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THERMOANALYTICAL STUDIES OF RUBBER OXIDATION: PREDICTION OF ISOTHERMAL INDUCTION TIME

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ABSTRACT

The oxidation induction times of natural rubber stabilized by various antioxidants were measured by differential scanning calorimetry (DSC). Various Arrhenius plots could be superimposed to form a single plot by using a shift factor dependent on the oxidation peak temperature obtained from a dynamic DSC test. The superimposed plot provides a simple means to predict the induction time from a dynamic DSC test result.

INTRODUCTION

Thermoanalytical techniques such as DSC, DTA and TG can provide a rapid and simple means to estimate the service life of polymers [1–3]. The isothermal induction time of a sample is obtained by heating the sample isothermally in the intended environment and recording the time required for a deviation in the DSC/DTA baseline or a pre-determined weight loss in TG to occur. The logarithm of the induction time is a linear function of the reciprocal of the test temperature. The Arrhenius plot is usually extrapolated to low temperature to predict the service life of the sample. However, such extrapolation is sometimes extended through the region in which the material changes in physical state. In such a case, notably for polyethylene and polypropylene, non-linearity of the Arrhenius plot is observed when passing through the melting range of the polymer [1,4]. Previous works on the use of DSC/DTA to determine the induction time of a polymer have been reviewed recently by Billingham et al. [1]. The present communication reports the DSC measurement of the oxidation induction time of natural rubber stabilized by various antioxidants. It will be shown that various Arrhenius plots can be superimposed to form a single plot by using a shift factor dependent on the oxidation peak temperature obtained from a dynamic DSC test. The superimposed plot provides a simple means to predict the induction time at various temperatures.

EXPERIMENTAL

Materials

Natural rubber of pale crepe grade was used. It was purified by extraction with acetone for 24 h and then precipitation of the benzene solution of the extracted natural rubber in methanol.

The following antioxidants were used: A, 2,6-di-tert-butyl-*p*-cresol (Gasoline AO-29, E.I. DuPont de Nemours&Co.); B, 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (Merck); C, *N*-phenyl-β-naphthylamine (Agerite Powder, R.T. Vanderbilt Co., Inc.); D, *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (4010NA, Bayer); E, zinc diethyldithiocarbamate (Ethyl zimate, R.T. Vanderbilt Co., Inc.); F, *N,N'*-diphenyl-*p*-phenylenediamine (JZF, Uniroyal); and G, *p*-(*p*-toluene-sulfonylamido)diphenylamine (Aranox, Uniroyal).

Equipment

A Perkin-Elmer DSC-1B differential scanning calorimeter was used. The instrument was purged with oxygen at a flow rate of 20 ml min^{-1} during operation.

Sample preparation

To ensure a good contact between sample and sample pan, solution cast samples were used as previously described [5–7]. Appropriate amounts of rubber and antioxidant were dissolved in benzene separately. The solutions were then mixed, droplets of solution placed in the sample pan, and then dried in a vacuum oven at room temperature. The amount of antioxidant used was 0.0025 mol per 100 g rubber.

Measurement of induction time

The sample was brought to the desired temperature with a heating rate of up to 64 K min^{-1} and the time taken for the oxidation exotherm to appear was taken as the induction time. Dynamic DSC tests using various heating rates were also made to locate the oxidation peak temperatures.

RESULTS AND DISCUSSION

Plots of the logarithm of induction time against the reciprocal of the absolute temperature of various samples are shown in Fig. 1. Also given in Fig. 1 are the results for raw natural rubber and synthetic polyisoprene rubber (Natsyn 2200, Goodyear) without antioxidant.

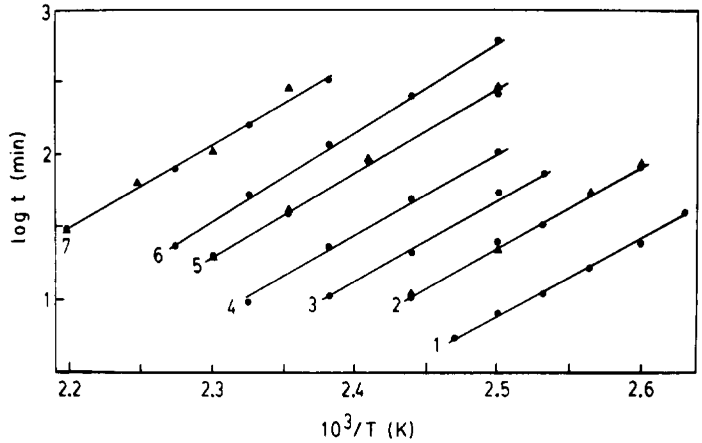

Fig. 1. Effect of temperature on the oxidation induction time of various samples: (1) polyisoprene rubber; (2) ▲ purified natural rubber (NR), ● NR + antioxidant A; (3) NR + antioxidant B; (4) NR + antioxidant C; (5) ● NR + antioxidant D, ▲ NR + antioxidant E; (6) raw natural rubber; (7) ● NR + antioxidant F; ▲ NR + antioxidant G.

The addition of antioxidant prolongs the induction time. Based on the induction time, the effectiveness of the antioxidant is in the order $A < B < C < D \simeq E < F \simeq G$. The results also show that natural rubber has a better oxidative stability than synthetic polyisoprene rubber, and that the extraction of natural antioxidant in natural rubber reduces its oxidative stability. The different oxidative stabilities of natural and synthetic polyisoprenes allows their differentiation as previously reported [7].

The oxidation peak temperatures (T_p) of various samples are given in Table 1. The addition of antioxidant increases the T_p value. The order of effectiveness of the antioxidant based on the T_p value is generally the same as that based on the induction time.

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}
Natural rubber (NR)	422	443	456	493
NR + A	422	444	456	493
NR + B	431	452	464	498
NR + C	438	461	473	504
NR + D	452	473	482	514
NR + E	451	471	482	510
NR + F	477	497	509	541
NR + G	477	495	505	532
Raw natural rubber	459	479	490	520
Polyisoprene rubber	405	428	443	487

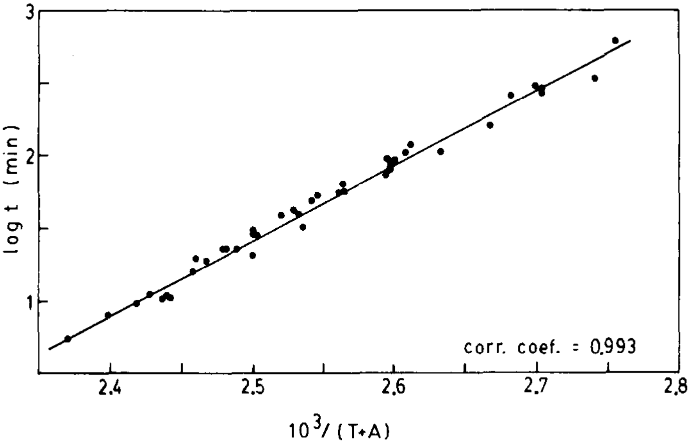

Fig. 2. Superimposed plot of log t against $1/(T+A)$ using a shift factor based on the T_p value obtained at a heating rate of 2 K min^{-1}.

The induction time measured by DSC/DTA is limited to the range of a few minutes to a few hundred minutes [1]. The lower limit is due to the time required to establish thermal equilibrium in the sample and the upper limit is due to the sensitivity of the instrument as long induction time is usually accompanied by a low post-induction rate of oxidation [1]. This work covers the induction time ranging from 5 to 600 min and the temperature range 380–455 K. Within this time and temperature range, it is noted that the various Arrhenius plots in Fig. 1 have the same slopes. It is therefore possible to shift the Arrhenius plots horizontally to form a single plot. The shift factor A is related to the T_p value of the sample. Using the Arrhenius

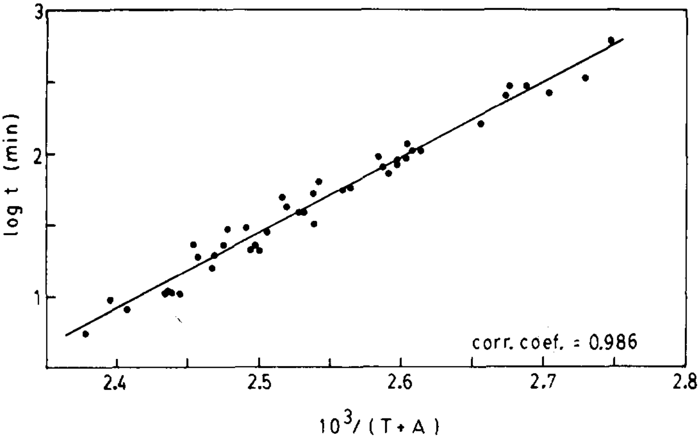

Fig. 3. Superimposed plot of log t against $1/(T+A)$ using a shift factor based on the T_p value obtained at a heating rate of 8 K min^{-1}.

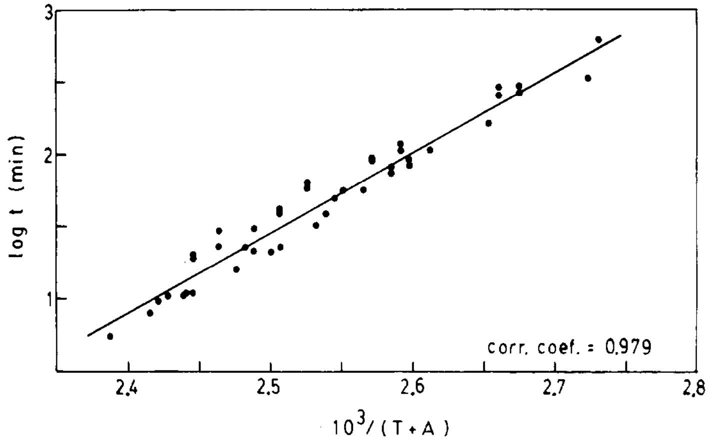

Fig. 4. Superimposed plot of log *t* against $1/(T+A)$ using a shift factor based on the T_p value obtained at a heating rate of 16 K min^{-1}.

plot of purified natural rubber without additive as the reference and $A = T_p(\text{reference}) - T_p(\text{sample})$ based on a particular heating rate, plots of log *t* against $1/(T+A)$ can be obtained as shown in Figs. 2 to 5.

Straight lines with correlation coefficients > 0.97 are obtained when shift factors are based on the T_p value obtained at a slow or moderate heating rate. However, the plot using a shift factor based on the T_p value obtained at a fast heating rate of 64 K min^{-1} has a poor correlation coefficient. Figures 2 to 4 correspond to eqns. (1) to (3), respectively, viz.

$$\log t = 5.151 \times 10^3/(T+A) - 11.457 \qquad (1)$$

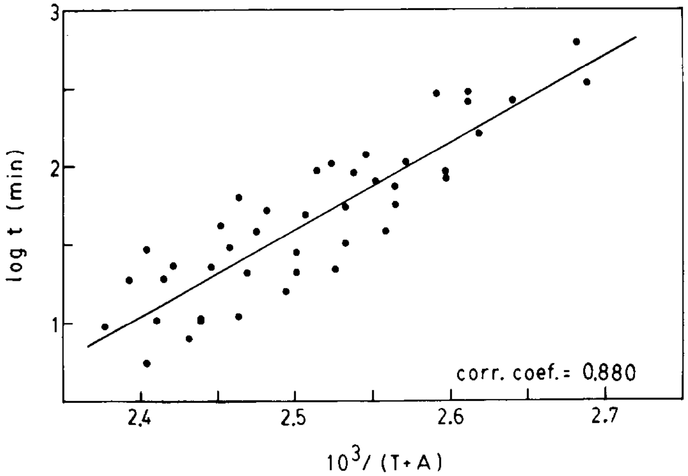

Fig. 5. Superimposed plot of log *t* against $1/(T+A)$ using a shift factor based on the T_p value obtained at a heating rate of 64 K min^{-1}.

$$\log t = 5.262 \times 10^3/(T + A) - 11.712 \qquad (2)$$

$$\log t = 5.562 \times 10^3/(T + A) - 12.446 \qquad (3)$$

These equations allow the prediction of the isothermal induction time at various temperatures using data from the more rapid dynamic DSC tests. For example, if natural rubber stabilized by a certain antioxidant shows a T_p at 460 K using a heating rate of 2 K min^{-1}, the shift factor A is then -38 K (i.e., 422–460). From eqn. (1), it is predicted that the sample will have an induction time of 592 min at 400 K and 48 min at 430 K. A similar study will be extended to other rubber systems in order to test the general applicability of this method.

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