EFFECT OF CURING TEMPERATURE ON THE THERMAL DEGRATION OF AN EPOXIDE POLYMER

H. T. Lee

Picatinny Arsenal
Dover, New Jersey

February 1968

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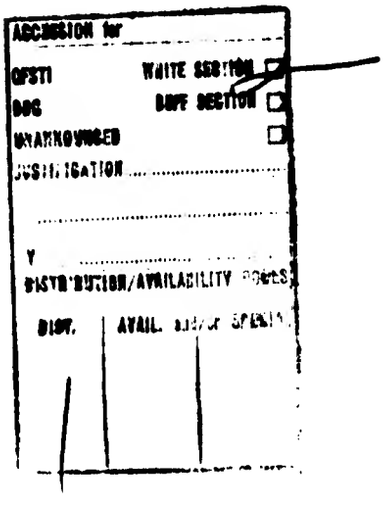

Technical Report 3624

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by

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OBJECT

To study the effect of curing temperature of an epoxide resin on its kinetic parameters of thermal degradation.

To compare the thermogravimetric thermograms of isothermal and dynamic thermal degradation.

To apply a simple method in estimating the order of reaction from dynamic thermogravimetric thermograms.

SUMMARY

A conventional bisphenol-A epoxide was cured with m-phenylenediamine under five different curing temperatures. The thermal degradation of the cured and uncured resins took place at both constant temperature and constant heating rate. The thermal stability, based on the overall energy of activation and the order of reaction, was generally higher for the resin cured at a higher temperature. The highest curing temperature was 200°C.

INTRODUCTION

Several investigations have been reported (Ref 1 - 4) involving kinetic and mechanism studies of the thermal degradation of epoxide resins. These studies appear to have been made mostly on the epoxide resins cured under the same temperature conditions. Work in these laboratories has been directed toward study of the effect of different curing temperatures of the epoxide resins on their kinetic parameters during thermal degradation. This report compares the changes of kinetic parameters of thermal degradation of a conventional epoxide resin cured at five temperatures. In addition, a simple method of estimating the order of reaction is applied.

RESULTS AND DISCUSSION

The epoxide resin used in this study was DER 332 of Dow Chemical Co. It is diglycidyl ether of bisphenol-A, a conventional epoxide, with an epoxy equivalent of 175. The resin was cured with m-phenylenediamine.

Primary thermograms of the dynamic thermogravimetric analysis (TGA) at constant heating rates for the five temperature-cured and for the uncured DER were normalized, based on the total weight loss as 100%, and corrected for the nonlinearity of the temperature scale. These normalized and temperature-scale-corrected TGA thermograms are shown in Figures 1 to 6 (pp 11 to 16).

Primary thermograms of isothermal degradation at 4 constant temperatures between 200° and 350°C for the DER cured at 5 different temperatures and for the uncured DER are shown in Figures 7 to 12 (pp 17 to 22).

The thermal degradation, using both isothermal and dynamic TGA, was carried out under a nitrogen atmosphere. The energy of activation, E, for each sample, cured and uncured, was obtained from both the isothermal and the dynamic TGA thermograms. The order of reaction, n, was obtained from the dynamic TGA thermogram.

Flynn and Wall's method (Refs 6 & 7) was used to determine the energy of activation. A similar approach was reported by Ozawa (Ref 10). This method does not require graphical differentiation and is applicable to the dynamic TGA thermograms acquired in this study. These authors used Doyle's approximation (Ref 9),

$$\log p\left(\frac{E}{RT}\right) \doteq -2.315 - 0.4567\,\frac{E}{RT} \qquad 60 > \frac{E}{RT} > 20 \qquad (1)$$

Here p $\left(\frac{E}{RT}\right)$ was calculated from values of $\frac{e^{-E/RT}}{E/RT}$ and $Ei\left(\frac{E}{RT}\right)$ for the equation of a TGA thermogram. At constant percentage of conversion,

$$\frac{d \log \beta}{d(1/T)} \doteq 0.4567 \frac{E}{R} \qquad (2)$$

$$E \doteq 4.351 \frac{d \log \beta}{d(1/T)} \qquad (3)$$

E is the energy of activation in cal/mole, β is the heating rate in °K/sec, T is °K, and R is 1.987 cal/mole -°K.

The plot of the common logarithms of the heating rate versus the reciprocal of absolute temperature from the dynamic TGA would result in a linear relationship. The slope of this linear plot multiplied by the constant 4.35 would give the approximate value of E. By reevaluating this constant, the corrected value of E was calculated. Doyle's table of -log p(x) (Ref 12) and Akahira's tables of e^{-x}, x and $\int_x^\infty \frac{e^{-u}}{u} du$ (Ref 8) were used to calculate the function p(x). Here x is E/RT in

$$\log p \left(\frac{E \text{ app.}}{RT}\right) = m \left(\frac{E \text{ app.}}{RT}\right) + b \qquad (4)$$

m and b are the same as in equation 1. After a reevaluated value, m', was acquired from either one of the tables of the exponential-integrals, then

$$E \text{ corr.} = \frac{R}{m'} \frac{d \log \beta}{(1/T)} \qquad (5)$$

The E corr. value for each sample is shown in Table 1 (p 8).

Doyle's approximation of equation 1 also gave the energy of activation from the isothermal degradation curve by matching a dynamic TGA thermogram,

$$E \cong K \, d \log t_i \; d(1/T) \tag{6}$$

A linear plot of the common logarithms of t_i, the time scale on the isothermal, against the reciprocal of absolute temperatures of the corresponding percentage of weight loss on the dynamic trace would give the value of E by multiplying the slope of the plot by the constant, K. Instead of the figure 1.351 in equation (3), the reevaluated value m' in Table 1 was adopted here for this constant, K.

The weight changes of several of the isothermal curves of each sample were used to match the temperatures of the corresponding weight changes on the sample's dynamic TGA at any one heating rate. The average slope, $d \log t_i \; d(1/T)$, was used to calculate the E. The results of the E values from isothermal degradation are shown in Table 2 (p 9).

It has been stated that the isothermal degradation of a polymer would give more reliable information on its kinetic parameters (Refs 9, 11, and 13). However, the values of activation energy obtained from the isothermal degradation curves (Table 2) in this study do not seem to be more consistent than those obtained from the dynamic TGA traces (Table 1). Thus the average value of E for each sample from the isothermal and the dynamic TGA (Tables 2 and 1) was taken as the reported value of E for this study. This reported value of E was used to determine the order of reaction, n, for each sample by a simplified method utilizing the dynamic TGA thermogram.

The rate of weight change in the Arrhenius equation,

$$\log \frac{dw}{dt} = \log A - \frac{E}{2.3RT} + n \log w \tag{7}$$

is $\frac{dT}{dt} \cdot \frac{dw}{dT}$. Equation 7 can be rewritten as

$$\log \frac{dT}{dt} = \log A - \log \frac{dw}{dT} - \frac{E}{2.3RT} + n \log w \tag{8}$$

Letting $\log \frac{dT}{dt} = 0$,

$$\frac{E}{2.3RT} = \log A - \log \frac{dw}{dT} + n \log w \tag{9}$$

A sinusoidal curve like a dynamic TGA trace of weight change versus temperature has at least two points of equal slope, i.e., two points having the same dw/dT. At these points of equal slope on a TGA thermogram, the second term of the right hand side of equation 9 is a constant. Assuming that the frequency factor, A, is temperature independent, the first term is also a constant.

By plotting 1/T of these constant dw/dT points against the common logarithms of their w, a straight line would yield a slope of n(2.3R/E). Knowing the average E value of a sample from Tables 1 and 2 (pp 8 and 9), one can determine its order of reaction, n. Since a single pair of equal dw/dT points cannot prove the linear relationship of 1/T vs log w, several pairs are necessary. If all the pairs give parallel or nearly parallel lines, the slope or the average slope, d(1/T)/d log w, would give some confidence as to the value of n. For a very steep curve, like the uncured and the lower temperature cured sample, a rapid and almost linear change in weight with respect to temperature was found near the maximum inflection points. In those cases, a number of consecutive weight changes were used as equal slope points.

Due to the deposit of pyrolysis product on the balance system at conversions over 70 - 75% (normalized), the more accurate values of n were obtained only up to 70% conversion. The plots of these equal slope points are shown in Figures 25 to 30 (pp 35 to 40). The overall values of E and n for all the samples, cured and uncured, are shown in Table 3 (p 10). The previously reported value for the dynamic TGA under vacuum of the uncured DER is also listed for comparison.

CONCLUSION

The values of E and particularly that of n reported in the present study show only very small changes due to the effect of curing temperature. These small changes, however, would probably imply the consistent effect of different curing temperatures, between 100° and 200°C, on the kinetic parameters during thermal degradation. The general trend found was higher values of E and n for the DER cured at higher temperature, and the lowest value for the uncured DER. It is believed that this trend agrees with some suggested mechansims of the thermal breakdown of cross-linked polymers (Ref 5).

EXPERIMENTAL

Five samples of DER 332 epoxide resin, as received from the Dow Chemical Co., were cured with m-phenylenediamine stoichiometrically at 75°C for 24 hours. Each sample was then cured at different temperatures between 100° and 200°C for another 24 hours. The recorded temperatures of curing were:

Sample No.	Curing Temperature for Each 24-Hour Period
1	75° ± 5°C and 100° ± 6°C
2	75° ± 6°C 125° ± 8°C
3	75° ± 4°C 150° ± 12°C
4	75° ± 5°C 175° ± 11°C
5	75° ± 4°C 200° ± 14°C

The cured sample was broken into pieces of 5-10 mm size and then ball milled in dry ice. After milling, the sample was vacuum dried and stored in a desiccator. Particle sizes between 400 and 200 mesh were used for the experiment.

A DuPont 950 Thermogravimetric Analyzer in connection with the 900 Differential Thermal Analyzer recorder was used for both isothermal and dynamic TGA. Nitrogen gas with a flow rate of 120 cc per minute was purged into the furnace tube. The actual weight of each sample was between 10.05 and 10.9 mg. The 100% span control was used to bring the recorder pen to the 100% line. The temperature for the isothermal degradation was held within ± 1°C of the reported constant temperature. The constant heating rates for the dynamic TGA had a linearity of ± 1% during the range of ± 150°C from the maximum inflection points on the thermograms. Some condensed pyrolysis product was found deposited on the balance system, near the cold beam. A propane torch was used to burn the condensed material after each run.

ACKNOWLEDGEMENT

The author is grateful to Dr. D. W. Levi for helpful discussion.

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TABLE 1

Corrected values of the activation energy from dynamic TGA by the reevaluated constant

Samples	Average $\frac{d \log \beta}{d (1/T)}$	E app., cal/mole, from Figures 13 - 18	T, °K[a]	$\frac{E \text{ app.}}{RT}$	Reevaluated Constant	E corr., cal/mole
5	7.15	31,100	642	24.22	1.430	31,670
4	6.95	30,230	634	23.84	1.281	29,730
3	6.09	26,490	611	21.68	1.205	25,580
2	6.01	26,150	578.5	22.60	1.272	25,520
1	4.75	20,700	553.4	17.72	1.143	19,670
Uncured	3.38	14,700	543.4	13.53	1.027	13,590

[a]Taken at the 50% conversion point on the lowest heating rate thermogram of each sample.

TABLE 2

Activation energy values from isothermal degradation

Samples	Isothermal Temperature, °C	Heating Rate of Matching Dynamic TGA, °/min	$\frac{d \log t_i}{10^3/°K}$	Average $\frac{d(\log t_i)}{d(10^3/°K)}$	Reevaluated Constant from Table 1	E, cal/mole
5	310	3.11	6.70	7.21	4.430	31,940
	317	3.11	7.90	7.21		
	328	3.11	7.85	7.21		
4	312	9.57	6.48	6.51	4.281	27,870
	320	9.57	6.53	6.51		
	326	9.57	6.54	6.51		
3	290	10.00	6.25	6.25	4.205	25,250
	297	10.00	6.24	6.25		
	301	10.00	6.26	6.25		
2	224	9.86	5.82	5.84	4.272	24,930
	229	9.86	5.84	5.84		
	243	9.86	5.86	5.84		
	254	9.86	5.84	5.84		
1	210	10.00	5.35	5.24	4.143	21,710
	225	10.00	4.89	5.24		
Uncured	205	18.19	3.09	3.10	4.027	12,470
	215	18.19	3.11	3.10		

TABLE 3

Kinetic parameters of DER 332

Samples	Energy of Activation, E, cal/mole: Isothermal Degradation	Dynamic TGA	Average	Order of Reaction, n
5	31,940	31,670	31,810	0.8
4	27,870	29,730	28,800	0.6
3	25,250	25,580	25,420	0.5
2	24,930	25,520	25,230	0.4
1	21,710	19,670	20,690	0.3
Uncured	12,470	13,590	13,030	0.2
Reported value of the uncured (Ref 2, under vacuum)			17 ± 2 Kcal/mole	0.08 ± 0.09

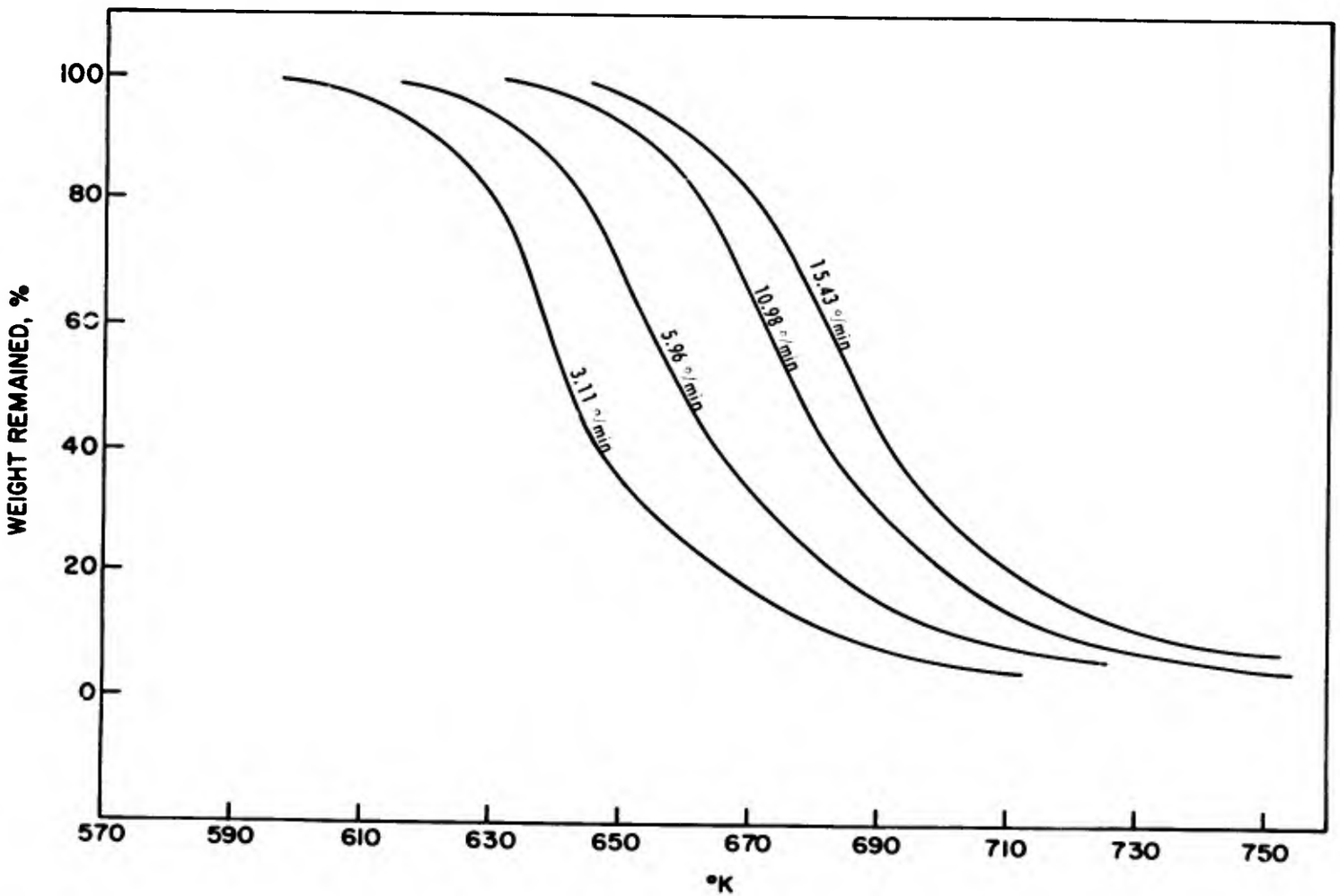

Fig 1 Normalized TGA thermograms of DER cured at 200°C

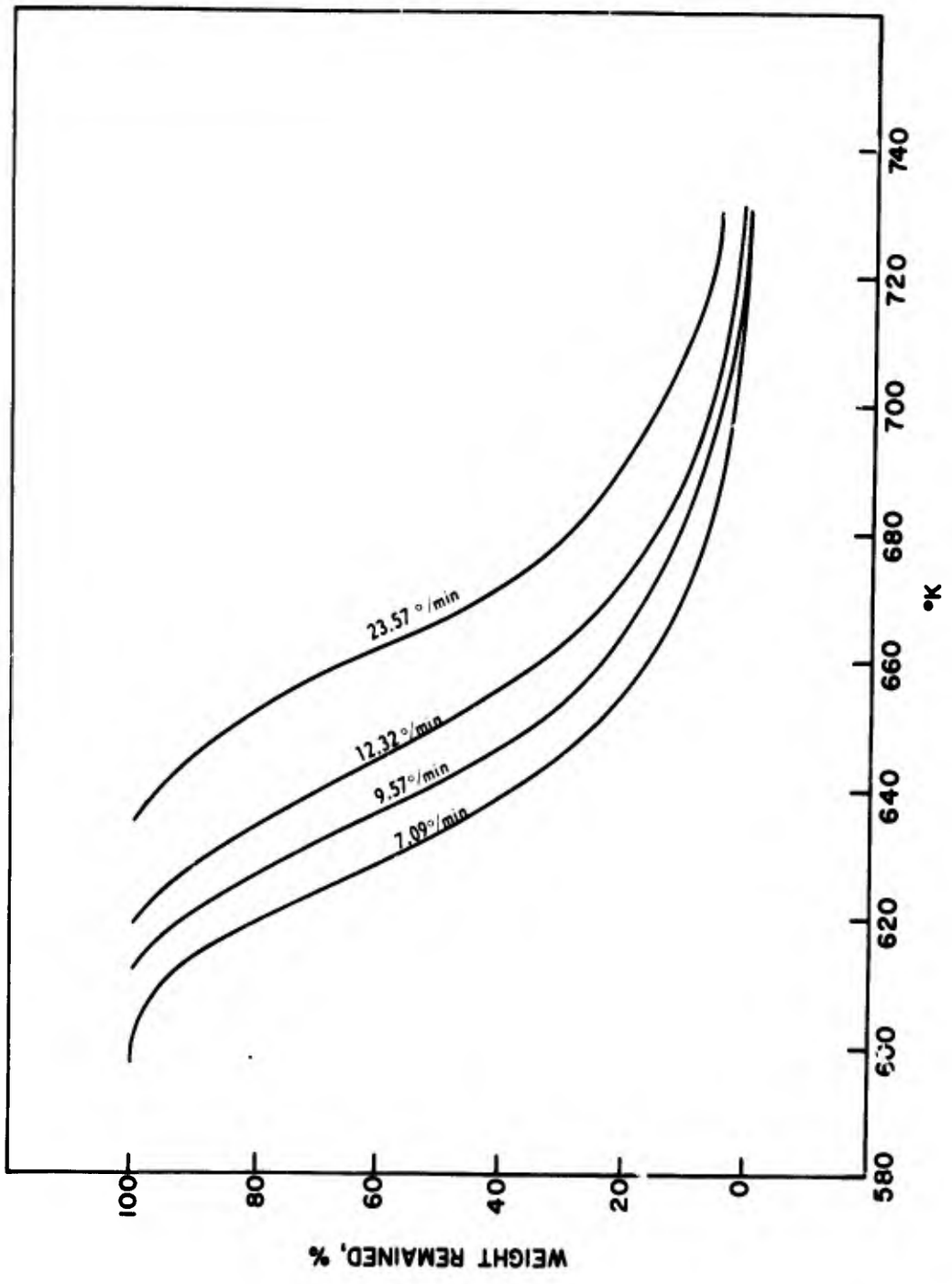

Fig 2 Normalized TGA thermograms of DER cured at 175°C

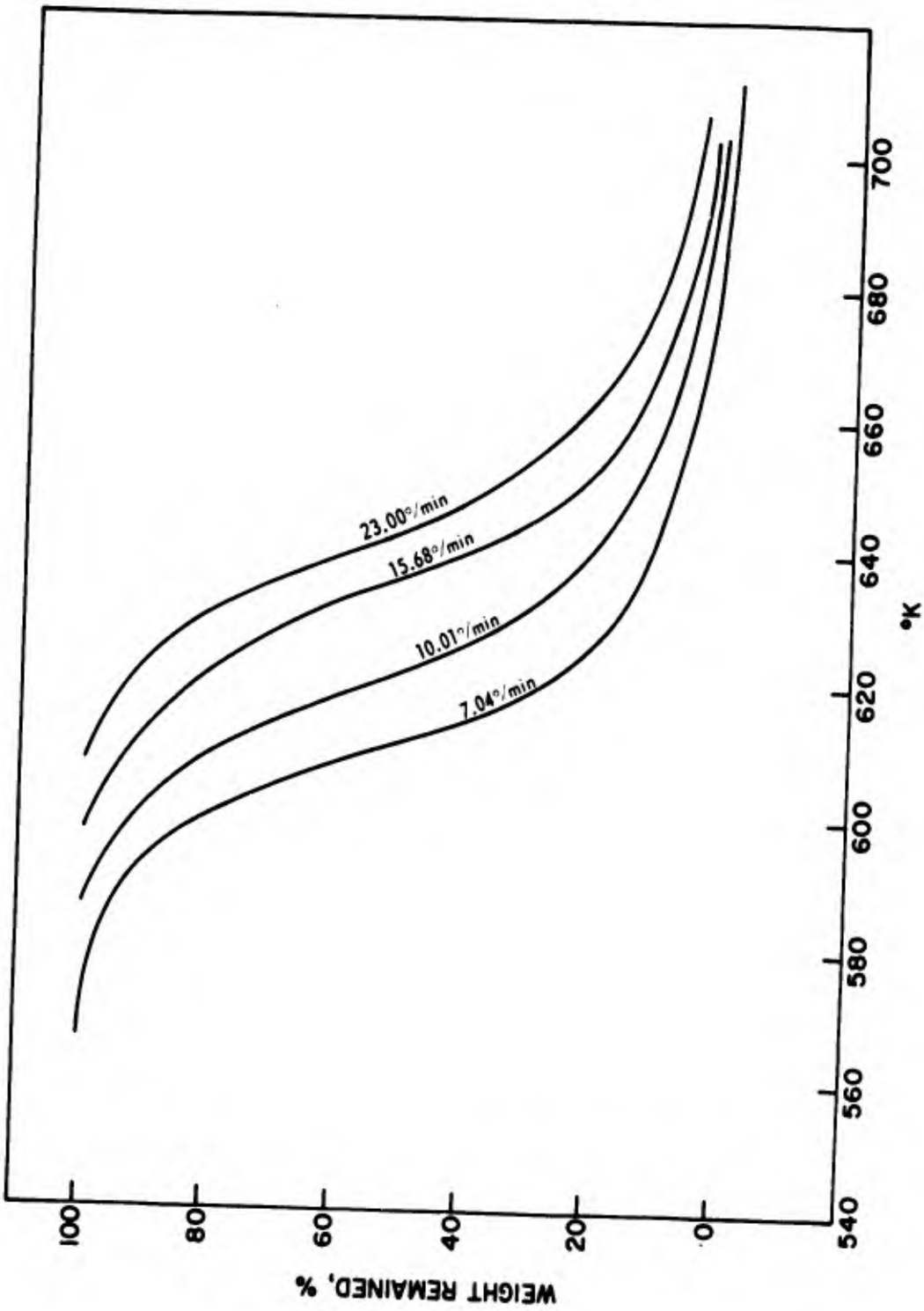

Fig 3 Normalized TGA thermograms of DER cured at 150°C

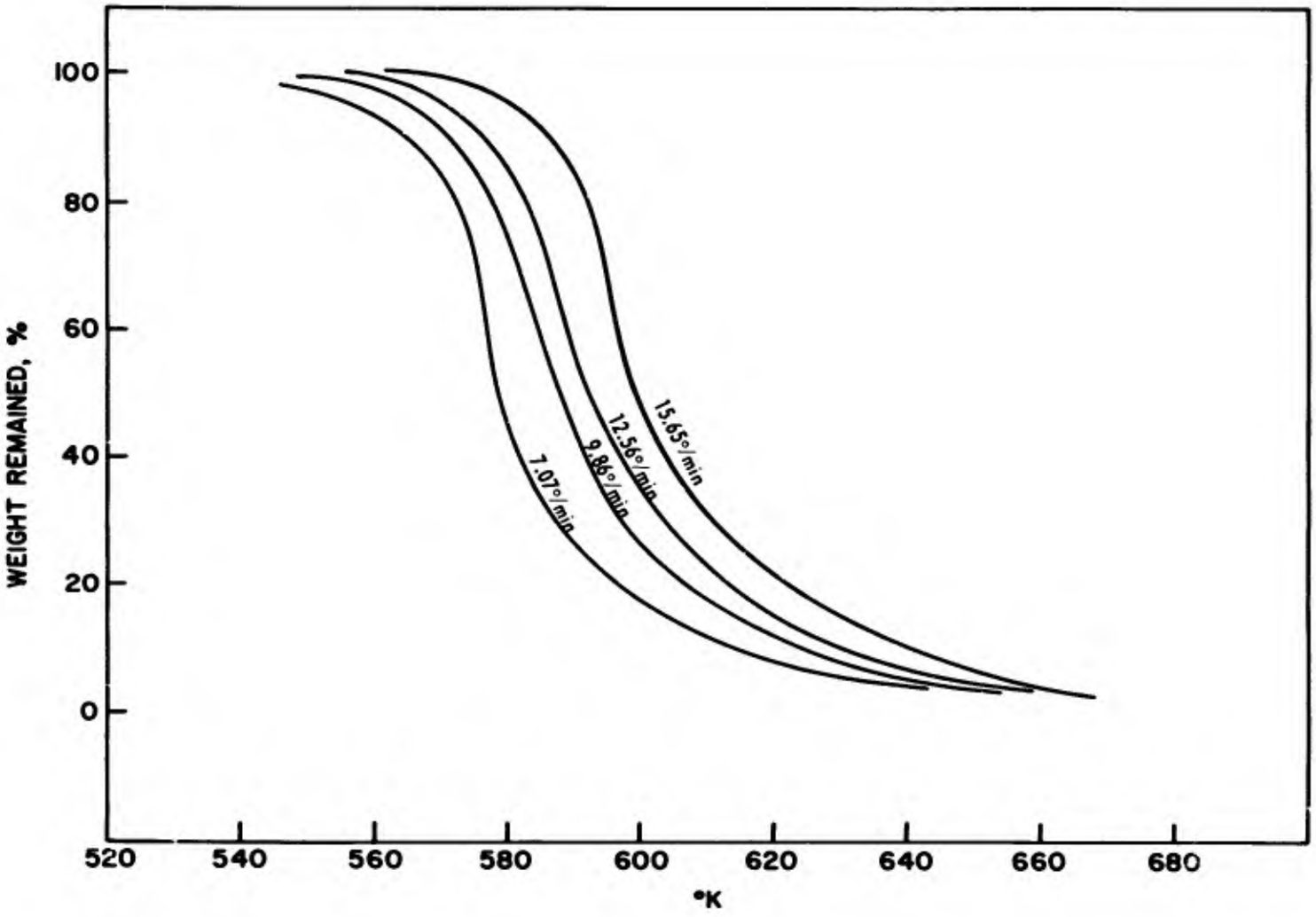

Fig 4 Normalized TGA thermograms of DER cured at 125°C

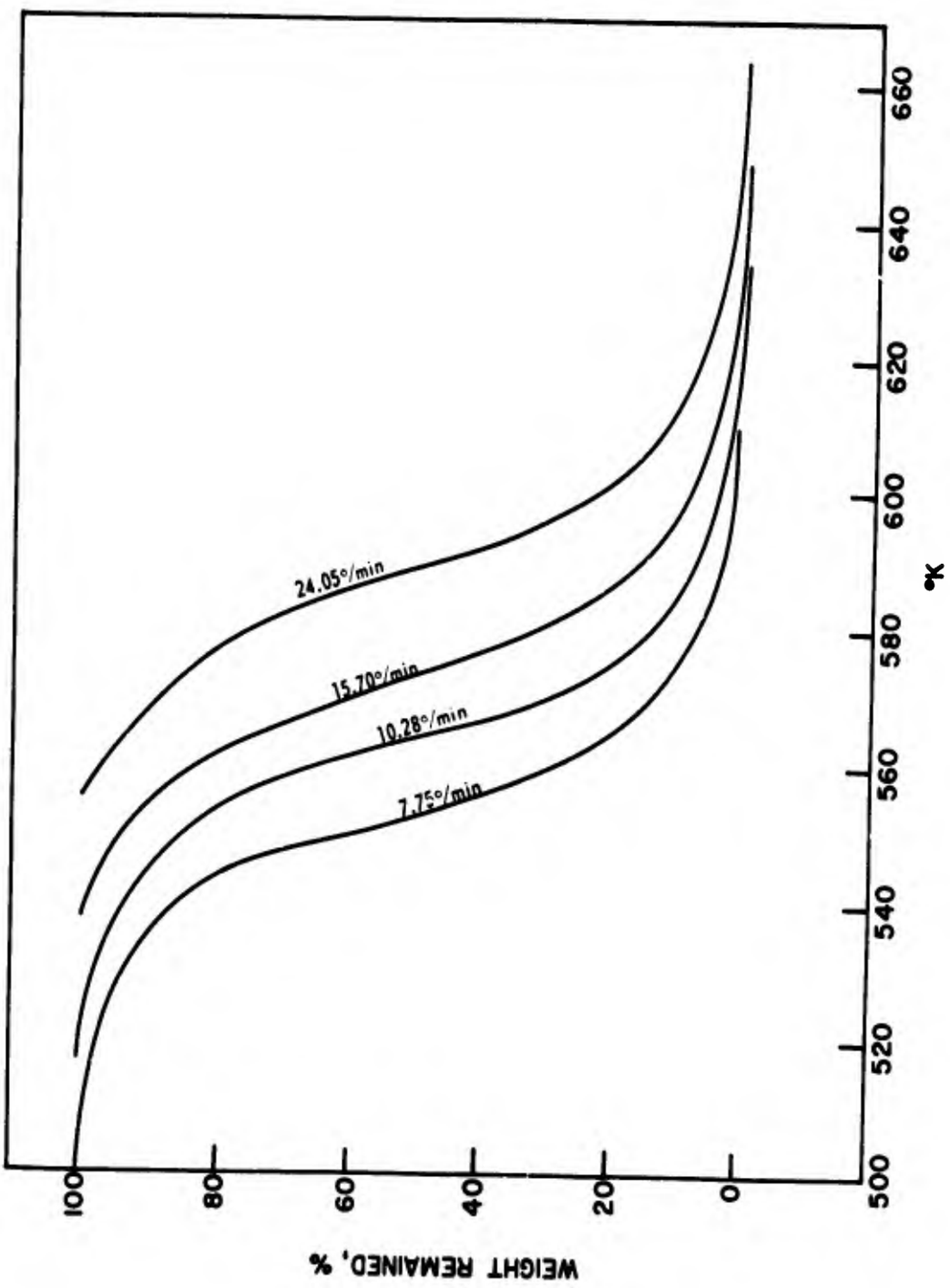

Fig 5 Normalized TGA thermograms of DER cured at 100°C

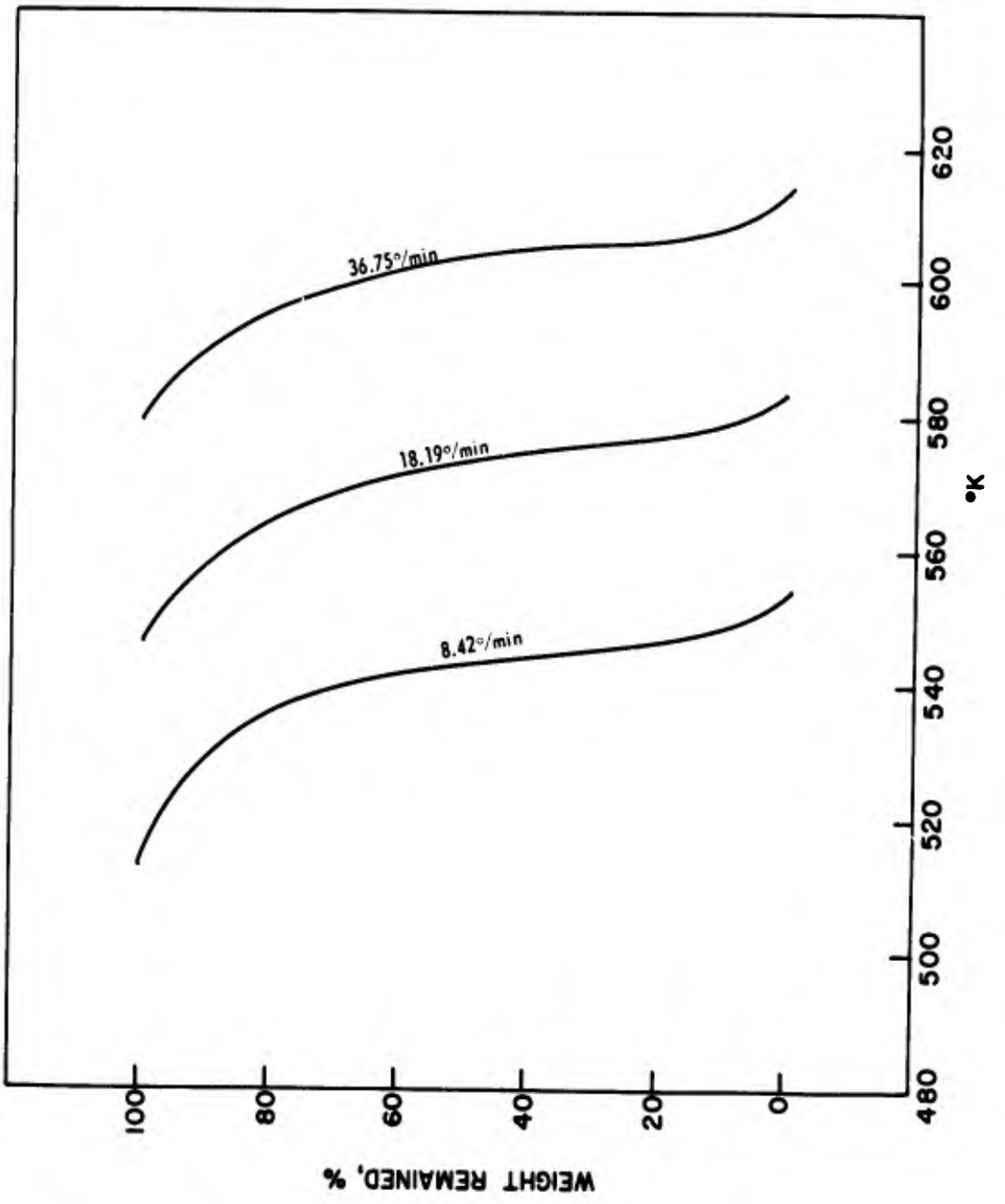

Fig 6 Normalized TGA thermograms of uncured DER

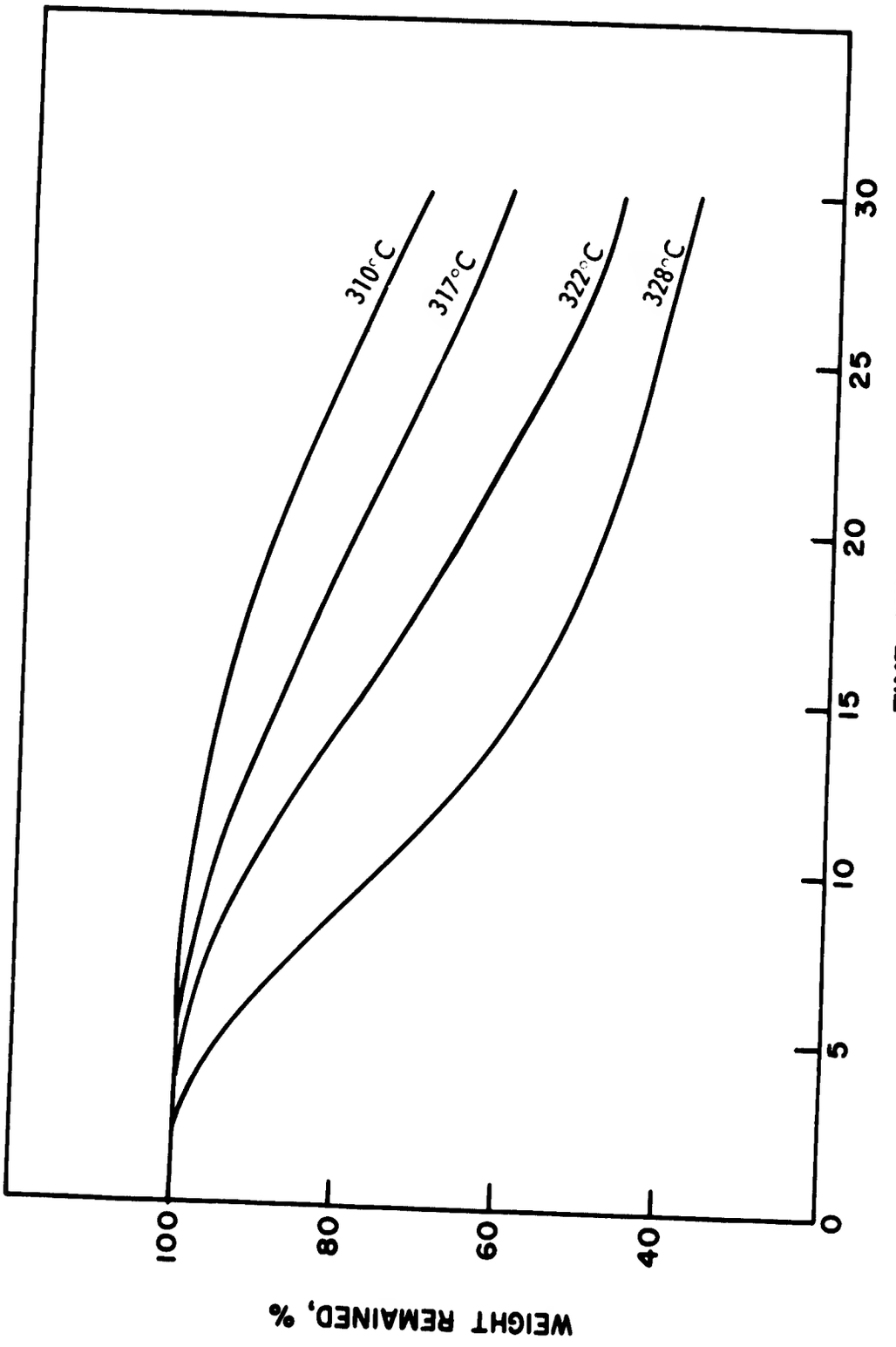

Fig 7 Isothermal degradation of DER cured at 200°C

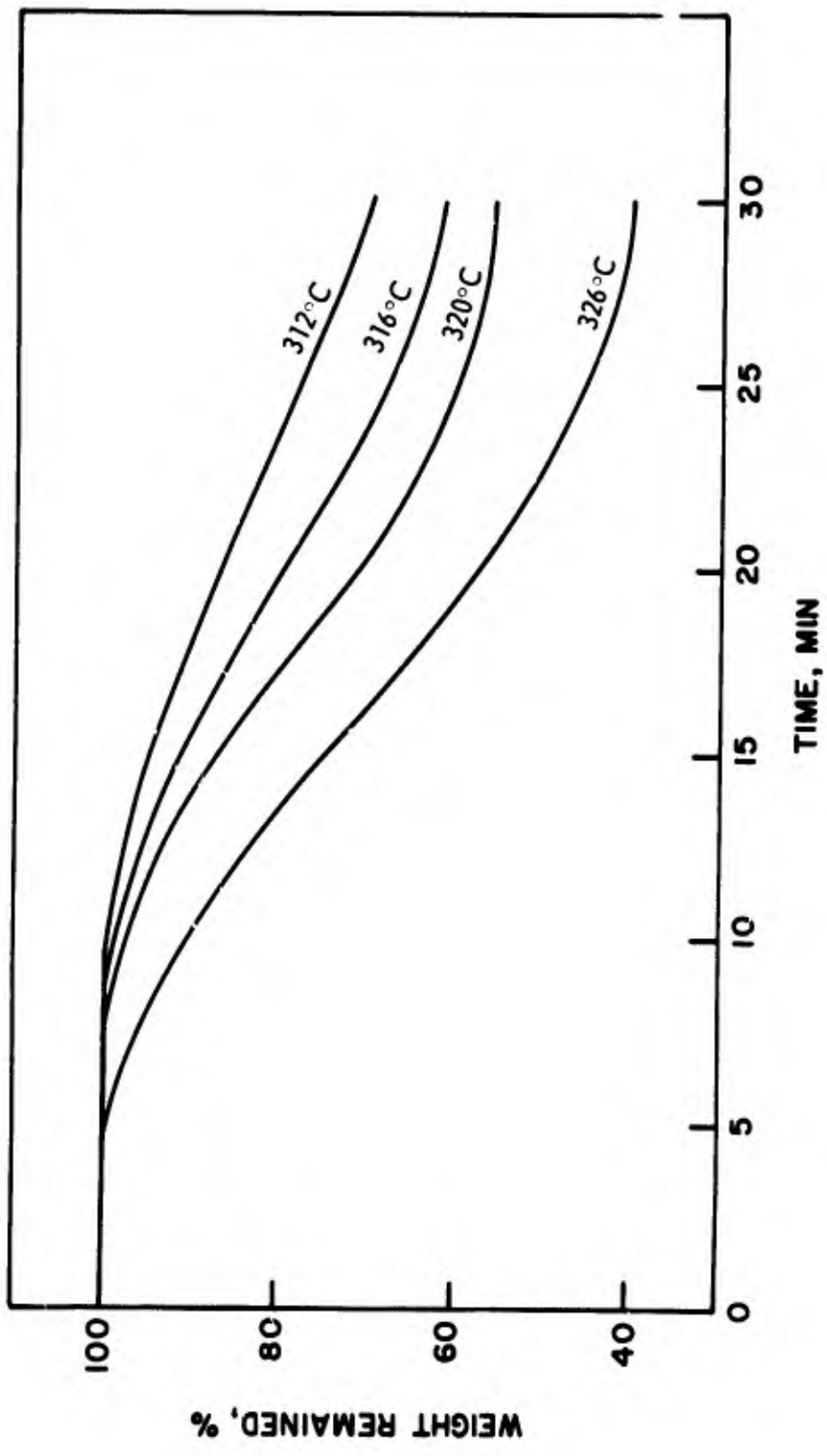

Fig 8 Isothermal degradation of DER cured at 175°C

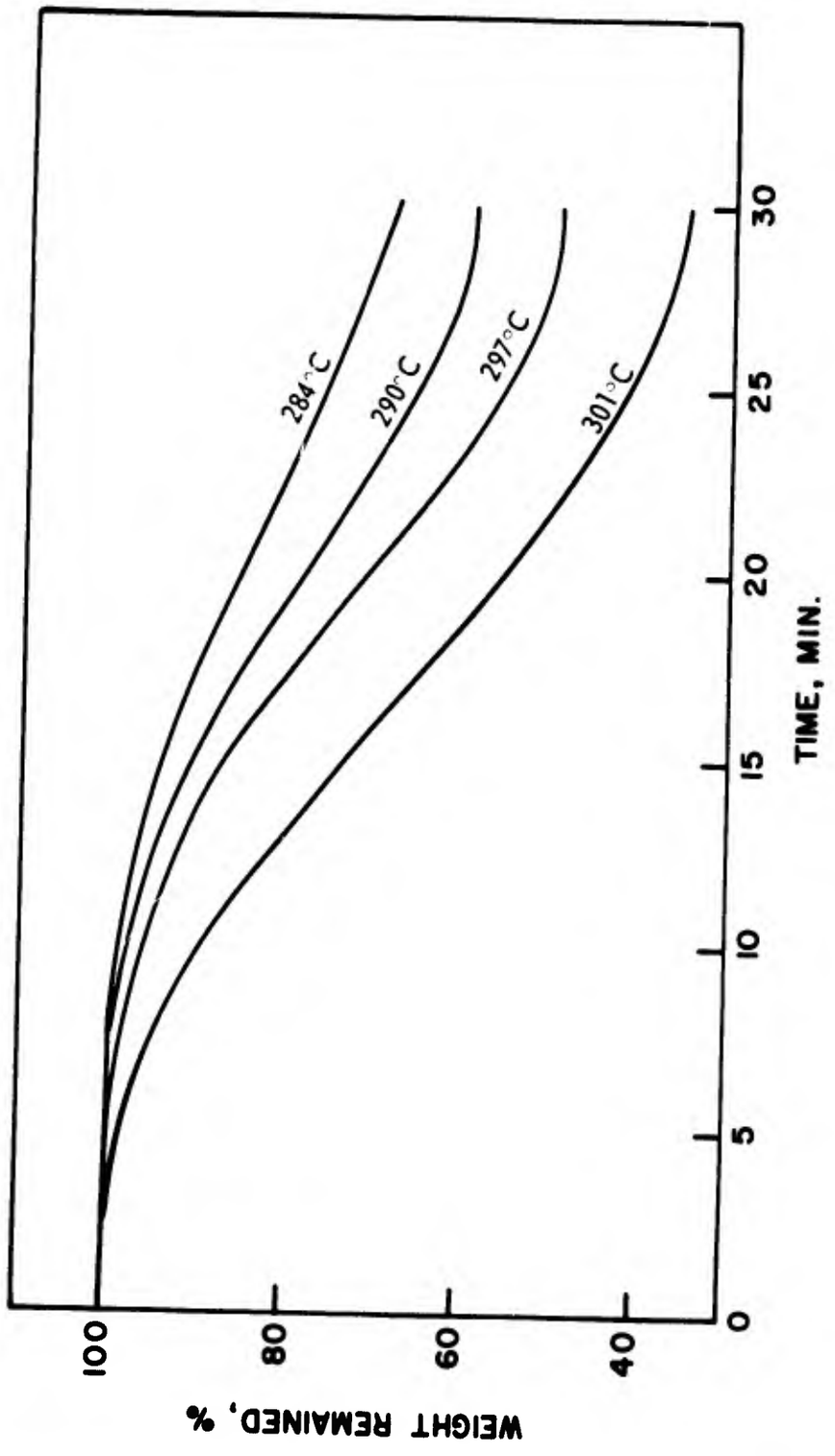

Fig 9 Isothermal degradation of DER cured at 150°C

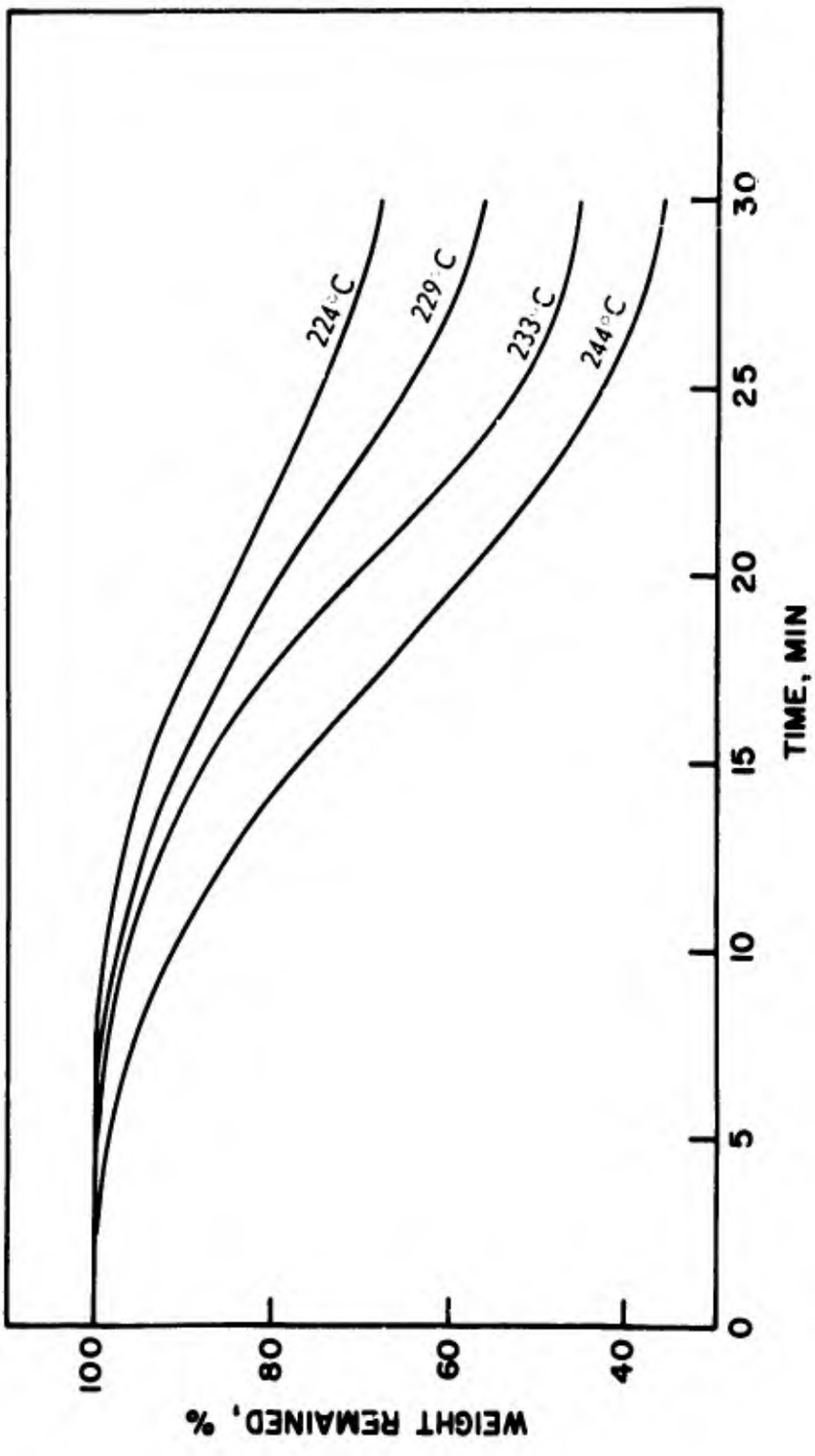

Fig 10 Isothermal degradation of DER cured at 125°C

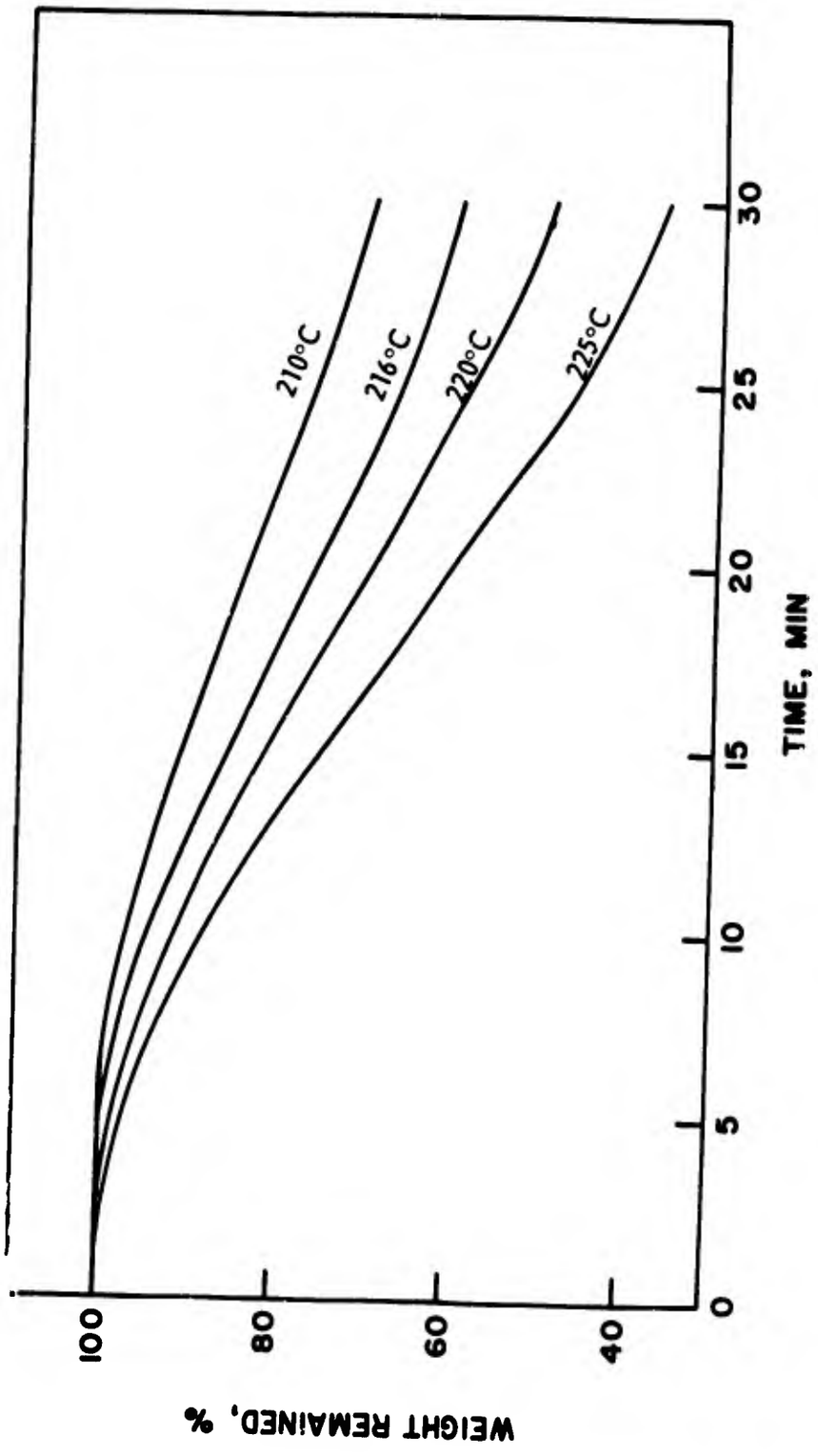

Fig 11 Isothermal degradation of DER cured at 100°C

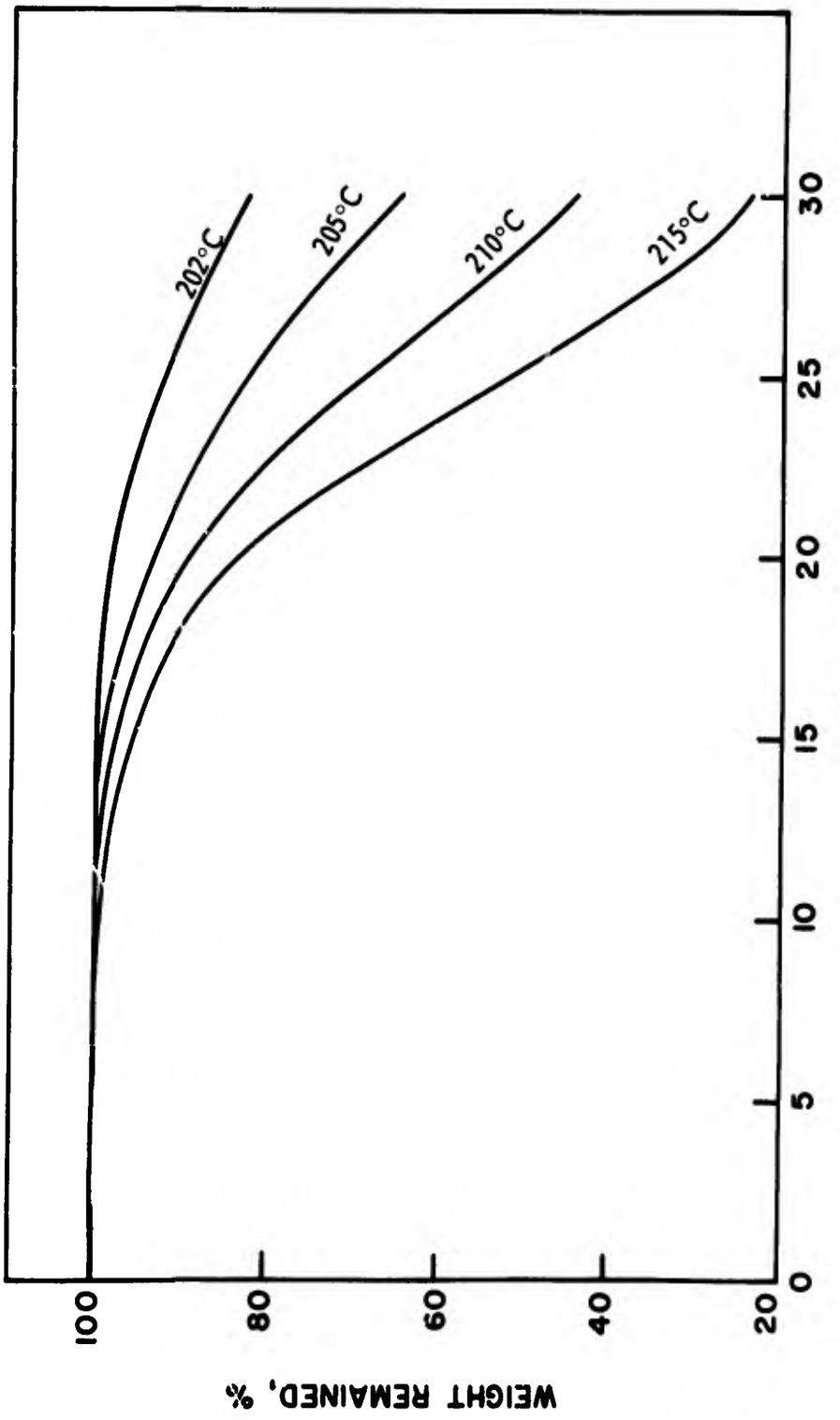

Fig 12 Isothermal degradation of uncured DER

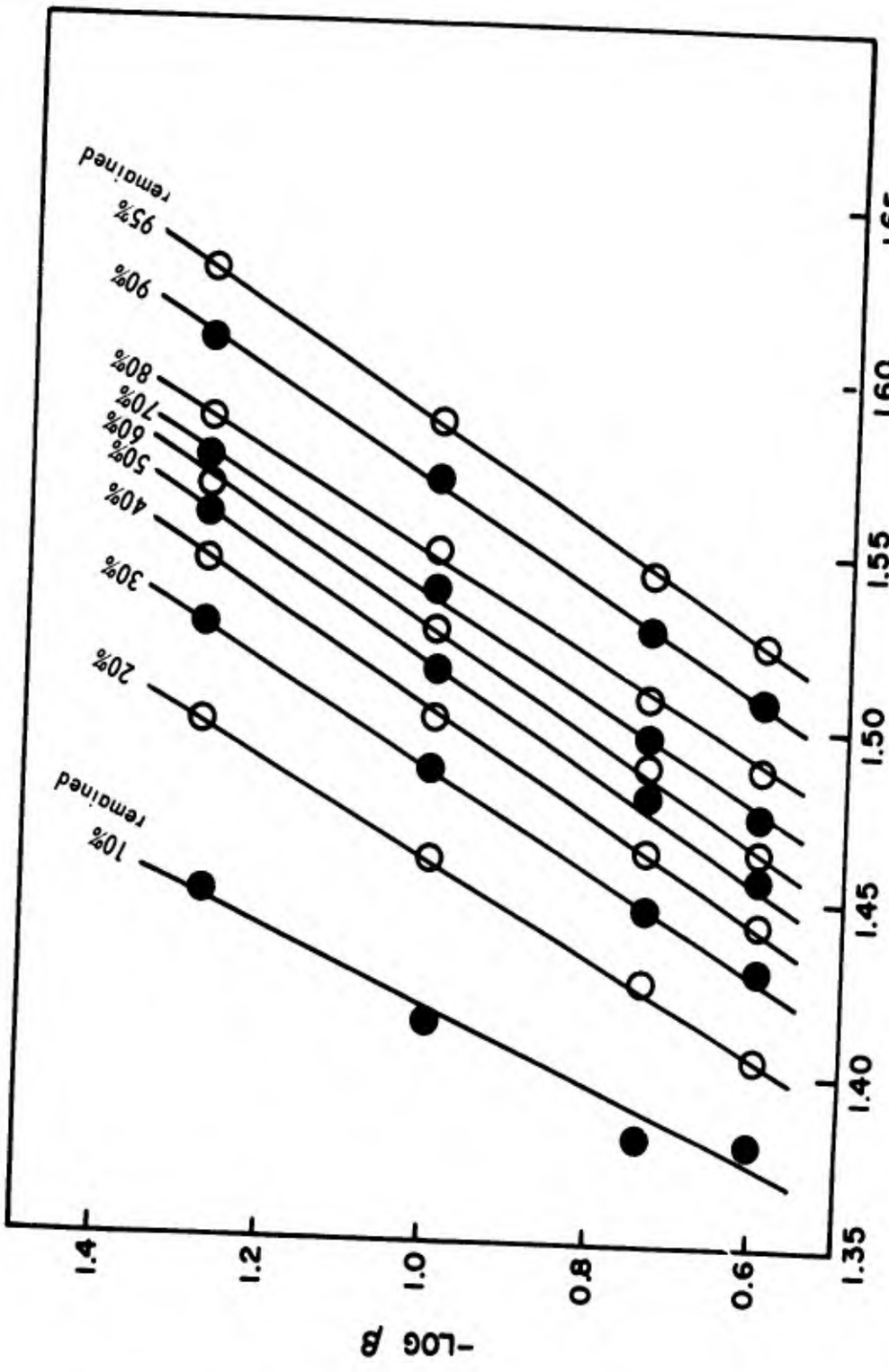

Fig 13 Logarithm of heating rate vs reciprocal of absolute temperature of DER cured at 200°C

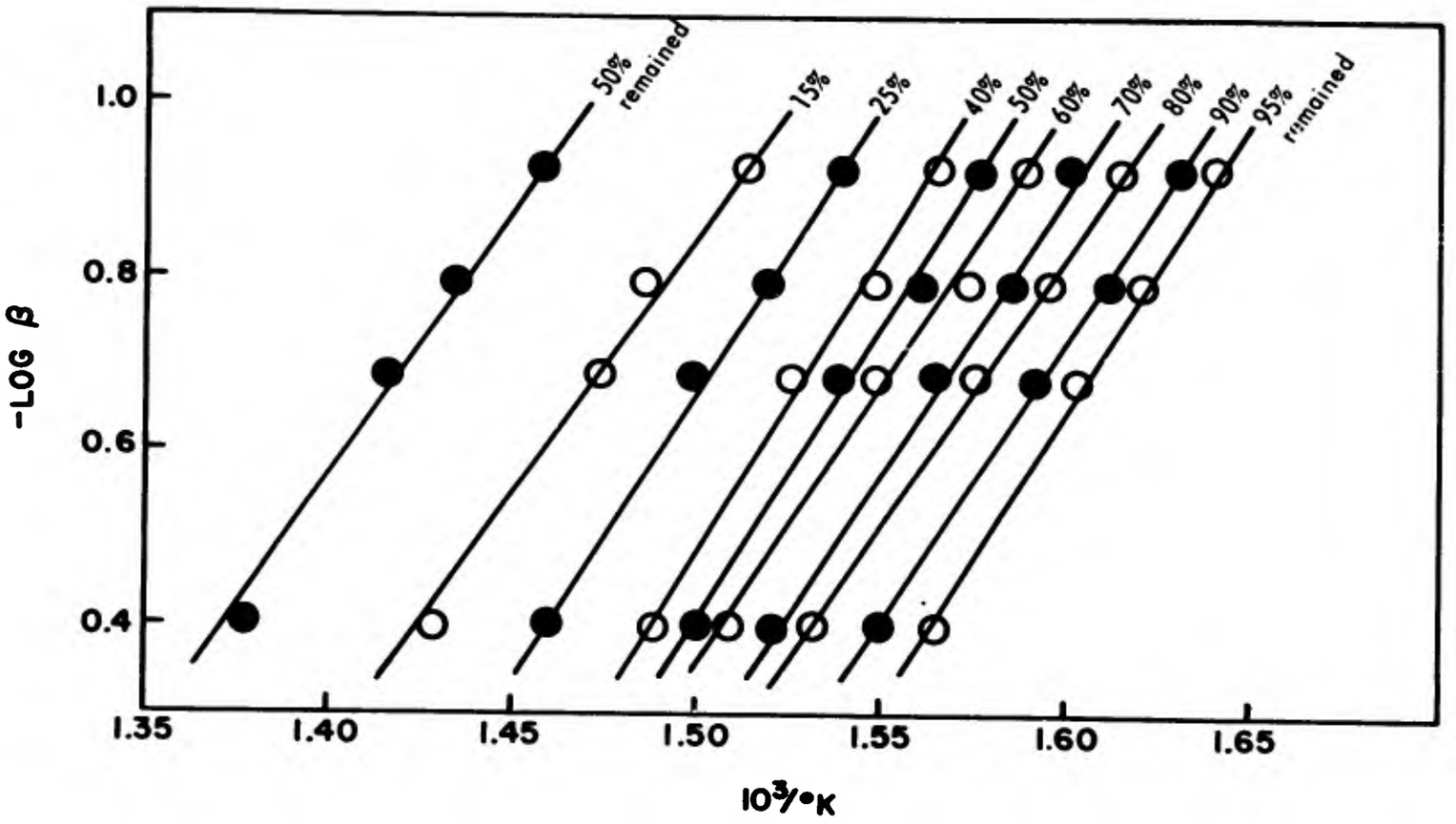

Fig 14 Logarithm of heating rate vs reciprocal of absolute temperature of DER cured at 175°C

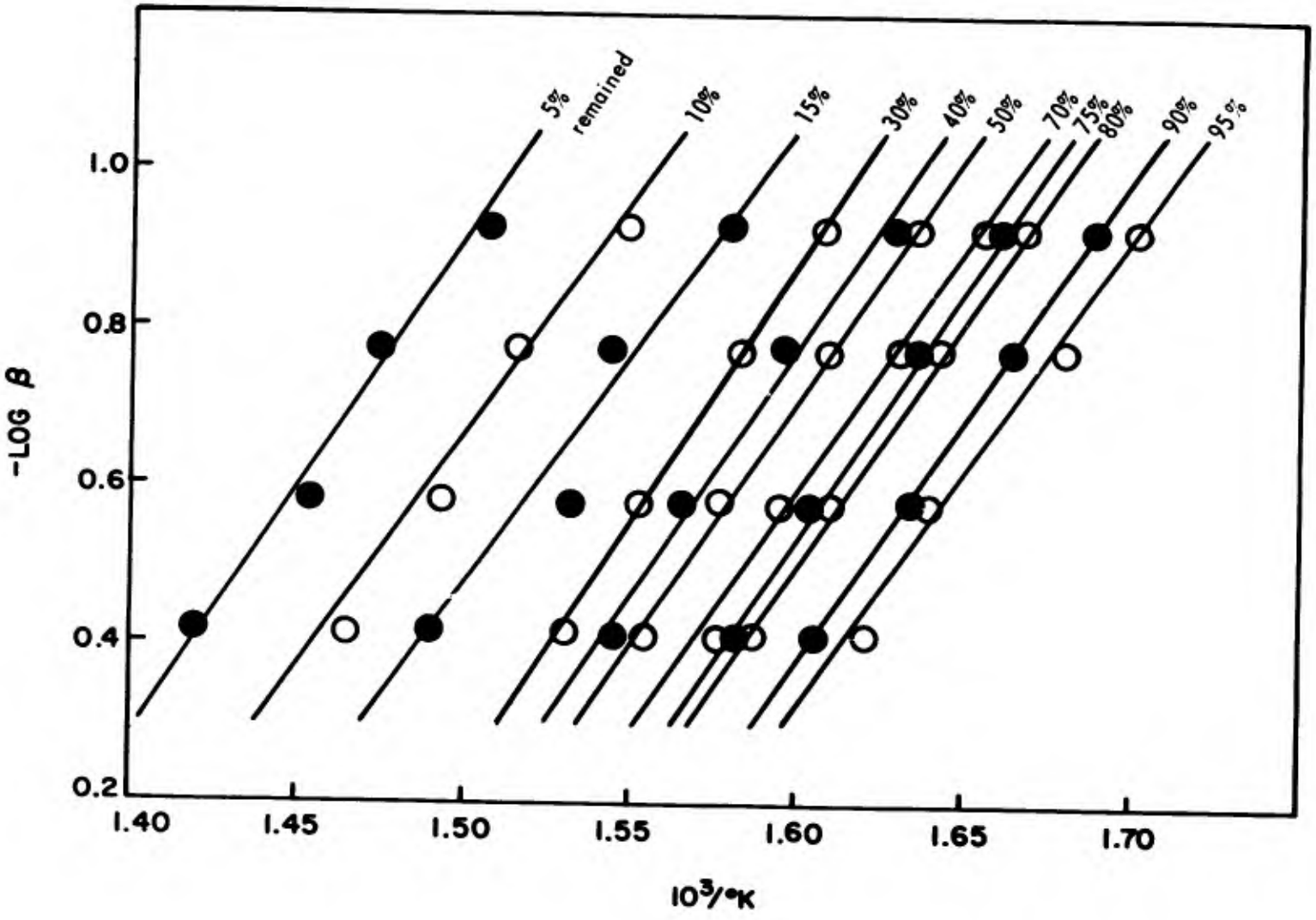

Fig 15 Logarithm of heating rate vs reciprocal of absolute temperature of DER cured at 150°C

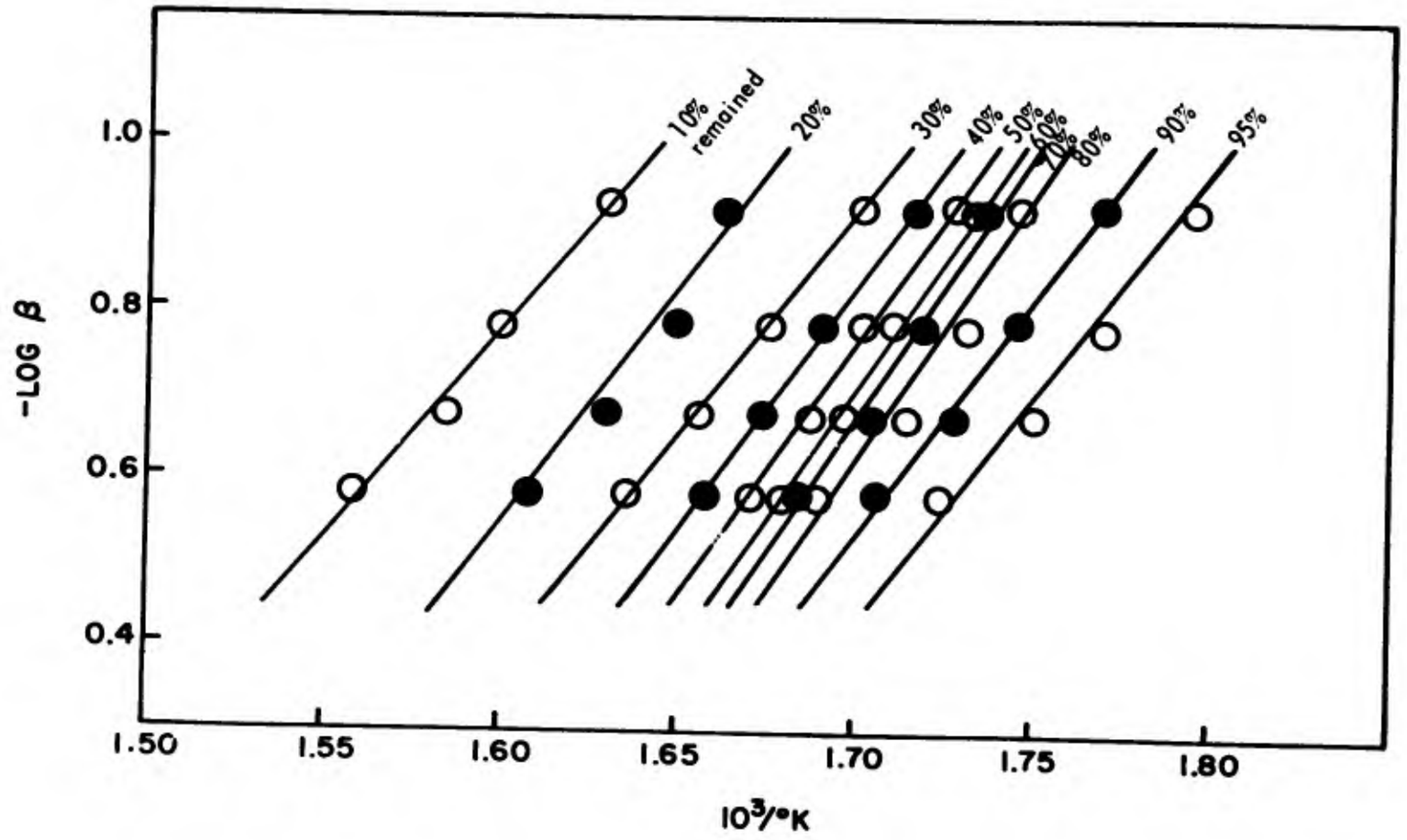

Fig 16 Logarithm of heating rate vs reciprocal of absolute temperature of DER cured at 125°C

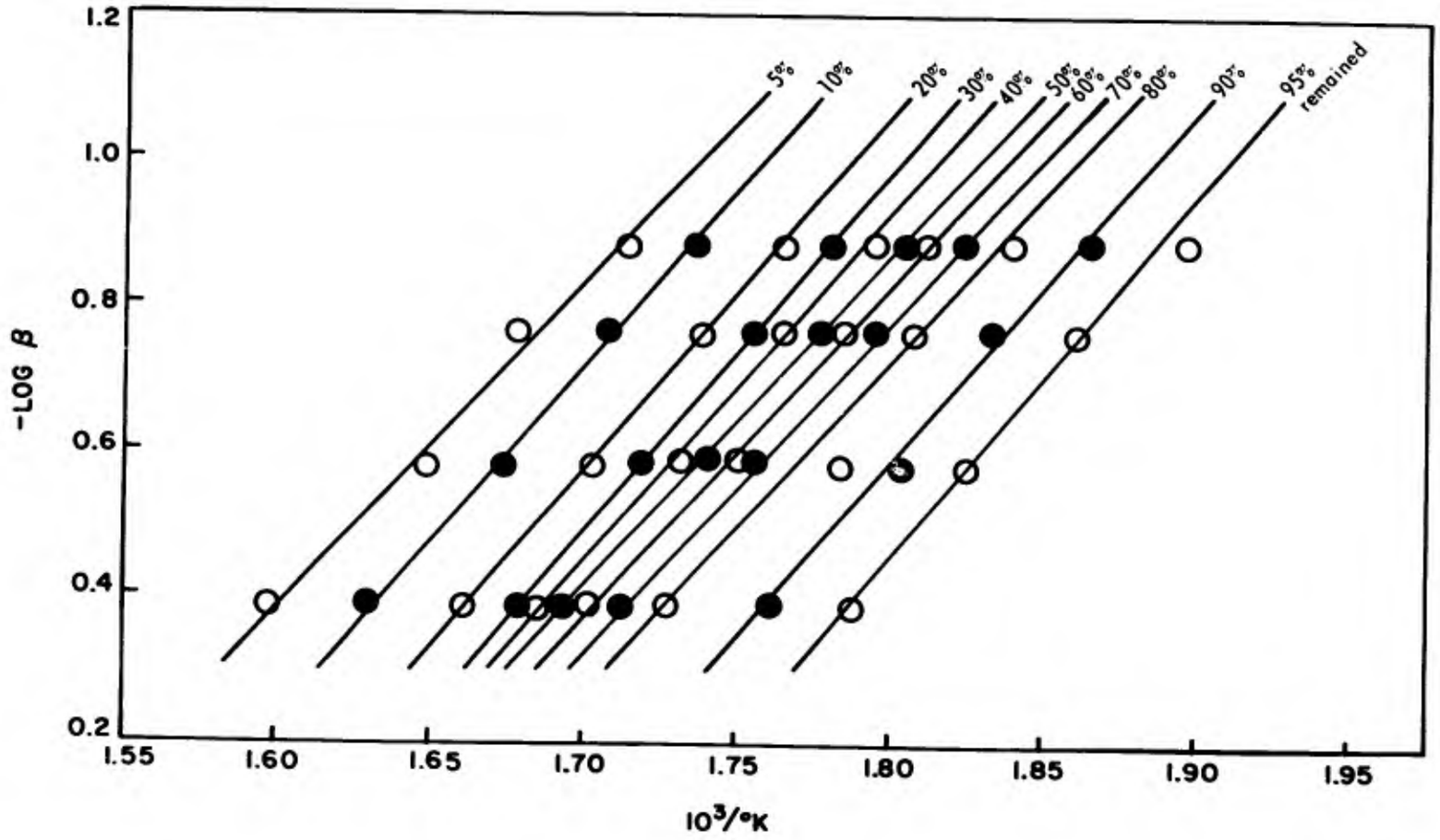

Fig 17 Logarithm of heating rate vs reciprocal of absolute temperature of DER cured at 100°C

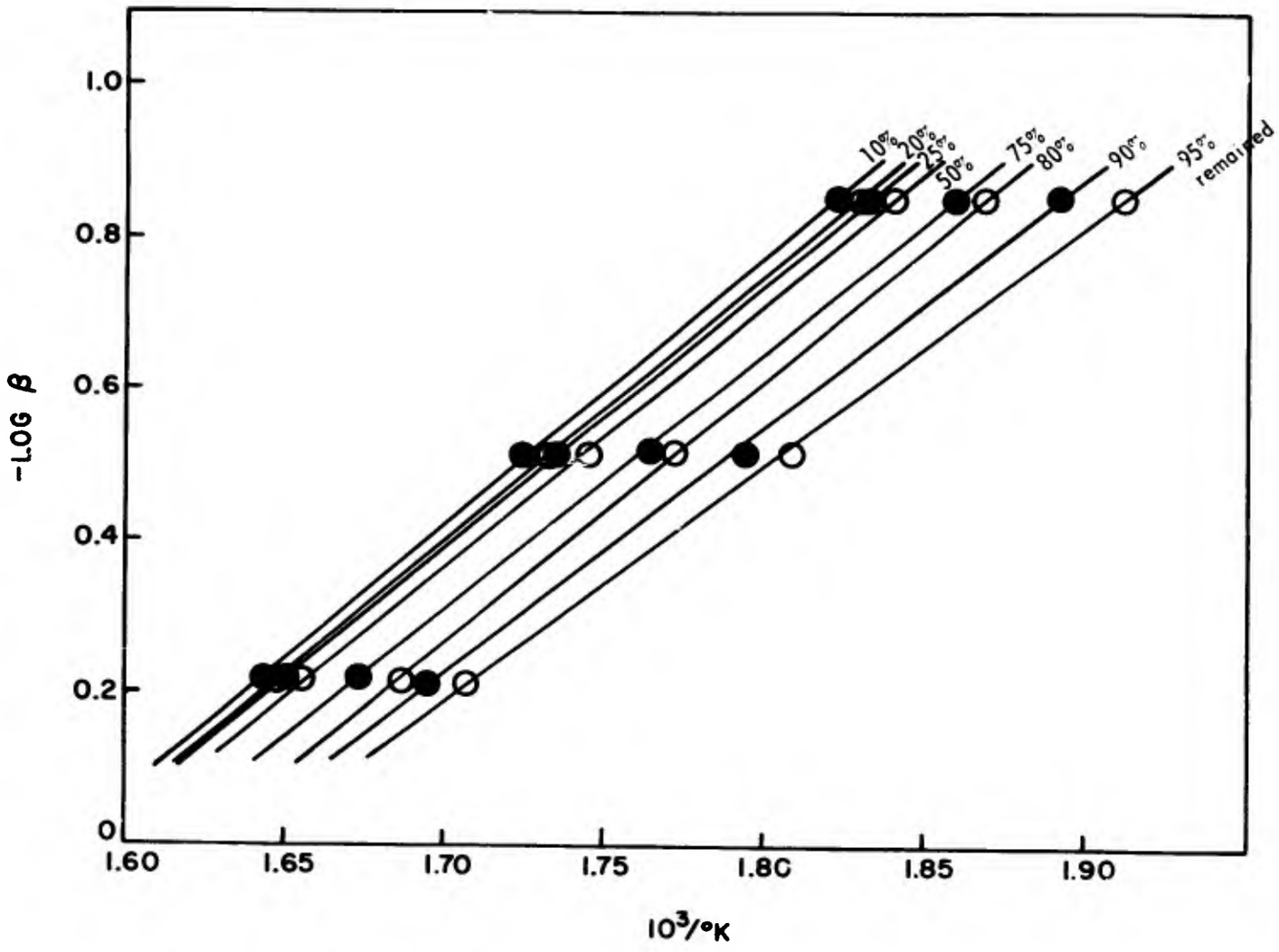

Fig 18 Logarithm of heating rate vs reciprocal of absolute temperature of uncured DER

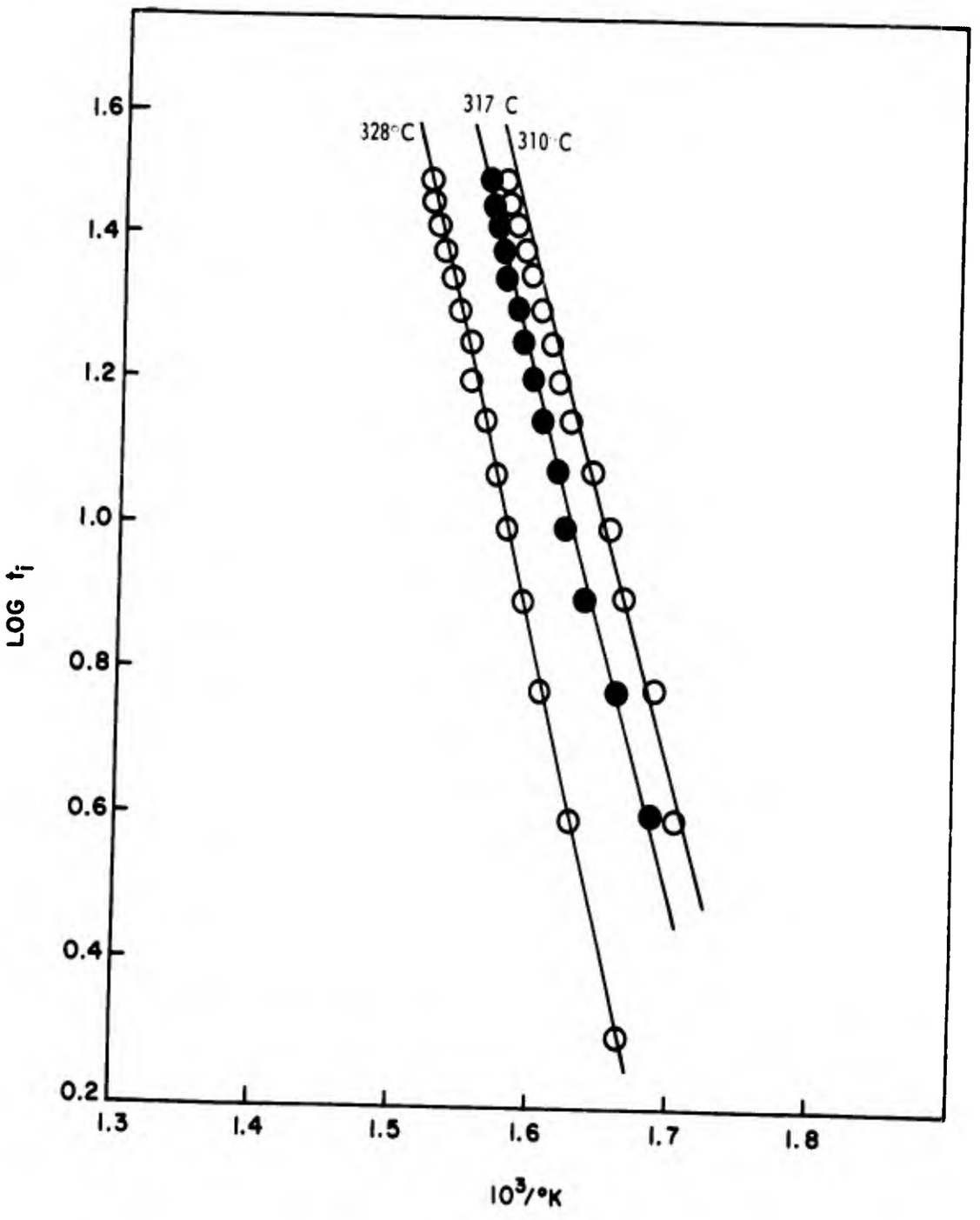

Fig 19 Logarithm of isothermal time vs reciprocal of absolute temperature of DER cured at 200°C

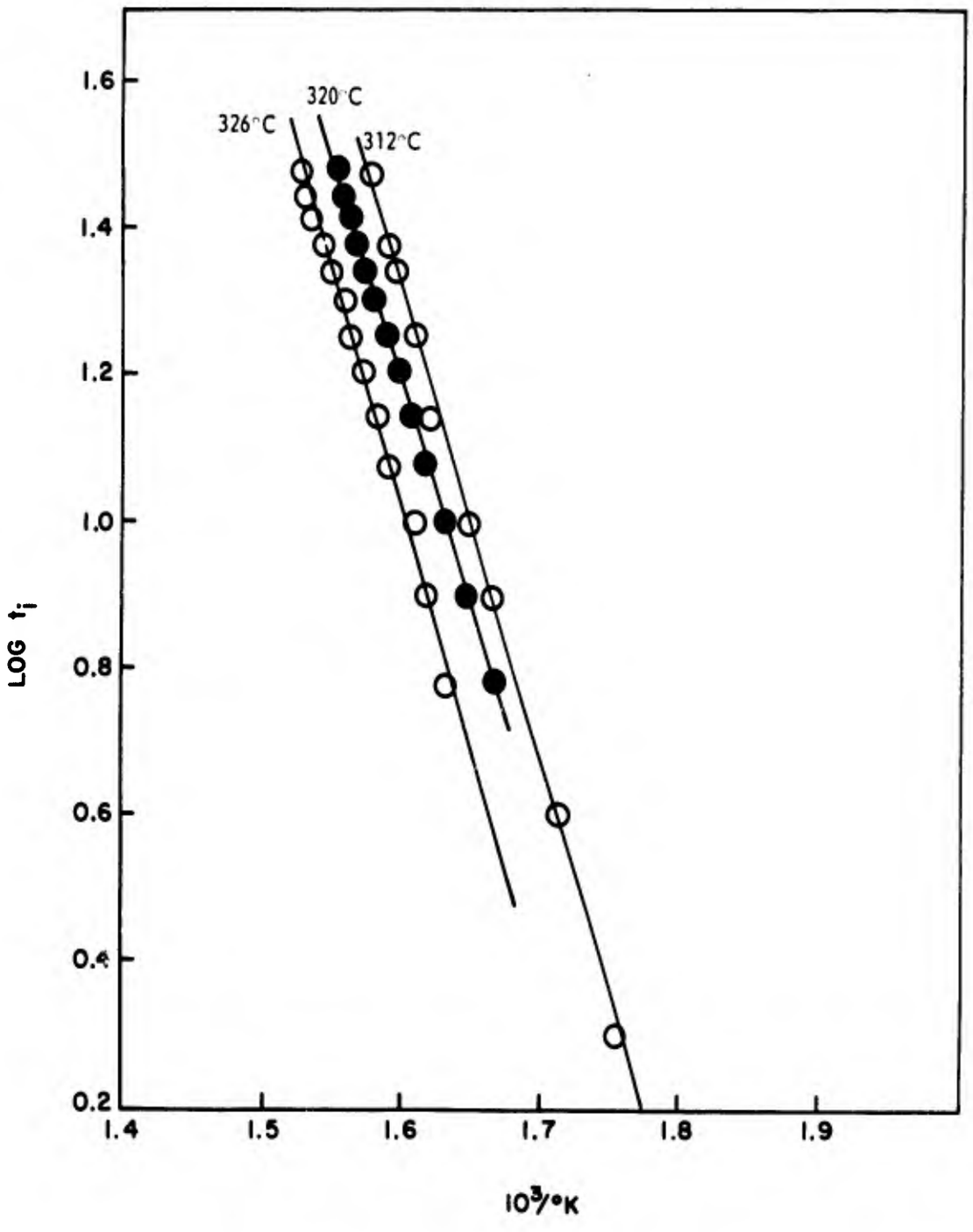

Fig 20 Logarithm of isothermal time vs reciprocal of absolute temperature of DER cured at 175°C

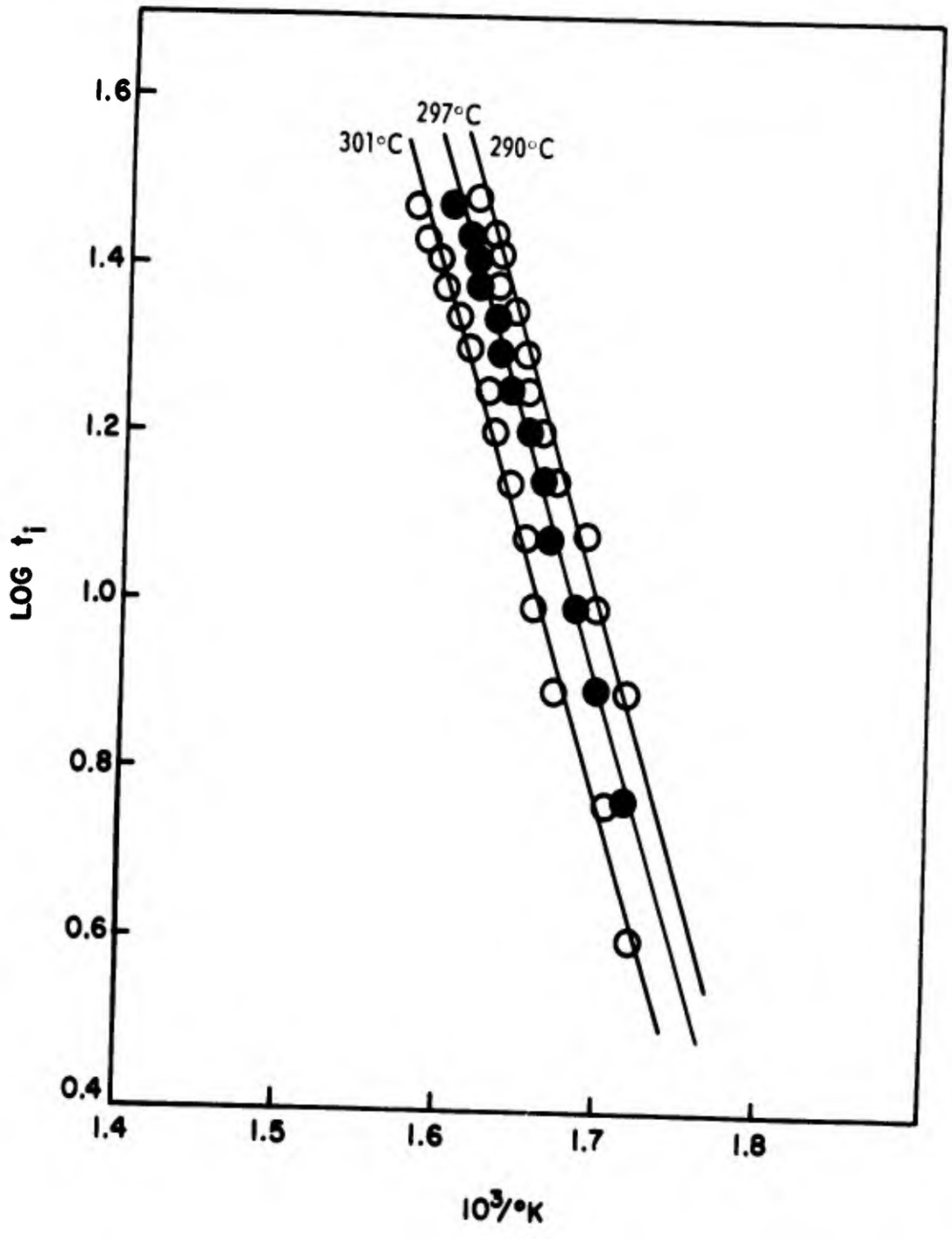

Fig 21 Logarithm of isothermal time vs reciprocal of absolute temperature of DER cured at 150°C

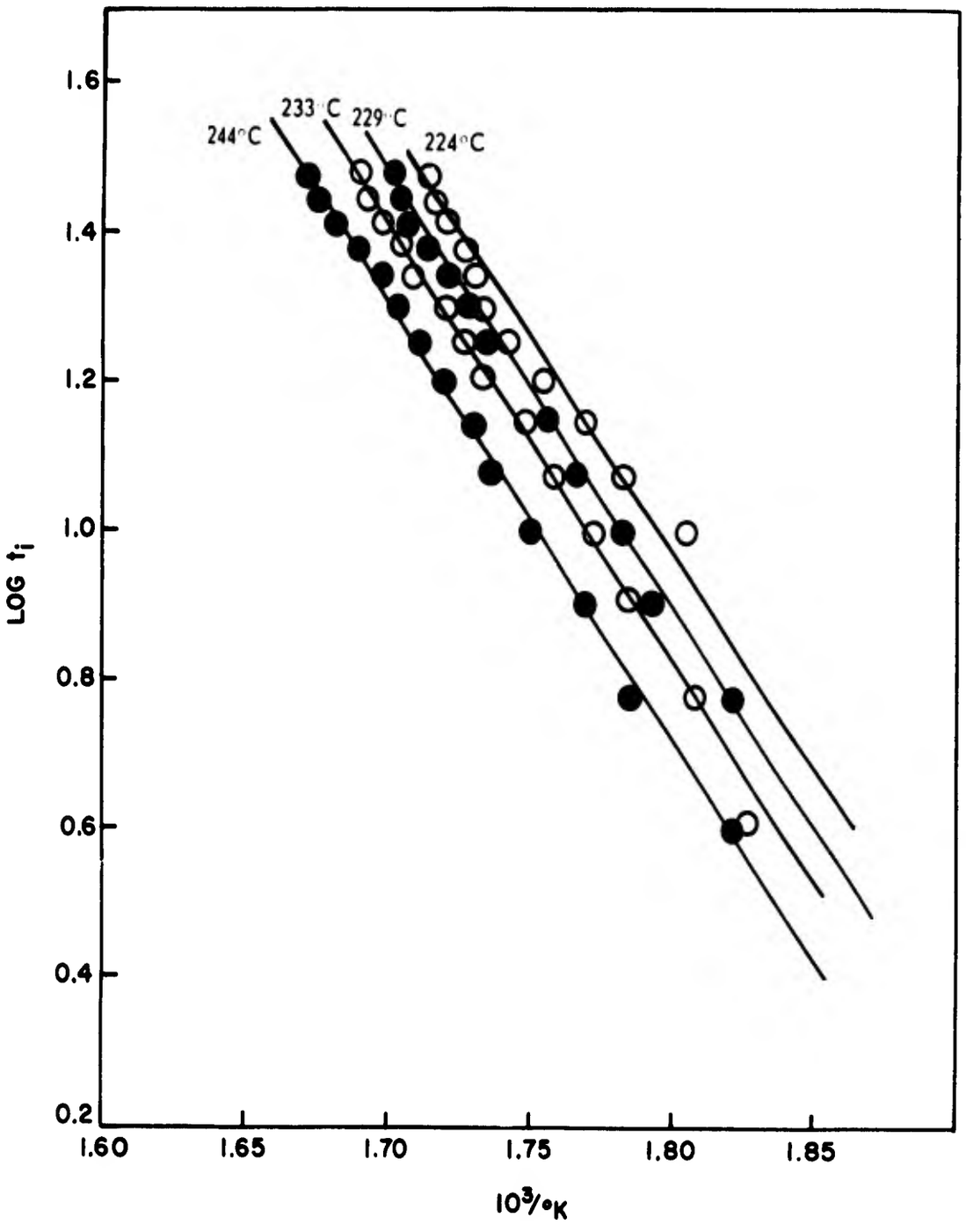

Fig 22 Logarithm of isothermal time vs reciprocal of absolute temperature of DER cured at 125°C

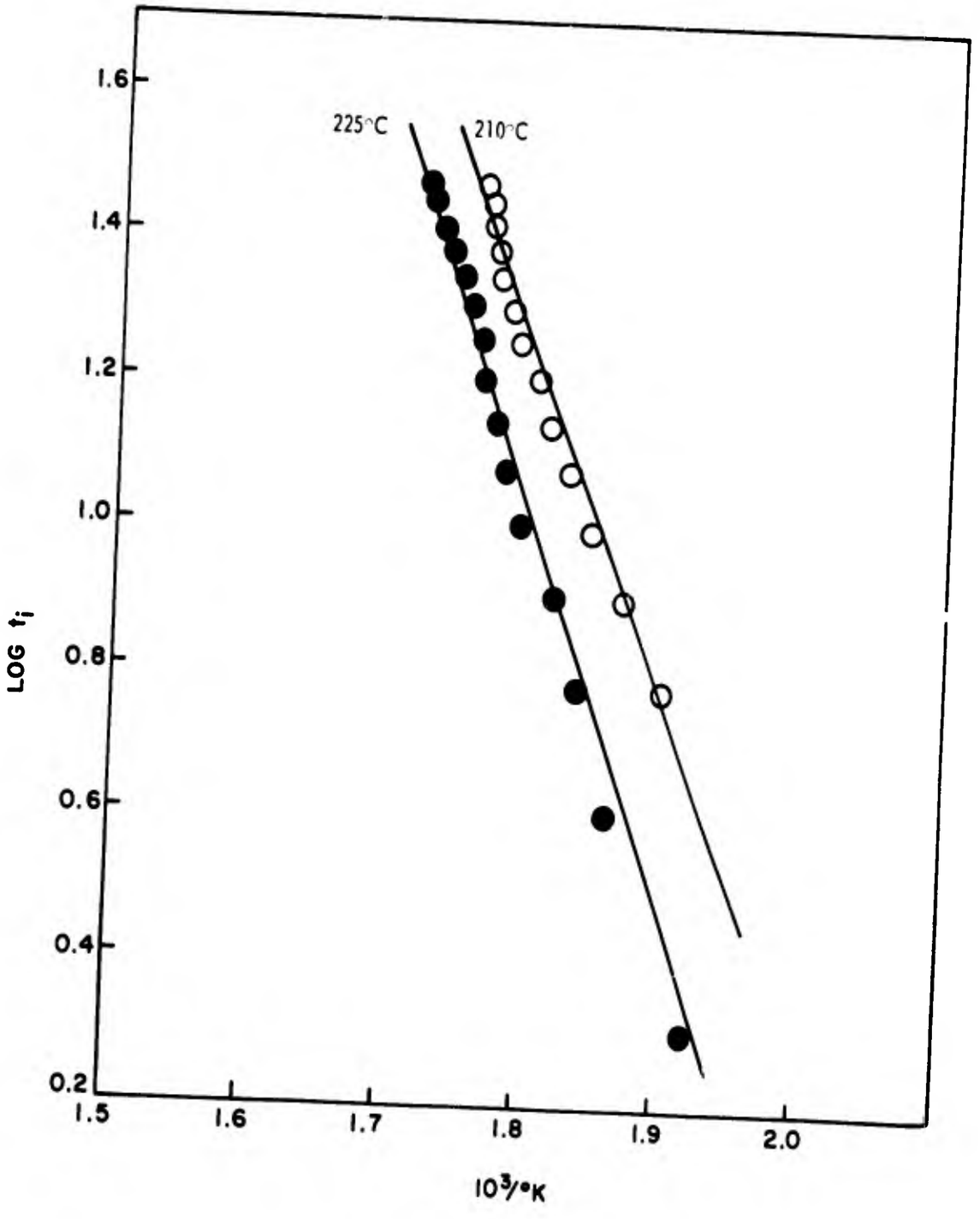

Fig 23 Logarithm of isothermal time vs reciprocal of absolute temperature of DER cured at 100°C

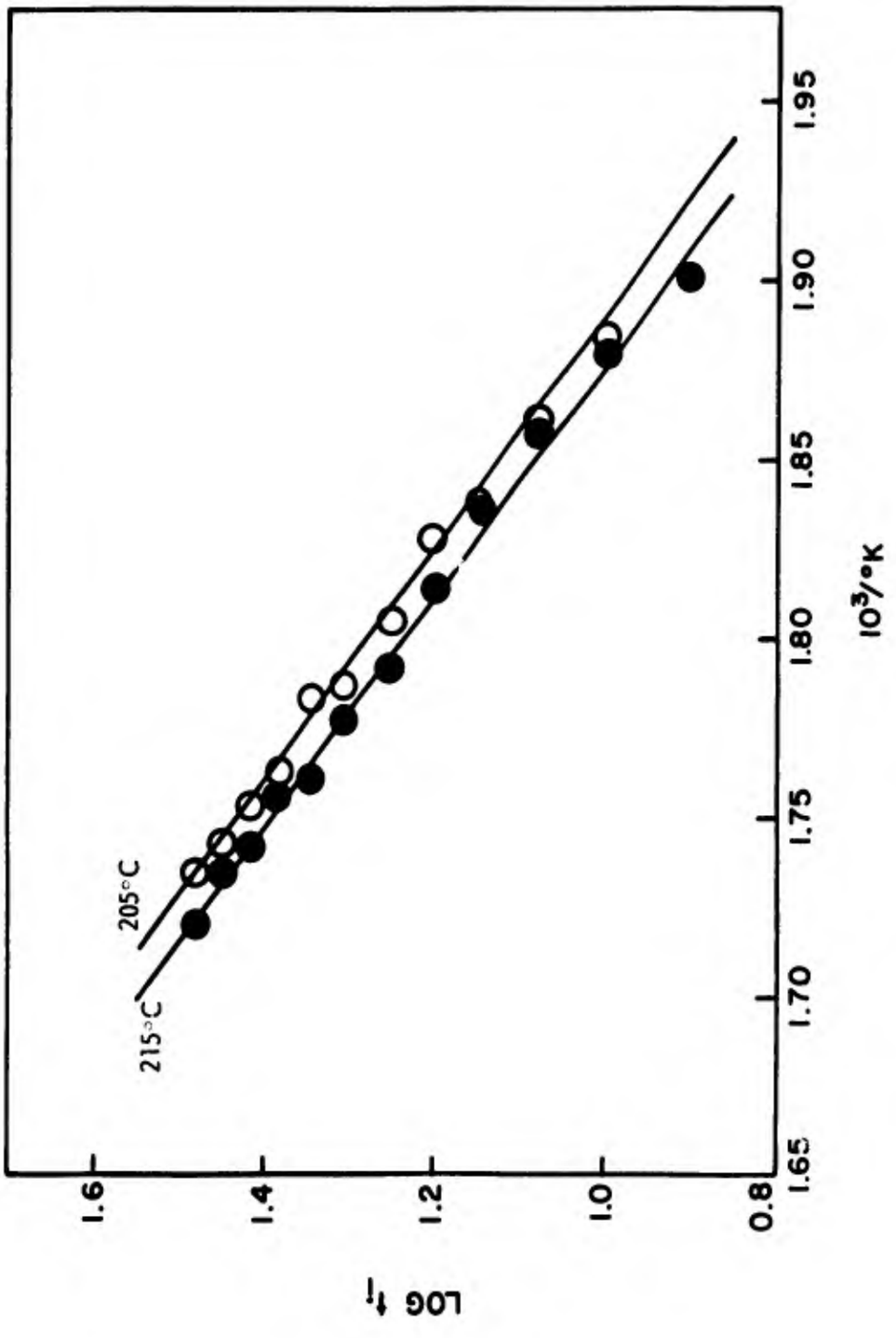

Fig 24 Logarithm of isothermal time vs reciprocal of absolute temperature of uncured DER

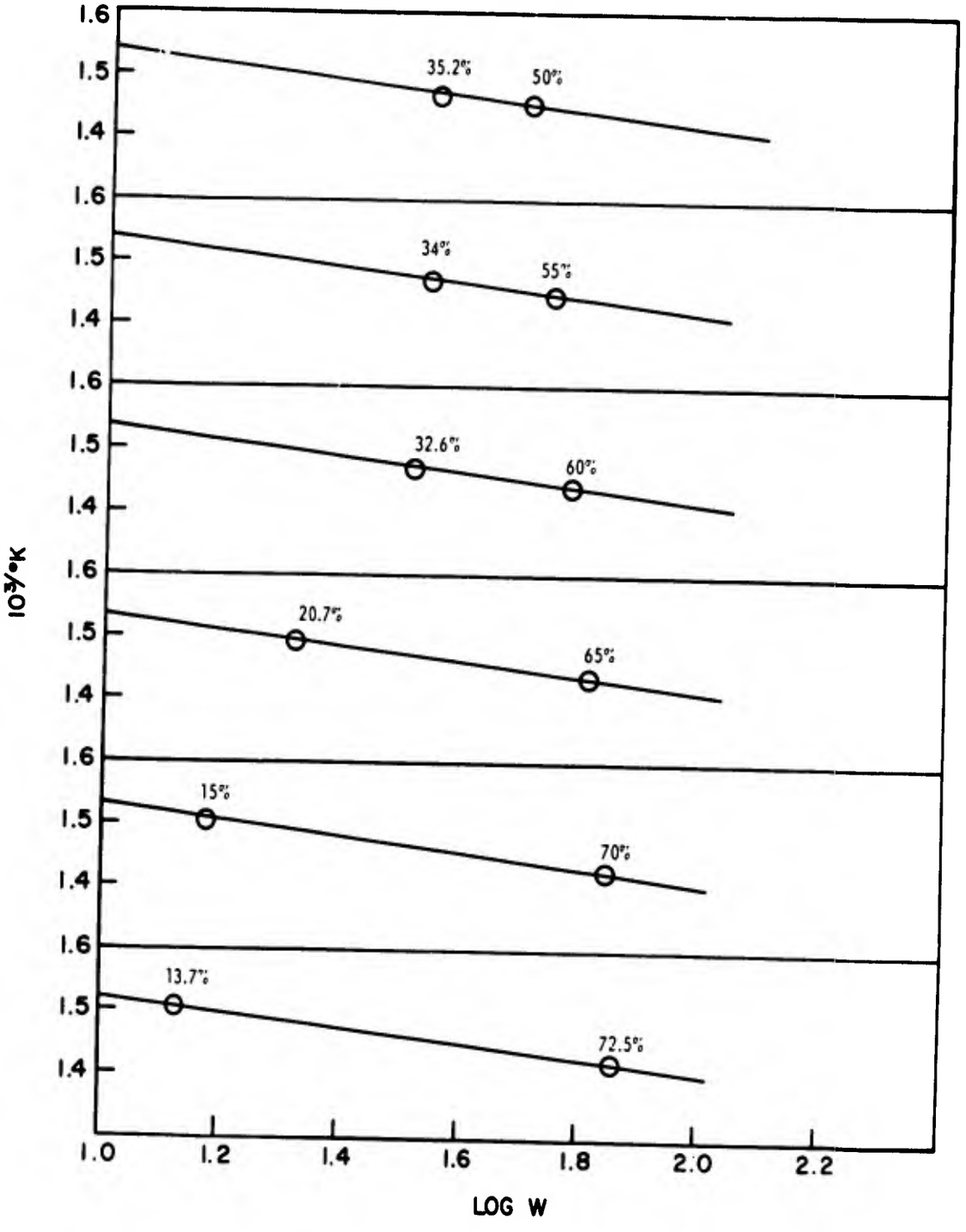

Fig 25 Reciprocal of absolute temperature vs logarithm of weight of DER cured at 200°C

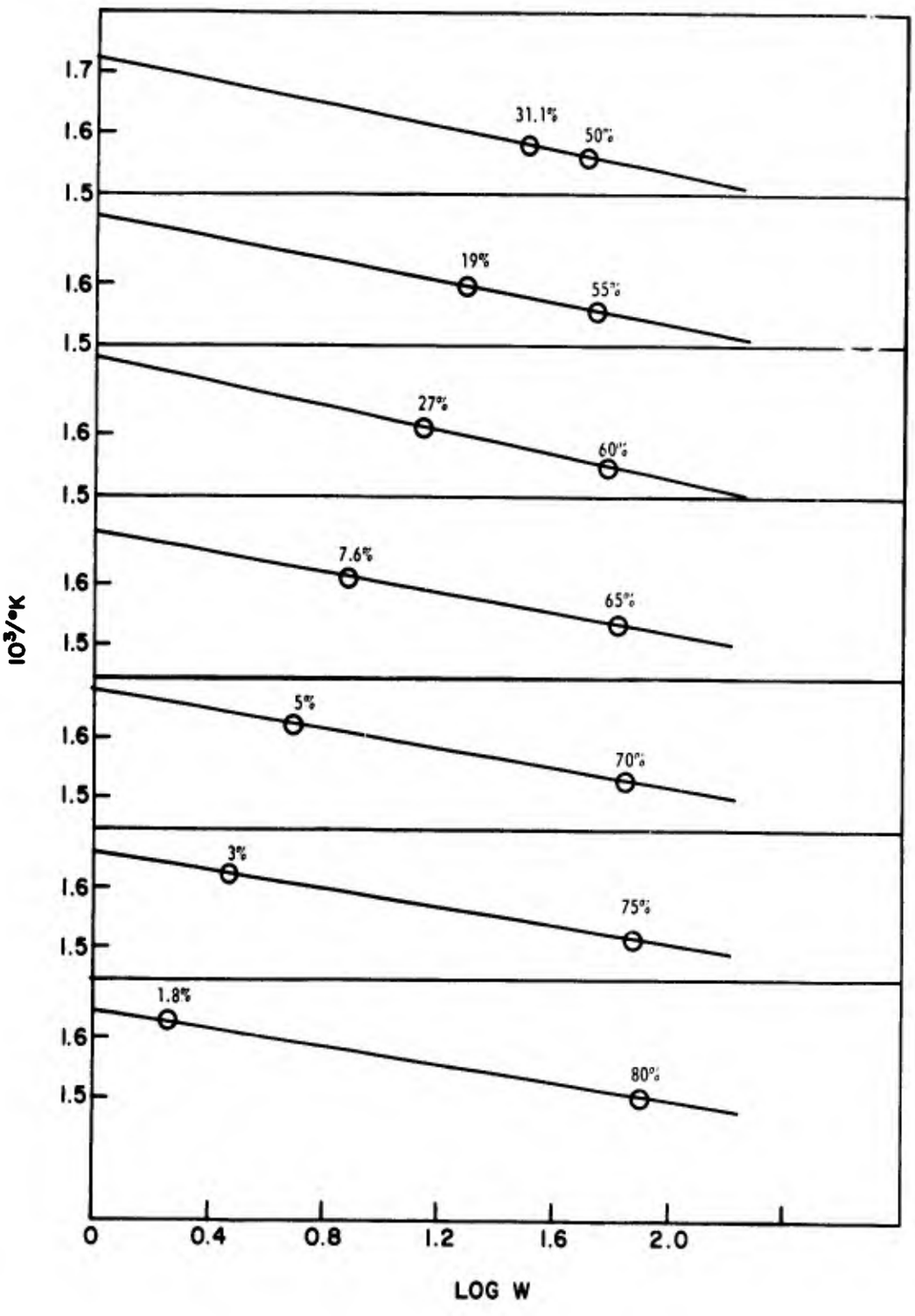

Fig 26 Reciprocal of absolute temperature vs logarithm of weight of DER cured at 175°C

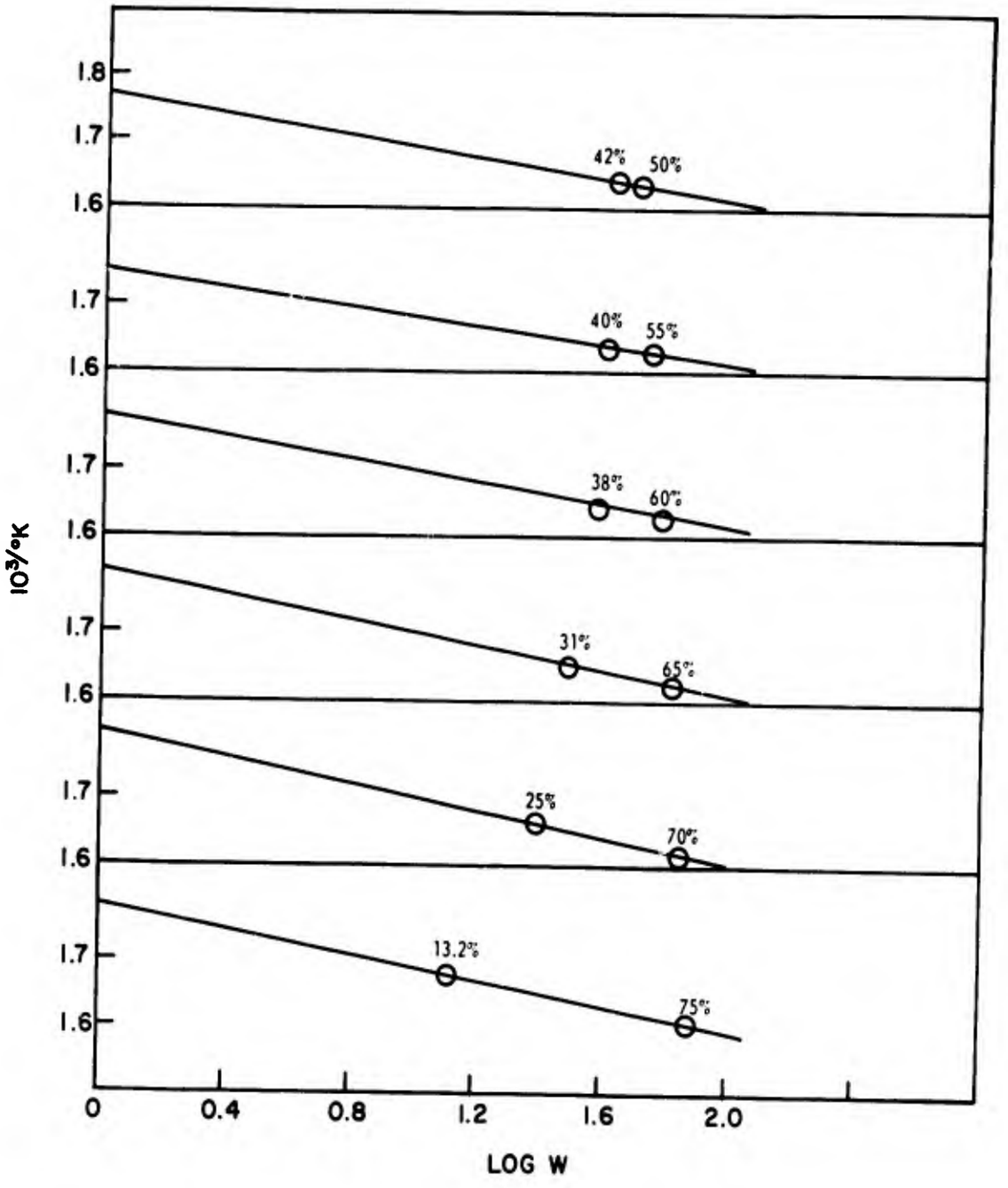

Fig 27 Reciprocal of absolute temperature vs logarithm of weight of DER cured at 150°C

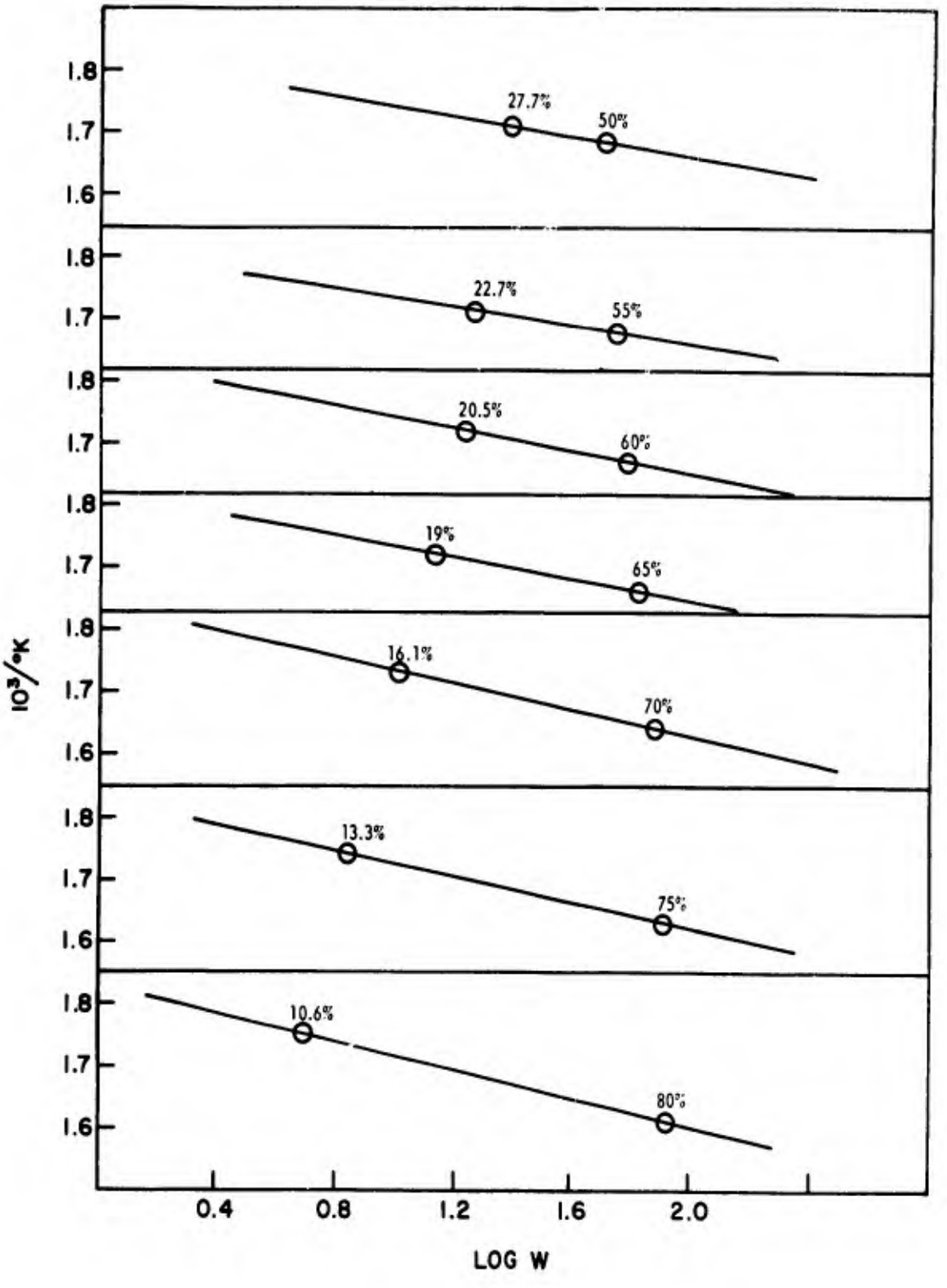

Fig 28 Reciprocal of absolute temperature vs logarithm of weight of DER cured at 125°C

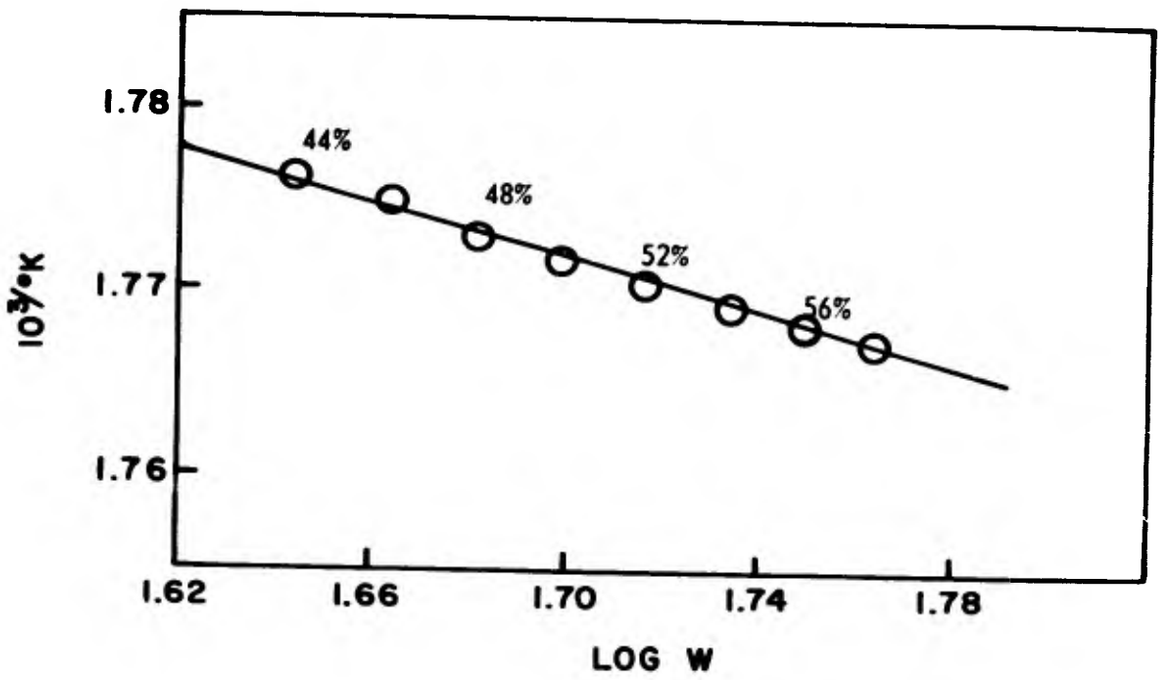

Fig 29 Reciprocal of absolute temperature vs logarithm of weight of DER cured at 100°C

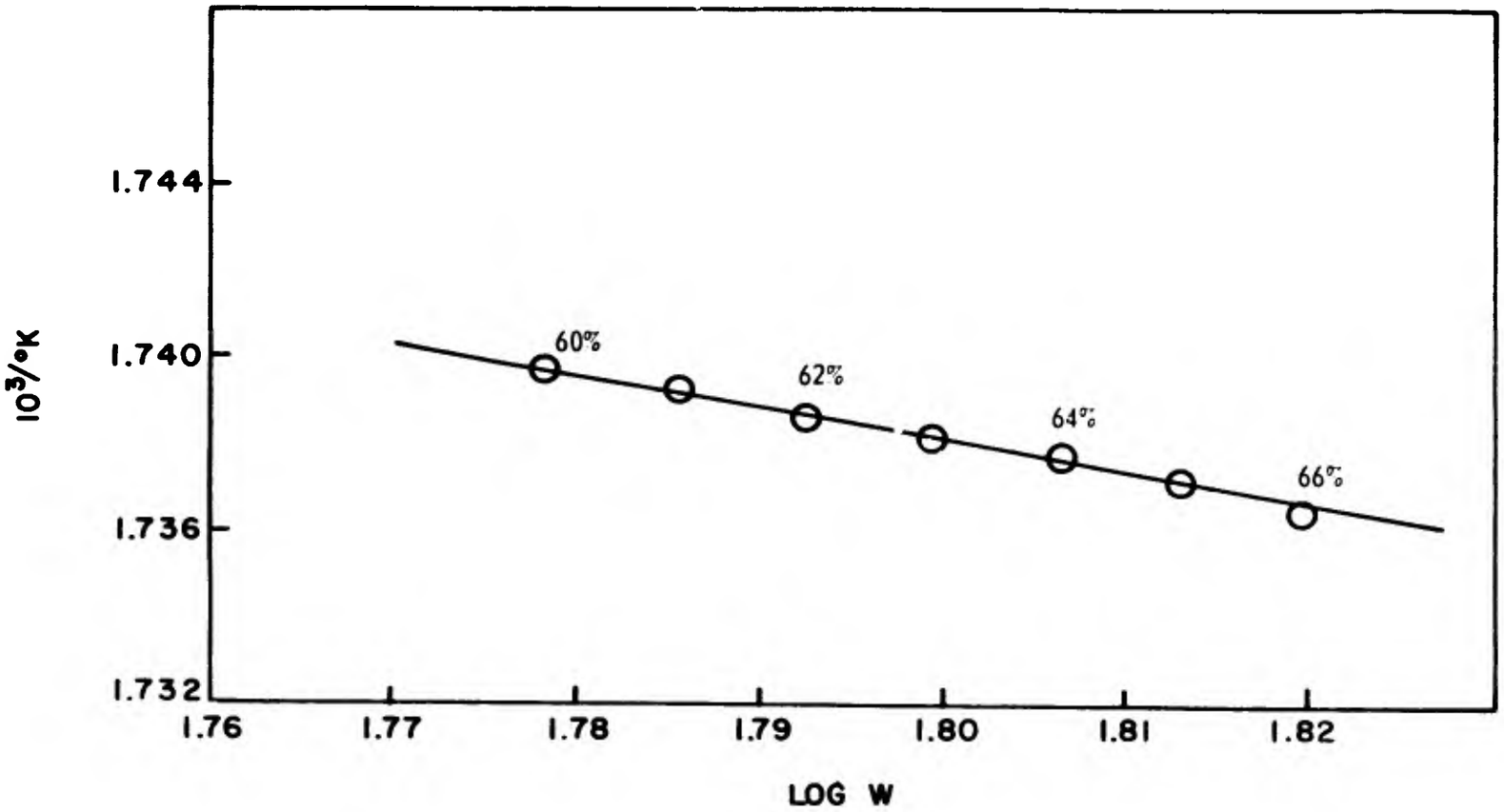

Fig 30 Reciprocal of absolute temperature vs logarithm of weight of uncured DER

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13. ABSTRACT

A conventional bisphenol-A epoxide was cured with m-phenylenediamine under five different curing temperatures. The thermal degradation of the cured and uncured resins took place at both constant temperature and constant heating rate. The thermal stability, based on the overall energy of activation and the order of reaction, was generally higher for the resin cured at a higher temperature. The highest curing temperature was 200°C.

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Epoxide resin						
Thermal degradation						
Curing temperature						
Thermal stability						
bisphenol-A						
m-phenylenediamine						
Thermogravimetric analysis						
Kinetic parameters						
Activation energy						