

Determination of Effectivenesses of 2,6-Ditertiarybutyl Cathecol Tri(Mono-and-Di-Nonyl-Phenyl Mixtures) Phosphite and Their Mixtures as Antioxidants for CBR, By DSC

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Synopsis

Effectivenesses of 2,6-ditertiarybutyl cathecol (Dnx), tri(mono-and-di-nonyl-phenyl mixture) phosphite (Plg), and their mixtures as antioxidants for CBR are determined. The activation energies of oxidative degradation for CBR are calculated. An attempt is made to corrolate the results obtained from experimental studies to storage time of CBR under ambient conditions. The relevant experiments are done mainly by differential scanning calorimetry. IR spectroscopy is used for effectiveness studies near room temperatures. Quantitative determinations of antioxidants in CBR samples are carried out by UV spectroscopy. It is found that, as an antioxidant, Dnx is more effective than Plg. When their mixture is used, 60% addition of Plg to Dnx gives almost the same effectiveness. When 45% Plg is added, maximum effectiveness is achieved and Plg is synergist to Dnx. Activation energies calculated are in good agreement with the values given in the literature. To corrolate the retarded oxidation periods obtained from DSC studies to room temperatures, DSC studies at temperatures where relative effectivenesses of different antioxidants to each other do not change by temperature must be carried out.

INTRODUCTION

Cis-1,4-polybutadiene (CBR) is one of the synthetic elastomers which is used extensively. CBR replaces styrene-butadiene rubber (SBR) and/or natural rubber in the formulations to improve various properties of these materials. Therefore, CBR has a special importance for the rubber tire industry and thus is utilized in this area extensively. Production of footwear, transport belts, "V" belts, houses, floor tiles, ebonite, etc. are other important application areas of CBR. This rubber is also used in the production of antishock polystyrene and acrylonitrile-butadiene-styrene (ABS) plastics to improve their impact properties.¹

As in the case of other polymeric materials, CBR oxidizes by reacting with oxygen. Since oxidation affects the properties of CBR in an undesirable way, various antioxidants are used to retard or preferably inhibit its oxidation during production, storage, processing as well as usage under the application conditions. Nowadays, various antioxidants are produced which are mainly phenolic compounds, alkyl aryl phosphites, dithiocarbonate or thiozyl derivatives. Furthermore, their number on the market is continuously increasing.^{2,3} Therefore, selection of the most suitable antioxidants

or their mixtures is very important from both technical and economical points of view.

In this work we determined the effectiveness of 2,6-ditertiarybutyl cathecol, tri(mono-and-di-nonyl-phenyl mixture) phosphite, and their mixtures as antioxidants for CBR. The activation energies of oxidation process are calculated. An attempt is made to correlate the results obtained from experimental studies to storage time of CBR under ambient conditions.

EXPERIMENTAL

Various techniques are used to study the oxidation of polymeric materials and the effectiveness of antioxidants used with them.⁴⁻¹⁰ In this work, the relevant experiments are done mainly by differential scanning calorimetry (DSC).¹¹⁻¹³ IR-Spectroscopy is used for effectiveness studies near room temperatures.⁶⁻⁸ Quantitative determinations of antioxidants in CBR samples are carried out by UV spectroscopy.

Materials

CBR is obtained as 13% solution in benzene from the production plant of PETKIM, Petrochemicals Corp., Izmit, Turkey. 2,6-Ditertiary butyl cathecol (Deenax) was a product of Kasching GmbH. Tri(mono-and-di-nonyl-phenyl mixture) phosphite (Polygard) was a product of Uniroyal Chimie SpA. Other chemicals and solvents such as benzene, cyclohexane, etc. were reagent grade chemicals.

Procedure

Sample Preparation

Rubber samples are prepared by precipitating rubber from its 13% solution in benzene by evaporating the solvent on a two-roll mixer. First, desired amounts of Deenax (Dnx) and Polygard (Plg) are dissolved in benzene. This solution is added to the rubber solution to obtain the desired percentage of Dnx + Plg. Then, this solution is poured slowly on to the rolls of a two-roll mixer whose rolls are kept at 85°C with 1.400 ± 0.127 mm clearance. To assure total evaporation of the solvent, after few passages, the sample is weighed. Milling is continued until constant weight of the sample is obtained. To obtain homogenous distribution of the antioxidants (Dnx + Plg) in CBR, milling is done for five more passages by cutting the sample sheet into two during the second and forth passages.¹⁴

Test Methods

Quantitative determination of Dnx and Plg in the rubber samples was performed in accordance with ASTM D 1416-76 by using UV spectroscopy.

For IR studies 2.5% solution of rubber samples in benzene are prepared. A few drops of this solution are placed on KBr cells, and the solvent is evaporated at room temperature and further dried in vacuum oven. To obtain the same film thicknesses each time, the number of drops is kept

approximately constant. The film thicknesses are checked for the same IR absorbances at 1458 cm^{-1} .^{8,9} These films on KBr cells are then kept in an oven at the desired temperature in contact with air. At various intervals, the cell is removed from the oven for quick IR spectrum recordings at desired wave numbers so that absorptivities of the carbonyl group at 1715 cm^{-1} are calculated to follow up the oxidation.

For DSC studies, about 0.0250 g samples of similar areas are cut from the sample prepared before by milling. They are placed in DSC capsules which are then placed in the DSC cell with their cups open to secure air-rubber interaction. Isothermal studies at various temperatures are done to determine antioxidant effectiveness. To determine rubber specifications, ASTM methods are used.

Equipment

For DSC studies, a DuPont Model 990 thermal analysis system with DSC unit, for IR studies, a Perkin-Elmer Model 377 IR Spectrophotometer, and for quantitative antioxidant determinations, a Varian Techtron Model 635 UV-Vis are used. A spectrophotometer, and, for rubber precipitation and testing, routine laboratory equipment in accordance with ASTM standards is used.

RESULTS AND DISCUSSIONS

Retarded Oxidation Periods from DSC Thermograms

The period during which no endothermic or exothermic reactions are observed at the DSC thermograms (t_1) is generally used as the retarded oxidation period.^{11,12} However, usage of the time necessary for the formation of the peak at the DSC thermograms (t_2) is also used by some workers.¹³ To clarify this point, DSC and IR studies are carried out in parallel at 150°C . In Figure 1, change by time of carbonyl absorption at 1715 cm^{-1} of CBR samples containing 1% Dnx + Plg (Dnx/Plg, 30/70) is given. Figure 2 shows the change of carbonyl absorbance values calculated from the spectrums in Figure 1: a DSC thermogram of the same sample is also shown in this figure for comparison. Oxidation is almost complete, when the DSC peak is formed (Fig. 2). Therefore, the real retarded oxidation period is t_1 , during which no chemical reaction, either endothermic or exothermic, is observed on the DSC thermograms.

To see the effect of the two different retarded oxidation periods reported in the literature,¹¹⁻¹³ on the antioxidant effectiveness determinations, DSC studies at 150°C with CBR samples containing 1% Dnx + Plg of various Dnx/Plg values are carried out. In Figure 3 DSC thermograms of these samples, and in Figure 4 variation of the retarded oxidation periods by the change of Dnx/Plg value, are given.

Figure 4 shows that if antioxidant effectiveness (retarded oxidation periods) are compared, both of the definitions of the retarded oxidation periods (t_1 and t_2) will give the same results. However, when the real value of the retarded oxidation period is needed, the period during which no chemical

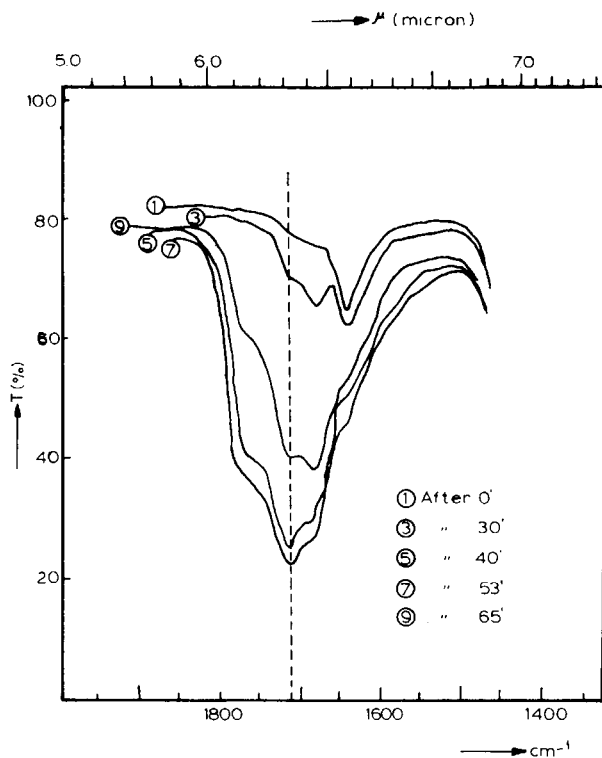


Fig. 1. Change of carbonyl peak by time at 150°C IR Spectrum of the CBR samples containing 1% (Dnx + Plg), Dnx/Plg, 30/70. After (min): (1) 0; (3) 30; (5) 40; (7) 53; (9) 65.

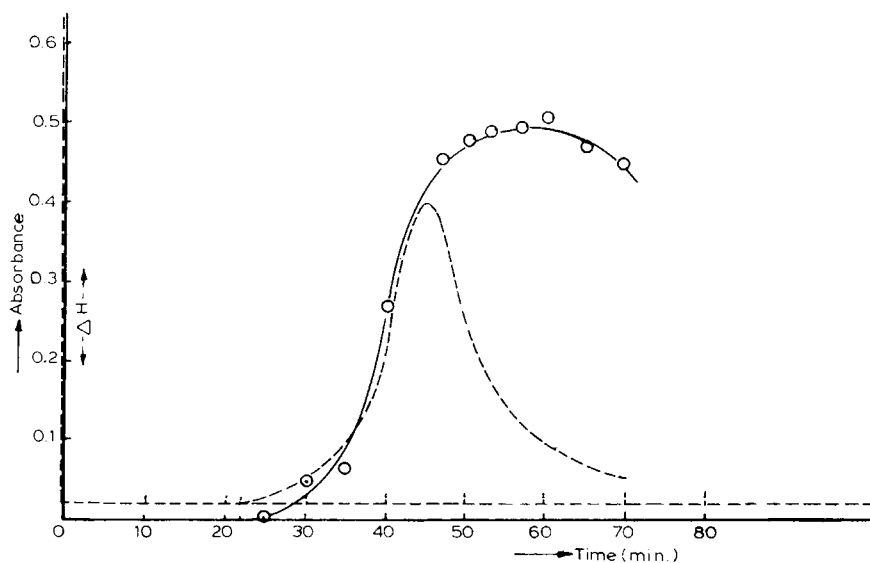


Fig. 2. Change of 150°C carbonyl absorbance by time of CBR samples containing 1% (Dnx + Plg), Dnx/Plg, 30/70, and the 150°C DSC thermogram of the same sample.

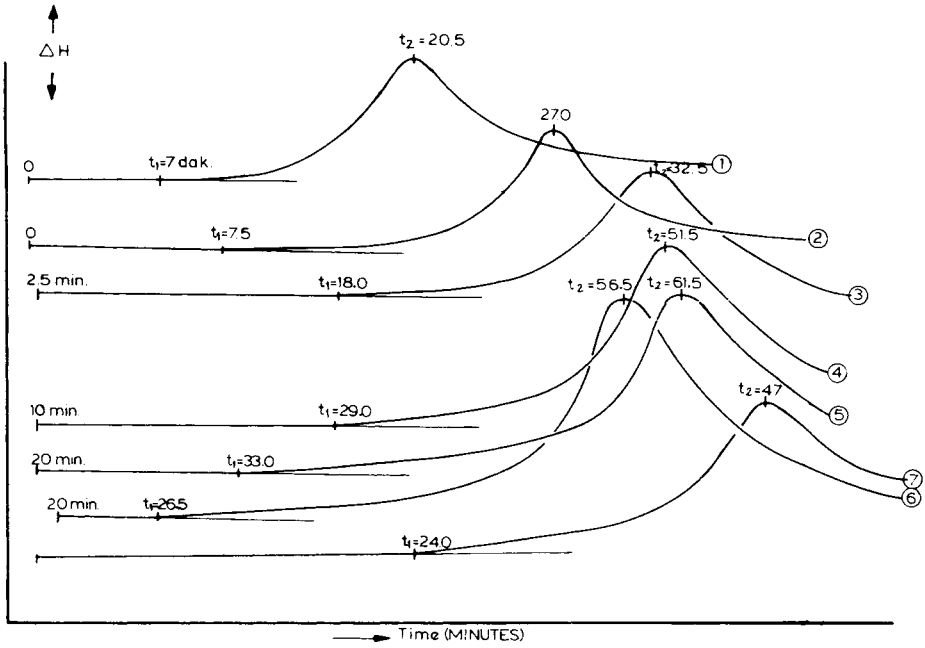


Fig. 3. 150°C DSC thermograms of CBR samples containing 1% (Dnx + Plg), Dnx/Plg: (1) 0/100; (2) 20/80; (3) 30/70; (4) 50/50; (5) 55/45; (6) 70/30; (7) 80/20.

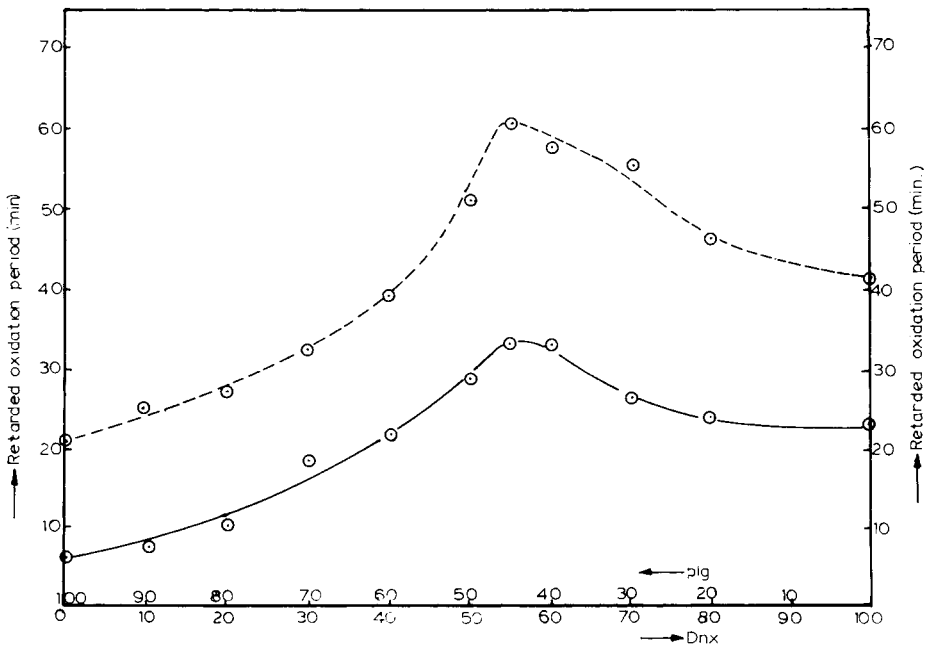


Fig. 4. Variation of 150°C retarded oxidation periods of CBR samples containing 1% (Dnx + Plg) by (Dnx/Plg): (○) according to t_1 ; (○) according to t_2 .

reaction, either endothermic or exothermic is observed on DSC thermograms, (t_1) is to be used. Therefore, in our studies, we refer to t_1 as the retarded oxidation period.

The Amounts of Dnx + Plg to be Used with CBR

When antioxidants are added to polymeric materials, their effectiveness changes linearly with the change of antioxidant concentration. However, if their concentration is lower than a minimum critical concentration (min c.c.) or higher than a maximum critical concentration (max c.c.), the obtained effectiveness is lower than the expected value. Therefore, the concentration chosen is desired to be between min c.c. and max c.c.¹⁴ Since we have chosen to use 1% Dnx + Plg for our experiments, to see if min or max c.c. are exceeded, DSC experiments at 130, 140, and 150°C are carried out with CBR samples containing various amounts of Dnx + Plg (Dnx/Plg, 30/70). Variation of retarded oxidation periods by percentage of Dnx + Plg at three temperatures is shown in Figure 5. Since linearity is still retained, addition of 1% Dnx + Plg to CBR as antioxidant provides suitable protection.

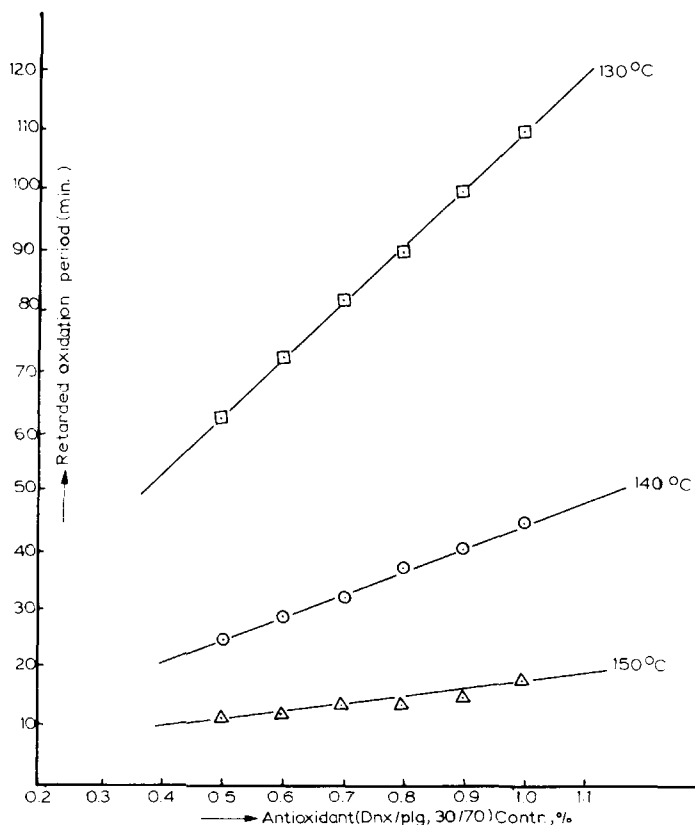


Fig. 5. Retarded oxidation periods of CBR samples containing various amounts of Dnx + Plg (Dnx/Plg, 30/70) at three temperatures.

Antioxidant Effectivenesses of Dnx, Plg, and Their Mixtures When Used With CBR

To study the antioxidant effectiveness of Dnx, Plg, and their mixtures; CBR samples containing 1% Dnx + Plg with various Dnx/Plg values are prepared and DSC thermograms at 120, 130, 140, 150, and 170°C are recorded. Figure 6 shows the graphs obtained when retarded oxidation periods (t_1) read from the DSC thermograms are plotted against the fraction of Dnx in the Dnx + Plg mixtures. Figure 6 shows that the more effective antioxidant in the mixture is Dnx. In addition, at Dnx/Plg, 55/45 value, a synergistic effect is obtained. Furthermore, when Dnx/Plg, 40/60 is used, the antioxidant effect is almost equal to that of Dnx alone. Since Dnx is about 2.5 times more expensive than Plg, using Dnx, Plg mixtures, particularly at a Dnx/Plg, 40/60 value, has an economical importance.

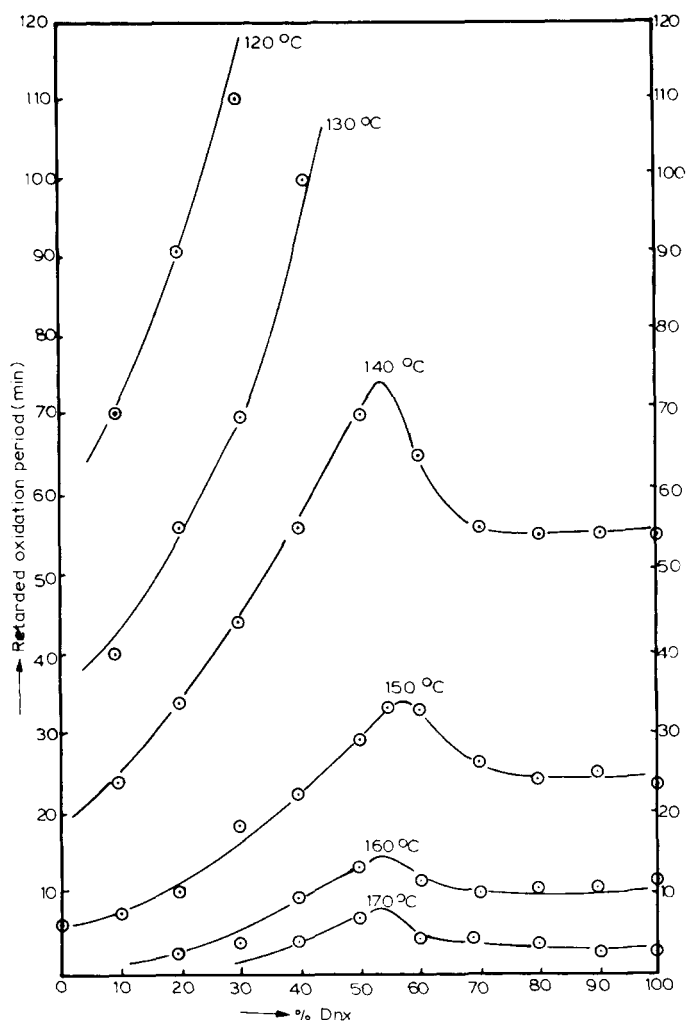


Fig. 6. Variation of retarded oxidation periods of CBR samples containing 1% (Dnx + Plg) by % Dnx.

Activation Energies of Oxidation for CBR

The retarded oxidation periods (t_1 or t_2) are dependent on rate constants of reactions taking place in this period, initial concentrations (C_1, C_2), and percent conversions (X).¹³ Therefore, for a particular oxidation temperature,

$$t = (C_1, C_2, X)/K_c \quad (1)$$

where K_c shows the overall rate constant. For CBR samples containing equal amounts of antioxidants of particular Dnx/Plg

$$f(C_1, C_2, X) = B = \text{const.} \quad (2)$$

Therefore we can write

$$t = B/K_c \quad (3)$$

Relative Antioxidant Effectivenesses and Correlation of DSC Results to Room Temperatures

To compare antioxidant effectivenesses, the value obtained from DSC studies for effectiveness (retarded oxidation period) of 1% (Dnx + Plg) of Dns/Plg, 40/60, is assumed to be 100% for each temperature. Retarded oxidation periods of other samples (Dnx/Plg, 30/70, 20/80, 10/90) corresponding to the same temperature is divided by these values, respectively. Thus, antioxidant effectiveness values are obtained for each sample. When these values are plotted against temperature, Figure 11 is obtained. The graphs in Figure 11 indicates that, at high temperatures, antioxidant effectiveness values change with temperature. At relatively lower temperatures (120–140°C), however, it is seen that the antioxidant effectiveness is almost constant and does not change with temperature. Assuming that the constant effectiveness values obtained for 120–140°C can be extrapolated to ambient temperatures, antioxidant effectiveness values of 68, 58, and 45% at 25°C for the samples of Dnx/Plg, 30/70, 20/80, and 10/90, are obtained respectively.

As given above, a 6-month retarded oxidation period of $25 \pm 5^\circ\text{C}$ for the CBR sample of Dnx/Plg, 40/60, is finalized. Calculations made using this value as a reference and using the above-given relative effectiveness value of 58% for the CBR sample of Dnx/Plg, 20/80, gives a retarded oxidation period of 3.5 months at $25 \pm 5^\circ\text{C}$. This value is again in very good agreement with the value obtained in Figure 10. From these results, we can draw a conclusion that, when an antioxidant is taken as a reference whose retarded oxidation period at room temperature is known, and DSC studies are carried out at temperatures where relative antioxidant effectiveness values do not change with temperature, the results obtained from the DSC thermograms can be directly extrapolated to room temperatures. Thus storage times at room temperatures can easily be predicted. If we write the Arrhenius equation for K_c , eq. (3) can be rearranged to give

$$\ln t = \ln \frac{B}{A} + \frac{Ea}{R} \frac{1}{T} \quad (4)$$

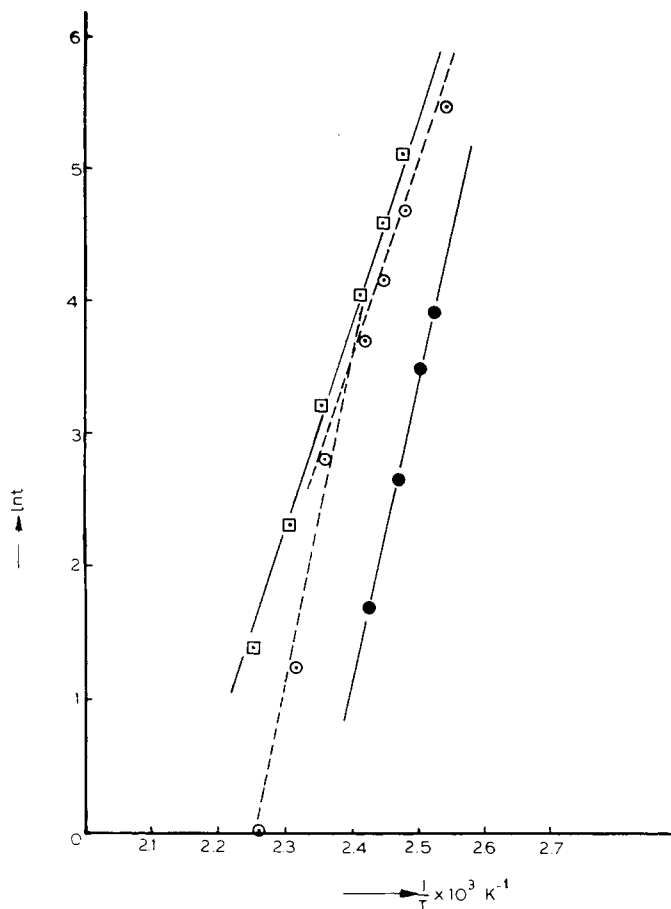


Fig. 7. Modified Arrhenius plot of CBR samples containing 1% (Dnx + Plg): (□) Dnx/Plg, 40/60; (○) Dnx/Plg, 30/70; (●) without antioxidant.

where A stands for preexponential factor. The activation energies are calculated by plotting logarithms of retarded oxidation periods ($\ln t$) read from DSC thermograms against $(1/T)$. A typical plot is given in Figure 7. The calculated activation energies are given in Table I.

TABLE I
Activation Energies of Oxidative Degradation of CBR Samples Containing 1% (Dnx + Plg)

Dnx/Plg	Activation energies (kJ/mol)	
	120°C(experiment temp (°C) 150°C	170°C(experiment temp (°C) 150°C
100/0	109.5	109.6
90/10	109.5	109.5
50/50	116.2	116.2
40/60	126.6	126.6
30/70	126.2	182.7
20/80	178.5	178.5
10/90	178.5	178.5
CBR (without antioxidant)	179.7	179.7

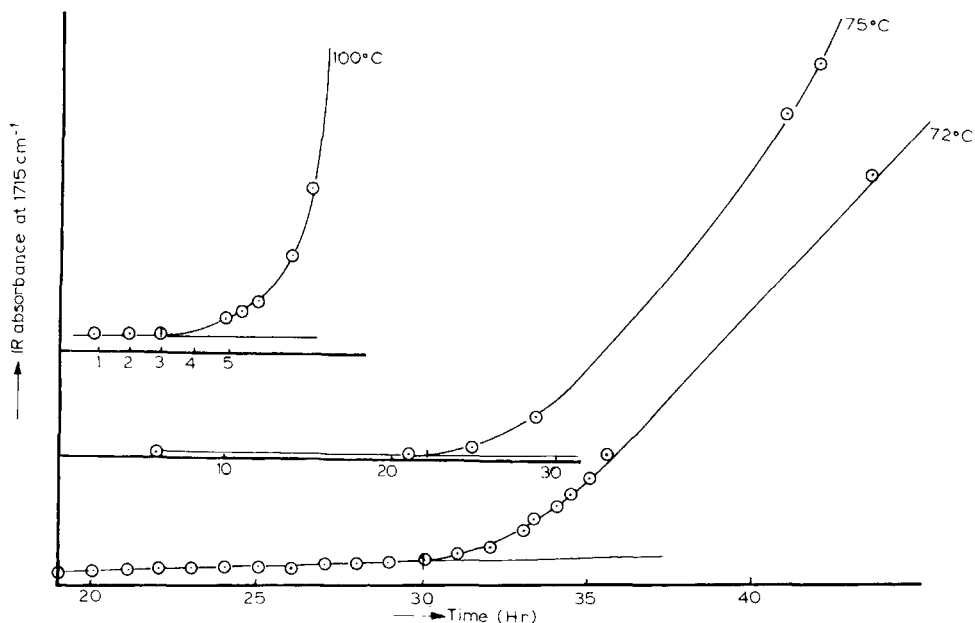


Fig. 8. Variation of IR carbonyl absorbance of 1715 cm^{-1} at 72, 75, and 100°C of CBR samples of Dnx/Plg, 40/60, in contact with air.

The values at Table I show that around our experiment temperatures ($120\text{--}170^\circ\text{C}$), depending on the temperature and the Dnx/Plg value, activation energies of oxidation of CBR are 27.5 and 42 kcal/mol.

When the values for E_a and $\ln B/A$ are obtained from the plots in Figure

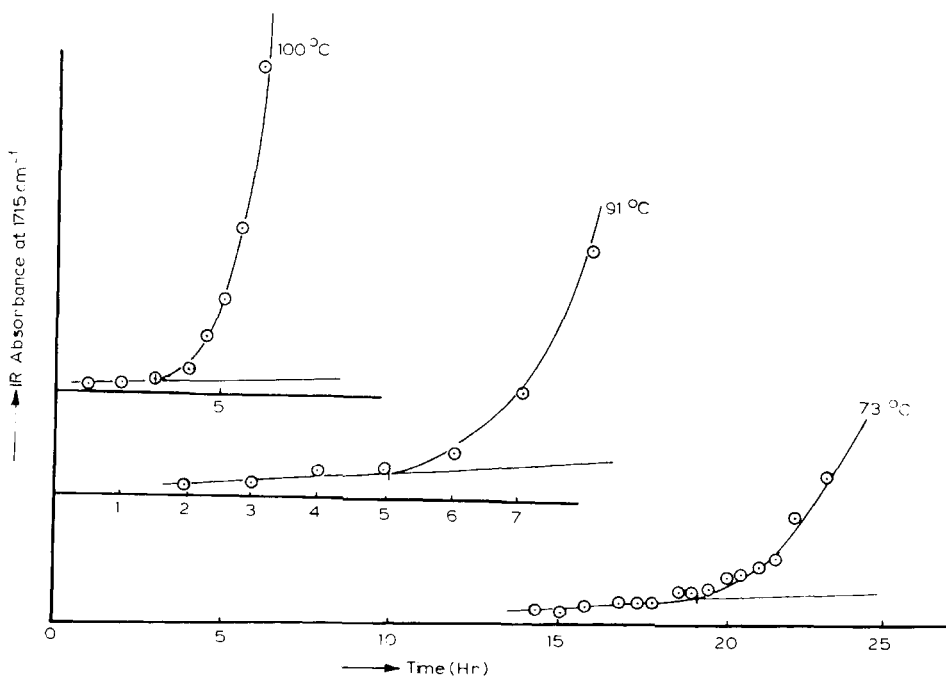


Fig. 9. Variation of IR carbonyl absorbance at 100, 91, and 73°C of CBR samples of Dnx/Plg, 20/80, in contact with air.

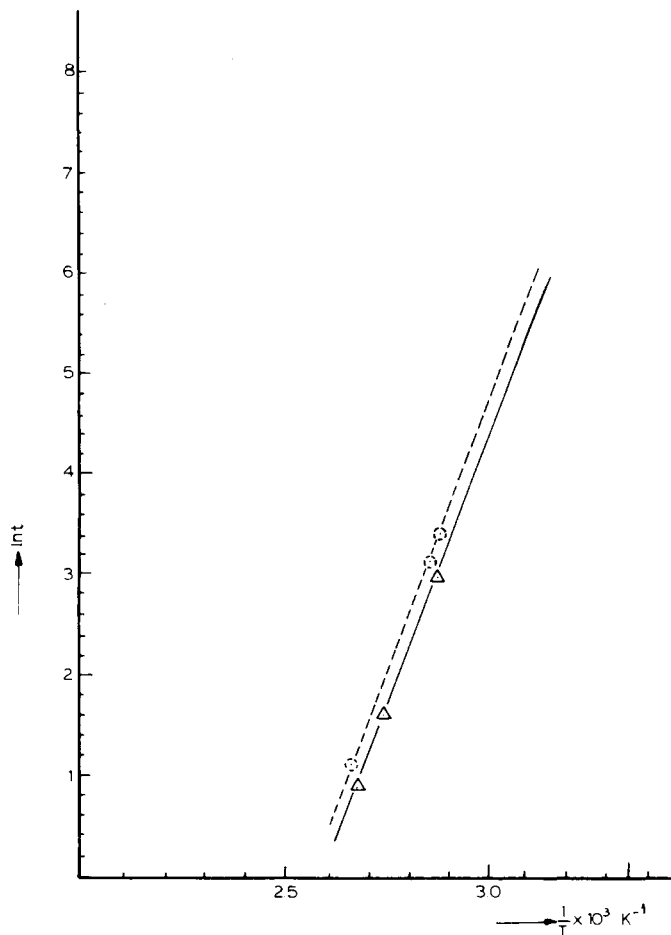


Fig. 10. Modified Arrhenius plot of CBR samples containing 1% (Dnx + Plg) (○) Dnx/Plg, 40/60; (△) Dnx/Plg, 20/80.

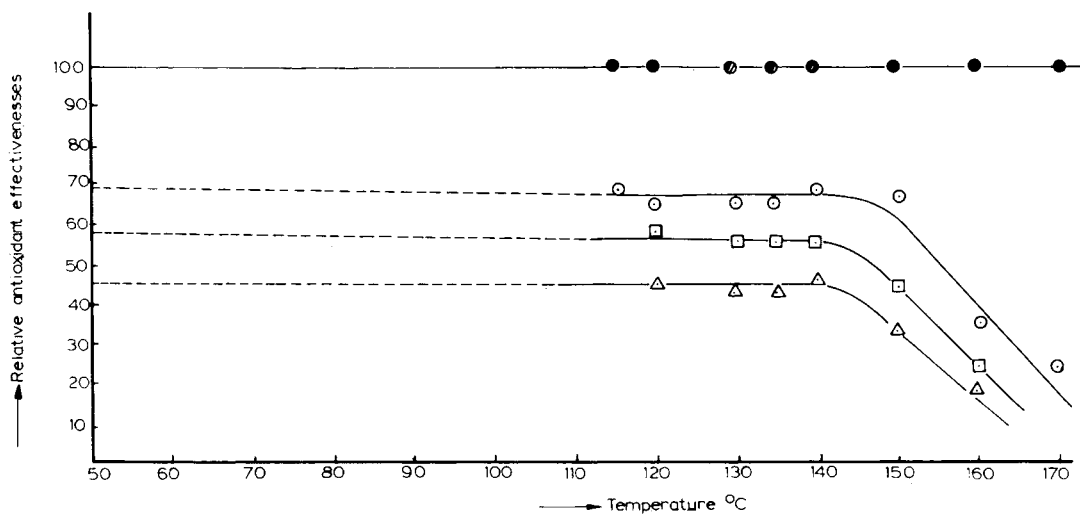


Fig. 11. Chance of antioxidant effectiveness values of (Dnx + Plg) mixtures when used 1% with CBR. Dnx/Plg: (○) 40/60 assumed as standard; (○) 30/70; (□) 28/80; (△) 10/90.

7 and plugged into eq. (4), and retarded oxidation periods for 25°C are calculated, rather unrealistic values such as 120 years are obtained. Taking into account these unrealistic values and the fact that CBR, like many other polymeric materials, might have a different oxidation pattern depending on temperature,¹⁵ further experiments are carried out at lower temperatures.

In this case the IR spectroscopic technique given above is used. In Figure 8 variation by time of the carbonyl group at 1715 cm⁻¹ for CBR samples of Dnx/Plg, 40/60, are given. Similar plots for CBR samples of Dnx/Plg, 20/80, are shown in Figure 9. The logarithm of retarded oxidation periods obtained from Figures 8 and 9 is then plotted against 1/T, and, from the slopes of the straight lines shown in Figure 10, activation energies for temperatures lower than 100°C are calculated as 17.5 kcal/mol. By using the ln B/A and E_a values obtained from Figure 10, eq. (4) gives retarded oxidation periods of 6 and 3.5 months at 25 ± 5°C for CBR samples of Dnx/Plg, 40/60, and 20/80, respectively.

To check these retarded oxidation periods obtained from Figure 10, CBR samples of Dnx/Plg, 40/60, are prepared and they are stored at 25 ± 5°C in contact with air. The results obtained from the periodical specification tests of these samples are given in Table II. It is shown that, even after 9.5 months, these samples retained their quality control test values. On the other hand, between 6 and 7.5 months, the samples developed a pale yellow to yellow color which was due to a rather thin layer on their surfaces. Since oxidation of polymeric materials starts from the surface and proceeds to the inner parts of the diffusion of oxygen, and color development is one of the results of this process, this is attributed to the initiation of oxidation. Therefore, this result is assumed to be in agreement with the approximately 6-month retarded oxidation period at 25 ± 5°C obtained in Figure 10.

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