

Pyrolysis kinetics of rubber mixtures

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Abstract

The pyrolysis kinetics of a rubber mixture was investigated by a dynamic thermogravimetry reaction system at heating rates of 3, 5 and 7 K/min, in a nitrogen atmosphere, over the temperature range of 400 to 950 K. The results indicated that the pyrolytic reaction rates of rubber mixture can be represented by the summation of the corresponding reaction rates of the rubber components, based on their mass fractions. Satisfactory agreements between the proposed reaction model and the experimental results could be obtained. The results of this study are useful for the utilization of scrap rubber mixtures as an energy resource. © 1998 Elsevier Science B.V.

Keywords: Pyrolysis; Rubber; Dynamic thermogravimetry; Mixtures

1. Introduction

In Taiwan, polybutadiene rubber (BR) and styrene–butadiene rubber (SBR) are classified as two of the principal manufacturing products of the rubber industry. The cumulative quantities of BR and SBR production between 1984 and 1994 are about 379 134 and 667 154 metric tons [1], respectively. Most of BR and SBR are used in tires [2]. About 78 000 metric tons of used tires were discarded in 1992, while the amount was estimated to be 58 000 metric tons in 1989 [3]. The growth rate in the generation of scrap tires is very high. Therefore, the treatment of rubber wastes and scrap tires has become a major environmental problem. Because of the high calorific value of synthetic rubber, about 40 000 kJ/kg, the conversion of rubber wastes or scrap tires to market-ready products has become a principal focus from both environmental and economical viewpoints.

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Several pyrolytic processes, such as batch processes [4–6], vacuum process [7], molten processes [8–10], fluidized bed processes [11–13] and coprocessing with waste oil [14,15] have been studied for the treatment of rubber wastes, scrap tires and automobile shredder wastes. A feasibility study for scrap tires treatment indicated that the optimization of pyrolysis processes was necessary [16]. The gas products obtained from the pyrolysis of rubber wastes or scrap tires may contain hydrogen, methane, ethane, propylene, butene, butadiene, etc. And benzene, toluene, xylene, limonene, naphthalene, etc. could be identified in the oil products [6,12,13]. The conversion of solid residues into activated carbon may be one of the most effective usages of char obtained through pyrolysis, and the desired characteristics of final carbon product could be also acquired [5,17,18]. Several pyrolytic reaction parameters of scrap tires and rubber wastes were reviewed [19,20] with the activation energies of about 50–600 kJ/mol. In Taiwan, some studies concerning pyrolysis of rubber wastes [19–21], scrap tires [13,22], and mixtures of plastics [23] or papers [24] have been investigated. However, mixtures of rubber wastes are needed to be studied with much more attention [25,26]. Therefore, there is a need to study the pyrolytic reaction rates of rubber mixtures and to develop a simple kinetic model describing the pyrolysis behavior of rubber mixtures.

It is, thus, the aim of the present work to deal with the pyrolysis of rubber mixture to provide a simple reaction model for engineering purposes. The pyrolyzer was a dynamic thermogravimetry system at three nominal heating rates of 3, 5 and 7 K/min, respectively, in a nitrogen atmosphere. A kinetic model was proposed for the pyrolysis of the typical rubber mixture. The reaction rates of rubber mixture were correlated with the corresponding reaction rates of the rubber components, based on their mass fractions. These results are useful for the pyrolytic treatment of rubber mixtures.

2. Experimental

2.1. Materials

The commercial-grade BR and SBR were used in this study. They were supplied by the Taiwan Synthetic Rubber Corporation. Some analytical properties of these samples are listed in Table 1. Nitrogen, with 99.99% purity, was used as purge gas. The mass fraction of rubber mixture is BR/SBR = 1.45/2.55, which can be deduced from the cumulative production quantities of BR and SBR mentioned previously [1].

2.2. Apparatus and procedures

The experimental flow diagram for the pyrolysis of rubber mixture is shown in Fig. 1. Details of this experimental procedures have been discussed previously [19]. The ultimate analyses of samples were made on the Perkin-Elmer, CT 2400 elemental analyzer with 0.3 wt.% accuracy.

3. Results and discussion

3.1. Mass-loss behaviors of individual rubber samples

The residual mass fraction of active reactant (M) is expressed on a normalized basis, $M = (W - W_f)/(W_0 - W_f)$, where W , W_0 , W_f = mass, initial mass, and final mass of sample, respectively. The mass-loss characteristics of SBR and BR pyrolysis with reaction temperature (T) are shown in Figs. 2 and 3, respectively [19,20].

The comparison of BR and SBR pyrolysis, at heating rate of 7 K/min, is shown in Fig. 4. It may be figured out that the on-set decomposition temperature is about 450–500 K for SBR, 550–600 K for BR, respectively. From the point of view of chemical bond energy, the bond dissociation energy of $\text{CH}_3\text{-H}$ is 435 kJ/mol, while that of $\text{CH}_3\text{-C}_6\text{H}_5$ is 389 kJ/mol [27]. This could be one of the main reasons why the on-set decomposition temperature of BR is higher than that of SBR, which means the thermal stability of BR is better than that of SBR under the same experimental conditions.

The variations of reaction rates ($r = dX/dt = -dM/dt$) for BR and SBR with reaction temperature (T), at heating rate of 7 K/min, are shown in Fig. 5. Two peaks of maximum reaction rates could be identified from Fig. 5 for BR pyrolysis, and three peaks of rates could be distinguished for SBR pyrolysis. This suggests that three different reaction paths might be proposed for SBR pyrolysis [19] and two different paths for BR pyrolysis [20]. The related kinetic parameters for SBR and BR pyrolysis are listed as Tables 2 and 3. Generally, the formulation of pyrolysis reaction rate may be regarded as:

$$r = \frac{dX}{dt} = -\frac{dM}{dt} = k(1 - X)^n \quad (1)$$

where $r = dX/dt$ is the instantaneous reaction rate, $X (= 1 - M)$ is the degree of

Table 1
Some properties of BR and SBR samples used in this study

Properties	BR	SBR
<i>Proximate analysis (wt.%)</i>		
Moisture	0.22	0.38
Combustible ^a	99.70	99.47
Ash	0.08	0.15
<i>Ultimate Analysis (wt.%)</i>		
C	88.72 (0.005) ^b	87.58 (0015)
H	11.17 (0.01)	10.41 (0.005)
N	ND ^c	ND
O	< 0.1	0.84 (0.015)
S	2.04 (0.01)	1.91 (0.07)
Cl	0.36 (0.01)	0.27 (0.045)
Lower heating value (kJ/kg)	45,690	43,350

^a 1-moisture-ash.

^b Numbers in parentheses are standard deviations.

^c Not detected.

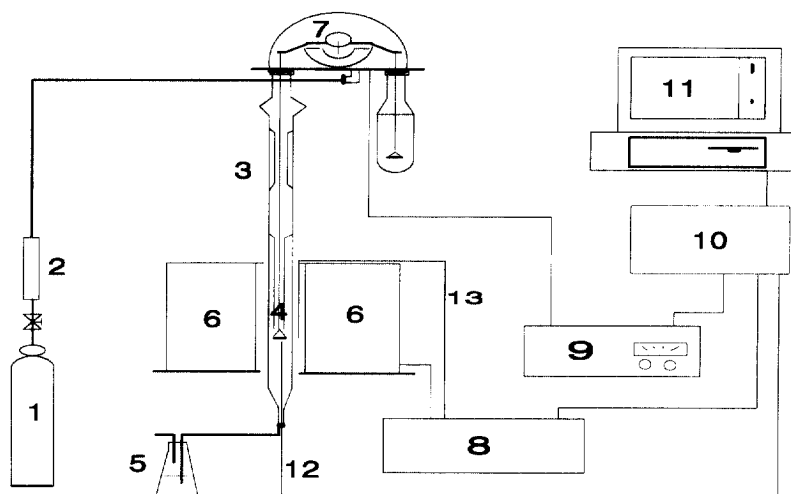


Fig. 1. Schematic diagram of apparatus for the pyrolysis experiment. (1) Nitrogen; (2) Flow meter with needle valve; (3) Reactor; (4) Extension wire and sample disk; (5) Trap; (6) Furnace; (7) Electrobalance; (8) Temperature controller; (9) Electrobalance controller; (10) Data acquisition unit; (11) Personal computer; (12), (13) K-type thermocouples [19].

conversion, n is the reaction order, k is the reaction rate constant according to the Arrhenius law. The overall mass balance for pyrolysis reaction can be expressed as:

$$X_j = 1 - M_j = \sum_i m_{v,i,j} \quad (2)$$

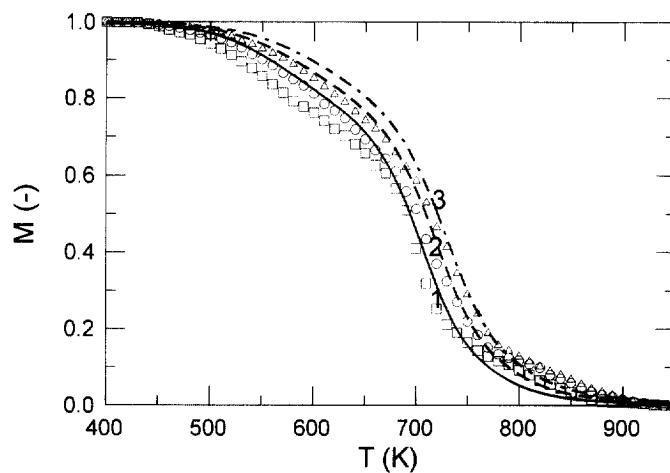


Fig. 2. Comparison of residual mass fraction (M) by model prediction with experimental data at different heating rates (β) for pyrolysis of SBR. \square and 1, \circ and 2, and \triangle and 3: experimental and predicted results for $\beta = 3, 5$, and 7 K/min, respectively [19].

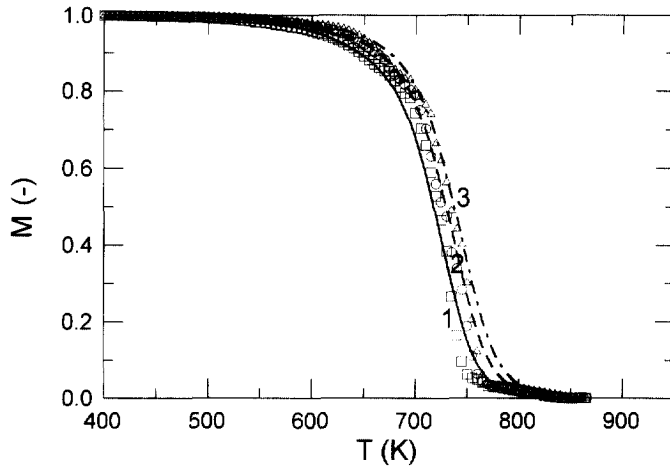


Fig. 3. Comparison of residual mass fraction (M) by model prediction with experimental data at different heating rates (β) for pyrolysis of BR. \square and 1, \circ and 2, and \triangle and 3: experimental and predicted results for $\beta = 3, 5,$ and 7 K/min, respectively [20].

where $m_{V_{i,j}}$ is the volatile released from i th reaction path of j th component, and in this study:

$$X_{BR} = 1 - M_{BR} = m_{V_{1,BR}} + m_{V_{2,BR}}, \quad i = 2 \tag{2A}$$

$$X_{SBR} = 1 - M_{SBR} = m_{V_{1,SBR}} + m_{V_{2,SBR}} + m_{V_{3,SBR}}, \quad i = 3 \tag{2B}$$

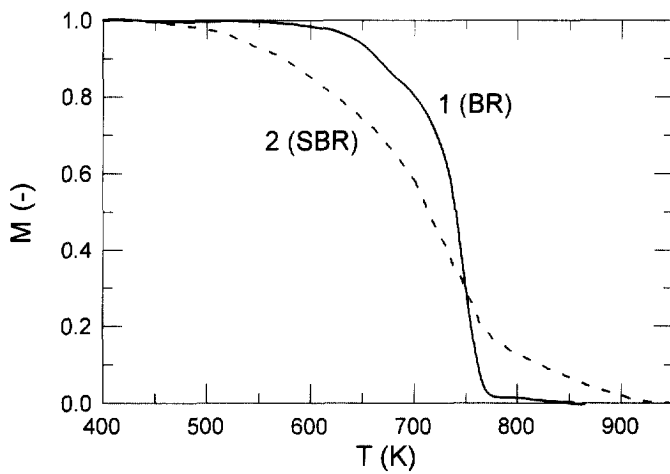


Fig. 4. Comparison of residual mass fractions (M) for pyrolysis of BR and SBR at $\beta = 7$ K/min.

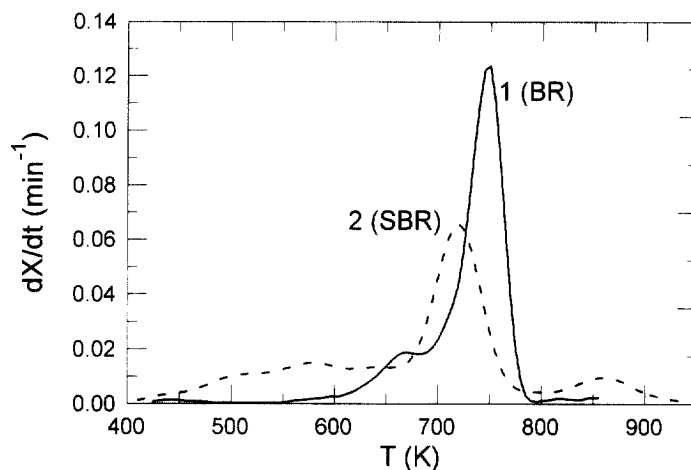


Fig. 5. Comparison of reaction rates (dX/dt) for pyrolysis of BR and SBR at $\beta = 7$ K/min.

The production rate of volatile ($m_{V_{i,j}}$) can be written as:

$$\frac{d\left(\frac{m_{V_{i,j}}}{F_{i,j}}\right)}{dt} = A_{i,j} \exp\left(-\frac{E_{i,j}}{RT}\right) \left[1 - \left(\frac{m_{V_{i,j}}}{F_{i,j}}\right)\right]^{n_{i,j}} \quad (3)$$

The initial condition for Eq. (3) is:

$$t = 0 \text{ for } M_j = 0, m_{V_{i,j}} = 0 \quad (4)$$

Satisfactory agreements between the proposed model and the experimental results have been obtained previously [19,20].

3.2. Pyrolysis of rubber mixtures

The variations of instantaneous reaction rates (r) of rubber mixture with temperature (T) under the three pre-set heating rates are shown in Fig. 6. It is noted that three peak

Table 2

Activation energies, frequency factors, reaction orders and weighting factors for the three reactions of SBR pyrolysis [19]

	First reaction	Second reaction	Third reaction
E (kJ/mol)	52.2	150.6	169.4
A (1/min)	2.3×10^3	1.5×10^{10}	3.5×10^{10}
n	2.09	1.28	1.90
F	0.35	0.50	0.15

F: fraction contributed by each reaction.

Table 3
Activation energies, frequency factors, reaction orders and weight factors for the two reactions of BR pyrolysis [20]

	First reaction	Second reaction
E (kJ/mol)	59.8	197.0
A (1/min)	2.8×10^3	1.9×10^{13}
n	1.27	1.49
F	0.195	0.805

F: fraction contributed by each reaction.

rates can be identified from the rate curves. A higher heating rate would shift the reaction rate curve to a higher temperature range and also result in a higher peak rate. The variations of residual mass fraction (M) with reaction temperature (T) at different heating rates are shown in Fig. 7. Three distinct mass changes might be identified over the experiment conditions.

3.3. Kinetic model for rubber mixture

Because of the similarity of reaction rate curves between rubber mixture and single constituent, we assume that: (a) the reaction of mixture could be expressed by the weighting combination of each component, (b) the corresponding reaction rate could be described by of Eq. (1), and (c) the reaction rate constant is a function of temperature according to the Arrhenius law.

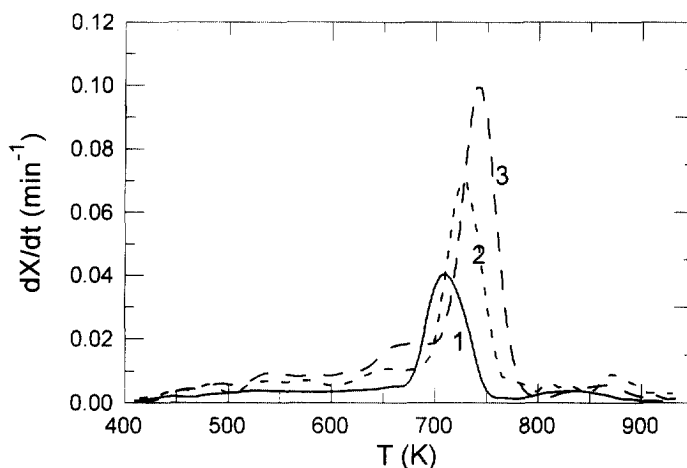


Fig. 6. Variations of instantaneous reaction rates (dX/dt) with temperature (T) for pyrolysis of rubber mixture at various heating rates (β). 1, 2 and 3: $\beta = 3, 5$ and 7 K/min.

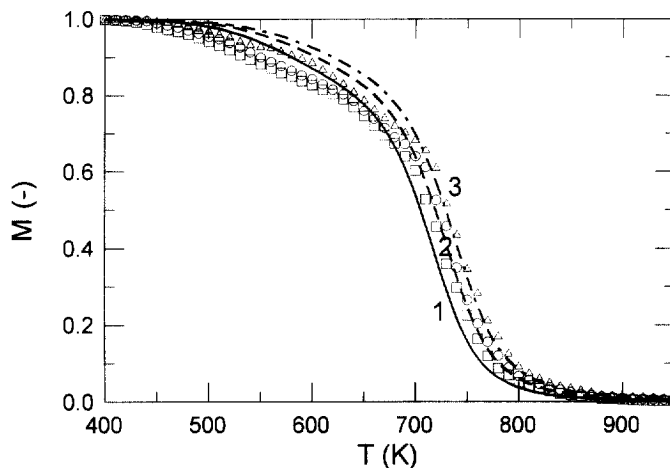


Fig. 7. Comparison of residual mass fraction (M) by model prediction with experimental data at different heating rates (β) for pyrolysis of rubber mixture. \square and 1, \circ and 2, and \triangle and 3: experimental and predicted results for $\beta = 3, 5,$ and 7 K/min, respectively.

The total conversion (X) of rubber mixture can be deduced from the individual conversions (X_j) of each components, i.e.

$$X = \sum_j \alpha_j X_j = \alpha_{BR} X_{BR} + \alpha_{SBR} X_{SBR} \quad (5)$$

where α_j is the mass fraction of j component, i.e. $\alpha_{BR} = 0.3625$ and $\alpha_{SBR} = 0.6375$. The differential form of Eq. (5) is:

$$\frac{dX}{dt} = \sum_j \alpha_j \frac{dX_j}{dt} \quad (6)$$

The kinetic parameters of BR and SBR pyrolysis are listed in Tables 2 and 3. By substituting the parameters and solving the Eqs. (2A), (2B), (3), (5) and (6), the simulated results, mass-loss history of rubber mixtures, can be obtained. The comparison of residual mass fractions predicted by the proposed model and those obtained by experiments is shown in Fig. 7. To verify the applicability of the proposed model, the coefficients of determination (R^2) are examined for $0.05 < M$ (predicted) < 0.95 , the value of R^2 are 0.9804, 0.9831 and 0.9857 for the heating rates of 3, 5 and 7 K/min, respectively. This, thus, indicates the validity and practical applicability of the proposed model which combines the corresponding rate of single rubber component with no detailed chemical composition of pyrolysis product.

4. Conclusions

The pyrolysis experiments of rubber mixture with pre-defined mass ratio were carried out by a dynamic TG reaction system in a nitrogen atmosphere, over the temperature

range of 400 to 950 K, at nominal heating rate of 3, 5 and 7 K/min. A simple kinetic model for the pyrolysis of rubber mixture was proposed. The mass-loss behavior of rubber mixture can be adequately described by the weighting sum of mass-loss of their components. This study surely assists the reutilization of wasted rubber mixture as an resource.

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