Thermochimica Acta, 80 (1984) 75–80
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

FURTHER STUDY ON THE PREDICTION OF ISOTHERMAL INDUCTION TIME BY DYNAMIC DIFFERENTIAL SCANNING CALORIMETRY

S.H. GOH

Department of Chemistry, National University of Singapore, Singapore 0511
(Republic of Singapore)

(Received 13 April 1984)

ABSTRACT

To test the applicability of dynamic DSC for predicting isothermal oxidation induction time, further study was carried out on butadiene rubber samples. Similar to the natural rubber samples, various Arrhenius plots of the butadiene rubber samples could be superimposed to form a single plot using a shift factor dependent on the oxidation peak temperature obtained from a dynamic DSC test. The superimposed plot can then be used to predict the oxidation induction times of other butadiene rubber samples from dynamic DSC test results.

INTRODUCTION

Thermoanalytical techniques such as DSC and DTA have been widely used to study rubber oxidation [1–3]. The oxidative stability of rubber and the effectiveness of various antioxidants can be evaluated by DSC/DTA based on the heat change during oxidation, the activation energy of oxidation, the isothermal induction time, the onset temperature of oxidation, and the oxidation peak temperature.

The logarithm of the induction time is a linear function of the reciprocal of the test temperature. Such an Arrhenius plot is usually extrapolated to lower temperatures to predict the service life of the polymer [4–7]. However, a separate Arrhenius plot is needed for each polymer sample and the measurement of induction time is a lengthy process, especially at low temperatures.

It was recently reported that, for natural rubber stabilized by various antioxidants, the Arrhenius plots could be superimposed to form a single plot using a shift factor dependent on the oxidation peak temperature obtained from a dynamic DSC test [8]. The superimposed plot provides a rapid means for predicting the oxidation induction time from the more rapid dynamic DSC test. To test the general applicability of this method, a similar study is now extended to butadiene rubber.

EXPERIMENTAL

Materials

The butadiene rubber used was BUNA CB-10 manufactured by Bayer. The rubber was used as received. Tests were also made on purified butadiene rubber obtained by precipitation of the benzene solution of the rubber in methanol.

The following antioxidants were used: A, *N*-phenyl-β-naphthylamine (Agerite Powder, R.T. Vanderbilt); B, *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (4010 NA, Bayer); C, zinc diethyldithiocarbamate (Ethyl Zimate, R.T. Vanderbilt); D, *N,N*′-diphenyl-*p*-phenylenediamine (JZF, Uniroyal); E, *N*-phenyl-*N*′-cyclohexyl-*p*-phenylenediamine (Flexzone 6-H, Uniroyal) and F, *p*-(*p*-toluene-sulfonylamido)diphenylamine (Aranox, Uniroyal).

Copper naphthenate was obtained from K&K Laboratories.

Equipment

A Perkin-Elmer DSC-1B differential scanning calorimeter was used to measure the induction time and the oxidation peak temperature of the sample. The instrument was purged with oxygen at a flow rate of 20 ml min^{-1} during operation.

Sample preparation

The samples for DSC tests were prepared by solution casting as previously described [8]. The amount of antioxidant used was 0.0025 mol per 100 g of rubber, and the amount of copper naphthenate used was 0.2 g per 100 g of rubber.

RESULTS AND DISCUSSION

Plots of the logarithm of induction time against the reciprocal of the absolute temperature for butadiene rubber containing various antioxidants are shown in Fig. 1. Based on the induction time, the effectiveness of the antioxidant is in the order $A < B < C < D \simeq E < F$. The slopes of the various Arrhenius plots are the same except that of the sample containing antioxidant F.

Also shown in Fig. 1 are the results for butadiene rubber containing copper naphthenate, purified butadiene rubber and purified butadiene rubber containing antioxidant A. The catalytic effect of copper ion is evidenced by a reduction in the induction time. The removal of antioxidant from the butadiene rubber also leads to a reduction in the induction time. The

TABLE 1

Effect of heating rate on the oxidation peak temperature (T_p) of various samples

	T_p(K)			
	2 K min^{-1}	8 K min^{-1}	16 K min^{-1}	64 K min^{-1}
Butadiene rubber (BR)	444	466	476	506
BR + copper naphthenate	436	457	468	497
BR + A	451	473	485	513
BR + B	453	475	486	517
BR + C	463	484	491	521
BR + D	469	492	504	534
BR + E	470	492	506	539
BR + F	470	491	502	531
BR (purified)	433	453	466	496
BR (purified) + A	447	468	480	512

addition of antioxidant A to the purified butadiene rubber prolongs the induction time. The slopes of the Arrhenius plots of these three samples are the same as those containing antioxidants A–E.

The oxidation peak temperatures (T_p) of various samples are given in Table 1. The order of effectiveness of the antioxidants based on T_p is the same as that based on the induction time. A linear relationship between log t and $1/T_p$ for natural rubber samples was recently reported [9].

The various Arrhenius plots in Fig. 1 can be shifted horizontally using a

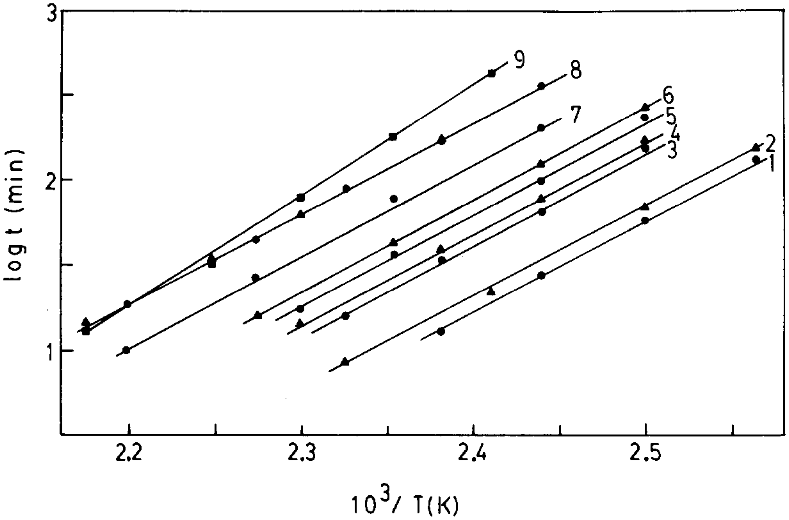

Fig. 1. Effect of temperature on the oxidation induction time of various samples: (1) purified butadiene rubber; (2) butadiene rubber (BR)+copper naphthenate; (3) BR; (4) purified BR+antioxidant A; (5) BR+antioxidant A; (6) BR+antioxidant B; (7) BR+antioxidant C; (8) ●, BR+antioxidant D, ▲, BR+antioxidant E; (9) BR+antioxidant F.

shift factor, A, where $A = T_p$ (reference) $- T_p$ (sample). In the present work, butadiene rubber without additive (line 3 in Fig. 1) is chosen as the reference. The superimposed plots of log t against $1/(T+A)$ are shown in Figs. 2 to 5 which correspond to eqns. (1) to (4), respectively, viz.

$$\log t = 5274/(T+A) - 11.061 \quad (1)$$

$$\log t = 5221/(T+A) - 10.919 \quad (2)$$

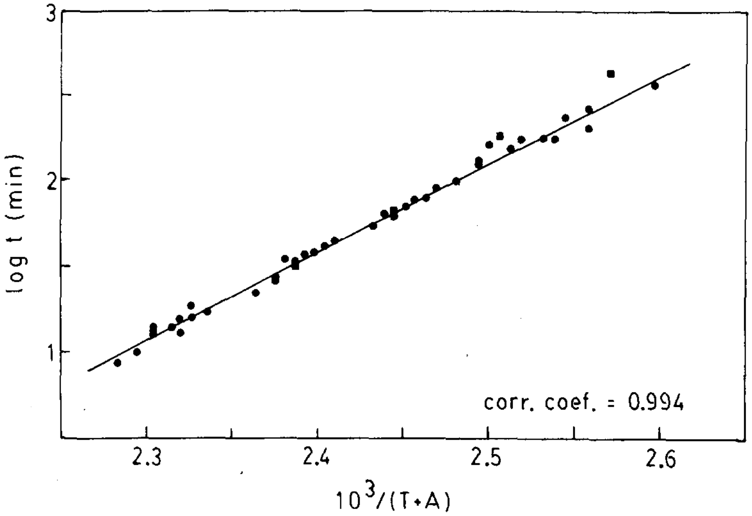

Fig. 2. Superimposed plot of log t vs. $1/(T+A)$ using a shift factor based on the T_p value obtained at a heating rate of 2 K min^{-1}. (■) BR + antioxidant F.

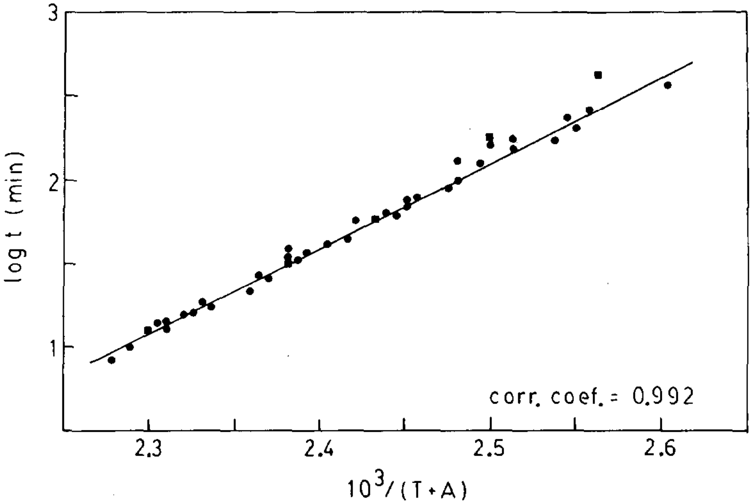

Fig. 3. Superimposed plot of log t vs. $1/(T+A)$ using a shift factor based on the T_p value obtained at a heating rate of 8 K min^{-1}. (■) BR + antioxidant F.

$$\log t = 5114/(T + A) - 10.700 \qquad (3)$$

$$\log t = 4914/(T + A) - 10.211 \qquad (4)$$

The correlation coefficients of these plots are better than those of the natural rubber samples [8]. Similar to the natural rubber samples, the correlation coefficient of the plot is better when T_p is based on a slow heating rate. The results once again confirm the importance of using a slow

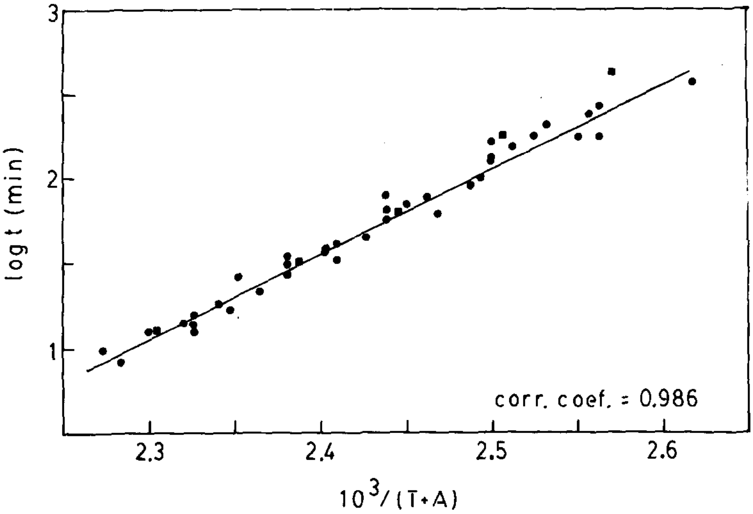

Fig. 4. Superimposed plot of log t vs. $1/(T + A)$ using a shift factor based on the T_p value obtained at a heating rate of 16 K min^{-1}. (■) BR + antioxidant F.

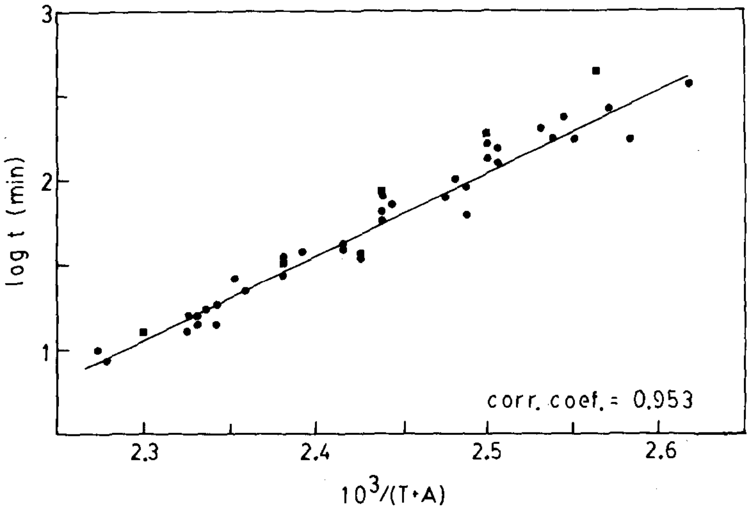

Fig. 5. Superimposed plot of log t vs. $1/(T + A)$ using a shift factor based on the T_p value obtained at a heating rate of 64 K min^{-1}. (■) BR + antioxidant F.

or moderate heating rate in a dynamic DSC test. Although the slope of the Arrhenius plot for butadiene rubber containing antioxidant F (line 9 in Fig. 1) is different from the others, the experimental results still fit quite well in the superimposed plot, except at low temperatures.

Equations (1) to (4) allow the prediction of the induction time using T_p values obtained from a dynamic DSC test. Even in the absence of the superimposed plot, prediction of the induction time can still be made by using the Arrhenius plot of one particular sample, for example, butadiene rubber without additive. If a butadiene rubber sample, X, shows a T_p value of 464 K when scanned with a heating rate of 2 K min^{-1}, the shift factor A is then -20 K (i.e., 444–464 K). The induction time of sample X at 420 K can then be taken as that of the reference sample at 400 K. From line 3 in Fig. 1, the induction time of sample X at 420 K is estimated to be 150 min. Equation (1) gives a value of 133 min.

It is also noted that eqns. (1) to (4) are different from those equations for the natural rubber samples [8], showing that separate equations are needed for different rubber systems. Nonetheless, the use of T_p values obtained from a dynamic DSC test to predict the induction time is applicable to both natural rubber and butadiene rubber systems.

REFERENCES

1 D.W. Brazier, Rubber Chem. Technol., 53 (1980) 437.
2 J.J. Maurer, in E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic Press, New York, 1981, Chap. 6.
3 A.K. Sircar, J. Sci. Ind. Res., 41 (1982) 536.
4 H.E. Bair, Polym. Eng. Sci., 13 (1973) 435.
5 D.I. Marshall, E. George, J.M. Turnispeed and J.L. Glenn, Polym. Eng. Sci., 13 (1973) 415.
6 W.L. Hawkins, W. Matreyek and F.H. Winslow, J. Polym. Sci., 41 (1959) 1.
7 N.C. Billingham, D.C. Bott and A.S. Manke, in N. Grassie (Ed.), Developments in Polymer Degradation—3, Applied Science Publishers, London, 1981, Chap. 3.
8 S.H. Goh, Thermochim. Acta, 75 (1984) 323.
9 S.H. Goh, Thermochim. Acta, 77 (1984) 275.