

High-Resolution Thermogravimetry/Coupled Mass Spectrometry Analysis of Flame-Retardant Rubber

Y. N. Gupta, Amitabh Chakraborty, G. D. Pandey, D. K. Setua

Defence Materials & Stores Research & Development Establishment PO, G.T. Road, Kanpur 208013, India

Received 11 May 2002; accepted 26 August 2002

ABSTRACT: A bromobutyl rubber composition containing a variety of conventional flame retardants, such as Saytex (decabromodiphenyl oxide), Sb_2O_3 , chlorinated paraffin wax, and polychloroprene rubber, was prepared and used to coat nylon 6 fabric in a laboratory-coating device. An attempt was made to evaluate the decomposition profile, the evolved gases, and the kinetics of the decomposition process at a dynamic heating rate with high-resolution thermogravimetric analysis (HR-TGA). HR-TGA was used with mass spectrometry for evolved gas analysis (EGA). The HR-TGA results were compared with results from conventional thermogravimetric analysis (TGA) at a constant heating rate; the former offered sharp transitions, an economic timescale, and an accurate activation energy. The resolution optimization

for stability analysis and the effect of its variation on the kinetic parameters offered better results for HR-TGA than conventional TGA. A lifetime and temperature relationship was evaluated in HR-TGA with Toop's method, and it was observed that the shelf life decreased sharply with temperature. The effluents HBr, HCl, Br · , and Cl · , generated between 210 and 496°C during EGA, were correlated with the thermal stability and fire-retardancy behavior of the material. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2051–2057, 2003

Key words: thermogravimetric analysis (TGA); mass spectrometry; degradation; flame retardance; rubber

INTRODUCTION

Fire-retardant polymers have acquired importance in industrial and technological development. For many years, a material was regarded as flame-retardant if it did not burn, regardless of how this was accomplished. However, recent surveys on the number of deaths in fire due to toxic gases and smoke production, rather than fire itself, have resulted in growing public awareness and a need for a comprehensive study of the efficacy of fire-retardant materials. In evaluating these materials, we must consider the effect of flame retardants on degradation products and the degradation kinetics.

ASTM procedures (D 568-61, D 635-63, D 757-49, D 1692-57T, and D 1360-58) can be used to evaluate the flammability of materials. However, all these methods suffer from the disadvantages of being empirical in nature and time-consuming. However, thermal analysis methods are fast, reproducible, and sensitive.

The burning of substances, such as rubber in the gas phase, generates fuel for the flame and provide energy to sustain the pyrolytic reactions and flame propagation. Therefore, an accurate estimation of the gaseous materials evolved is important.¹ In thermogravimetric

analysis (TGA), evolved gas analysis (EGA) is done by its coupling with mass spectrometry (MS).²

For kinetic studies, traditionally both isothermal and nonisothermal methods are applied. However, experiments with a constant heating rate are faster than a series of isothermal experiments. In conven-

TABLE I
Composition of the Rubber Coating Material

Ingredient	Chemical composition/Source	phr
BIIR	Bromobutyl rubber (BIIR-2244), Polysar (Ottawa, ON, Canada)	100
CR	Neoprene (CR-WM1), DuPont (Wilmington, DE)	20
Chlorinated paraffin wax	58% Chlorine content	5
Stearic Acid		1
PBNA	Phenyl β -naphthyl amine	1
ZnO		10
Sb_2O_3		10
Saytex	Decabromodiphenyl ether	20
CPE	Chlorinated polyethylene (Tyrin-0136), D Chemical (Midland, MI), 36% chlorine content	5
MgO		4
Sulfur		1.5
TMTD	Tetramethyl thiuram disulphide	1.5
MBTS	Mercaptobenzothiazyl sulphenamide	1.5
ZDC	Zinc diethyl dithiocarbamate	0.5

phr = Parts per hundred parts of rubber.

Correspondence to: D. K. Setua (dmsrde@sancharnet.in).

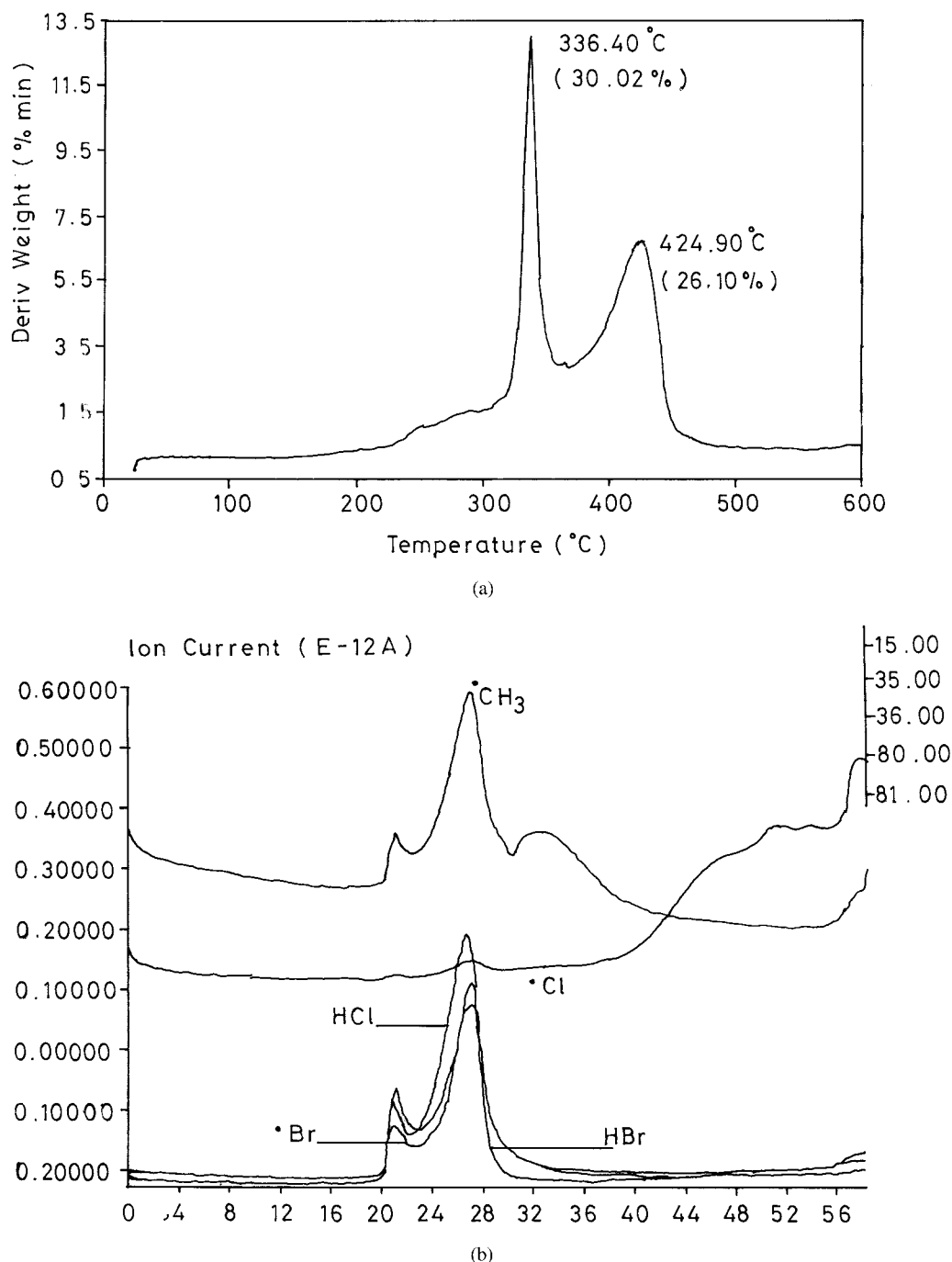


Figure 1 (a) DTG thermogram of conventional TGA at a constant heating rate of 15°C/min and (b) mass spectrograph of the conventional TGA mode.

tional TGA, the requirement of a high resolution necessitates a low heating rate and, therefore, an increased experimental time.³⁻⁵ For a balance between the experimental time and high resolution, high-resolution thermogravimetric analysis (HR-TGA) has been developed. In this method, the heating rate is dynamically varied to maximize the resolution and to separate closely occurring events. Furthermore, as the reaction rate is increased, the heating rate is automatically reduced and vice versa. Therefore, a good

resolution coupled with an acceptable time frame can be obtained in a single experiment.

The effects of various chemical additives [e.g., brominated phenyl ether (decabromo diphenyl oxide), chlorinated paraffin wax, inorganic oxides (e.g., Sb₂O₃), and halogenated rubber [e.g., polychloroprene rubber (CR)] on the flame-retardancy behavior of brominated isobutylene-*co*-isoprene rubber (BIIR) have been discussed elsewhere.⁶ An appropriate formulation consisting of the aforementioned materials was

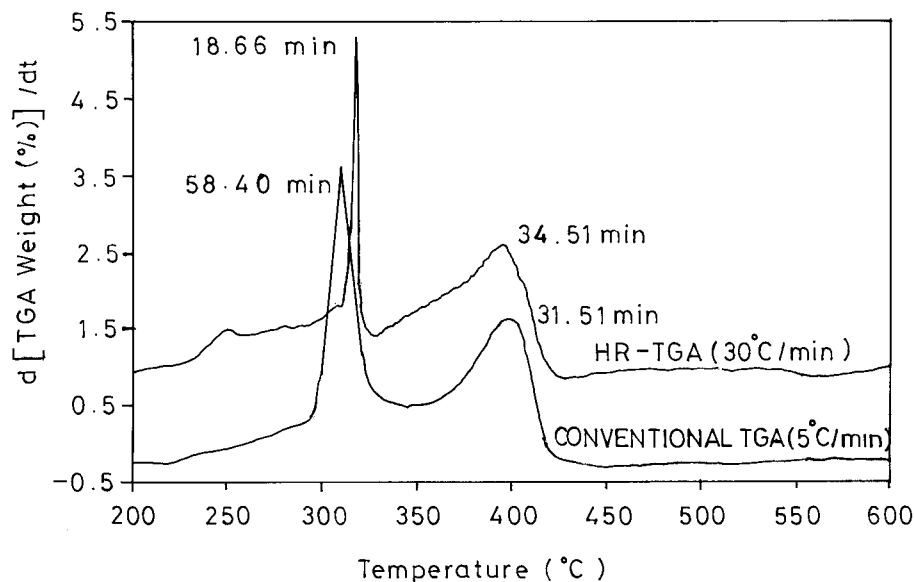


Figure 2 Comparison of the DTG thermograms for conventional TGA and HR-TGA.

used to prepare a rubber cement to coat a nylon 6 fabric in a laboratory coating machine and was cured to yield a flame-retardant rubberized fabric for defense applications. The objective of this study was to identify the decomposition products by MS and to study the thermal degradation kinetics of the rubber coating with both conventional TGA and HR-TGA. The methodology of determining the kinetic parameters from variable heating rate data has been developed only recently.⁷ Kinetic results have also been used for a lifetime estimation of the rubber.

EXPERIMENTAL

The fire-retardant rubber coating (0.15 mm thick) was removed from the nylon fabric through swelling in toluene and then was vacuum-dried in an oven at 70°C to a constant weight. The composition of the rubber coating is given in Table I. The experiments were performed in an HR-TGA 2950 from TA Instruments (New Castle, DE). In the constant heating rate mode

(conventional TGA), experiments were performed at 5, 10, and 15°C/min, respectively, between the ambient temperature (25°C) and 600°C under a nitrogen atmosphere (purge rate = 60 mL/min). For the variable heating rate mode (HR-TGA), first the initial heating rate was kept at 30°C/min, and the resolution was varied from 2 to 6 in steps of 2. Second, the resolution was fixed at 4, and the initial heating rate was varied from 25 to 35 to 45°C/min, respectively. The temperature range and the nitrogen flow rate were kept the same as those for conventional TGA. HR-TGA was also coupled with MS (Thermostat GD 300, Balzers Instruments, Germany) for EGA. The scan speed was kept at 0.5 s/amu up to the mass range of 300 amu. The resolution of the mass spectrometer was taken to be 25.

CALCULATIONS

The activation energy (E_a) for the conventional TGA was calculated with Flynn and Wall's procedure:⁸

TABLE II
Summary of the DTG Results for Conventional TGA

Heating rate (°C/min)	Time for maximum decomposition (min)	Peak temperature (°C)	Maximum decomposition rate (%/min)	Weight loss (%)
First step of decomposition				
5	58.40	309.85	4.405	32.20
10	30.17	319.40	7.383	28.24
15	21.27	336.42	12.360	29.06
Second step of decomposition				
5	75.73	398.31	2.153	23.27
10	39.40	411.71	4.610	26.81
15	27.16	424.88	6.752	26.24

TABLE III
Summary of the DTG Results for HR-TGA at the Initial Heating Rate of 30°C/min

Resolution	Time for maximum decomposition (min)	Peak temperature (°C)	Maximum decomposition rate (%/min)	Weight loss (%)
First step decomposition				
2	11.98	347.44	24.620	28.58
4	18.66	316.22	4.973	25.68
6	95.54	268.25	0.316	29.00
Second step of decomposition				
2	16.37	431.58	8.774	27.05
4	34.51	395.55	2.202	27.49
6	212.05	352.28	0.272	22.96

$$E_a = - (R/b)[\{d \ln \beta / d(1/T)\}] \quad (1)$$

where b is a constant (0.457) with a reaction order of $n = 1$, β is the heating rate (°C/min), T is the temperature at a constant conversion (K), and R is the gas constant (8.314 J/mol K). With a point of equivalent weight loss, a plot of $\ln \beta$ versus $1/T$ can be drawn. The slope of the straight-line plot was used to calculate E_a .

The calculation of E_a for HR-TGA was performed with the equation developed by Salin and Seferis:⁷

$$\ln(q/T^2) = (-E_a/RT) + \ln[(AR/Ea)n(1-\alpha)^{n-1}] \quad (2)$$

where q is the minimum heating rate (°C/min), T is the temperature (K), R is the gas constant, A is the pre-exponential factor (1/min), n is the reaction order, and α is the fraction of decomposition. E_a was calculated with the slope of the plot of $\ln(q/T^2)$ versus $(1/T)$.

The lifetime of the product was calculated with the following equation after Toop:⁹

$$\ln t_f = \{E_a/RT_f\} + \ln[(E_a/\beta R) \times P(X_f)] \quad (3)$$

where t_f is the estimated time to failure (min), T_f is the failure temperature (K), R is the gas constant, β is the heating rate (°C/min), and $P(X_f)$ is a function whose values depend on E_a at T_f .

RESULTS AND DISCUSSION

Figure 1(a) shows the derivative thermogravimetry (DTG) thermogram of a rubber composition in the conventional TGA mode at a constant heating rate of 15°C/min. Two successive steps of weight loss can be recognized. The first one is between 210 and 369°C, and the second one is between 369 and 496°C. The corresponding peak temperatures are at 336.40°C with a weight loss of 30.02% and at 424.90°C with a weight loss of 26.10%. Figure 1(b) shows the simultaneous mass spectrum of the material, in which the decomposition can be observed to be accompanied by a release of fragments (Br·, Cl·, HCl, HBr, and CH₃). The formation of hydrogen halides is due to the combination of antimony oxide with organic halogen compounds that produce antimony trihalide, which carries the halogen into the flame, where it is released as hydrogen halide. The decomposition also favors cleavage of the carbon-halogen bonds, yielding Br· and Cl· fragments, which act as vapor-phase inhibitors.

Figure 2 compares the derivative thermograms of the coating for both conventional TGA (constant heating rate = 5°C/min) and HR-TGA (initial heating rate = 30°C/min at a resolution of 4). The time required to reach the peak of the first thermal decomposition step for conventional TGA is 58.40 min, whereas that for HR-TGA is only 18.66 min. Moreover, it is apparent that the conventional mode does not give a resolution

TABLE IV
Temperature Difference Between the Minimum Heating Rate and the Maximum Decomposition Rate

Resolution	First step of decomposition			Second step of decomposition			
	T_1 (°C) ^a	T_2 (°C) ^b	$(T_2 - T_1)$ (°C)	T_1 (°C) ^a	T_2 (°C) ^b	$(T_2 - T_1)$ (°C)	
2	344.95	347.44	2.49	435.37	431.58	3.79	
4	316.35	316.22	0.13	395.41	395.55	0.14	
6	267.56	268.25	0.69	351.72	352.28	0.56	

^a Temperature at the minimum heating rate.

^b Temperature at the maximum rate of thermal decomposition.

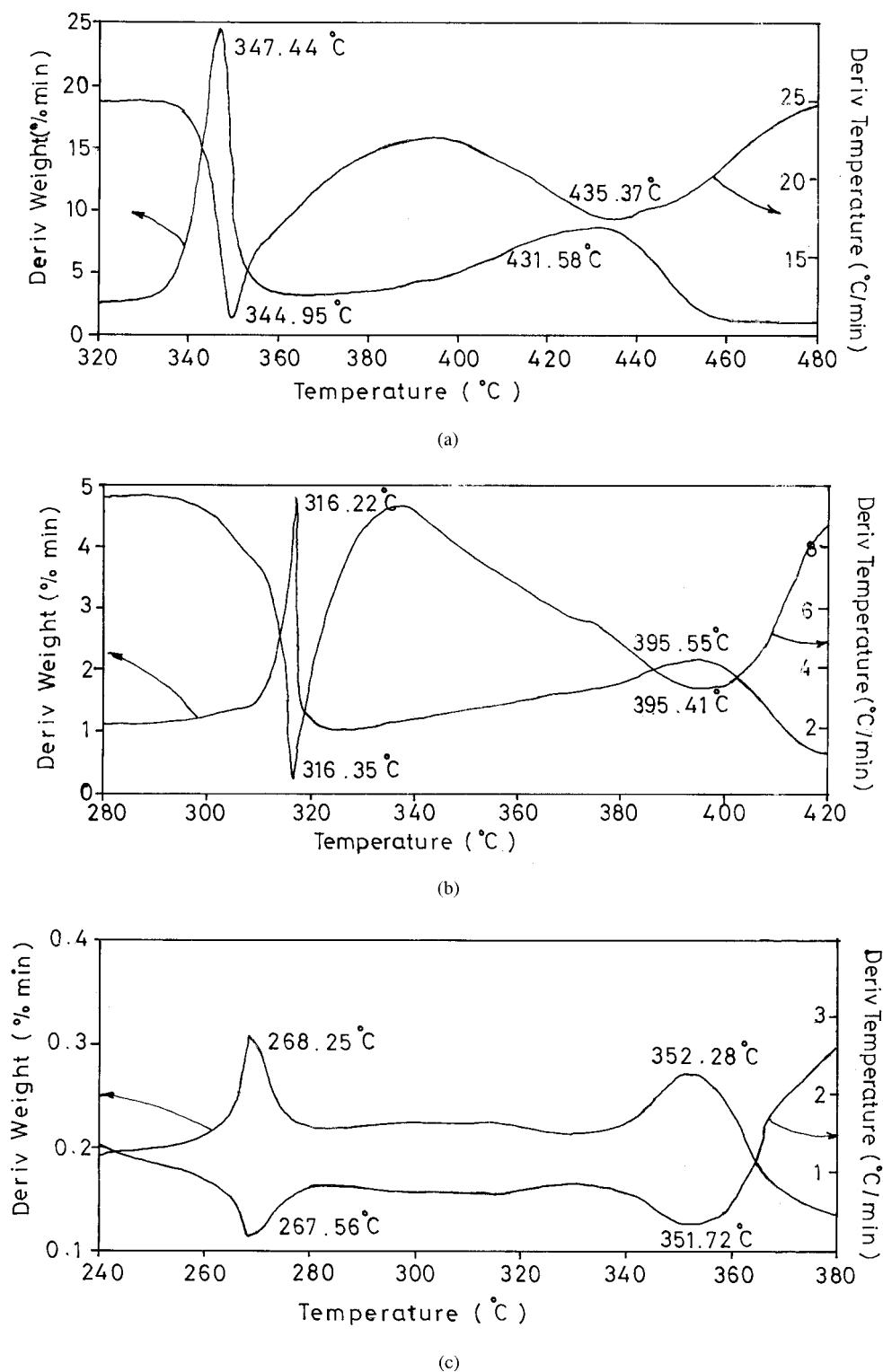


Figure 3 Comparison of the thermograms of the thermal decomposition and heating rate at resolutions of (a) 2, (b) 4, and (c) 6.

as good as that of HR-TGA, which also offers sharp transitions and an economic timescale.

Table II shows a summary of DTG data for conventional TGA at constant heating rates of 5, 10, and 15°C/min. It is evident that the increase in the heating

rate results in a shifting of the peak temperatures toward the higher side for both the first and second steps of decomposition. The results also indicate that with the heating rate increasing, the maximum rate of thermal decomposition is increased. The weight-loss

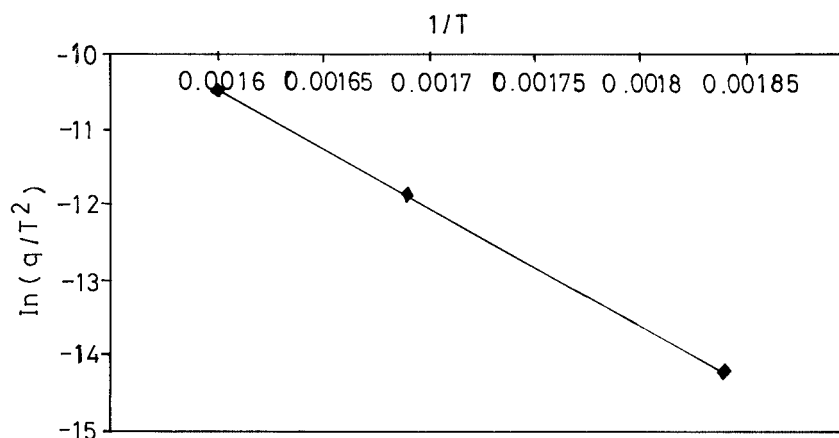
TABLE V
Summary of DTG Results for HR-TGA at a Fixed Resolution of 4

Initial heating rate (°C/min)	Time for maximum decomposition (min)	Peak temperature (°C)	Maximum decomposition rate (%/min)	Weight loss (%)
First step of decomposition				
25	21.23	312.68	4.592	25.65
35	17.15	312.98	4.910	24.70
45	14.86	317.32	5.522	25.75
Second step of decomposition				
25	37.42	392.55	2.007	26.69
35	31.46	394.71	2.281	27.33
45	28.00	397.18	2.378	26.83

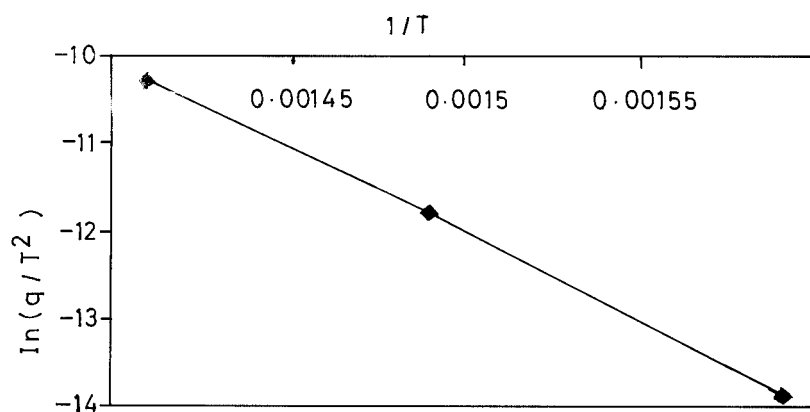
percentage, however, does not vary much with the heating rate.

Table III summarizes the DTG results for HR-TGA when a resolution sweep is made from 2 to 6 in steps of 2 at an initial heating rate of 30°C/min. As the resolution is increased, the corresponding peak temperatures are shifted toward the lower values, as the high resolution generated a minimum heating rate at a

maximum thermal decomposition. This enabled us to obtain more accurate measurements of the peak temperatures at sharp transition points. The results also show that the resolution sweep from 2 to 6 causes a concomitant decrease in the maximum thermal degradation rate. This agrees with the high-resolution approach. A comparison of the results of Tables II and III indicates that the variation of the resolution is analo-



(a)



(b)

Figure 4 Plots of $\ln(q/T^2)$ versus $1/T$ for (a) the first step of decomposition and (b) the second step of decomposition by HR-TGA.

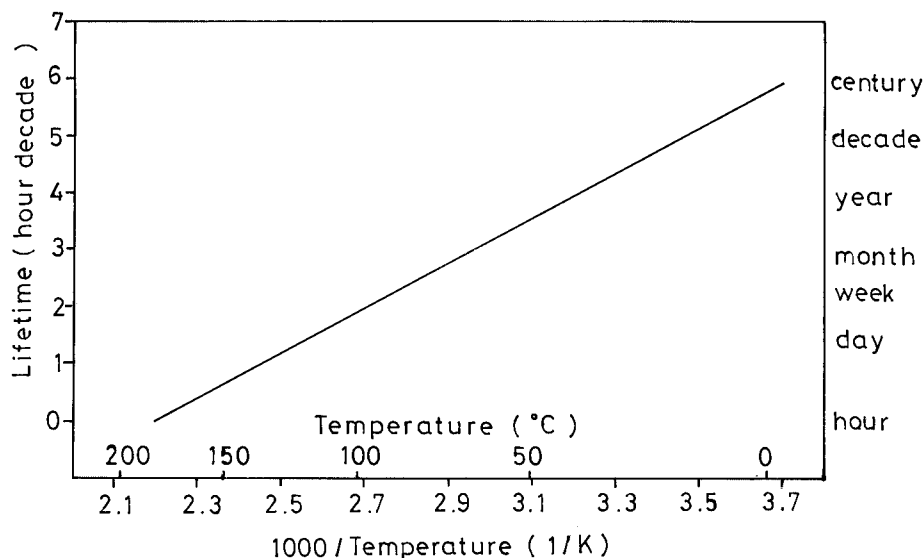


Figure 5 Estimated shelf life versus the temperature.

gous to a change in the heating rate in conventional TGA experiments. It is further apparent from Table IV and Figure 3(a–c) that at a resolution of 4, the minimum heating rate and maximum rate of thermal decomposition coincide, and this makes a resolution of 4 the optimum choice for further study.

Table V summarizes the DTG results of HR-TGA experiments in which the initial heating rate is varied from 25 to 45°C/min in steps of 10°C/min at a fixed resolution of 4. The influence of the variation of the initial heating rate is apparently insignificant on the variation of the peak temperatures. A comparison of Tables III and V shows that the peak temperature is strongly affected by the resolution but less so by the initial heating rate. Therefore, fixing the initial heating rate and varying the resolution has been found to be the best approach for generating kinetic information. An initial heating rate of 30°C/min was, therefore, chosen for further analysis.

Figure 4(a,b) shows plots of $\ln(q/T^2)$ versus $1/T$ for the first and second steps of decomposition in HR-TGA (with data from Table III). The corresponding E_a value obtained for the first step of decomposition is 129.23 kJ/mol, and for the second step, it is 165.87 kJ/mol. Contrary to HR-TGA, for conventional TGA, the corresponding values are 88.8 (first step) and 125.5 kJ/mol (second step), respectively (with data from Table II). The poor agreement may be due to the fact that the decomposition kinetics does not follow Flynn and Wall's⁸ approximations.

A plot of the shelf life versus the temperature is shown in Figure 5. At an ambient temperature of 25°C and at a conversion level of 20%, the shelf life is calculated to be 4.18 years. The shelf life decreases sharply with an increase in the temperature; for exam-

ple, at 50°C, the value is about 145 days. The lower shelf life of the sample has been attributed to the addition of fire retardants, which accelerates the decomposition reaction.¹⁰

CONCLUSIONS

1. The thermal decomposition of bromobutyl rubber is accompanied by the evolution of Br ·, Cl ·, HBr, HCl, and CH₃.
2. The best approach for analyzing thermal stability is to optimize the resolution; for generating kinetic information, the best approach is to vary the resolution through the HR-TGA method.
3. The initial heating rate has no significant effect on the kinetics of decomposition of rubber in HR-TGA.
4. The E_a value determined from HR-TGA is more accurate than that from conventional TGA.
5. The shelf life decreases sharply with an increase in temperature.

References

1. Liepins, R. J. *Fire Flamm* 1975, 6, 326.
2. Stafford, G. C. *J Mass Spectrom Ion Process* 1984, 60, 85.
3. Rouquerol, J. *Bull Soc Chim* 1964, 31.
4. Paulik, F.; Paulik, J. *Anal Chim Acta* 1971, 56, 328.
5. Sorenson, S. *J Therm Anal* 1978, 13, 429.
6. Setua, D. K.; Pandey, A. K.; Debnath, K. K.; Mathur, G. N. *Kautsch Gummi Kunstst* 1999, 7, 486.
7. Salin, I. M.; Seferis, J. C. *J Appl Polym Sci* 1993, 47, 874.
8. Flynn, J. H.; Wall, L. A. *Polym Lett* 1966, 19, 323.
9. Toop, D. J. *IEEE Trans Electr Insul* 1971, EI-6, 2.
10. *Calorimetry and Thermal Analysis of Polymers*; Mathot, V. B. F., Ed.; Hanser: New York, 1994; p 36.