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THERMOANALYTICAL STUDIES OF RUBBER OXIDATION: CORRELATION OF ACTIVATION ENERGY, ISOTHERMAL INDUCTION TIME AND OXIDATION PEAK TEMPERATURE

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ABSTRACT

The activation energy of oxidation, E_a, isothermal oxidation induction time, t, and oxidation peak temperature, T_p, obtained from DSC/DTA, are widely used to evaluate the oxidative stability of rubbers and the effectiveness of antioxidants. Based on the analysis of 127 sets of data, E_a, t and T_p were found to be correlated by the following equations

$$E_a = 443.13 - 1.545 \times 10^5/T_p$$

$$\log t = 15.177 - 5.809 \times 10^3/T_p$$

$$\log t = 0.0363 E_a - 1.377$$

A good correlation is obtained if T_p is based on a slow heating rate.

INTRODUCTION

Oxidation is a problem for most rubbers. The presence of unsaturation in the rubber, for example natural rubber, makes it particularly susceptible to oxidation which eventually leads to the deterioration of its mechanical properties. Oxidation is accelerated by heat, light and some metal ions. Antioxidants are, therefore, added to rubbers during the manufacturing process in order to protect the rubber from oxidation during finishing, packaging and storage.

Thermoanalytical techniques such as DSC and DTA have been widely used to study rubber oxidation [1–3]. The oxidative stability of rubbers 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. DSC is used to study the oxidation of natural rubber, the catalytic effects of metal ions on the oxidation of natural rubber, the inhibition of the metal-ion catalyzed oxidation of natural rubber

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by macrocyclic ligands and the oxidation of natural rubber/polyisoprene rubber blends [4–10]. This communication reports the analysis of previous results in an attempt to establish a correlation between activation energy of oxidation, E_a, isothermal induction time, t, and oxidation peak temperature, T_p.

EXPERIMENTAL

The details of the experiments are given in previous publications [4–10]. The main feature of these works is the use of small sample size (< 1 mg) and solution cast samples (film thickness ~ 0.01 mm) to improve the thermal contact between sample and sample pan. The oxidation of rubber films with such thicknesses is not diffusion controlled [11].

The activation energy of oxidation, E_a, was calculated from the oxidation peak temperatures at various heating rates using Kissinger's method [12].

All the isothermal oxidation tests were conducted at 400 K. The time required for the appearance of the oxidation exotherm was taken as the induction time.

RESULTS AND DISCUSSION

A plot of log t against $1/T_p$, where T_p is based on a heating rate of 2 K min^{-1}, is shown in Fig. 1. The plot contains 127 sets of data from previous work [5–10]. A linear relation, viz.

$$\log t = 15.177 - 5.809 \times 10^3/T_p$$

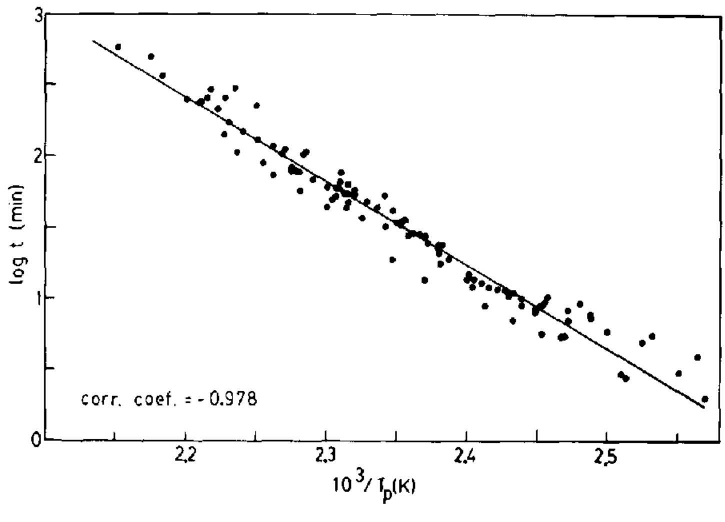

Fig. 1. Log t vs. $1/T_p$ (T_p based on a heating rate of 2 K min^{-1}).

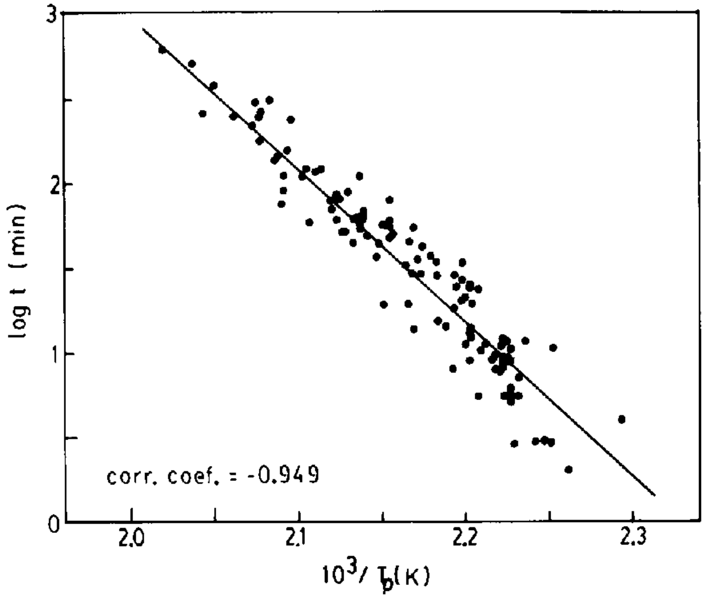

Fig. 2. Log t vs. $1/T_p$ (T_p based on a heating rate of 16 K min^{-1}).

is obtained by regression analysis. Similar plots using T_p based on heating rates of 16 and 64 K min^{-1} are shown in Figs. 2 and 3, respectively. It is apparent that as the heating rate increases, the correlation coefficient of the straight line is reduced. In the study on the catalytic effects of metal ions on the oxidation of natural rubber, it was noted that the T_p values of various samples were quite similar at a fast heating rate while substantial differences in T_p were observed at a slow heating rate [5]. Therefore, a slow or moderate

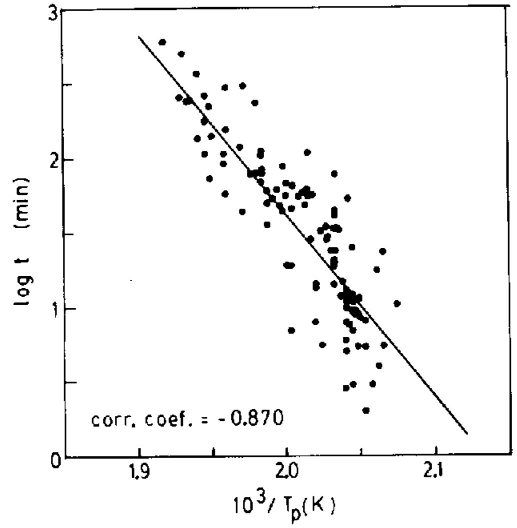

Fig. 3. Log t vs. $1/T_p$ (T_p based on a heating rate of 64 K min^{-1}).

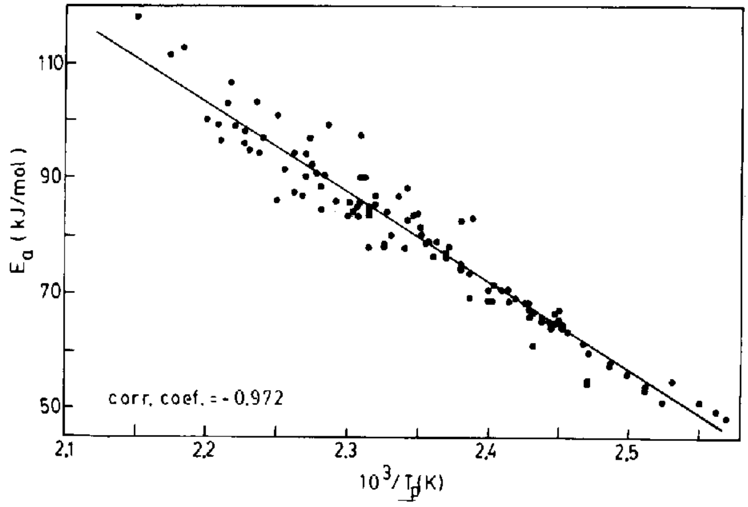

Fig. 4. E_a vs. $1/T_p$ (T_p based on a heating rate of 2 K min^{-1}).

heating rate must be employed if T_p is used to evaluate the oxidative stability of rubbers and the effectiveness of antioxidants.

Similarly, the activation energy of oxidation, E_a, is also a linear function of $1/T_p$ as shown in Figs. 4–6. Once again, a better correlation between E_a and $1/T_p$ is obtained when T_p is based on a slow heating rate. The linear

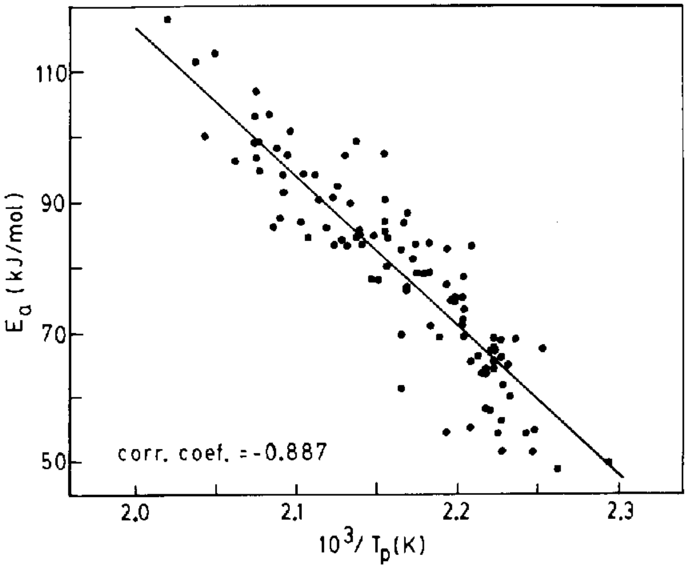

Fig. 5. E_a vs. $1/T_p$ (T_p based on a heating rate of 16 K min^{-1}).

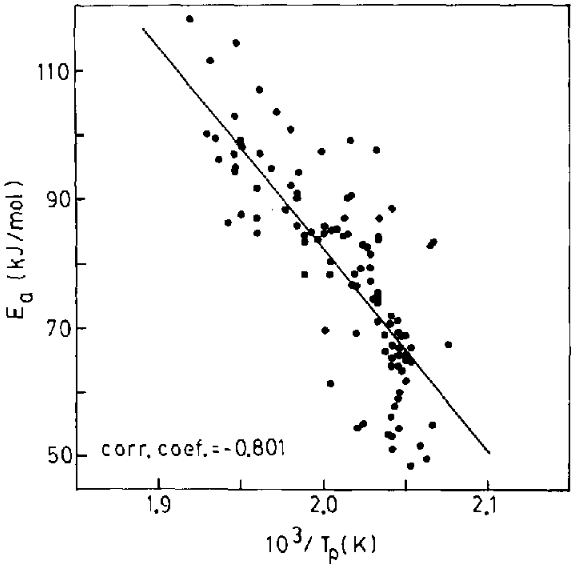

Fig. 6. E_a vs. $1/T_p$ (T_p based on a heating rate of 64 K min^{-1}).

relation, viz.

$$E_a = 443.14 - 1.545 \times 10^5/T_p$$

is obtained where T_p is based on a heating rate of 2 K min^{-1}.

Lastly, the isothermal induction time at 400 K is also linearly related to

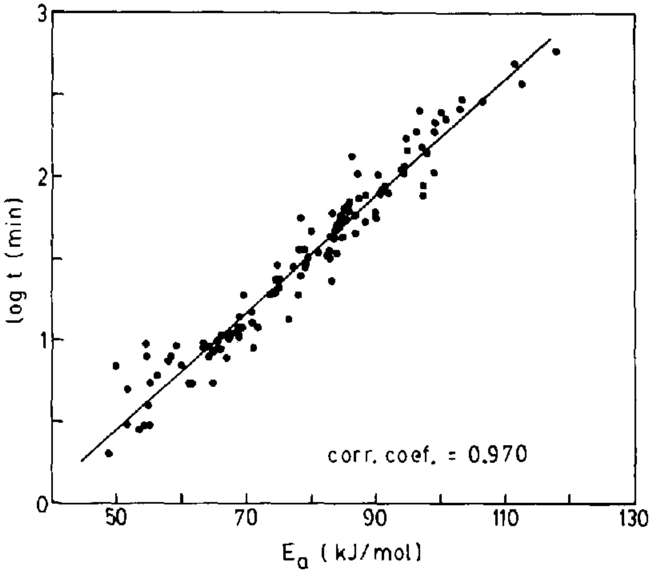

Fig. 7. Log t vs. E_a.

the activation energy of oxidation, viz.

$$\log t = 0.0363E_a - 1.377$$

as shown in Fig. 7.

It has been shown that the activation energy, isothermal induction time and oxidation peak temperature are inter-related and hence they can all be used to evaluate the oxidative stability of rubbers and the effectiveness of antioxidants. The use of induction time has the disadvantage that a long test time is needed for a sample of good stability. The evaluation of the activation energy by the Kissinger method [12] requires several scans at various heating rates. The use of the oxidation peak temperature based on a single scan is the most convenient method. However, as discussed earlier, T_p values based on a slow heating rate provide a better result, however, a longer test time is needed. In this respect, a moderate heating rate of 10–20 K min^{-1}, commonly used in DSC/DTA tests, provides a fast and yet reasonably good result.

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