

Kinetics of Nonisothermal Thermal Degradation of Styrene-Butadiene Rubber

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Abstract—The kinetics of thermal degradation of styrene-butadiene rubber (SBR) was studied by conventional thermogravimetric technique with various heating rates under nitrogen. A kinetic model which accounts for the effects of scission of polymeric chain at any time was proposed to describe the thermal degradation of SBR. Results showed that the contribution of the thermal degradation of zero-order reaction is greater than that of first-order and second-order reactions. The activation energy of the thermal degradation of SBR was calculated to be 172 kJ/mol using the Arrhenius equation.

Key words : Styrene-Butadiene Rubber, Thermal Degradation Kinetic, Thermogravimetric Technique

INTRODUCTION

As quantities of municipal and industrial organic wastes increase, the thermal treatment of solid wastes by pyrolysis or incineration has received considerable attention. A proper thermal treatment system not only resolves the disposal problems but also recovers energy from these wastes. The kinetics of thermal degradation of such solid wastes must be studied to provide a more detailed thermal and flow analysis [Coonely et al., 1983; Ebbinghaus, 1995; Arisawa and Brill, 1997]. The thermal degradation kinetics in polymers are generally quite complicated due to the nature of polydispersity of polymer chains.

Thermogravimetric analysis (TGA) cannot be used to elucidate clear mechanism of thermal degradation. Nevertheless, dynamic thermogravimetric analysis has been frequently used to study the overall thermal degradation kinetics of polymers because it gives reliable information on the frequency factor, the activation energy, and the overall reaction order [Park et al., 1985; Petrovic and Zavargo, 1986; Nam and Seferis, 1991; Nam and Seferis, 1992; Salin and Seferis, 1993; Jimenez et al., 1993]. Chen and Yeh [1997] investigated the kinetics of thermal decomposition of styrene-butadiene rubber (SBR) using Friedman's method, which cannot yield the information on thermal degradation behavior of polymers at a desired time. Deng et al. [1997] developed a model based on the assumption that the rate constant at any weight loss fraction is approximately equal to the rate constant of its neighboring weight loss fraction, which accounts for the type of a bond scission and the state of a scission of the polymeric chain at any time.

In this work, a kinetic model which accounts for not only the effects of scission of polymer chain at any time, but also the degree of contribution of multi-order reactions to the overall reaction was proposed to describe the thermal degradation behavior of polymers, and was applied to the thermal degradation of SBR under nonisothermal conditions. Numerical method was proposed to solve the thermal degradation rate equation based on

the kinetic model used in this work. The activation energy of the thermal degradation of SBR was calculated using the Arrhenius equation. To verify the performance of the kinetic model and the numerical method used in this work, the calculation results were compared to TGA data.

EXPERIMENTAL

The kinetics of thermal degradation of SBR for nonisothermal conditions has been investigated thermogravimetrically. The thermogravimetric analysis was performed with a Shimadzu TG model TGA-50. The SBR samples from commercial rubber (grade 1502 USA from Korea Kumho Petrochemical Co., Ltd.) were studied at various heating rates (2, 10 and 20 °C/min). The initial mass of the sample was 8.1–9.3 mg. The experiments were carried out in nitrogen atmosphere with a flow rate of 50 ml/min and a purge time of 20 min.

KINETIC ANALYSIS

1. Kinetic Model

When polymers are subject to heating condition, complicated processes occur, such as random-chain scission, end-chain scission, chain stripping, cross-linking, and coke formation [Fried, 1995]. In this work, there is no intention to describe fundamental chemical mechanisms of the thermal degradation. This work focuses on the measurement of apparent kinetic parameters useful for chemical engineering design. In general, the overall rate equation of conversion α for thermal degradation in nitrogen atmosphere is expressed in the Arrhenius form as

$$\frac{d\alpha}{dt} = A \exp\left\{-\frac{E}{(RT)}\right\} (1-\alpha)^n \quad (1)$$

where A, E, T and R are the frequency factor (1/min), the activation energy (J/mol), the temperature of reaction (K), and the gas constant (8.314 J/mol·K), respectively, and n denotes the overall reaction order. However, though Eq. (1) gives a reliable estimation of kinetic parameters, it cannot account for the thermal de-

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gradation behavior of polymer at any time. Denq et al. [1997] proposed a model based on the assumption that the overall thermal degradation rate of a polymer could be represented as a combination of zero-order, first-order, and second-order reactions. The thermal degradation rate equation which accounts for each of the three reaction orders can be written as

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = K_0 + K_1(1-\alpha) + K_2(1-\alpha)^2 \quad (2)$$

where β is the heating rate (K/min) and K_0 , K_1 , and K_2 are the summations of rate constants (1/min) that represent the zero-order, first-order, and second-order reactions respectively. Each of the above three rate constants changes, depending on reaction temperature and state of chain scission. Physically, a zero-order reaction would reflect the monomer scission from a polymer chain end, and the small molecule scission from a side chain. A first-order and second-order reaction would reflect the weight loss related to the random scission of a main chain and the two random polymer segments combination due to colliding, respectively [Denq et al., 1997].

2. Numerical Model

In order to solve Eq. (2), Denq et al. [1997] used the assumption that the rate constant at any weight loss fraction is approximately equal to the rate constant of its neighboring weight loss fraction as the following:

$$\begin{aligned} K_{0,\alpha-\Delta\alpha} &\approx K_{0,\alpha} \approx K_{0,\alpha+\Delta\alpha} \\ K_{1,\alpha-\Delta\alpha} &\approx K_{1,\alpha} \approx K_{1,\alpha+\Delta\alpha} \\ K_{2,\alpha-\Delta\alpha} &\approx K_{2,\alpha} \approx K_{2,\alpha+\Delta\alpha} \end{aligned} \quad (3)$$

Eq. (3) can effectively be used for numerical estimation of the rate Eq. (2) when the thermal degradation rate $d\alpha/dt$ is slow, but it produces serious numerical error at high thermal degradation rate. And though the thermal degradation rate was slow, Eq. (3) could not give reasonable accuracy for low ($\alpha < 0.05$) and high ($\alpha > 0.96$) conversion ranges in this work because TGA data could be influenced by noise where thermal degradation rate was too slow. For instance, it estimates negative values of K_i , and a negative reaction order can be obtained. Therefore, in this work the optimization technique using constraints was used in the estimation of rate constants. The optimization problem can be formulated by the form

$$\text{Minimize } f(\mathbf{K}) = (\alpha_e - \alpha_e(\mathbf{K}))^2 \quad (4a)$$

$$\text{subject to } K_i \geq 0 ; i = 0, 1, 2 \quad (4b)$$

where \mathbf{K} denotes the rate constant vector which consists of K_0 , K_1 and K_2 . In Eq. (4a) α_e is the weight loss fraction obtained by thermogravimetric analysis and α_e is the weight loss fraction calculated by the 4th Runge-Kutta integration method from Eq. (2) and \mathbf{K} . To solve the constrained minimization problem of Eq. (4a) the complex method was used. The calculation procedure of the complex method used in this work is described elsewhere [Rao, 1984] and only important steps are summarized in this article.

Step 1. Feasible point \mathbf{K}_h which satisfies the constraints (4b) is calculated by the following equation.

$$k_{i,j} = k_i + r_{i,j}(k''_i - k'_i); \quad i=0,1,2 ; j=1,2,\dots,p \quad (5)$$

where $k_{i,j}$ is the i th component of a point \mathbf{K}_h , and $r_{i,j}$ is a random number lying in the interval (0, 1), and l , u , i and j denote the lower and upper bound of the rate constants, the reaction order and the calculation point, respectively. If p is not sufficiently large, the complex tends to collapse. In this work, $p=3m$ where m is the number of \mathbf{K} was used.

Step 2. The objective function (4a) is evaluated at each of the p points. If the point \mathbf{K}_h corresponds to the largest function value, the process of reflection is used to find a new point \mathbf{K}_r as

$$\mathbf{K}_r = (1+\alpha)\mathbf{K}_c - \alpha\mathbf{K}_h \quad (6)$$

where $\alpha \geq 1$ for initial values and \mathbf{K}_c is the centroid of all points except \mathbf{K}_h . The centroid \mathbf{K}_c is given by

$$\mathbf{K}_c = \frac{1}{p-1} \sum_{i=1, i \neq h}^p \mathbf{K}_i \quad (7)$$

Step 3. If the point \mathbf{K}_r is feasible, and $f(\mathbf{K}_r) < f(\mathbf{K}_h)$, the point \mathbf{K}_h is replaced by \mathbf{K}_r and go to step 2. If $f(\mathbf{K}_r) \geq f(\mathbf{K}_h)$, a new trial point \mathbf{K}_r is found by reducing the value of α in Eq. (6) by a factor 2. A value of 1.3 for the initial value of α in Eq. (6) was used in this work. If $f(\mathbf{K}_r) \geq f(\mathbf{K}_h)$, the procedure of finding a new point \mathbf{K}_r with a reduced value of α is repeated again. If an improved point \mathbf{K}_r with $f(\mathbf{K}_r) < f(\mathbf{K}_h)$ cannot be obtained even with the small value of α , the point \mathbf{K}_r is discarded and the whole procedure of reflection is restarted by using a point \mathbf{K}_p which has the second highest function value.

Step 4. Each time the worst point \mathbf{K}_h of the current complex is replaced by a new point, the following criteria can be used to terminate the iterative process:

$$\left\{ \frac{1}{k} \sum_{i=1}^k [f(\mathbf{K}_i) - f(\mathbf{K}_c)]^2 \right\}^{1/2} \leq \epsilon \quad (8)$$

where \mathbf{K}_c is the centroid of all the k points of the current complex, and ϵ is the specified small number. If an improved point satisfying the convergence criteria (8) cannot be found, the iterative process can be terminated when the distance between any two points among \mathbf{K}_1 , \mathbf{K}_2 , \dots , \mathbf{K}_k becomes smaller than a pre-described small quantity.

The average reaction order and rate constant can be obtained from Eqs. (9) and (10) as the following :

$$\bar{n} = \sum_{i=0}^2 n P_i \quad (9)$$

$$\bar{K} = \frac{\beta \cdot \left(\frac{d\alpha}{dT} \right)}{(1-\alpha)^n} \quad (10)$$

In Eq. (9) P_0 , P_1 and P_2 are the relative contributions to the entire thermal degradation rate for the zero-order, first and second-order reactions, respectively, and calculated by the Eq. (11) as the following:

$$P_0 = \frac{K_0}{K_0 + K_1(1-\alpha) + K_2(1-\alpha)^2}$$

$$P_1 = \frac{K_1(1-\alpha)}{K_0 + K_1(1-\alpha) + K_2(1-\alpha)^2}$$

$$P_2 = \frac{K_2(1-\alpha)^2}{K_0 + K_1(1-\alpha) + K_2(1-\alpha)^2} \quad (11)$$

Finally, the activation energy was calculated using the Arrhenius equation from \bar{K} and absolute temperature.

RESULTS AND DISCUSSION

For the model proposed in this work, the relationships between the rate constants and weight loss fraction at heating rates of 2, 10 and 20 °C/min are shown in Figs. 1, 2 and 3. The ther-

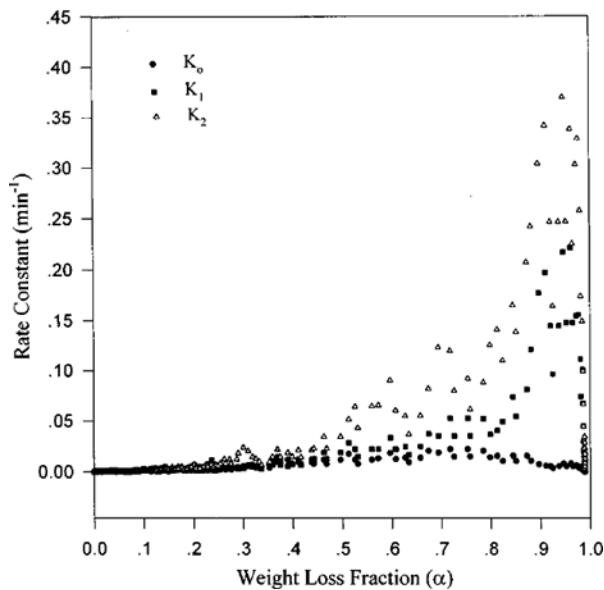


Fig. 1. Relationship between rate constants to different reaction order and weight loss fraction at a heating rate of 2 °C/min under nitrogen atmosphere.

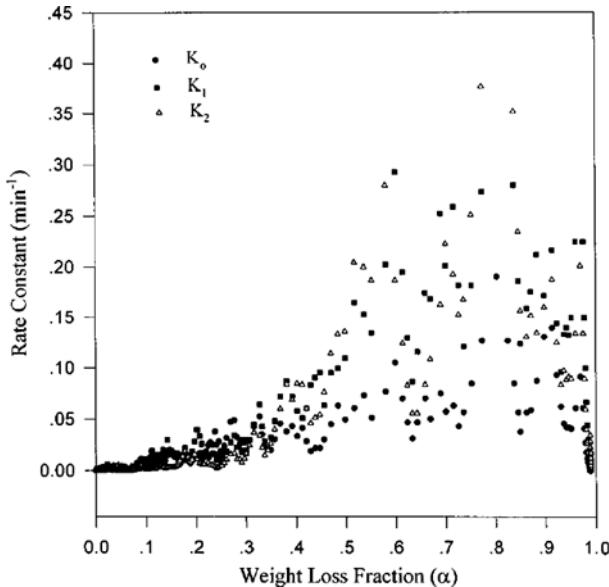


Fig. 2. Relationship between rate constants of different reaction order and weight loss fraction at a heating rate of 10 °C/min under nitrogen atmosphere.

mal degradation took place in nitrogen atmosphere. As can be seen, the rate constant of the second-order reaction is greater than those of the zero-order and first-order reactions. However, it is not rational to use these rate constants in kinetic analysis, because the effects of reaction order upon the thermal degradation must be assessed with degradation rates such as K_0 , $K_1(1-\alpha)$ and $K_2(1-\alpha)^2$ in Eq. (2). Figs. 4, 5 and 6 show the contribution to the thermal degradation rates for different reaction orders as a function of temperature. From these figures, we note that the contribution of the thermal degradation of the zero-order reaction is greater than those of the first-order and second-order

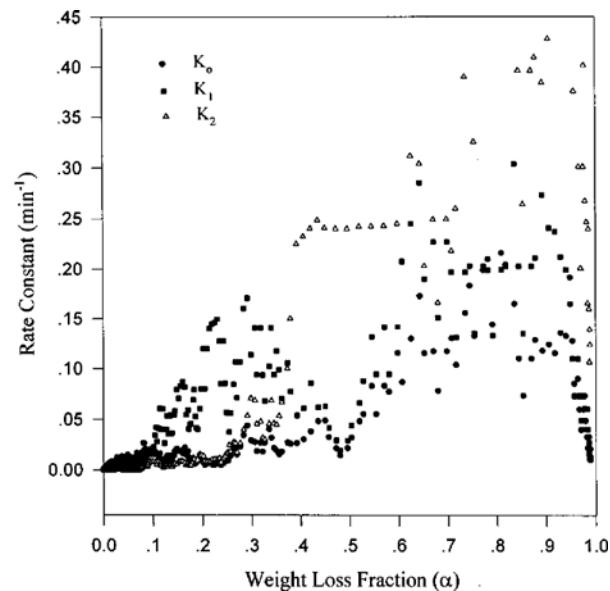


Fig. 3. Relationship between rate constants of different reaction order and weight loss fraction at a heating rate of 20 °C/min under nitrogen atmosphere.

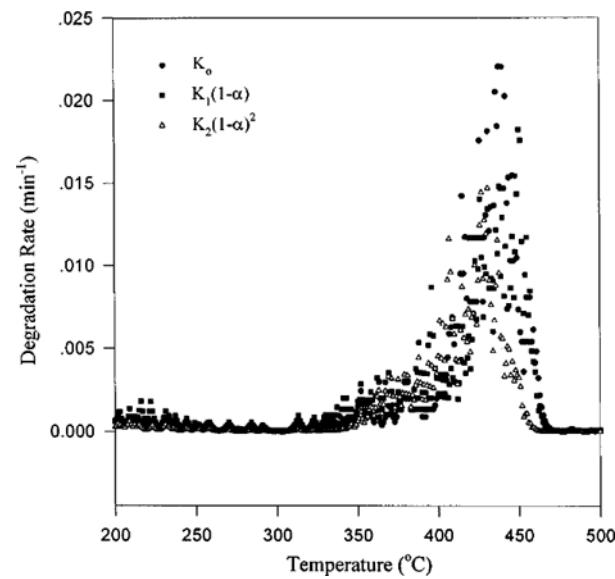


Fig. 4. Thermal degradation rate of a different reaction order as a function of temperature at a heating rate of 2 °C/min under nitrogen atmosphere.

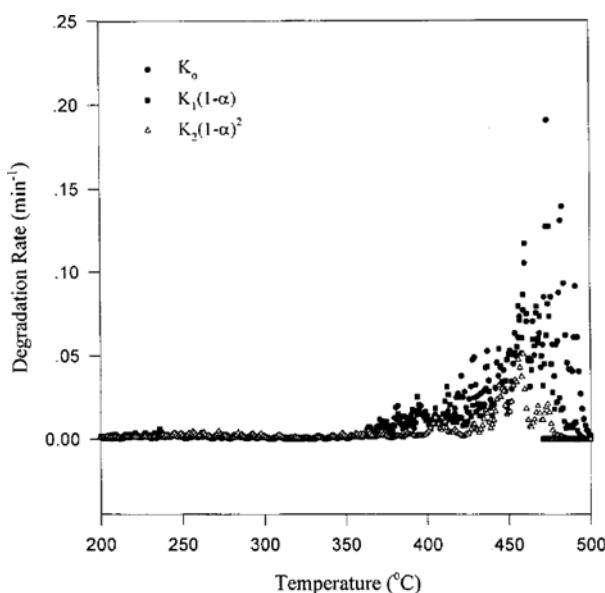


Fig. 5. Thermal degradation rate of a different reaction order as a function of temperature at a heating rate of 10 °C/min under nitrogen atmosphere.

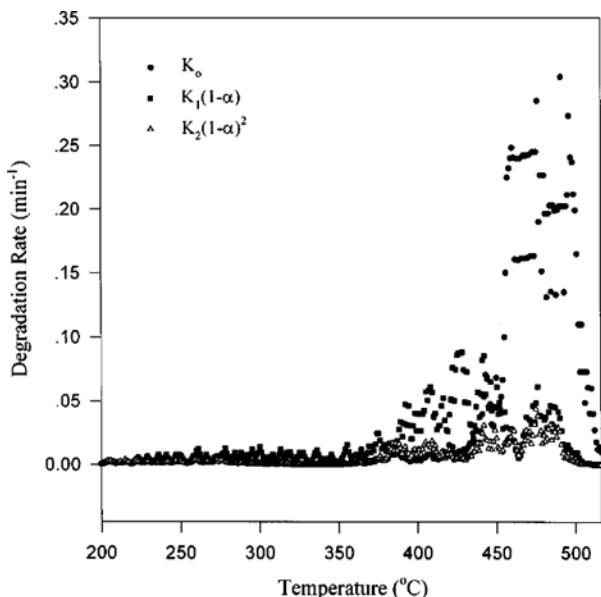


Fig. 6. Thermal degradation rate of a different reaction order as a function of temperature at a heating rate of 20 °C/min under nitrogen atmosphere.

reactions. Also the thermal degradation by the second-order reaction starts to occur at a higher temperature than that of the zero-order and first-order reactions. According to the model used in this work, the thermal degradation by zero-order reaction indicates the weight loss by the monomer scission from the polymer chain end and the small molecule scission from a side chain. The thermal degradation by first-order indicates the weight loss by the random scission of a main chain, and the thermal degradation by the second-order reaction indicates the weight loss related to the intermolecular transfer and scission. Considering that SBR is prepared by free radical polymerization

and that the model used in this work indicates that the important mechanisms of thermal degradation process include depropagation, random main chain scission, intermolecular transfer and the scission of small molecules from side chains, the thermal degradation rate data obtained from the model used in this work are reasonable and in agreement with literature [Mc-Neill, 1977].

The corresponding Arrhenius plot of the logarithmic value of average reaction rate constant at heating rates of 2, 10 and 20 °C/min versus the inverse of absolute temperature is shown in Fig. 7. From this figure the average apparent activation energy of SBR was calculated to be 172 kJ/mol. Fig. 8 shows the relation-

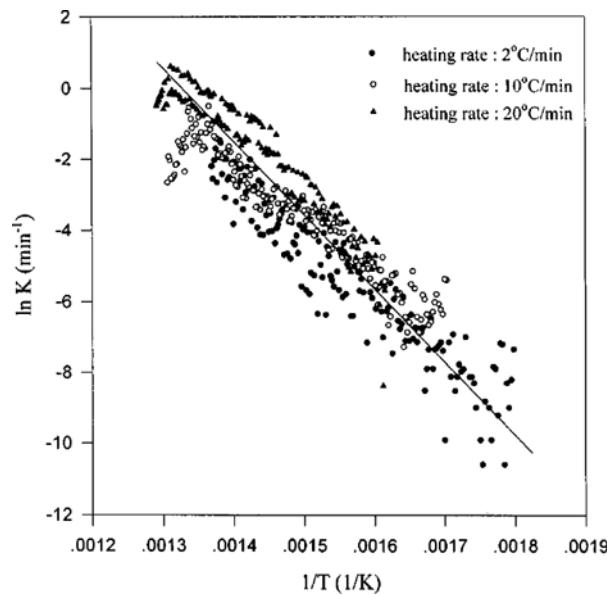


Fig. 7. Arrhenius plot of logarithmic value of the average reaction rate constant versus inverse of absolute temperature.

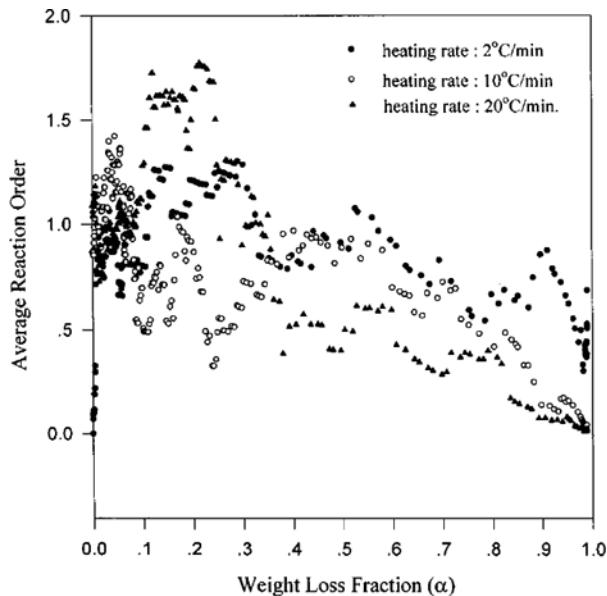


Fig. 8. Relationship between average reaction order and weight loss fraction for different heating rates under nitrogen atmosphere.

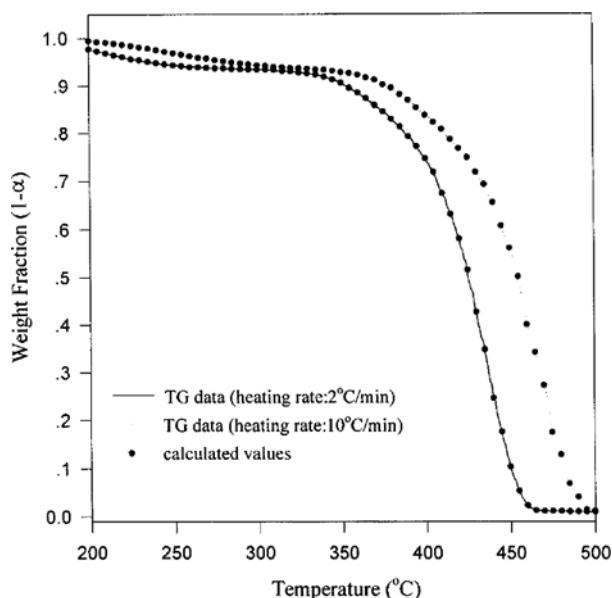


Fig. 9. Comparison of TG data and calculation results at different heating rates under nitrogen atmosphere.

ship between average reaction order and weight loss fraction at various heating rates. Fig. 9 shows TGA data and values calculated by using the kinetic analysis method proposed in this work. It is seen that calculated values agree very well with experimentally obtained TGA data. Further studies, such as the analysis of substances obtained from thermal degradation, are required to identify the heating rate dependence of the thermal degradation process.

CONCLUSION

The kinetics of thermal degradation of SBR was investigated by a kinetic model which accounts for the effects of scission of polymeric chains at any time. From the experimental results, we can see that the contribution of thermal degradation of the zero-order reaction reflecting a weight loss by the monomer scission from a polymer chain end and the small molecular scission from a side chain is greater than that of the first-order and second-order reactions. The average activation energy of the thermal degradation of SBR was estimated to be 172 kJ/mol using the Arrhenius equation. To verify the performance of the kinetic model and the numerical method proposed in this work, a comparison of TGA data and the calculation results was made, and it is seen that the calculated values agree very well with TGA data. Further studies are required to identify the heating rate dependence of each thermal degradation process.

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