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Thermal degradation kinetics of polybutadiene rubber

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The thermal degradation kinetics of polybutadiene rubber (BR) was investigated by dynamic thermogravimetry, in a nitrogen atmosphere, over the temperature range 177–577°C and at constant nominal heating rates of 3, 5 and 7°C/min, respectively. Two distinct mass change stages in the thermogravimetric analysis (TGA) curves indicated that the degradation of BR may be attributed to two reactions. The corresponding activation energies, frequency factors and reaction orders of the two reactions were determined. A simplified two-reaction model based on the TGA curves was also proposed for engineering purposes. Satisfactory agreements between the proposed model and the experimental results were obtained. The results of this study are useful for the utilization of scrap BR as an alternative energy resource. © 1996 Elsevier Science Limited

1 INTRODUCTION

In Taiwan, polybutadiene rubber (BR) is classified as one of the principal manufacturing products of the synthetic rubber industry. Production quantities of BR have increased from about 35 000 metric tons in 1986 to about 43 000 metric tons in 1993.[1] About 78 000 metric tons of used tyres were discarded in 1991, while the amount was estimated to be 58 000 metric tons in 1989.[2] The growth rate of scrap tyres is high. Therefore, the treatment and disposal of rubber wastes has become a problem because of concern for the environment and care of the globe. Some studies and review literature indicate that proper pyrolysis methods may be appropriate solutions for both problems of treatment and minimization of rubber waste or scrap tyres.[3–11] Scrap tyres contain a vast amount of synthetic rubber with extremely high calorific value, say 40 000 kJ/kg. Because of the high calorific value, the conversion of scrap tyre or rubber wastes to market-ready products has become a principal focus from both the economical and environmental standpoints.

Several types of pyrolysis processes, such as fluidized bed processes,[12–14] batch processes,[15–19] vacuum processes,[20] molten salt processes,[21–23] and coprocessing with heavy oil,[7,24] have been tried for the treatment of rubber wastes, scrap tyres and automobile shredder wastes. The gas products may contain hydrogen, methane, ethane, propylene, butene, butadiene, etc., while benzene, toluene, xylene, ethylbenzene, limonene, naphthalene, etc. are identified in the oil products.[13,14,19] The conversion of pyrolysis residues into activated carbon may be one of the most effective usages of chars obtained through pyrolysis of rubber wastes, and the desired characteristics of final solid products could also be obtained.[18,25,26]

Methods for the treatment of mass-loss curves, obtained through thermogravimetric analysis (TGA), have previously been studied and reviewed.[27–29] The thermal degradation of polybutadiene with an apparent activation energy of

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251 kJ/mol and maximum degradation rate of 0.0091 min^{-1} (375°C) has been performed by the use of derivative thermogravimetric analysis (DTG).[30] The decomposition of polybutadiene, studied by pyrolysis gas chromatography (PGC), is mainly by bond scission followed by unzipping to yield butadiene monomer at lower temperatures, while at higher temperatures the H transfer reaction is followed resulting in the formation of one saturated end and the other unsaturated.[31] A dynamic thermogravimetry study indicated that the pyrolysis of used tyres in the temperature range of 417–457°C follows first-order kinetics with an activation energy of 170 kJ/mol.[32] The activation energies for the pyrolysis of BR and styrene–butadiene rubber (SBR) were reported to be 263.4 and 253.6 kJ/mol with maximum degradation rate occurring at 473 and 460°C, respectively, but the pyrolysis schemes were not mentioned any further.[33] The pyrolysis of waste tyres, in the temperature range from 300 to 900°C, has been investigated by isothermal TG, and the activation energy was determined to be 613.0 kJ/mol with the second-order reaction.[34] For the temperature range 175–450°C, the activation energies for the pyrolysis of BR in an oxidative atmosphere were estimated to be 66.8 (175–275°C), 86.1 (275–350°C) and 209.4 (350–450°C) kJ/mol.[35] In the temperature range 300–500°C, a first-order reaction could be adequately used to describe the pyrolysis kinetics of BR with activation energy 215 kJ/mol and frequency factor 6.32×10^{14} min^{-1}.[36] Also, no reaction scheme was suggested. Therefore, there is a need to propose a convenient method to determine the reaction rate for the pyrolysis of BR and to suggest a simplified reaction model which may properly describe the pyrolysis history of BR.

It is thus the aim of the present work to deal with the degradation of BR to provide a simple reaction model for engineering purposes. The pyrolyzer was a dynamic thermogravimetry system at the temperature-programmed constant heating rates of 3, 5 and 7°C/min, respectively, in a nitrogen atmosphere. The corresponding activation energies, frequency factors and orders of reactions were determined. A simple reaction model is proposed for describing the pyrolysis of BR. All these results are useful for the pyrolytic treatment of rubber wastes of BR.

2 EXPERIMENTAL

2.1 Materials

A commercial-grade BR was used in this study. It was supplied by the Taiwan Synthetic Rubber Corporation. Property, elemental and calorific value analyses of the samples are listed in Table 1. Nitrogen gas, with 99.99% purity, was purchased from the Ching-Feng-Harng Co. Ltd in Taipei, Taiwan.

2.2 Apparatus and procedures

The experimental flow diagram for the pyrolysis of BR is shown in Fig. 1. Details of the experimental methods have been described in detail previously.[37]

3 RESULTS AND DISCUSSION

3.1 Effects of temperature and heating rate

The residual mass fraction of active reactant (M) is expressed on a normalized basis, $M = (W - W_f)/(W_o - W_f)$, where W, W_o, W_f = mass, initial mass and final mass of the sample, respectively. The variation of M with reaction temperature (T) is shown in Fig. 2. There are two principal reactions as distinguished by the two distinct mass changes in Fig. 2 over the experimental

Table 1. Some properties of BR used in this study

Item	Property
Trade name	TAIPOL BR 0150
Configuration	96%[a] Cis minimum
Elemental analysis (weight %)	
C	88.72(0.005)[b]
H	11.17 (0.01)
N	ND[c]
O	<0.1
S	2.04 (0.01)
Cl	0.36 (0.01)
Composition analysis (wt %)	
Moisture	0.22(0.0037)
Ash	0.08(0.0030)
Combustible	99.70[d]
Calorific value (kJ/kg)	45 600

[a] In weight percent.

[b] Numbers in parentheses are standard deviations.

[c] Not detected.

[d] Combustible = 1 − moisture − ash.

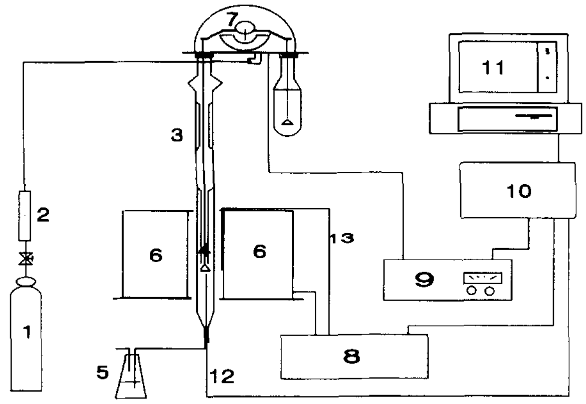


Fig. 1. Schematic diagram of apparatus for the pyrolysis of BR. 1: Nitrogen; 2: flow meter with needle valve; 3: reactor; 4: extension wire and sample disk; 5: trap; 6: furnace; 7: electrobalance; 8: temperature controller; 9: electrobalance controller; 10: data acquisition unit; 11: personal computer; 12, 13: K-type thermocouples.

range for the three different heating rates (β) under investigation. At a temperature of about 227°C (500 K), the first reaction of mass change begins and goes on up to about 427°C (700 K) with $M = 0.805$, which may also be judged by the use of plots of $\mathrm{d}X/\mathrm{d}t$ and $\mathrm{d}^2X/\mathrm{d}t^2$ versus T ($X = 1 - M$, t = reaction time). Afterwards, the second reaction proceeds and goes on to the end. The first reaction may be attributed to the thermal formation of volatiles V_1, which are much easier to form at lower temperatures and with a slower reaction rate. The second reaction, which is a reaction with a faster rate, may be the degradation of intermediates yielding volatiles V_2.

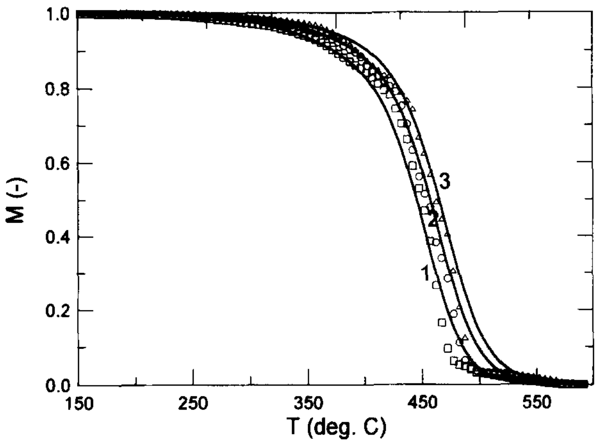


Fig. 2. Comparison of residual mass fraction (M) by model prediction with experimental data at different heating rates (β) for pyrolysis of BR. □ and 1, ○ and 2, and △ and 3: experimental and predicted results for β = 3, 5 and 7°C/min.

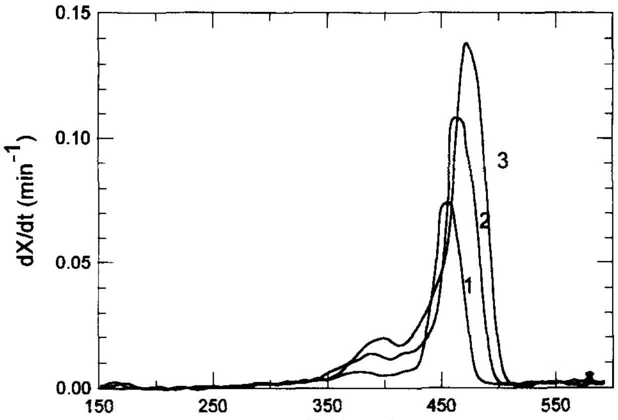


Fig. 3. Variations of instantaneous reaction rates ($\mathrm{d}X/\mathrm{d}t$) with temperature (T) for pyrolysis of BR at various heating rates (β). 1,2,3: β = 3,5,7°C/min.

The variations of instantaneous reaction rates ($r = \mathrm{d}X/\mathrm{d}t$) with temperature ($T$) under the three heating rates are shown in Fig. 3. It is noted that two peak rates can be identified from the rate curves. For instance, the first peak occurs at about 387°C (660 K) with a reaction rate of about 0.021 min^{-1} for a heating rate of 7°C/min; the second is around 467°C (740 K) with a reaction rate of 0.147 min^{-1} under the same heating rate. This may suggest that two major reactions proceed throughout the experimental conditions. The corresponding fractions F_1 and F_2 caused by the first and second reactions are determined to be 0.195 (= 1 − 0.805) and 0.805, respectively.

3.2 Kinetic parameters

The foundation for the study of kinetic data from the mass-loss curve is based on the basic rate equation:

$$r = \mathrm{d}X/\mathrm{d}t = kf(X) \qquad (1)$$

where

k = the Arrhenius rate constant, $k = A\exp(-E/\mathrm{R}T)$,
A,E = frequency factor, activation energy,
R,n = universal gas constant, reaction order,
$f(X)$ = the function of conversion X, $f(X) = (1-X)^n$.

The differential, iso-conversion method for determining the activation energy was employed in this study. The activation energies at various conversions are shown in Fig. 4. The results indicate that values of the activation energy for

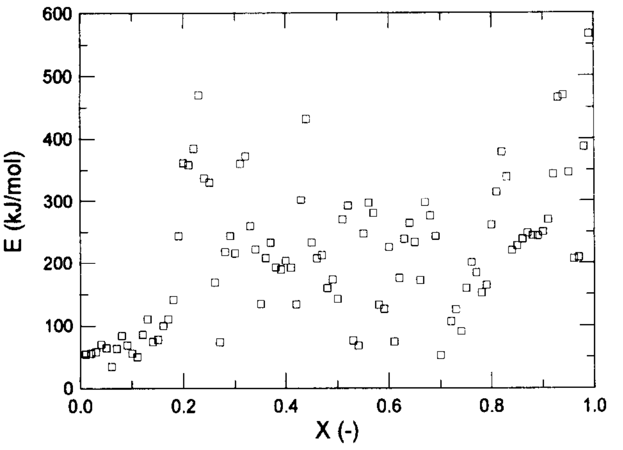


Fig. 4. Variations of activation energies (E) with conversion (X) for pyrolysis of BR.

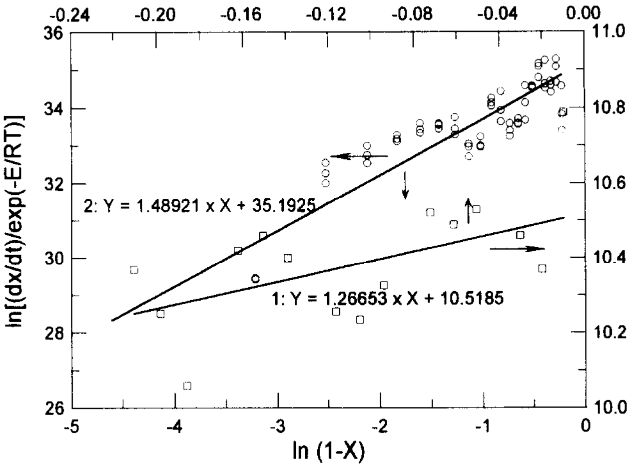


Fig. 5. Variations of $\ln[(dX/dt)/\exp(-E/(RT))]$ with $\ln(1-X)$ for determination of reaction order and frequency factor for pyrolysis of BR. □ and 1, and ○ and 2: experimental and correlated results of first and second reactions.

the pyrolysis of BR are about 50–500 kJ/mol. According to the results shown in Figs 2 and 3, two reactions are observed. The arithmetic means of the activation energies corresponding to the two reactions are 59.8 kJ/mol for the first reaction (X:0.02–0.11) and 197.0 kJ/mol for the second reaction (X:0.40–0.80), respectively. Some kinetic parameters of scrap tyres or rubber wastes are listed in Table 2 indicating that the activation energies are in the range of about 50–600 kJ/mol. The reaction order (n) can be obtained from the slope of the plot of $\ln[(dX/dt)/\exp(-E/(RT))]$ versus $\ln(1-X)$ for each reaction as shown in Fig. 5. Therefore, the reaction orders of the two different reactions are 1.27 ($E = 59.8$ kJ/mol) and 1.49 ($E = 197.0$ kJ/mol) for the first and second reactions, respectively. The frequency factors are determined by the use of temperature dependence of reaction rate constant, i.e. the Arrhenius law as shown in Fig. 6, which shows $\ln k$ versus $1/T$ with the slope of $-E/R$ and the intercept of $\ln A$. Thus, the values of frequency factors are 2.8×10^3 and 1.9×10^{13} min^{-1} for the first and second reactions, respectively. Values of E, A, n and F for the two reactions of BR pyrolysis are listed in Table 3.

Table 2. Comparison of kinetic parameters of pyrolysis of scrap tyres or rubber wastes

Material used	Test method	Activation energy (kJ/mol)	Max. reaction rate (min^{-1})	Reaction order	Frequency factor (min^{-1})
Polybutadiene[30]	Derivative TG	251	0.0091 (375°C)[a]	—	—
Tyre waste[15]	Batch process	125.5	—	1	1.1×10^9
Used tyre[32]	Dynamic TG	170.0	—	1	—
BR[33]	Dynamic TG	263.4	—(473°C)	—	—
SBR[33]	Dynamic TG	253.6	—(460°C)	—	—
Waste tyre[34]	Isothermal TG	613.0	—	2	3.3×10^5
BR[35]	Dynamic TG	66.8; 86.1; 209.4[b]	—	—	7.2×10^7; 4.9×10^6; 1.4×10^{15}
SBR[35]	Dynamic TG	112; 126.9; 331.1; 160.7[c]	—	—	3.7×10^{12}; 9.5×10^9; 7.9×10^{23}; 2.5×10^{10}
BR[36]	Derivative TG	215	—	1	6.32×10^{14}
SBR[36]	Derivative TG	152	—	1	1.78×10^{10}
BR[d]	Dynamic TG	59.8	0.021 (387°C)[e]	1.27	2.8×10^3
		197.0	0.147 (467°C)	1.49	1.9×10^{13}

[a] Numbers in parentheses are temperatures at which max. reaction rates occur.

[b] Temperature ranges: 175–275°C for 66.8, 275–350°C for 86.1, and 350–450°C for 209.4; under oxidative atmosphere.

[c] Temperature ranges: 175–275°C for 112, 275–350°C for 126.9, 350–450°C for 331.1, and above 450°C for 160.7; under oxidative atmosphere.

[d] This study.

[e] Data for heating rate of 7°C/min.

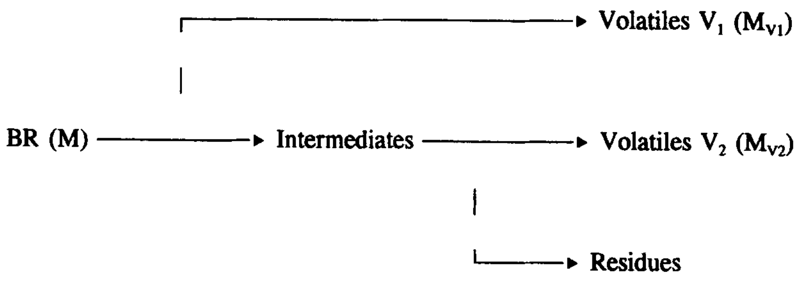
3.3 Kinetic model

According to the kinetic parameters obtained above and the temperature dependence of reaction rates (Fig. 6), there exist two reactions which may proceed for the pyrolysis of BR in this study. Thus, a reaction model based on the residual curves is proposed to represent the pyrolysis of BR as follows:

Table 3. Values of E, A, n and F for two reactions of BR pyrolysis in this study

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

F: fraction contributed by each reaction.



where V_1 and V_2 are the volatiles (with mass fractions of M_{V1} and M_{V2}, respectively) obtained from the pyrolysis of BR and its intermediates, respectively. It can be shown that

$$\frac{M_{Vi}}{F_i}=1-\left[1-(1-n_i)\frac{A_i RT^2}{\beta E_i}\exp\left(-\frac{E_i}{RT}\right)\sum(E_i,T)\right]^{1/1-n_i} \quad (2)$$

where

$$\sum(E_i,T)=\sum_{j=0}^{\infty}\left[\left(-\frac{RT}{E_i}\right)^j\prod_{k=0}^{j}(k+1)\right]$$
$$=1-2\frac{RT}{E_i}+6\left(\frac{RT}{E_i}\right)^2-24\left(\frac{RT}{E_j}\right)^3+120\left(\frac{RT}{E_i}\right)^4-\ldots \quad (3)$$

F_1 and F_2 are 0.195 and 0.805, respectively, as previously determined. The variations of M_{V1} and M_{V2} against T at 5°C/min heating rate are shown in Fig. 7. The accumulated release of V_1 increases

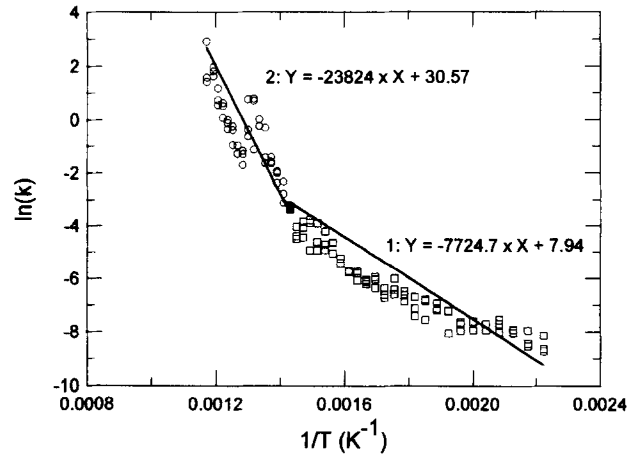


Fig. 6. Temperature dependence of the reaction rate constant (k) for Arrhenius' law. □ and 1, ○ and 2: experimental data and correlated results of first and second reactions.

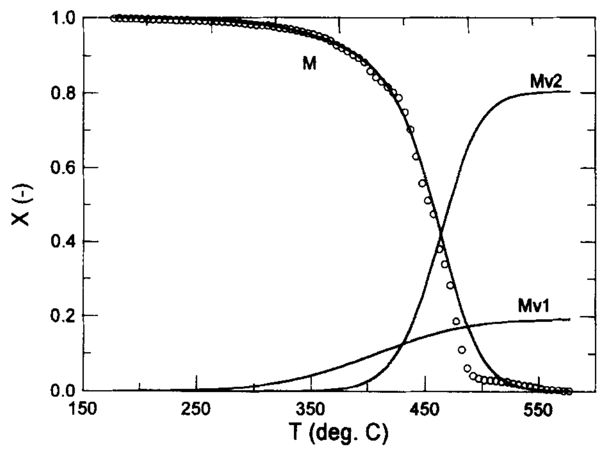


Fig. 7. Comparison of experimental data (○) and predicted values (•) of residue mass fraction (M), and computed values (•) of mass fractions of V_1(M_{V1}) and V_2(M_{V2}) for pyrolysis of BR at β =5°C/min.

steadily from about 277 to 487°C, whereas that of V_2 exhibits a rapid increase from about 377 to 507°C. Thus, the variation trends of M_{V1} and M_{V2} justify the two distinct mass changes of M in Fig. 2. A comparison of residual mass fractions predicted by the proposed model and those obtained by experiments is also shown in Fig. 2, indicating satisfactory agreements.

To verify the applicability of kinetic parameters and the validity of the proposed model, the coefficients of determination (R^2) are examined for $0.05 < M$ (predicted) < 0.95, and the values of R^2 are 0.981, 0.997 and 0.994 for the heating rates of 3, 5 and 7°C/min, respectively. This thus shows the validity and practical applicability of the proposed two-reaction model for describing the pyrolysis of BR without specifying the detailed chemical reactions involved.

4 CONCLUSIONS

Thermal degradation experiments on BR were carried out by a dynamic TG reaction system, in nitrogen atmosphere, over the temperature range 177–577°C and at pre-set heating rates. A simplified two-reaction model was proposed to model the experimental results. The activation energies, frequency factors and reaction orders were determined for the two reactions under experimental conditions. The pyrolysis of BR can be adequately described by the proposed model. This study greatly assists the reutilization of scrap BR as an energy resource.

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