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THERMAL ANALYSIS OF IRRADIATION AND SULPHUR VULCANIZED NATURAL RUBBER

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ABSTRACT

THERMAL ANALYSIS OF IRRADIATION AND SULPHUR VULCANIZED NATURAL RUBBER. Thermal behaviour of either irradiation or sulphur vulcanized natural rubber has been studied using thermogravimetric analysis. Thermal stability of irradiated natural rubber is found to be better than that of sulphur vulcanized natural rubber. However,the mechanism of thermal decomposition appears to be similar. The activation energy for thermal degradation increases with the increase of conversion, presumably due the the formation of higher degree of unsaturated compound during the heating. IR analysis shows the formation of $R_1R_2C = CH_2$ compound by heating natural rubber.

ABSTRAK

ANALISIS TERMAL KARET VULKANISASI RADIASI DAN BELERANG. Sifat termal karet vulkanisasi radiasi dan belerang dipelajari dengan menggunakan analisis termogravimetri. Kestabilan termal karet iradiasi ternyata lebih baik daripada karet alam vulkanisasi belerang. Tetapi mekanisme peruraiannya hampir sama. Energi aktivasi peruraian termal naik dengan naiknya konversi, yang mungkin disebabkan oleh terbentuknya senyawa yang derajat tidak jenuhnya lebih tinggi. Analisis IR menunjukkan terbentuknya senyawa $R_1R_2C=CH_2$ pada pemanasan karet alam.

INTRODUCTION

Natural rubber latice is a natural polymer latice which is produced by a large number of plant species, but only *Hevea brasiliensis* latice has assumed major industrial importance. Natural rubber is a polymer of isoprene in which all or nearly all of the repeating unit posseses

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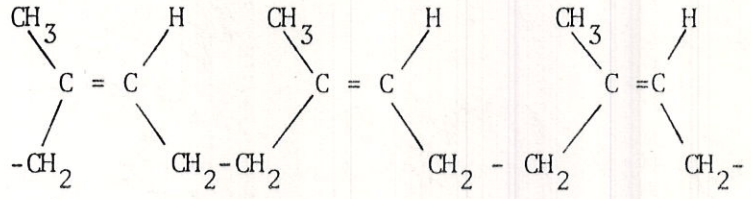
the cis configuration. It is clear that natural rubber contains a large number of double bonds, which are liable to oxydation. Crosslinked natural rubber is the most usefull for all practical applications (1).



cis-configuration

Crosslinked natural rubber can be obtained by sulphur, peroxide, or radiation vulcanization method. Each of these processes is able to produce a crosslinked natural rubber with a specific property. This paper presents the experimental results on the thermal behaviour of irradiation and sulphur vulcanized natural rubber. A non isothermic method, thermogravimetric analysis, was used to determine the kinetic parameter of thermal decomposition. Although the use of non isothermal kinetic method has been seriously questioned, this method has more advantages than the conventional isothermal method for determining the kinetic parameter (3). A number of investigators use this method to study the thermal behaviour of a large number of polymers (4 - 9).

Thermal decomposition of a polymer is a very complex reaction, and for simplifying the formulation, all kinetic reactions of thermal decomposition can be assumed to follow the basic rate equations as follows :

$$dC/dt = A\,(100-C)^n \exp - E_a/RT \quad \ldots\ldots\ldots\ldots \quad 1/$$

where C is the conversion (%), E_a is the activation energy for thermal decomposition, A is the pre-exponential factor, n is the reaction order, T is the absolute temperature (^oK), and R is the gas constant.

If the heating rate dT/dt can be defined as β, then equation 1/ becomes :

$$dC/dt = (A/\beta)(100-C)^n \exp - E_a/RT \quad \ldots\ldots\ldots\ldots \quad 2/$$

$$\text{or} \quad \ln\beta = \ln A(dT/dC)(100-C)^n - E_a/RT \quad \ldots\ldots\ldots\ldots \quad 3/$$

If at a given amount of conversion C, dC/dT and reaction order n are assumed to be constant, and do not depend on the rate of heating β , equation 3/ can be simplified as follows :

$$\ln \beta = \text{const} - E_a/RT \quad \ldots\ldots\ldots\ldots \quad 4/$$

By plotting ln β against 1/T, a straight line is obtained, which slope is $- E_a/R$, and hence the activation energy E_a can be computed.A number of experimental results showed to be in agreement with equation 4/.

Modification of equation 2/becomes :

$$\int_o^c \frac{dC}{(100-C)^n} = \frac{A}{\beta} \int_{To}^{T} (\exp - E_a/RT)\,dT \quad \ldots\ldots\ldots \quad 5/$$

where To is the temperature at zero conversion and T is the temperature at conversion C. Using this basic equation a number of investigators, such as REICH (4), determine the kinetic parameter for thermal decomposition.

REICH used the following expression :

$$E_a = \frac{4.6 \log \left({}_2 {}_1 \right) (T_1/T_2)^2}{(1/T_1 - 1/T_2)}$$

to determine the kinetic parameter for thermal degradation.

EXPERIMENTAL

Natural rubber used for this experiment was from West Java, Indonesia. Field natural rubber latex, about 40% dry rubber content , was concentrated up to 60% dry rubber content by using a centrifuge. This concentrated latex, about 200 ml, was mixed with a small amount of carbon tetrachloride (3 phr) in the form of an emulsion, and then irradiated with dose of irradiation 30 kGy and dose rate 2 kGy per hour. Irradiation was carried out in a Panoramic CO-60 irradiation of about 40 kCi activity. A small amout sulphur vulcanizing chemicals in the form of a dispersion was mixed with the irradiated latex. The sulphur vulcanizing chemicals such as ZnO , ZDC , sulphur and dispersol, were of technical grade. Dry rubber film was prepared by casting the latex on a glass plate, and evaporated at room temperature. The dried film was heated at 100^{o}C for about 60 minutes.

The dried rubber film of about 6 mg was use for TG analysis. The experiment was carried out under a steady flow of nitrogen. The heating rates were 2, 5, 10 and 30^{o}C per minute and the samples were heated up to 500^{o}C. Shimadzu thermal analyzer DT-30 was used for the TG analysis. The kinetic parameter of thermal decomposition was determine by computing the displacement of TG curves due to the difference in

heating retes. A Shimadzu Infrared Spectrophotometer IR-435 was used to analyse the chemical structure of the natural rubber film either before or after thermal decomposition.

RESULTS AND DISCUSSION

Figure 1 shows TG curves of irradiated natural rubber at various heating rates. The TG curves displace due to the difference in heating rate. It is found that irradiated natural rubber begin to decompose at a temperature of about 300^{o}C and complete the decomposition at about 400^{o}C. At a given amount of conversion, the decomposition temperature was found to decrease with a decrease in heating rate , and dC/dT appears to be constant and does not depend on the heating rates. Figures 2 and 3 show the TG curves of irradiated natural rubber which has been mixed with a small amount of sulphur vulcanizing agent. These figures show the same phenomena as Figure 1. It is clear that the addition of a small amount of sulphur vulcanizing chemicals on natural rubber does not influence the mechanism of thermal decomposition.

The kinetic parameter E_a at a given amount of conversion can be determined using the displacement of TG curves due to the difference in heating rate. Figures 4, 5, and 6 show the semilog plot of heating rate β vs 1/T for either irradiated natural rubber of irradiated natural rubber which has been mixed with a given amount of sulphur vulcanizing chemicals. Plots of log β vs 1/T are found to be straight lines. These results show that for the thermal decomposition of natural rubber, the reaction order n should be constant and not depend on

heating rate β, at a given amount of conversion. It is found that these results are in agreement with equation 4/. The slopes of the lines are equal to $-E_a/R$, and hence the activation energy for thermal decomposition E_a at a given amount of conversion can be computed. Table 1 shows the results of the computation of E_a at various degrees of conversion C. It is clear that E_a depends much on the degree of conversion C. The activation energy for thermal degradation E_a at 70% conversion was found to be much higher than at 50% or 30% conversion. Lower molecular weight of degraded products will evaporated first, and the rest is the higher molecular weight compound with a higher degree of unsaturation. Higher degree of unsaturation means higher E_a because C = C bond is stronger than C - C or C - H bond.

Figure 7 shows the relation between activation energy E_a and percent weight loss for thermal decomposition of various treated natural rubber, i.e. natural rubber, irradiated natural rubber and sulphur vulcanized natural rubber. The experimental results are obtained using Reich equation (4). It is found that E_a increases with an increase in conversion, and the rate of increase is much higher at conversion of more than 70%. The thermal stability of irradiated natural rubber appears to be better than the unirradiation one or sulphur vulcanized natural rubber. This experimental result is in agreement with the theory that C-C bond is stronger than C-S bond. C-S bonds are found in sulphur vulcanized natural rubber. The mechanism of decomposition appears to be similar for either untreated or treated natural rubber. This fact presumably is due to the very weak influence of sulphur on the mechanism of decomposition. At conversion between 20% and 60%,

E_a is about 50 kcal/mole, and at conversion of about 90%, E_a is about 100 kcal/mole. The reaction order n can be computed if it is assumed that n is constant throughout the decomposition reaction.

It appears that there are several steps of thermal decomposition which take place. In the first step of decomposition, the side chain presumably decompose and evaporate, and the residue of the decomposition is a compound with higher degree of unsaturation than natural rubber. The residue which is a solid compound, has lost its rubbery properties and is easily soluble in tetrahidrofuran. In the second step of decomposition, the compound with the high unsaturation will continue to decompose, and the product may be a compound with a very high degree of unsaturation, or a cyclic compound. High degree of unsaturation means high activation energy for thermal decomposition because C=C bond is believed to be stronger than C-H bond. Figure 8 shows DTA curve for thermal decomposition of natural rubber. Two endothemic peaks, at $330^{o}C$ and $405^{o}C$, appear in this DTA curve which indicate that there are two steps of thermal decomposition with different E_a.

Figures 9A shows IR absorption spectra of natural rubber. A strong absorption at wave number 2960 cm^{-1} is presumably due to C-H stretching vibration. A weak absorption at wave number 1660 cm^{-1} may be due to C=C stretching vibration. Strong absorption at 1450 and 1380 cm^{-1} may be due to C-H deformation. Medium absorption at 835 cm^{-1} may be due to C-H out of plane deformation of an alkene compound, $R_1R_2C{=}CHR_3$. These experimental results appear to be in agreement with the chemical structure of poly-isoprene. Figure 9B shows IR spectra of decomposed

natural rubber, after heating up to 360°C with a heating rate of 30° C per minute. The weight loss due to this heating is about 28% Figure 9B is found to be similar to Figure 9B in band absorption, but differs in the degree of absorption. Absorption at 880 cm^{-1}, which appears in this spectra, may be due to C-H out of plane deformation of an alkene compound, $R_1R_2C=CH_2$. The fact that there is no absorption at about 1700 - 1725 cm^{-1} indicates that there is no oxydation take place during the heating (11).

CONCLUSION

Thermal stability of irradiated natural rubber appears to be better than that of sulphur vulcanized natural rubber, the mechanism of thermal decomposition appears to be similar. Activation energy for thermal decomposition at a given of conversion increases with an increase in conversion.

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Table 1. Activation energy (kcal/mole) for thermal degradation of natural rubber.*

Rubber	Conversion, %		
	30	50	70
Irradiated, 30 kGy	60.35	69.64	82.42
Irradiated, 30 kGy with 0.5 phr sulphur	61.60	64.84	96.72
Irradiated, 30 kGy with 0.1 phr sulphur	57.96	56.66	69.22

Note : * Computed using equation 4/.

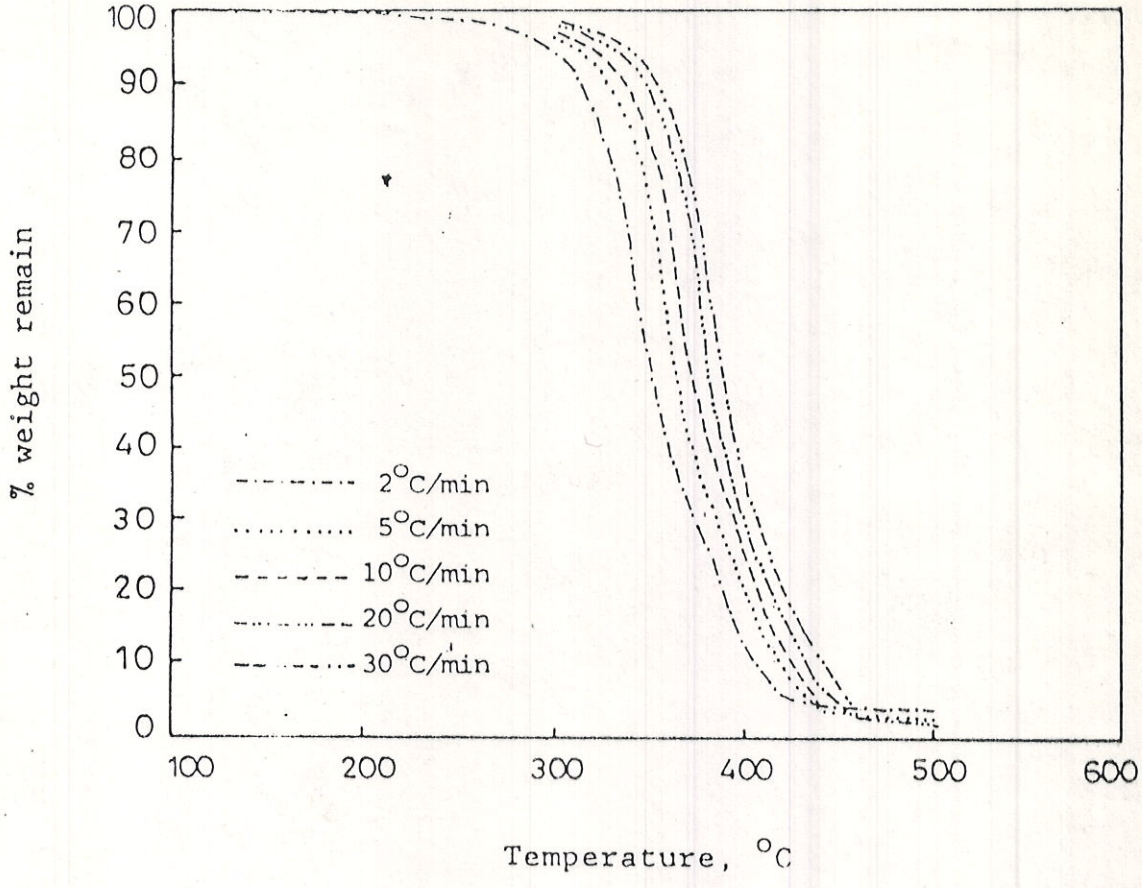

Fig.1 TG curves for irradiated natural rubber (30 kGy) at various heating rates.

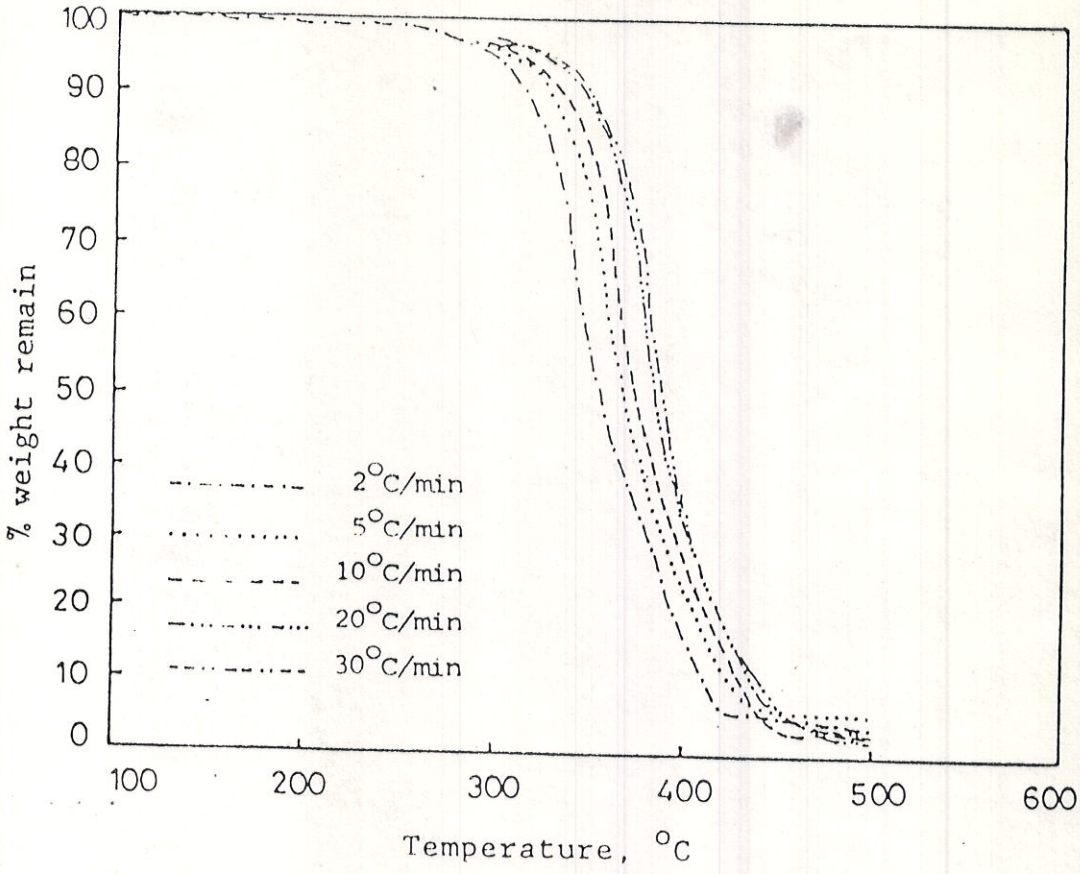

Fig.2 TG curves for irradiated natural rubber (30 kGy) mixed with S 0.5 phr, ZnO 0.5 phr and ZDC 0.5 phr, at various heating rates.

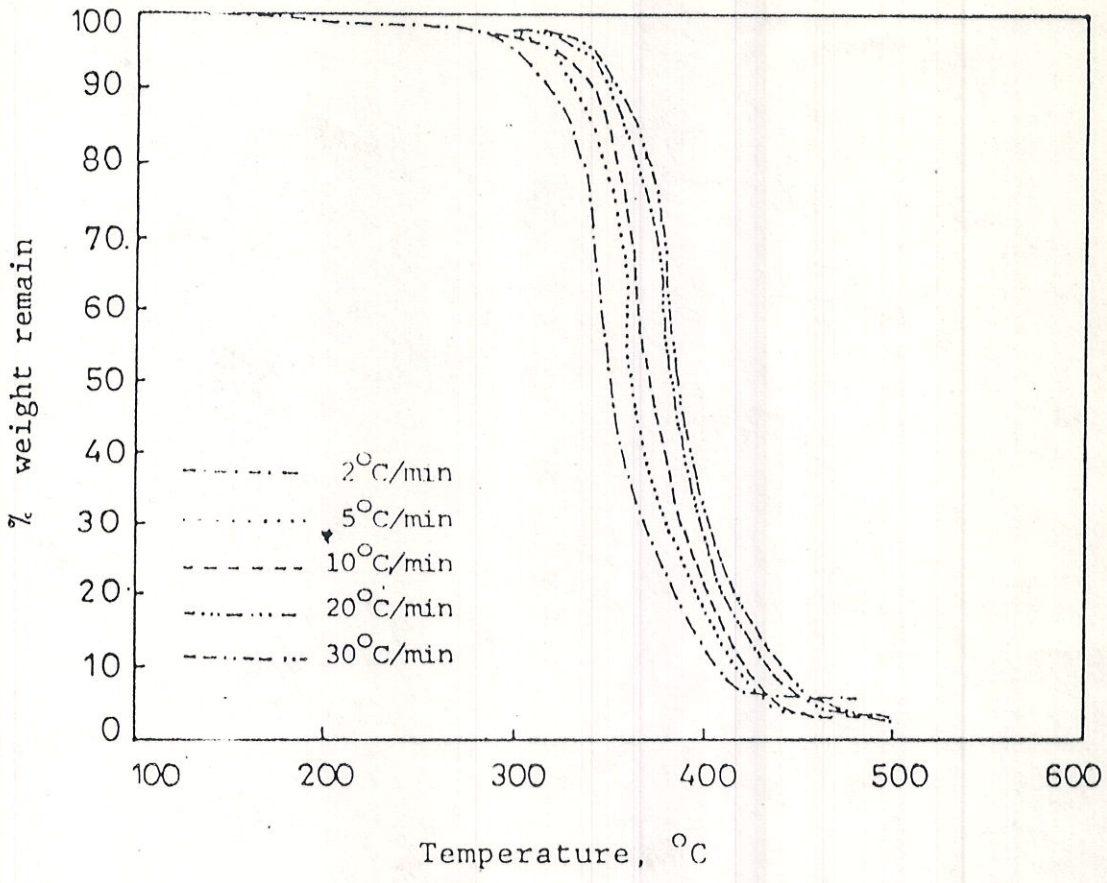

Fig.3 TG curves for irradiated natural rubber (30 kGy) mixed with S 1 phr, ZnO 1 phr and ZDC 1 phr, at various heating rates.

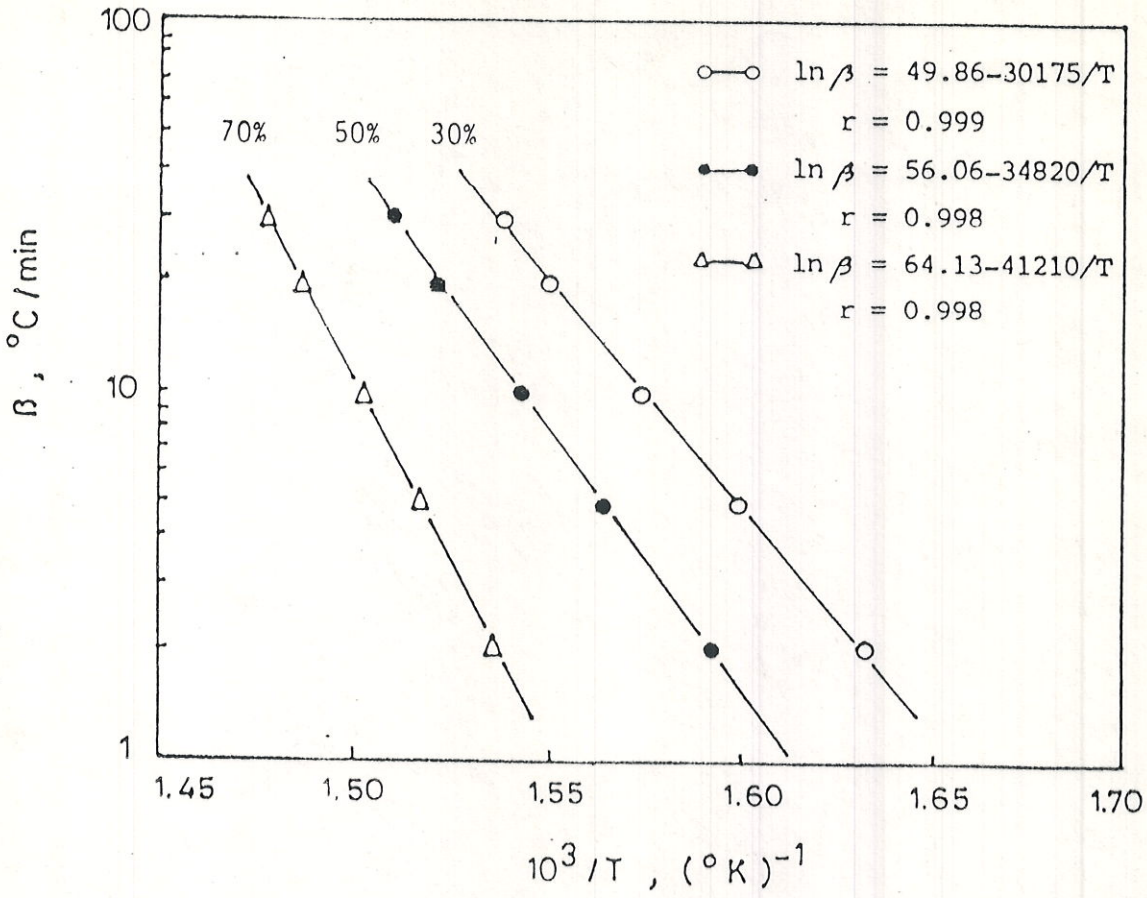

Fig.4 Plot of heating rates (β) vs 1/T for irradiated natural rubber (NR, 30 kGy) at various percentages of weight loss (30, 50 and 70%).

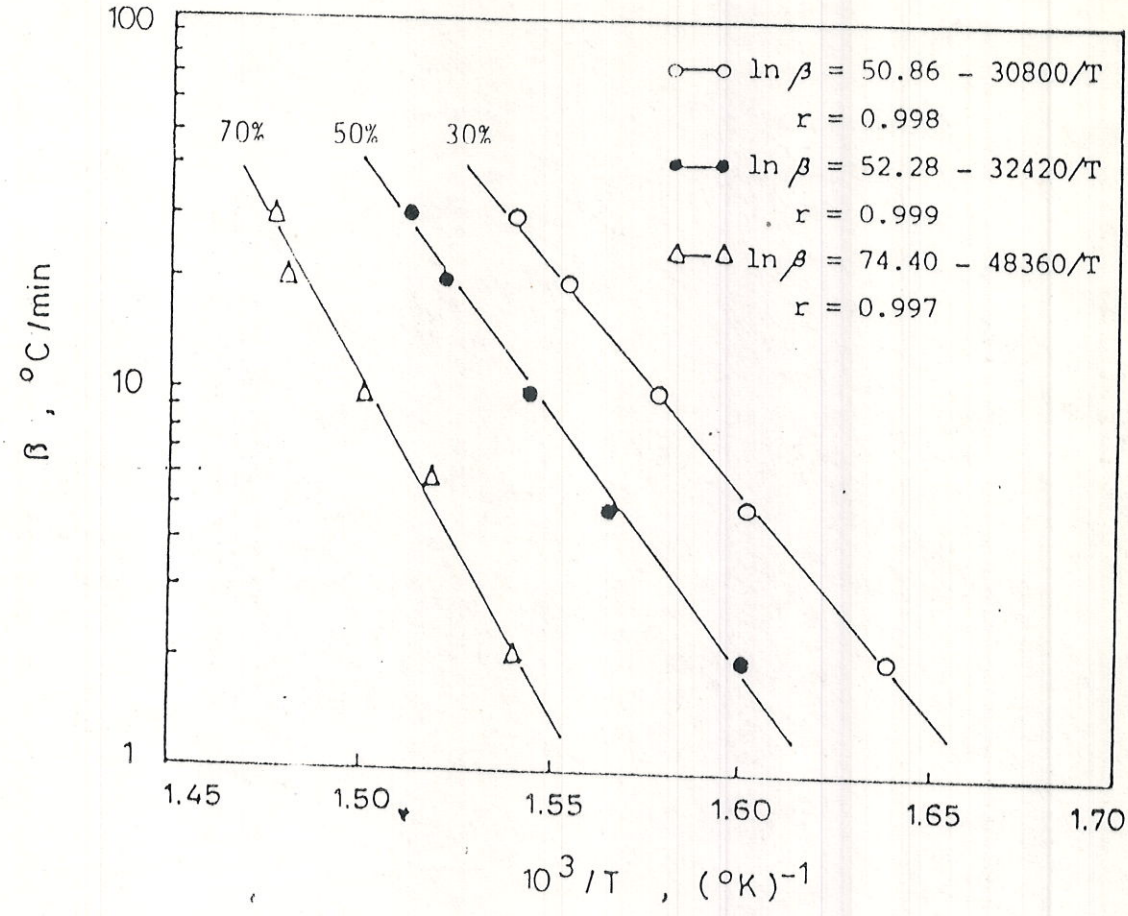

Fig.5 Plot of heating rates (β) vs 1/T for irradiated natural rubber (30 kGy) mixed with sulphur 0.5 phr, ZnO 0.5 phr and ZDC 0.5 phr, at various percentages of weight loss (30 , 50 and 70 %).

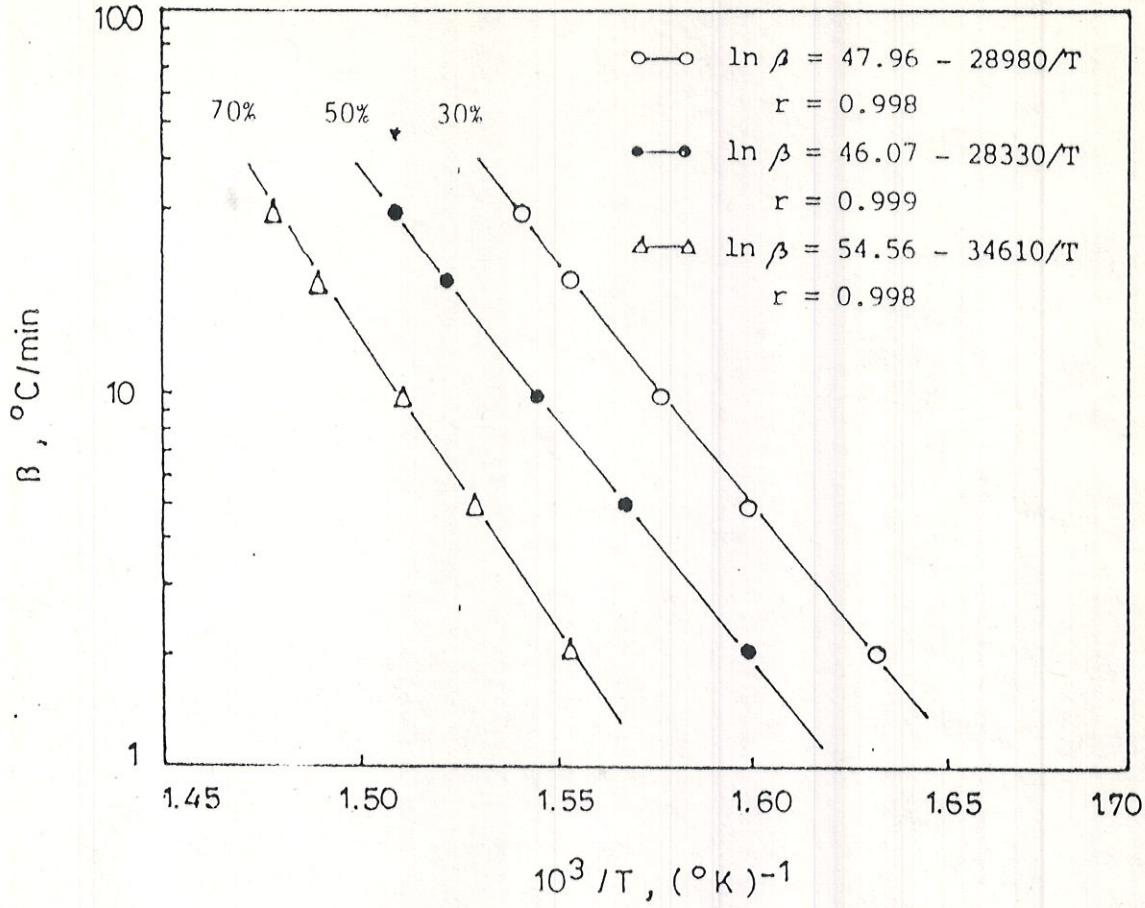

Fig.6 Plot of heating rates (β) vs 1/T for irradiated natural rubber (30 kGy) mixed with sulphur 1 phr, ZnO 1 phr and ZDC 1 phr, at various percentages of weight loss (30 , 50 and 70%)

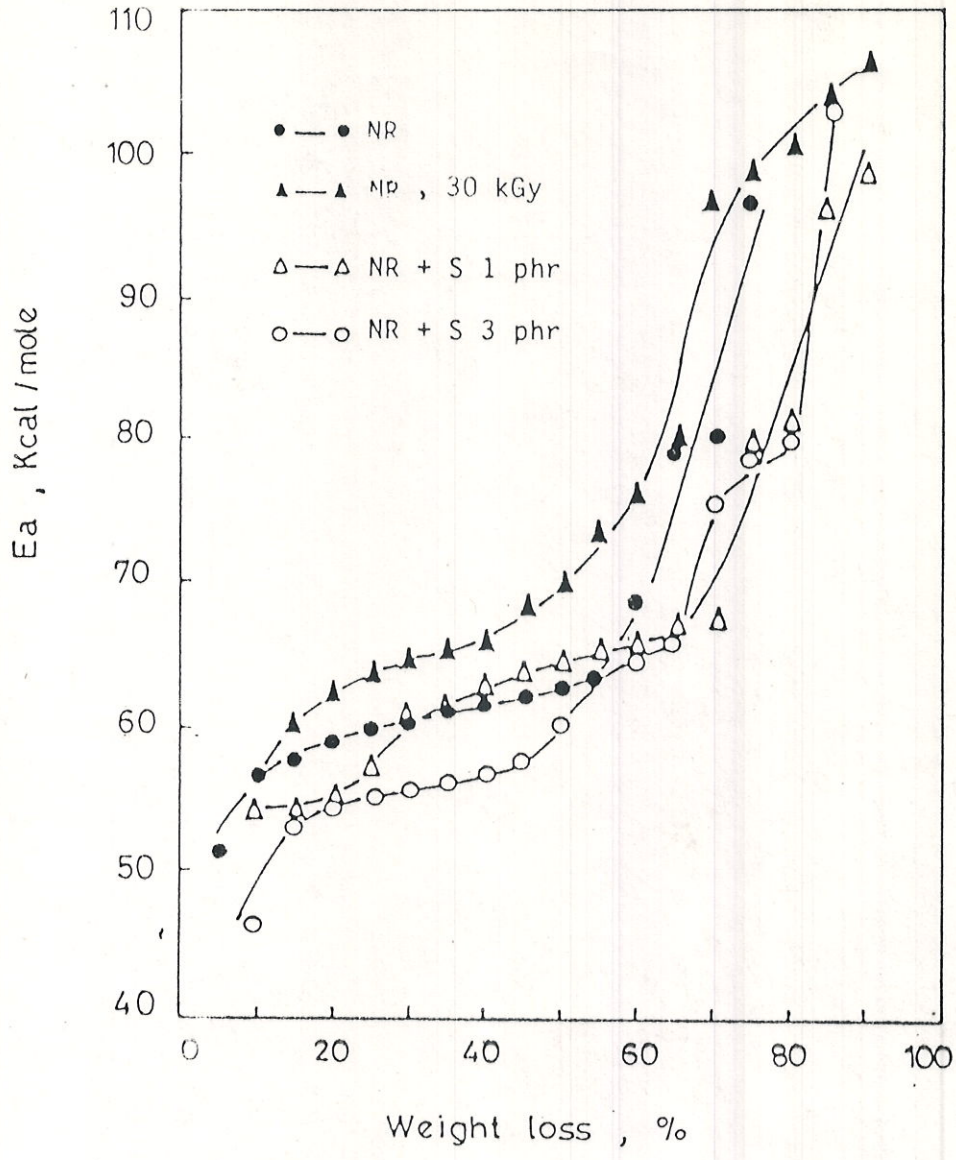

Fig.7 Relation between activation energy for thermal degradation, Ea, and the percentage of weight loss for various treated natural rubber (NR).

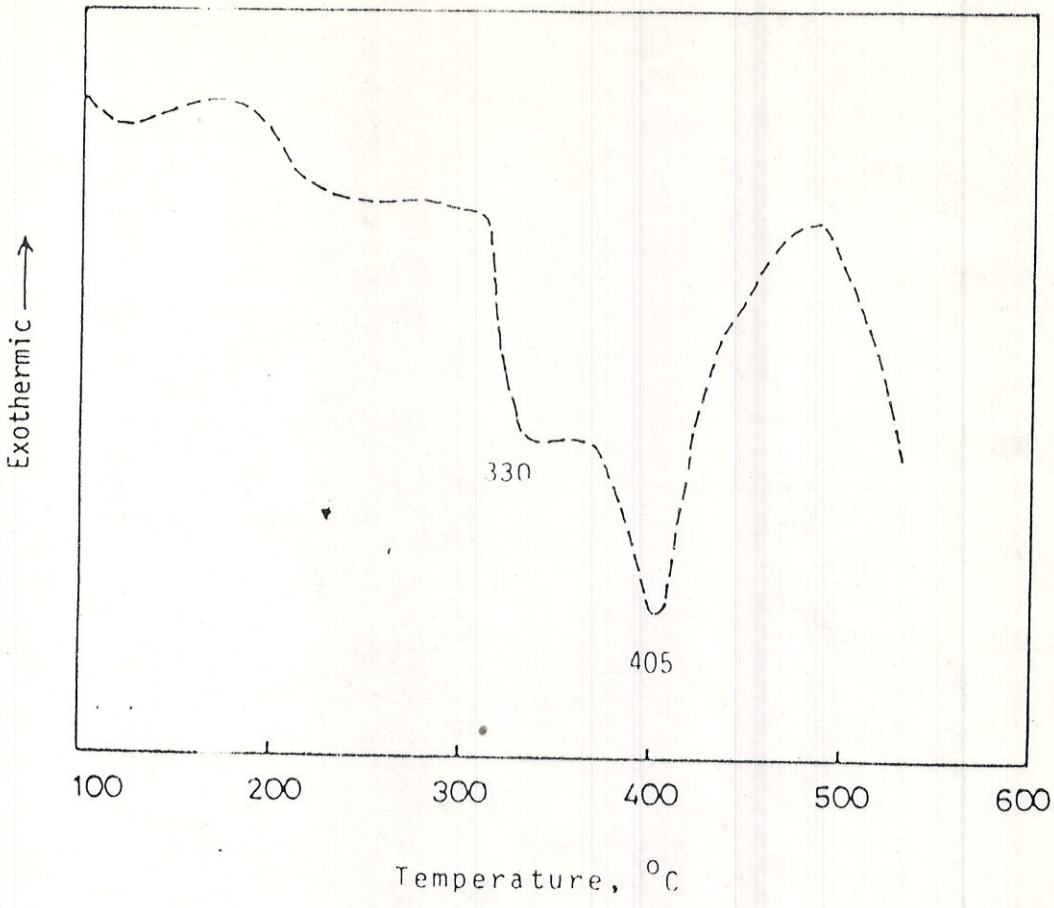

Fig.8 DTA curve for natural rubber at heating rate 30°/min

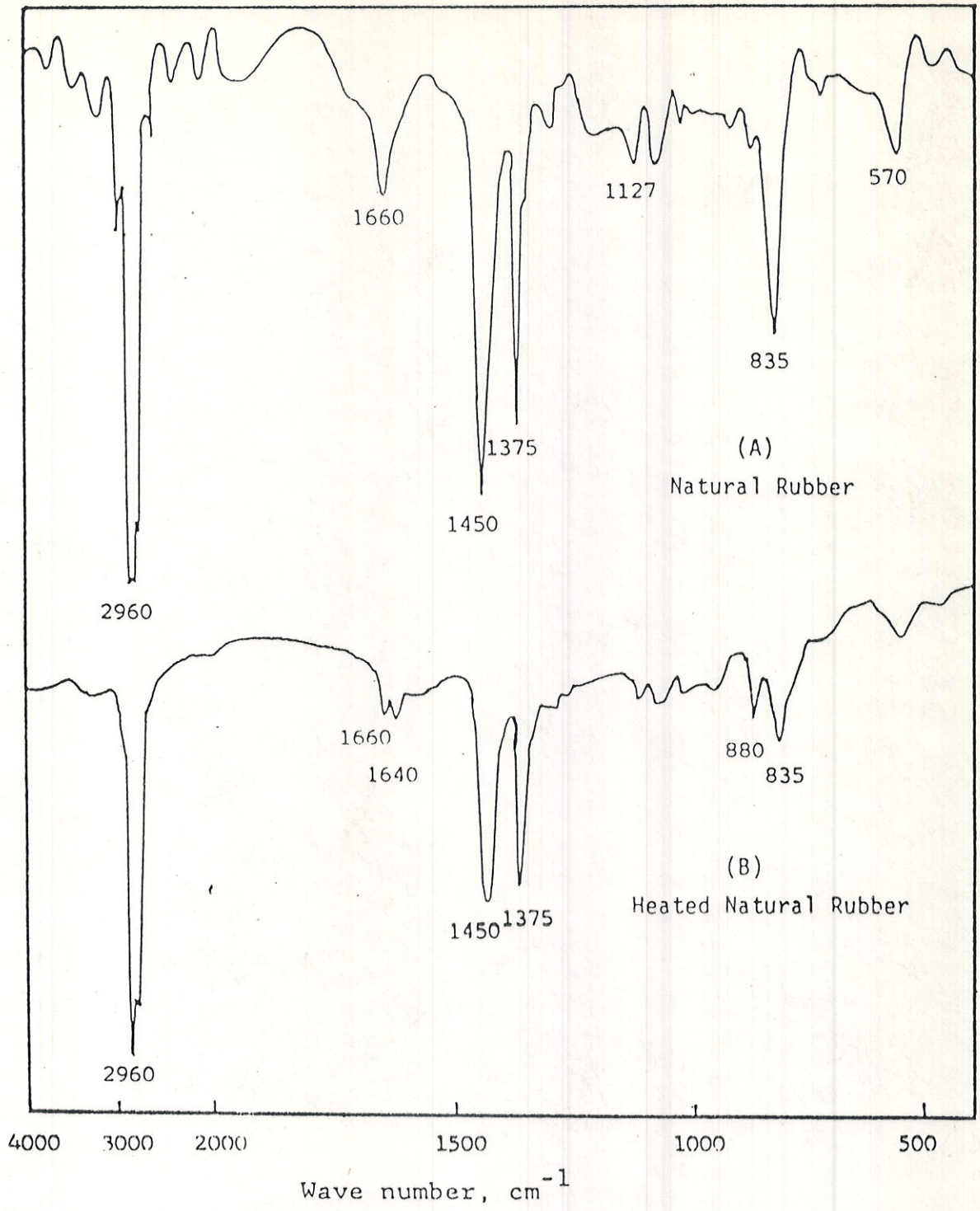

Fig.9 Absorption spectra of natural rubber (A) and heated natural rubber(B). For (B), the natural rubber was heated up to 360°C with a heating rate of 30°C/minute, and under a flow of nitrogen.