Study of Rubber Oxidation by Thermoanalysis*

P. H. LYE and H. K. TOH, *School of Applied Science, University Sains Malaysia, Minden, Penang, Malaysia*

Synopsis

A method using the DSC was utilized whereby the oxidation of natural rubber was studied by adapting the procedures developed by Kissinger, Doyle, and Ozawa for thermoanalysis. Thus oxidative induction time of several hours for a particular rubber sample can be estimated in a relatively short time. Some of the results of this method are compared with those from other established methods, the estimated oxidative induction time showing a good correlation with some of the systems tested. The validity and limitations of this method are discussed.

INTRODUCTION

Several methods using either the DSC or DTA to study oxidation of polymers have been proposed by several workers.[1–7]

May et al.[1] made comparisons of antioxidant efficiencies by comparing onset of oxidation, start of peak, and peak maximas. Horvath et al.[2] deduced elastomer stability from the temperature of oxidation onset when the sample was heated at 5 K/min in air. Smith and Stephens[3] related the effectiveness of antioxidants in rubber to its ability to suppress the enthalpy of the oxidation exotherm. Goh[4] tried to evaluate antioxidant efficiency in natural rubber by comparing the apparent activation energies obtained from Kissinger's plots. Ponce-Velez and Campos-Lopez[5] studied the thermal oxidation of Guayule and Hevea rubbers using three different kinetic treatments. Gonzalez[6] used the shift in peak temperature as a criterion to stability while Kotoyori[7] considered the activation energy, frequency factor, and specific reaction rate.

In this present work the procedures developed by Kissinger[8] for the DATA and Doyle[9,10] and Ozawa[11–14] for thermal analysis were adapted for this study. Thus, in addition to the apparent activation energy, the isothermal oxidative induction time at any particular temperature may be estimated. This procedure is then applied to a real system—the oxidation of natural rubber.

EXPERIMENTAL

Materials. SMR 5L was used as the base polymer. Commercial antioxidants used were: ZDC (zinc diethyl dithiocarbarmate), TDQ (polymerized 2,2,4-trimethyl-1,2-dihydroquinoline), IPPD (*N*-isopropyl-*N'*-phenyl-*para*-phenylenediamine), ZKF (2,2'-methylene-bis(4-methyl-6-cyclohexyl phenol), and DOD (4,4'-dihydroxy diphenyl). The antioxidants were obtained from BAYER

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Company and were used as received.   Dicumyl peroxide was obtained from RRIM.

Equipment and Procedure.   A Perkin-Elmer DSC 2B Differential Scanning Calorimeter and thermogravimetric system (TGS-2) were used.   Air at a rate of 20–25 mL/min was used as a purging agent.   The scanning rates used for analysis were 5, 10, 20, 40, and 80 k/min.   For the vulcanizate, scanning rates of 5, 10, and 20 K/min were used.   For isothermal tests, a heating rate of 160 K/min was used to achieve the desired temperature before timing commences. Oxygen at the same rate was used in the analysis of the peroxide-cured vulcanizates.

The temperature calibration for the DSC was carried out at the temperature range of interest (323–600 K) with indium (mp 429.8 K) and tin (mp 505.1 K).

For the infrared induction time study, rubber films were cast on sodium chloride cells and placed in a PRI oven at 140°C.   The increase in the concentration of the —OH and C=O group were checked using an infrared spectrophotometer.   The time to reach the greatest rate of increase of —OH and C=O groups were taken to be the induction time (IRIT).

Sample Preparation.   A 2% solution of acetone-extracted rubber in toluene was prepared.   Appropriate amounts of antioxidants were added to give the required concentration in parts per hundred (pph).   One or two drops of the resulting solution was placed in an aluminium sample pan and the solvent allowed to evaporate.   Sample weights were in the range of 0.3–0.8 mg.   The peroxide vulcanizate was made up of 2.2 pph dicumyl peroxide to SMR 5L and press-cured at 150°C for the 1 h 20 min in the form of thin films less than 0.1 mm thickness.

Data Analysis.   The temperature at which the oxidation peak occurs (see the Appendix) and the corresponding heating rate were recorded and the kinetic parameters analysed using the following equations:

Calculation of apparent activation energy of oxidation.   Two equations were used.   (A) The Kissinger equation[8]:

$$\frac{d \log(\phi/T_p^2)}{d(1/T_p)} = \frac{-\Delta E}{2.303R}$$

(B)   The Doyle–Ozawa equation[9–14]:

$$\frac{d \log \phi}{d(1/T_p)} = \frac{-0.4567\Delta E}{R}$$

where ϕ = heating rate, T_p = exotherm peak temperature, ΔE = apparent activation energy (E_a), and R = gas constant.

In the application of the Kissinger equation and the Doyle–Ozawa equation, certain important assumptions have to be made.   In the case of the Kissinger equation, the peak temperature during oxidation is assumed to be the point of maximum reaction rate of oxidation (shown to be valid for small samples, slow heating rate and moderate reaction rate of samples by Akita et al.[15]).   For the Doyle–Ozawa equation, the peak temperature is assumed to refer to the same degree of conversion of oxidation at any heating rate.

Estimation of isothermal induction time.   For the above, the equation deduced by Doyle[10] is used:

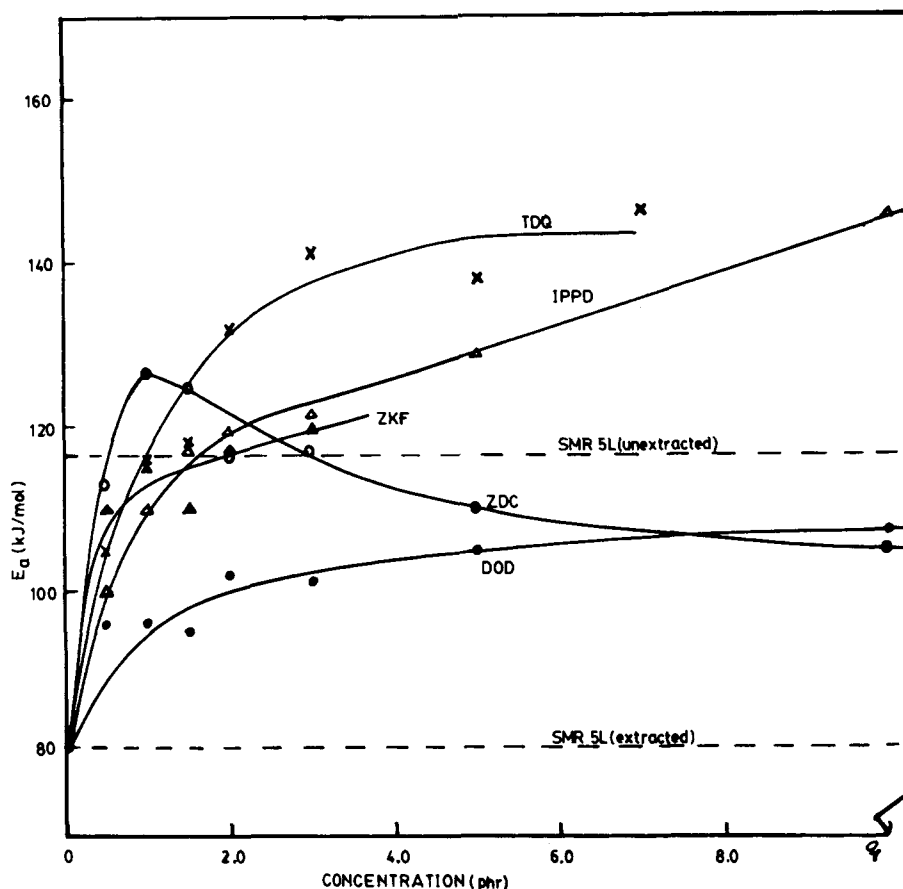(C) $\log t_0 \simeq \log \Delta E/R\phi - 2.315 + \Delta E/RT_0 \times (\log e) - 0.4567\Delta E/RT_p$

Fig. 1. Dependance of E_a upon antioxidant concentration (pph) for various antioxidants. Results are compared with extracted and unextracted SMR 5L.

where T_p = exotherm peak temperature, T_0 = reference temperature, and t_0 = isothermal induction time (IIT) or isothermal equivalent for the reaction.

This equation can only be used if $\Delta E/RT > 20$,[9,10] below which the approximation differ significantly from the exact value. $E/RT > 20$ for all the cases of rubber oxidation in this study. t_0 is calculated for all heating rates for each sample and the average taken.

DISCUSSION

Determination of Apparent Activation Energy (see Fig. 1). The apparent activation energy (E_a) as determined shows the greatest rate of increase for the lower concentrations at approximately below 2 pph. Above that, the increase is less or even showed a decrease as in ZDC. This increase of E_a over the E_a of acetone-extracted NR gives an idea of the temperature dependence of oxidative resistance of the various systems. E_a as obtained from Kissinger's equation gives a better correlation to experimental data when used in the oxidative isothermal induction time equation and thus is shown for all data in preference to that obtained by the Ozawa–Doyle method.
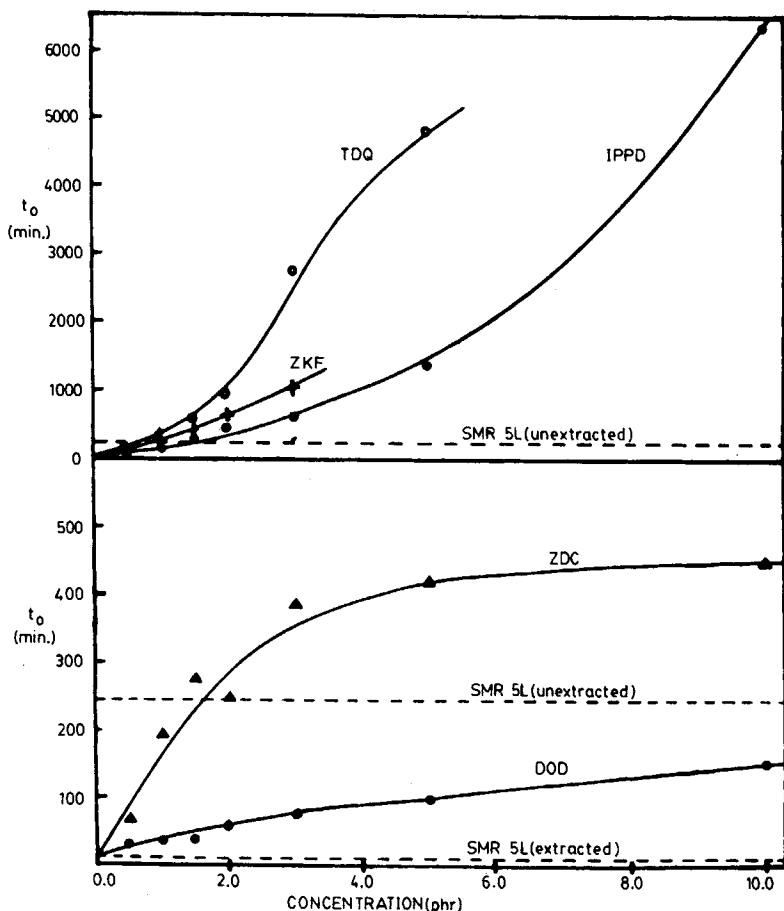
Fig. 2. Dependance of t_0 upon antioxidant concentration (pph) at 140°C for various antioxidants. Results are compared with extracted and unextracted SMR 5L.

Determination of Oxidative Isothermal Induction Time t_0. From Figure 2, the calculated t_0 at 140°C shows an increasing trend for all antioxidants studied, even for ZDC where E_a showed a decreasing trend with oxidation after 1.5 pph. Thus from Figure 2 it is deduced that increase of the antioxidants concentration for DOD and ZDC are 3 pphr and showed little improvement, but, overall, there is no real antagonistic effect for the pure gum system. For ZKF, TDQ, and IPPD for the pure gum system, there is no leveling off for the concentrations studied.

Figures 3–5 compared calculated t_0 with t_0 obtained experimentally. They showed good correlation for the systems under investigation at the temperature range used. Table I shows calculated to compared with experimentally obtained t_0 for some random samples. While most of the samples showed fairly good correlation, calculated values for ZDC were very high while, for ZKF, calculated t_0 also appeared to be on the high side.

The discrepancy for ZDC could provide useful information on the antioxidant used, such as its stability or volatility. Experiments with the TGS revealed that ZDC showed signs of decomposition starting from 423 K ($\simeq$150°C) at a heating rate of 20 K/min in N_2. Thus exposing the antioxidant at an elevated temper-
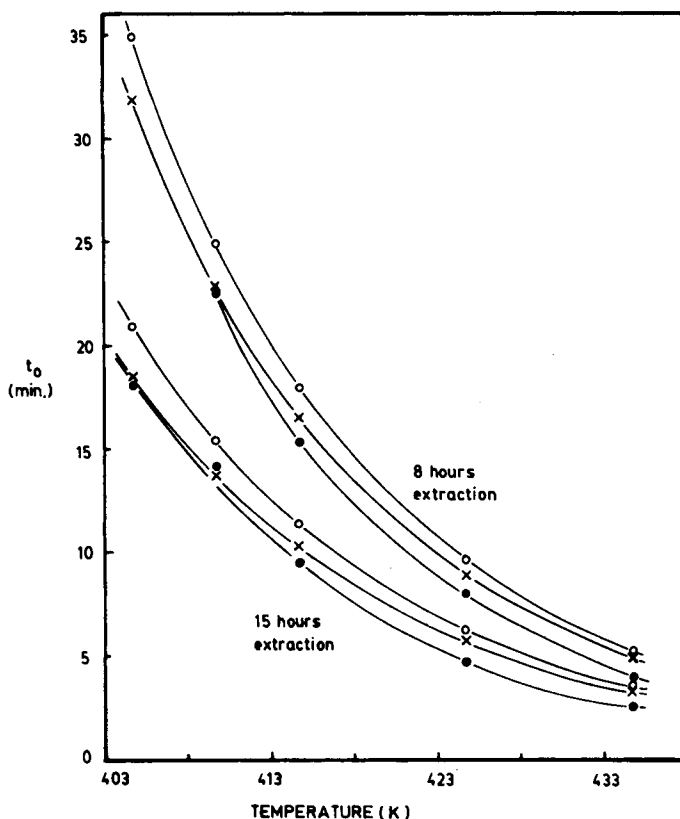
Fig. 3. Variation of t_0 (calculated and experimental) with temperature for two different samples of extracted SMR 5L: (●) experimental data: (▲) data using Ozawa–Doyle E_a; (×) data using Kissinger's E_a.

ature for a sustained period of time as would be required for isothermal tests could affect the effectiveness of the antioxidants. (For thermally stable antioxidants, calculated and experimental t_0 may be expected to be close.) The above consideration may also account for the drop in E_a with increasing concentration for ZDC. At the present moment, data pertaining to ZDC at high concentrations should be treated with caution.

From the above results, E_a as evaluated by Kissenger and the estimated isothermal time relationship devised by Doyle and adapted for the DSC appear to be valid for the evaluation of oxidative stability in natural rubber, subject to certain limitations to be discussed. The isothermal induction time method provide a better criterion for the evaluation than basing it as either E_a or peak temperature alone, e.g., comparing the E_a and induction time for different concentrations of TDQ in NR; after 3 pph, the E_a appears to level off but the calculated and experimental induction time still increases significantly. Furthermore, isothermal induction time would give a quantitative indication of antioxidant effectiveness. Unfortunately, in this work, it was not possible to determine accurately the enthalphy change for the above experiments as this would give further information on the oxidative nature of natural rubber, the reason being that the rubber started to pyrolyze a short time after the peak temperature was reached.
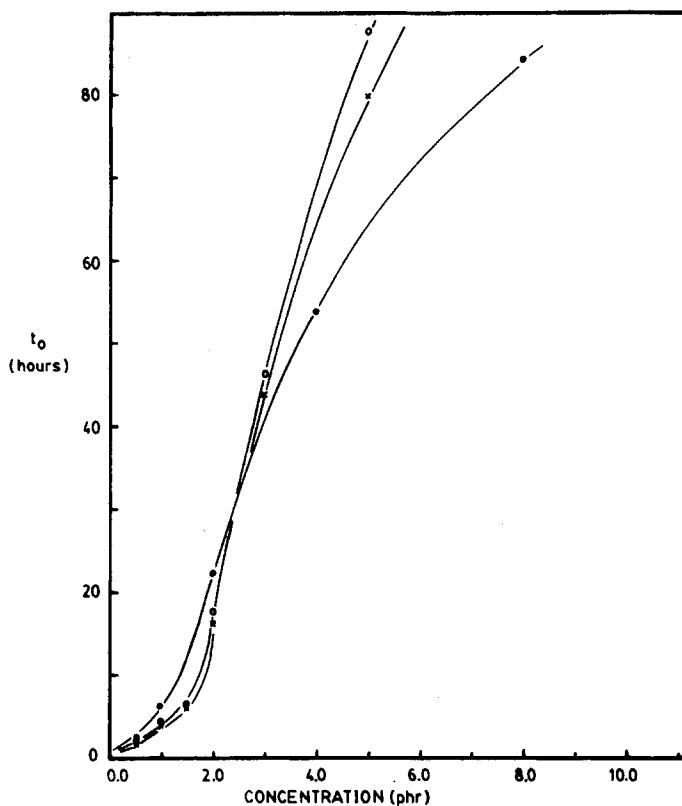
Fig. 4. A comparison of t_0 (calculated and experimental) at 140°C at different concentrations for TDQ protected NR: (●) experimental data (IRIT); (×) data using Kissinger's E_a; (▲) data using Ozawa–Doyle E_a.

Discussion of Accuracy, Validity, and Limitations. All temperature readings are made to the nearest degree K after correction for baseline slope and thermal log in the instrument. All slopes used for the calculation of the apparent activation energies have a correlation factor of better then -0.99. Generally, the correlation factors are better for samples with lower antioxidant concentrations. Peak temperature variation of 1 K normally causes the calculated isothermal inductin time (IIT) to vary by $\simeq 10\%$. This effect is lessened by calculating the t_0 at all heating rates and taking the average. A standard deviation over average of less than 15% is obtained for all calculated values of t_0.

The validity of the above calculations hold only as long as the oxidation mechanism remains unchanged at the temperature range studied and as long as the Arrhenius equation holds. Such deviations could arise from decomposition or volatilization of antioxidants, thermal log, and the increasing significance of other thermal reactions—e.g., thermal degradation. This could give rise to inconsistent peak temperature position or peak profile especially at a high heating rate, i.e., 40 and 80 K/min. This is a common occurence in the analysis of vulcanizates. However, such effects are not observed for low antioxidant concentrations (dependent on effectiveness of antioxidant) if the sample is in the form of a cost film.
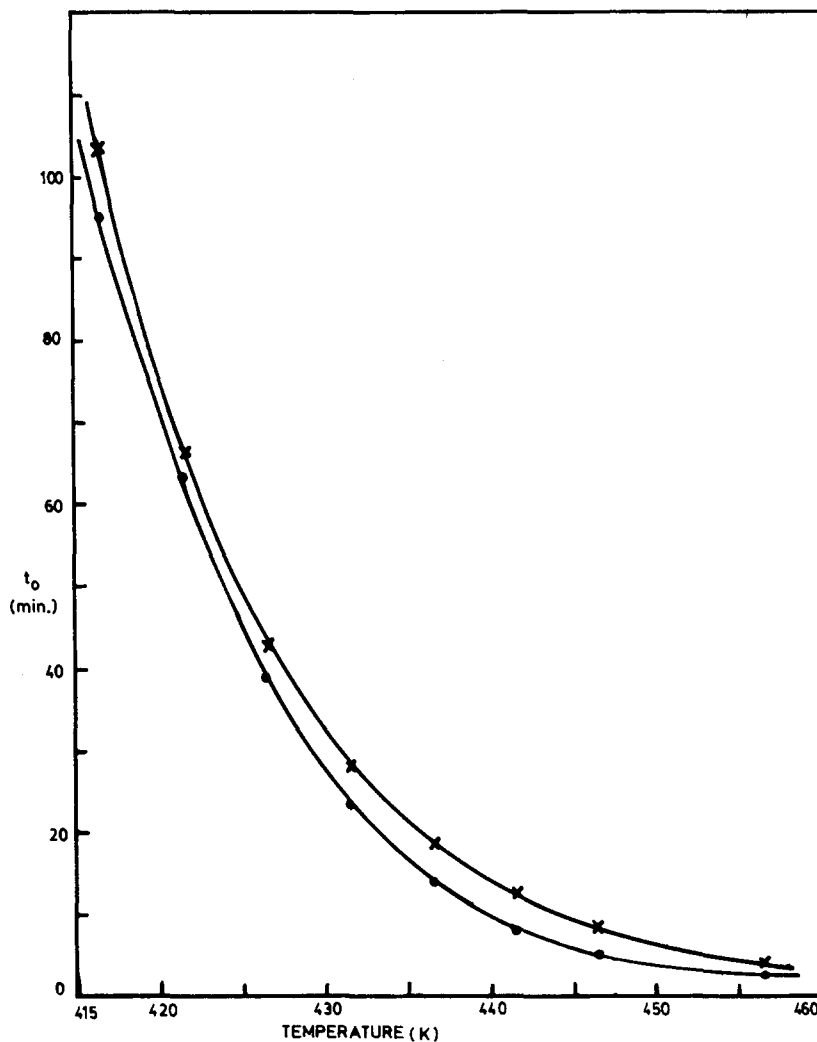
Fig. 5. Variation of t_0 [calculated using Kissinger's E_a ($\times$) and experimental ($\bullet$)] with temperature for peroxide cure vulcanizate.

Another limitation would be due to instrument sensitivity especially at a low heating rate (i.e., 5 K/min or 10 K/min); e.g., for ZKF, at 5 pph the oxidation exotherm is not very significant and not well defined.   Thus no data at low heating rates are available for ZKF protected rubber at a concentration of 5 pph and above.

Although the final equation in the model is derived by making a number of approximations,[8-14] the agreement between calculated and experimental values has been shown to be surprisingly good.

Comment: An Oxidation Peak Profile. For samples with the same anti-oxidant concentrations and same heating rates, it is observed that the oxidation peak of ZDC (a; peroxide decomposer) is sharp and narrow compared to the oxidation peaks of the other antioxidants, which tend to be broader and more gradual. The oxidation peak profile of IPPD is between that of ZDC and TDQ

TABLE I
Experimental and Calculated t_0 for Various Random Samples of Natural Rubber with
Antioxidants Added

Sample	Ref. temp	t_0 (exptl)	t_0 (calcd)
2246:TDQ (1:1)			
1.5pph total	473 K	5.7 min[a]	5.7 min
IPPD 1.5pph	453 K	18.5 min[a]	20.9 min
IPPD 1.5pph	443 K	35.4 min[a]	41.4 min
IPPD 1.5pph	413 K	6 h 45 min[b]	7 h
ZDC 1.5pph	413 K	1 h 10 min[b]	4 h 35 min
ZKF 1.5pph	413 K	4 h 50 min[b]	6 h 30 min
DOD 2.0pph	453 K	4.1 min[a]	4.8 min
DOD 1.0pph	453 K	5.6 min[a]	5.4 min

[a] Data from DSC.
[b] Data from IRIT.

at the lower antioxidant concentration. As IPPD is known to have both chain-breaking as well as peroxide-decomposing effects, the oxidation peak profile may also give an indication of the mechanism antioxidant action.

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