve due to the other compound (less stable one) was constructed by subtracting the decomposition rates of the more stable compound [Eq. (1)] from an original DTG curve [Eq. (2)]. Theoretical aspects were described clearly in the former paper [Kim et al., 1995a].

Figure 1 illustrates the subtraction method graphically. Three compositional components were identified for both tread and sidewall rubbers. As shown in Figure 1, the three components of tread rubber correspond to straight lines where the slopes are $-E_i/R$ (i =tire component i) and $\ln A_i$ are the Y intercepts. Figure 2 exhibits the excellent fit of the theoretical values to the experi-

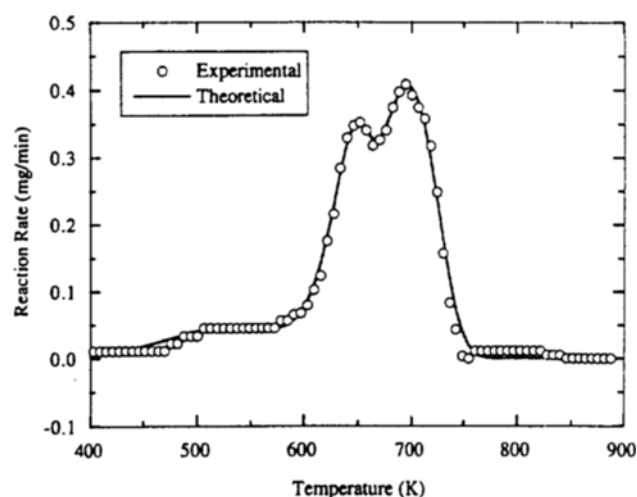


Fig. 2. Comparison of theoretical DTG curve for the tread rubber with experimental one at a heating rate of 7.5°C/min [Kim et al., 1995a].

mental DTG results. Table 1 summarizes frequency factors, activation energies, and weight fractions of the tire rubber components.

PEAK PROPERTIES IN DTG CURVE

Peak temperature and height (rate) in a DTG curve can be utilized to estimate the activation energy and pre-exponential factor of a reaction. For a single kinetic reaction, a DTG curve is mathematically represented by:

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) (1-x)^n \quad (5)$$

where x = weight conversion fraction of a compound at temperature $T = W_0 - W/W_0 - W_\infty$; W_0 = initial weight of tire rubber sample (kg); and n = reaction order.

At a peak temperature, differentiating the DTG equation with temperature is equal to zero [Flynn and Wall, 1966]:

$$\frac{E}{nRT_m^2(1-x_m)^{n-1}} = \frac{A}{\beta} \exp\left(\frac{E}{RT_m}\right) \quad (6)$$

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

Substituting Eq. (6) into Eq. (5) yields the expression for the activation energy [Flynn and Wall, 1966; Friedman, 1965]:

$$E = \frac{nRT_m^2 H_m}{(1-x_m)} \quad (7)$$

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

$$A = \frac{H_m \beta \exp(E/RT_m)}{(1-x_m)^n} \quad (8)$$

On the other hand, the activation energy can be derived from the functional relationship between peak temperature and heating rate. A linear relationship exists between the inverse peak temperature and natural logarithm of heating rate and is described as [Ozawa, 1970]:

$$\ln \beta = \ln\left(\frac{AE}{R}\right) - 5.3305 - 1.0516\left(\frac{E}{R}\right) \frac{1}{T_m} \quad (9)$$

Table 1. Frequency factors, activation energies and weight fractions of the compositional components of the sidewall and tread rubber at different linear heating rates of derivative thermogravimetry [Kim et al., 1995a]

Sidewall Rubber

HR ⁴ (K/min)	Compound 1 ¹			Compound 2 ²			Compound 3 ³		
	ln A ⁵	E (kJ/mol)	wt%	ln A ⁵	E (kJ/mol)	wt%	ln A ⁵	E (kJ/mol)	wt%
2.5	31.64	195.3	68.1	32.53	177.8	22.7	7.65	45.6	9.3
5.0	33.71	208.5	68.4	34.06	188.8	24.0	4.91	33.0	7.6
7.5	34.06	210.6	66.9	38.43	212.2	23.4	7.33	41.6	9.6
12.5	31.80	196.8	70.0	33.17	183.8	22.2	7.80	42.1	7.9
15.0	33.52	208.2	74.1	38.15	212.8	20.1	8.67	48.1	5.8
Average	32.95	203.9	69.5	35.27	195.1	22.5	7.27	42.1	7.7
95% C.I. ⁶	± 1.41	± 9.0	± 3.5	± 3.49	± 20.3	± 1.9	± 1.75	± 7.1	± 1.9

Tread Rubber

HR ⁴ (K/min)	Compound 1 ¹			Compound 2 ²			Compound 3 ³		
	ln A ⁵	E (kJ/mol)	wt%	ln A ⁵	E (kJ/mol)	wt%	ln A ⁵	E (kJ/mol)	wt%
5.0	19.34	122.2	58.4	38.87	211.4	23.4	5.10	32.8	18.3
7.5	19.80	123.0	70.3	36.52	199.6	17.2	7.35	41.1	12.5
10.0	19.37	119.6	69.7	42.29	229.7	14.8	5.93	33.6	15.5
12.5	22.46	136.7	62.9	38.57	209.6	26.0	7.25	39.6	11.1
15.0	21.96	135.0	57.0	34.60	194.9	25.3	8.55	46.4	17.7
Average	20.59	127.3	63.6	38.17	209.0	21.3	6.84	38.7	15.0
95% C.I. ⁶	± 1.87	± 9.8	± 7.7	± 3.57	± 16.7	± 6.3	± 1.67	± 7.0	± 3.9

^{1,2,3}: Compound decomposed at high, medium, and low temperature region, respectively;

⁴: Heating rate;

⁵: Natural logarithm of frequency factor (A : min⁻¹);

⁶: Confidence interval.

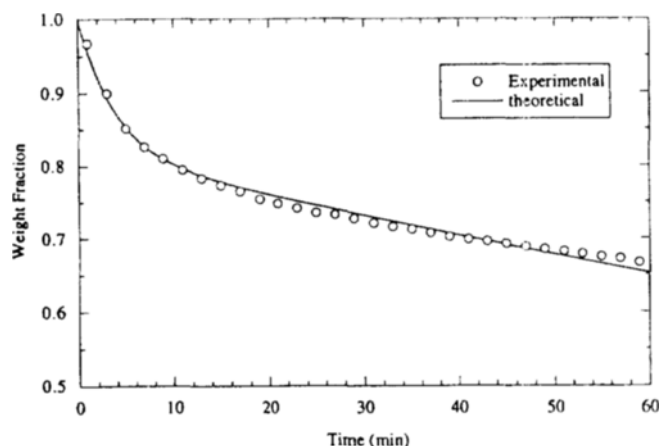


Fig. 3. Comparison of decomposition ratios of the tread rubber as a function of time between theoretical and experimental results at 300°C.

The above equations represent straight line where the slope is $-1.0516E_1/R$ and the Y intercept is $\ln(AE/R) - 5.3305$.

EXPERIMENTAL

Thermogravimetric experiments were conducted with SEIKO TG/DTA 300 which uses a horizontal differential balance mechanism. The sample balance beam and reference balance beam are each independently supported by a driving coil/pivot. When a weight change occurs at the beam end, the movement is conveyed to the opposite (rear) end of the beam via the driving coil/pivot and optical position sensors detect changes in the position of a slit. The detected optical position sensor signal is sent to the balance circuit. The current running to the driving coil on the sample side and the current running to the driving coil on the reference side are detected and converted into weight signals.

A scrap tire (195/60 R15 86H) produced by the Bridgestone Company in Japan was used throughout this study. The rubber samples were dried at 50°C for two hours and put in a desiccator before DTG and TGA analysis. Approximately 10 mg of the sample was subject to DTG and TGA at linear heating rates. Decomposition was carried out in a stream of dry helium to a maximum temperature of 850K.

RESULTS AND DISCUSSION

In a previous study [Kim et al., 1995a], the subtraction method was developed to estimate kinetic parameters and initial weight fractions of compositional components of scrap tire rubbers. According to the kinetic parameters, the tread rubber may consist primarily of three degradable components: natural rubber (NR), styrene butadiene rubber (SBR), and processing oils, while the sidewall rubber may be composed of NR, polybutadiene rubber (BR), and processing oils. It was also proposed that pyrolysis reaction of each component may be accounted for by a first-order irreversible independent reaction.

Although the subtraction method offered an insight into estimating the kinetic parameters of complex reactions, it was uncertain whether the kinetic parameters derived from the subtraction method were accurate or not. Thus, it was necessary to validate the subtraction method by means of comparing theoretical results with

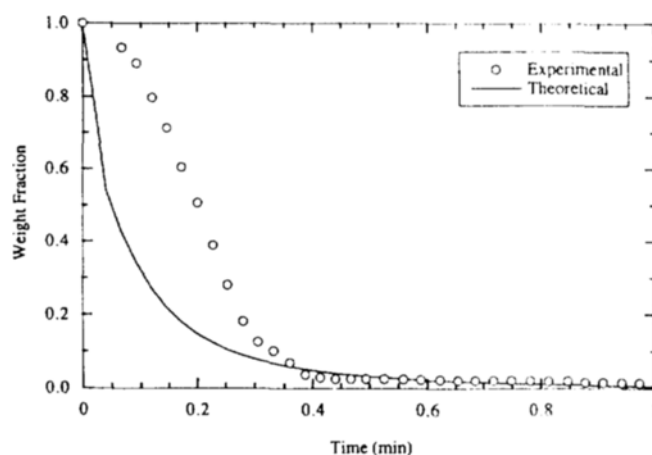


Fig. 4. Comparison of decomposition ratios of the tread rubber as a function of time between theoretical and experimental results at 600°C.

experimental ones under isothermal conditions. The decomposition ratio of scrap tire rubbers at an isothermal temperature is expressed as a function of time:

$$\alpha = f_1 \exp(-c_1 t) + f_2 \exp(-c_2 t) + f_3 \exp(-c_3 t) \quad (10)$$

where α = decomposition ratio = $(W - W_x) / (W_0 - W_x)$; f = weight fraction; $W_{i,0} / (W_0 - W_x)$; $W_{i,0}$ = initial weight of component i (kg); c_i = rate constant (min^{-1}) = $A_i \exp(-E_i / RT_0)$; T_0 = isothermal operating temperature; and t = time (min).

Figures 3 and 4 compare the theoretical results with the experimental ones at isothermal operating temperatures of 300 and 600°C, respectively. The theoretical results were obtained from a best fit to isothermal data by varying the kinetic parameters and initial weight fractions in Eq. (10) within a confidence level of 95% as to those reported in Table 1.

The theoretical results well duplicate the experimental ones at the low temperature (300°C), whereas the theoretical ones deviate significantly at the medium temperature (600°C). The deviation is noticeable particularly at the initial stage of test where the effect of heat transfer may be significant. Non-isothermal pyrolysis controlled the process before the entire tire sample reached the isothermal conditions. Hence, the degradation may have been initially retarded because of the non-isothermal operation and the lag period may be extended as the heat transfer limitations become significant. Although the heat transfer conditions may affect the pyrolysis kinetics more greatly at the low operating temperatures, their decomposition rates were rarely retarded at the beginning of test (Figures 3). Since chemical kinetics competes with the heat transfer conditions during the course of the pyrolysis reactions, the chemical kinetics may limit the reactions at the low operating temperatures, whereas the relative role of heat transfer may become significant at the medium temperature or higher because of fast decomposition reactions [Kim et al., 1995c].

On the other hand, the kinetic parameters can be obtained from the peak temperature, peak height and x_m at a heating rate [Eqs. (9) and (8)], but the overlapped peaks led to a difficulty in estimating the peak heights of individual elastomers separately. As shown in Figures 5 and 6, theoretical DTG curves of the binary elastomers (NR/SBR and NR/BR) used for the tire rubbers were simulated at three linear heating rates based on the assumption of independent reactions [Yang et al., 1993]. The NR/SBR elasto-

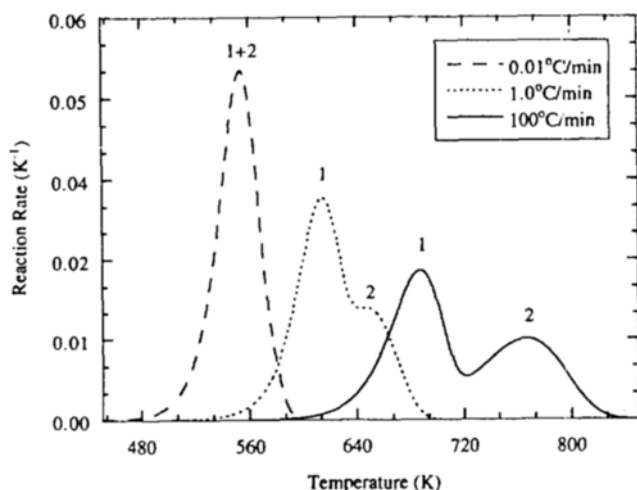


Fig. 5. Theoretical DTG curves of binary elastomer of NR and SBR at three heating rates of 0.01, 1.0 and 100°C/min (1: NR and 2: SBR).

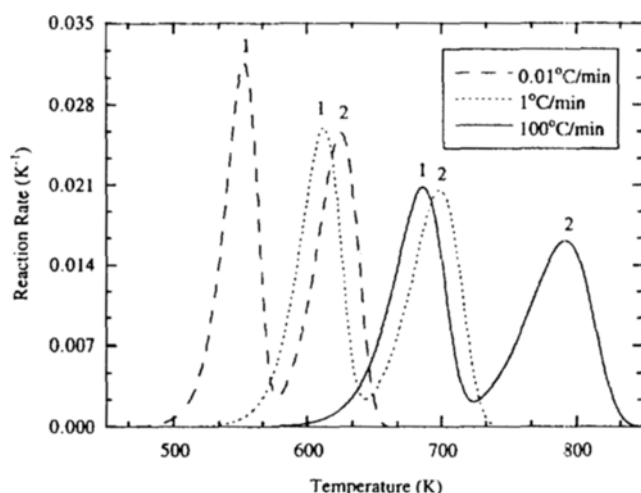


Fig. 6. Theoretical DTG curves of binary elastomer of NR and BR at three heating rates of 0.01, 1.0 and 100°C/min (1: NR and 2: BR).

mer may demonstrate no disturbance of the peak temperature at heating rates of higher than 100°C/min, whereas no disturbance was observed for the NR/BR elastomer at any heating rates. Hence, application of this method using peak properties in DTG curve may be carefully examined for some cases of complex reactions because the disturbance of peak temperatures arising from significant overlapping was problematic [Flynn, 1980].

As already mentioned, the above methods may run into a difficulty if the tire components exhibit quite similar thermal stability, thereby leading to a composite peak due to a significant superposition of various DTG peaks. However, overlapped peaks in a DTG curve may be separated by either increasing or decreasing constant heating rates [Flynn, 1980; Kim and Park, 1995b]. If the separation of overlapped peaks can be accomplished by manipulating the heating rates, the methods proposed here may be able to evaluate kinetic parameters of compositional compounds separately.

As shown in Eq. (9), the theoretical relationship between the

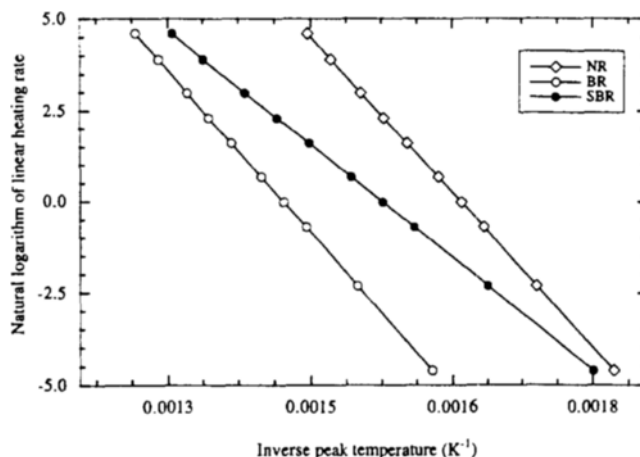


Fig. 7. Functional relationship between linear heating rate and peak temperature for the NR, BR, and SBR.

Table 2. Frequency factors and activation energies of processing oils, NR, BR, and SBR [Yang et al., 1993]

Compound	$\ln A^1$	E (kJ/mol)
Processing oils ²	7.84	48.0
Processing oils ³	7.56	43.3
NR	38.20	207.0
BR	34.08	215.0
SBR	24.02	148.0

¹: Natural logarithm of frequency factor (A: min⁻¹);

²: In natural rubber (NR) and polybutadiene rubber (BR); and

³: In styrene-butadiene rubber (SBR).

inverse peak temperature and natural logarithm of the heating rate is developed for the three straight elastomers (NR, BR, and SBR) (Figure 7). The slope of the straight line is accounted for by the activation energy, thus suggesting that reactions of lower activation energies may shift more with respect to heating rate. Since the activation energy for decomposition reaction of SBR is the lowest (Table 2), the shift pattern of SBR peak is more apparent. Hence, the peak is superimposed eventually with NR peak at high heating rates (Figure 5). On the other hand, the activation energy of the NR is similar to that of the BR, thus yielding similar shift pattern of both peaks (Figure 6). It was, thus, expected that the tire rubbers composed of the NR/SBR should be applied at high heating rates to introduce the subtraction method and the concept of peak properties, while those composed of the NR/BR can be determined regardless of heating rate.

CONCLUSIONS

1. The subtraction method is a reliable tool for estimating the kinetic parameters for a first-order irreversible independent reaction of each compositional component in a heterogeneous substance like tire rubber. The method may undergo a difficulty in determining the kinetic parameters provided that peaks would be superimposed one another. The method, however, may be applicable after separating the overlapped peaks by means of increasing and decreasing heating rates, because the peaks may shift differently as to the activation energies.

2. The peak temperature and height in a DTG curve can be utilized to estimate the kinetic parameters for a single reaction, whereas those may be problematic for complex reactions like thermal decomposition reactions of scrap tire rubbers because of disturbance of peak properties.

NOMENCLATURE

A	: pre-exponential factor [min^{-1}]
c	: rate constant [min^{-1}]
E	: activation energy [J/mol]
f	: weight fraction
H_m	: peak height
n	: reaction order
R	: gas constant [$\text{J/mol}\cdot\text{K}$]
T	: absolute temperature [K]
T_h	: absolute temperature at high-temperature region [K]
T_m	: peak temperature [K]
T_0	: isothermal operating temperature [K]
W	: weight of tire compound at a time t [kg]
W_a	: tire weight of degradable portion at time t [kg]
W_0	: initial weight of tire at time t [kg]
W_{10}	: initial weight of compound 1 [kg]
W_{20}	: initial weight of compound 2 [kg]
W_x	: residual weight [kg]
x	: conversion ratio of tire
x_m	: conversion ratio of tire at peak temperature

Greek Letters

α	: decomposition ratio of tire
β	: linear heating rate [$^{\circ}\text{C/min}$]

Subscripts

1	: compound 1
2	: compound 2
i	: compound i

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