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APPLICATION OF SUPERPOSITION TECHNIQUES TO THERMAL DEGRADATION OF EPOXIDE RESINS

H. T. LEE
ELISE MCABEE
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DECEMBER 1971

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13. ABSTRACT

Time-temperature superposition was successfully applied to thermogravimetric (TGA) data for the thermal degradation of a number of cured expoxide resins. For several epoxides and for two curing agents, the same values of log a_D were applicable. This suggests that the same chemical processes were occurring in all cases, at least up to conversions of about 50%. Since log a_D was linear with temperature, it also was possible to superpose W versus log T plots at various rates of heating. Once more, the same shift factors (log K) could be applied to all the epoxides studied.

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OBJECT

The object of this study was to apply temperature-time superposition to thermogravimetric (TGA) data involving the thermal degradation of epoxide resins.

ABSTRACT

Time-temperature superposition was successfully applied to thermogravimetric (TGA) data for the thermal degradation of a number of cured epoxide resins. For several epoxides and for two curing agents, the same values of log a_D were applicable. This suggests that the same chemical processes were occurring in all cases, at least up to conversions of about 50%. Since log a_D was linear with temperature, it also was possible to superpose W versus log T plots at various rates of heating. Once more, the same shift factors (log K) could be applied to all the epoxides studied.

INTRODUCTION

A widely used method of studying the thermal degradation of polymers involves measuring the volatiles given off by recording weight loss as a function of time and temperature. At least in certain cases, it should be possible to apply superposition methods in the treatment of such thermogravimetric analysis (TGA) data (Ref 1, 2). This report describes such an application to TGA results obtained in these laboratories for a number of epoxide polymers.

RESULTS AND DISCUSSION

A temperature-time superposition method should be valid for any rate process where the temperature influences only the rate constant k. Even where the effect of temperature is more complicated, it usually is to be expected that the major temperature dependence is through the rate constant (Ref 1, 2).

If k_o is the rate constant at the reference temperature and k the rate constant at any other temperature, then $\log (k/k_o) = \log a_D$ is the amount by which the data must be shifted along the log to axis. The rate constant is conventionally written

$$k = Ae^{-\Delta H/RT} \qquad (1)$$

Then the ratio of rate constants for temperatures T and T_o is

$$\log (k/k_o\_ = \log a_D = -\frac{\Delta H}{2.303R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \qquad (2)$$

where ΔH is the activation energy and R is the gas constant.

Thermogravimetric data for several epoxide polymers have been obtained in these laboratories over the past few years (Refs 3 through 7). These data were used to test the validity of applying the superposition method to TGA curves.

The epoxides studied and the abreviations that will be used in this report for them are shown in Table 1 (Ref 5). Each epoxide was cured with m-phenylenediamine (MPD) as described in the earlier reports (Ref 3, 4). In one case, the undecyl was cured with hexamethylenediamine (HMDA) (Ref 3).

The primary thermograms (Ref 3, 4) had been obtained as weight loss versus temperature traces at several rates of heating. Such curves, due to the usual nonlinear temperature dependence of the shift factor (Ref 8), would not be expected to superposable by horizontal shifts along the temperature axis. However, since traces for several rates of heating were available (Ref 3, 4), it was possible to plot weight loss versus log time from the information in the primary curves. Such plots are shown for DER 332 in Figure 1. These weight loss curves were shifted to the 400° C curve along the log time axis to give the curve shown in Figure 2. The shift distances along the log time scale are denoted log a_D (Ref 1). Figure 2 does indicate that a time-temperature superposition applies to this type of data. Figures 3 through 12 show the corresponding plots for the other MPD cured epoxides listed in Table 1. Figures 13 and 14 give the results for the undecyl epoxide cured with HMDA.

It is noteworthy that the same shift factors (a_D) could be used in constructing master curves, despite the structural differences in the epoxides. This was also true in the one case where the curing agent was changed; and it would seem to indicate that the degration was following the same course in each case, the primary process not depending on structural changes that were introduced into this series of polymers. In earlier work (Ref 3, 5), it was found that activation energy values for the degradation of MPD cured epoxides were essentially constant within the experimental error. This also indicated that chemical processes occurring in the degradation were the same for all the polymers. It is known that degradation of cured epoxide resins during early stages primarily involves destruction of the aromatic ether moieties (Ref 5, 9). The thermograms used in the present work are reliable up to around 50% degradation (Ref 3). Above this degree of conversion, deposition of material on the balance weighing system made the results somewhat suspect. So it would appear that the data obtained probably mainly reflects changes in the ether moiety. It is believed that such changes will be little affected by steric factors arising from side-chain effects (Ref 3, 5).

The same conclusions appear to hold for the single HMDA cured sample. As indicated above, the same a_D values that were used for the MPD cured samples could also be applied to this material. Lee, Reich, and Levi (Ref 3) found that in this case the activation energy for degradation appeared to some 15% lower than that for MPD cured epoxides. On the basis of the limited data at their disposal, however, they could not be certain whether this was a real effect or only experimental error. Our results here tend to support the latter view.

A plot of log a_D versus 1/T according to Equation (2) is shown in Figure 15. An activation energy of 15 kcal/mole was found from the Arrhenius plots for all of the cured epoxides studied. This constancy is to be expected if the same degradation processes are operating in all cases over the conversion range investigated.

Most kinetic parameters evaluated from TGA data based on the reaction rate equations were weight dependent. The prime parameters in these equations were concentrations expressed in terms of weight changes. The implication of weight dependency possibly would affect the values of the evaluated kinetic parameters. This probably would account for the differences between the values for the activation energy obtained in the present study and those from earlier work.

Figure 16 shows the temperature dependence of log a_D. The fact that log a_D is linear with temperature suggests that superposition might be applicable to W versus log T plots at various rates of heating (Ref 8). Visual inspection of such plots also indicated that they were nearly parallel.

Shift factors, designated in this case, as K for superposing the weight loss-log temperature plots were determined by inspection for each of the epoxides. Upon plotting the average log K values against rate of heating (RH), the curve shown in Figure 17 then were used in constructing the master curves shown in Figures 18 through 24. It appears that the superposition procedure is applicable to these curves and that the same log K values can be applied to all of them. This demonstrates once more that the same chemical processes seem to be occurring in the thermal degradation of all the epoxide resins studied.

CONCLUSION

Time-temperature superposition can be applied to thermogravimetric data for cured epoxide resins.

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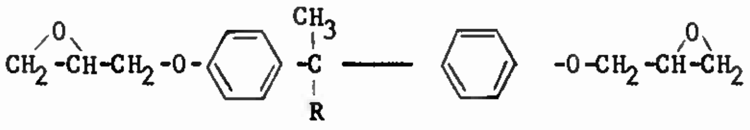
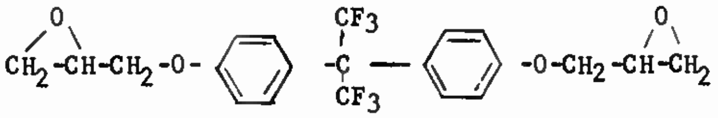
TABLE 1

List of epoxides studied



R	Abbreviation
$-CH_3$	Epon 820
$-CH_3$	DER 332
$-(CH_2)_6CH_3$	Heptyl
$-(CH_2)_{10}CH_3$	Undecyl
$-(CH_2)_{14}CH_3$	Pentadecyl



Halogenated 6F

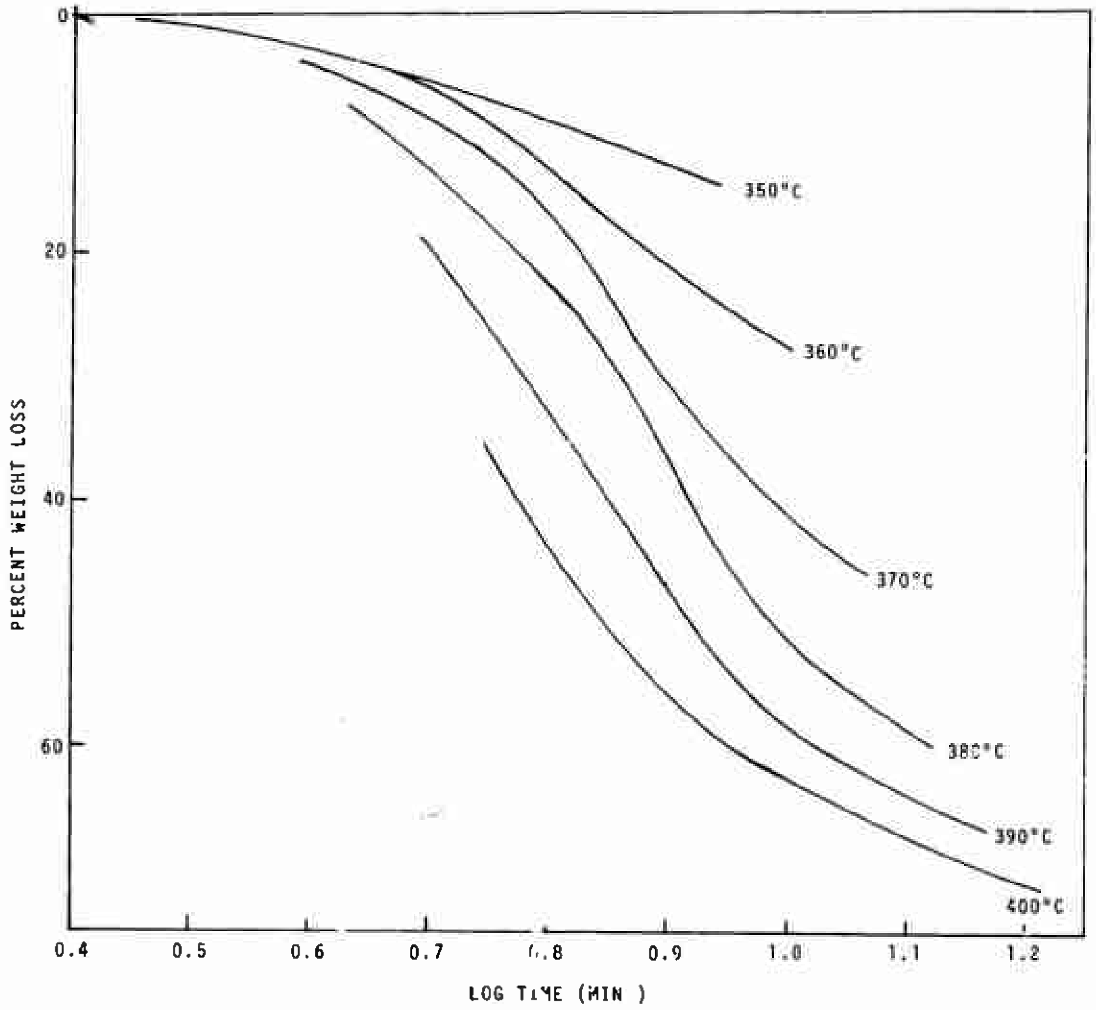


Fig 1 Weight loss of DER 332 as a function of time

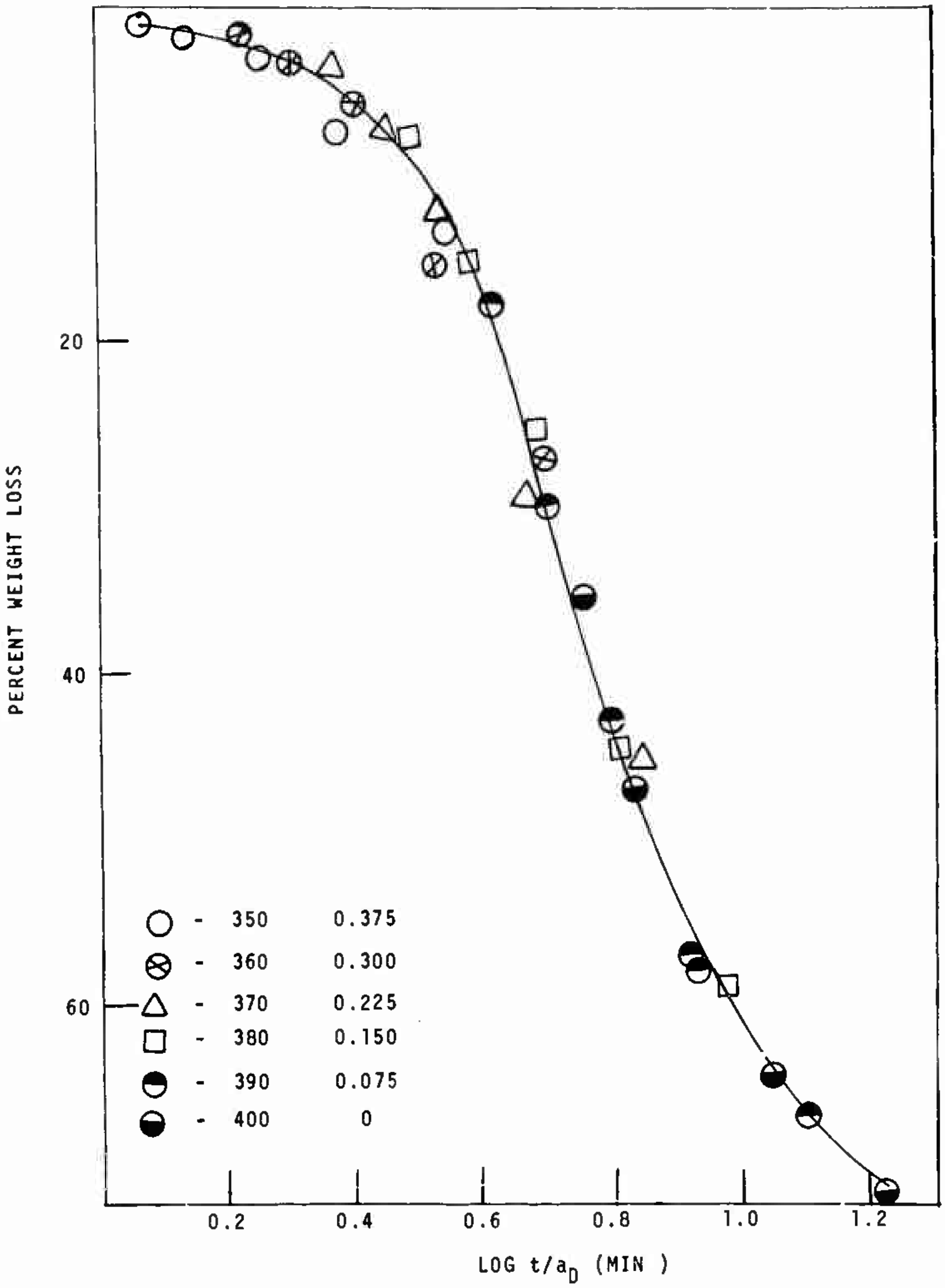


Fig 2 Master curve of weight loss versus reduced time for DER 332. Constructed from Fig 1 using the log a_D terms on the graph

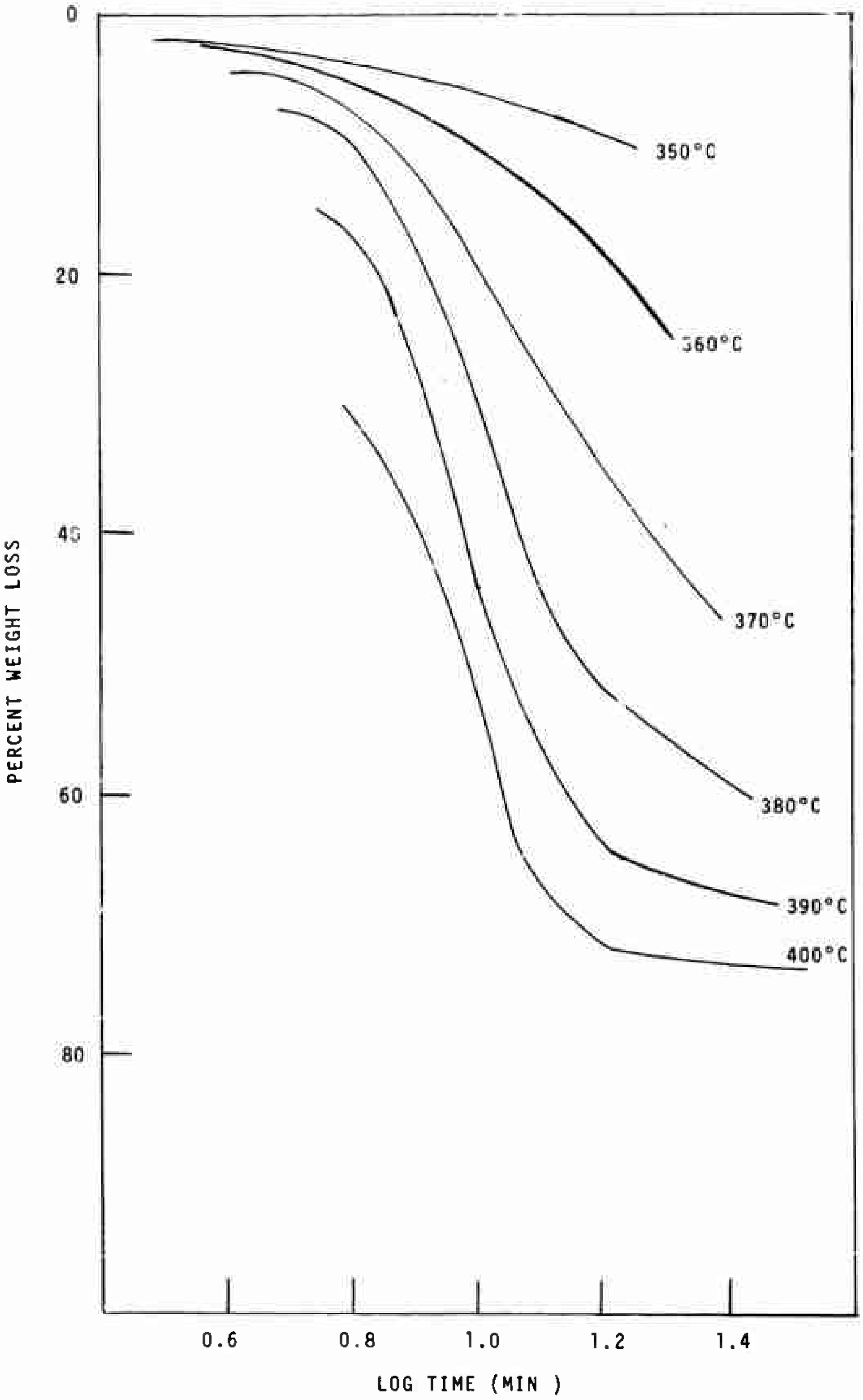


Fig 3 Weight loss of Epon 820 as a function of time

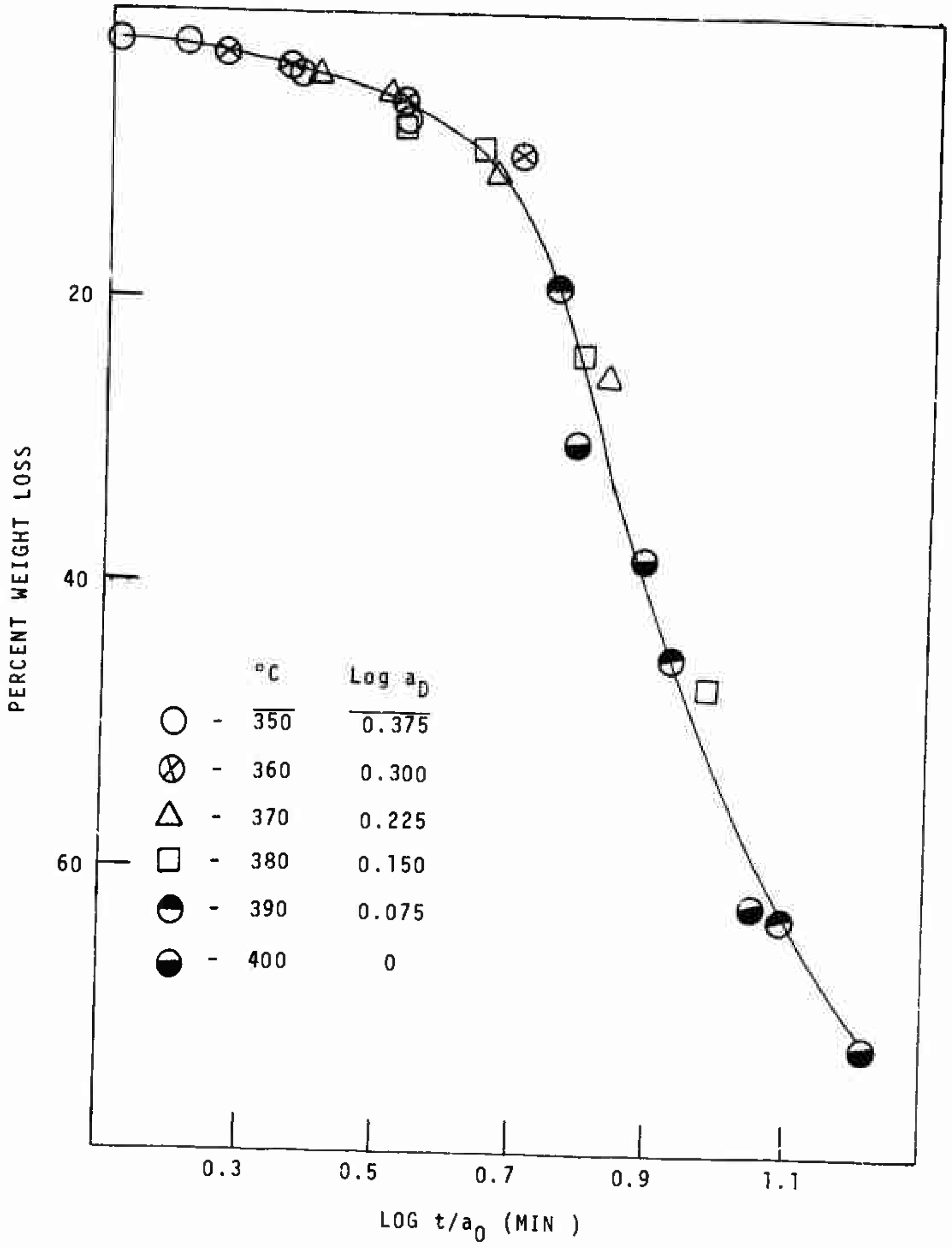


Fig 4 Master curve of weight loss versus reduced time for Epon 820. Constructed from Fig 3 using the log a_D terms on the graph

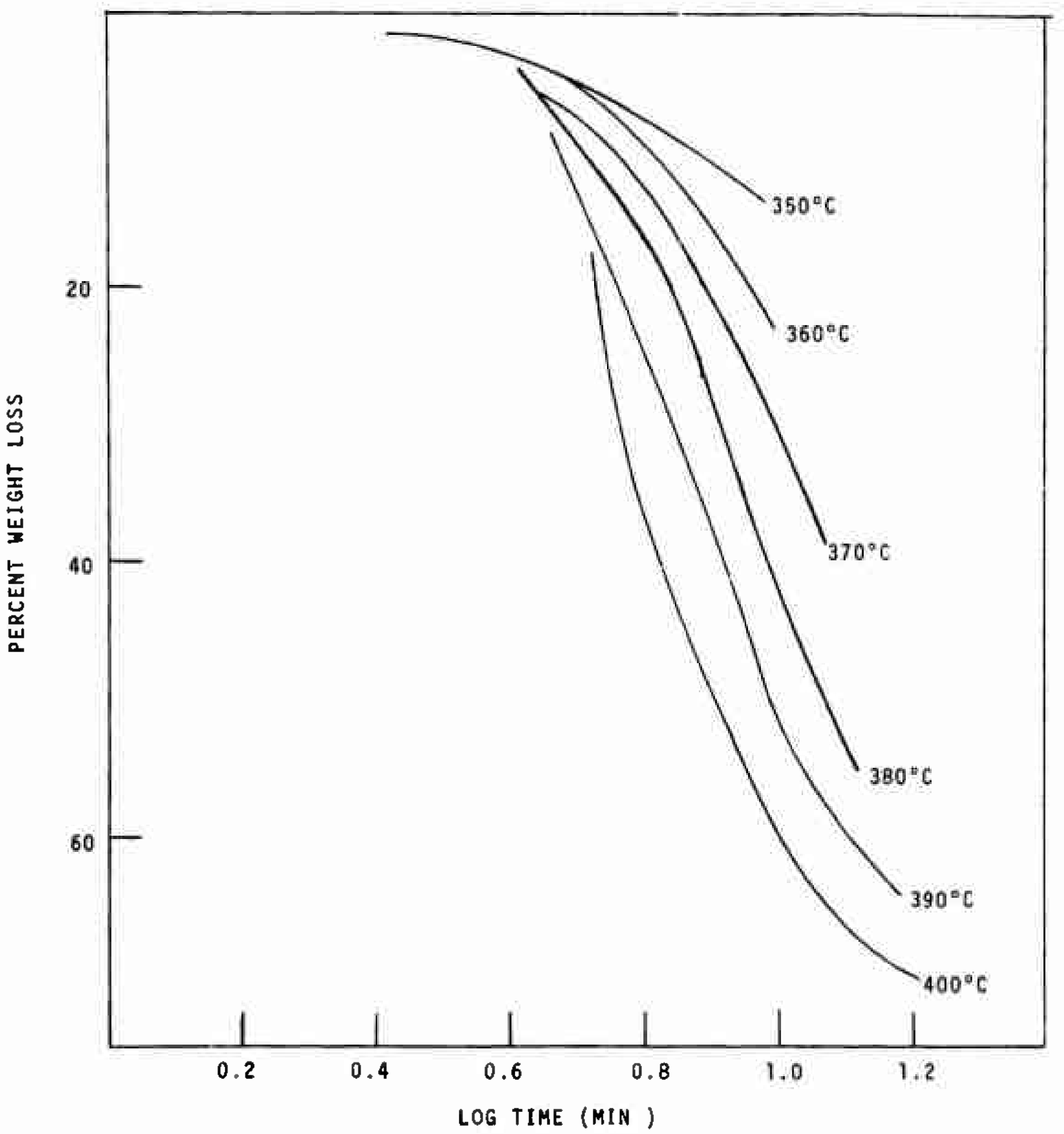


Fig 5 Weight loss of Heptyl as a function of time

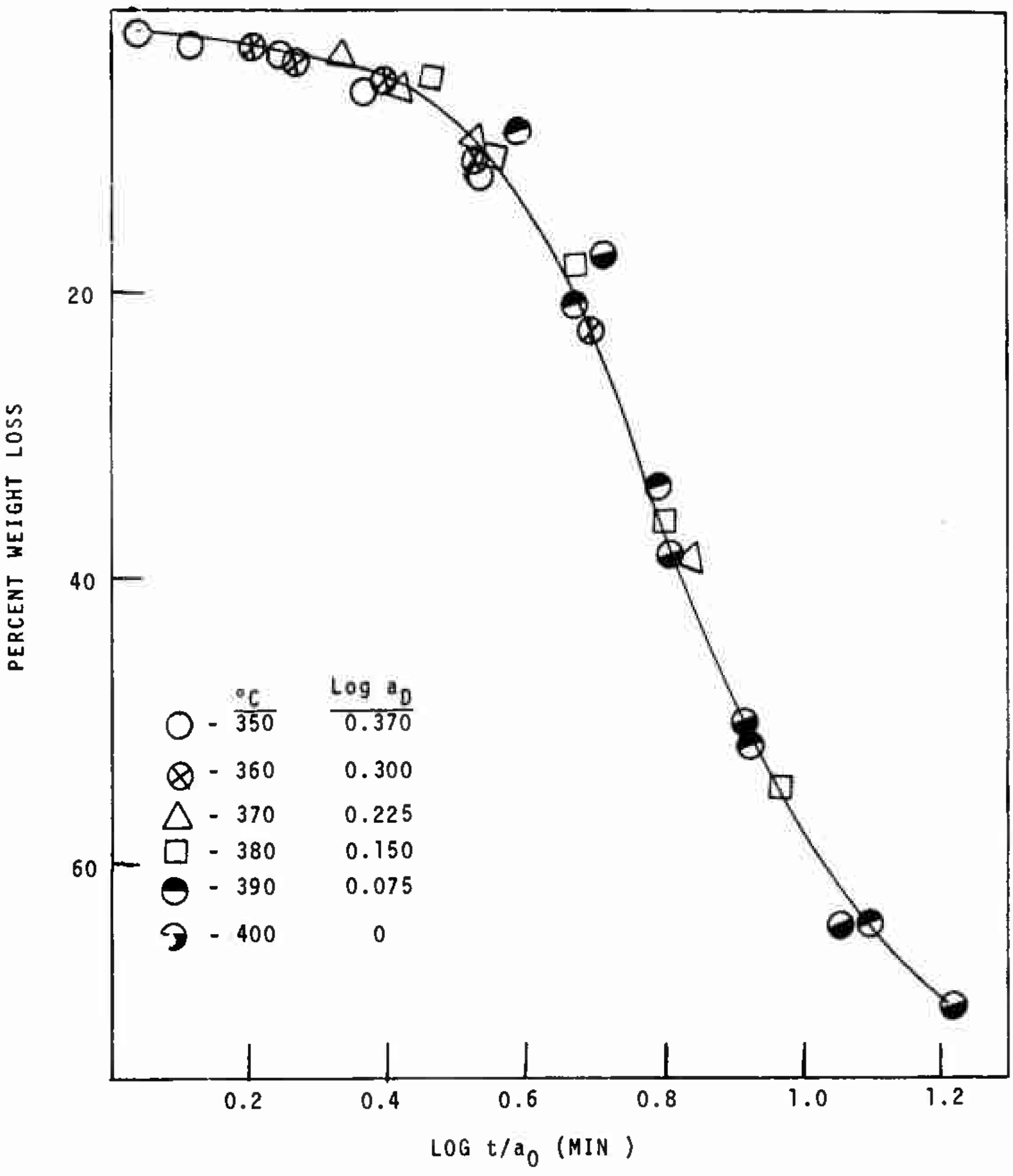


Fig 6 Master curve of weight loss versus reduced time for Heptyl. Constructed from Fig 5 using the log a_D terms on the graph

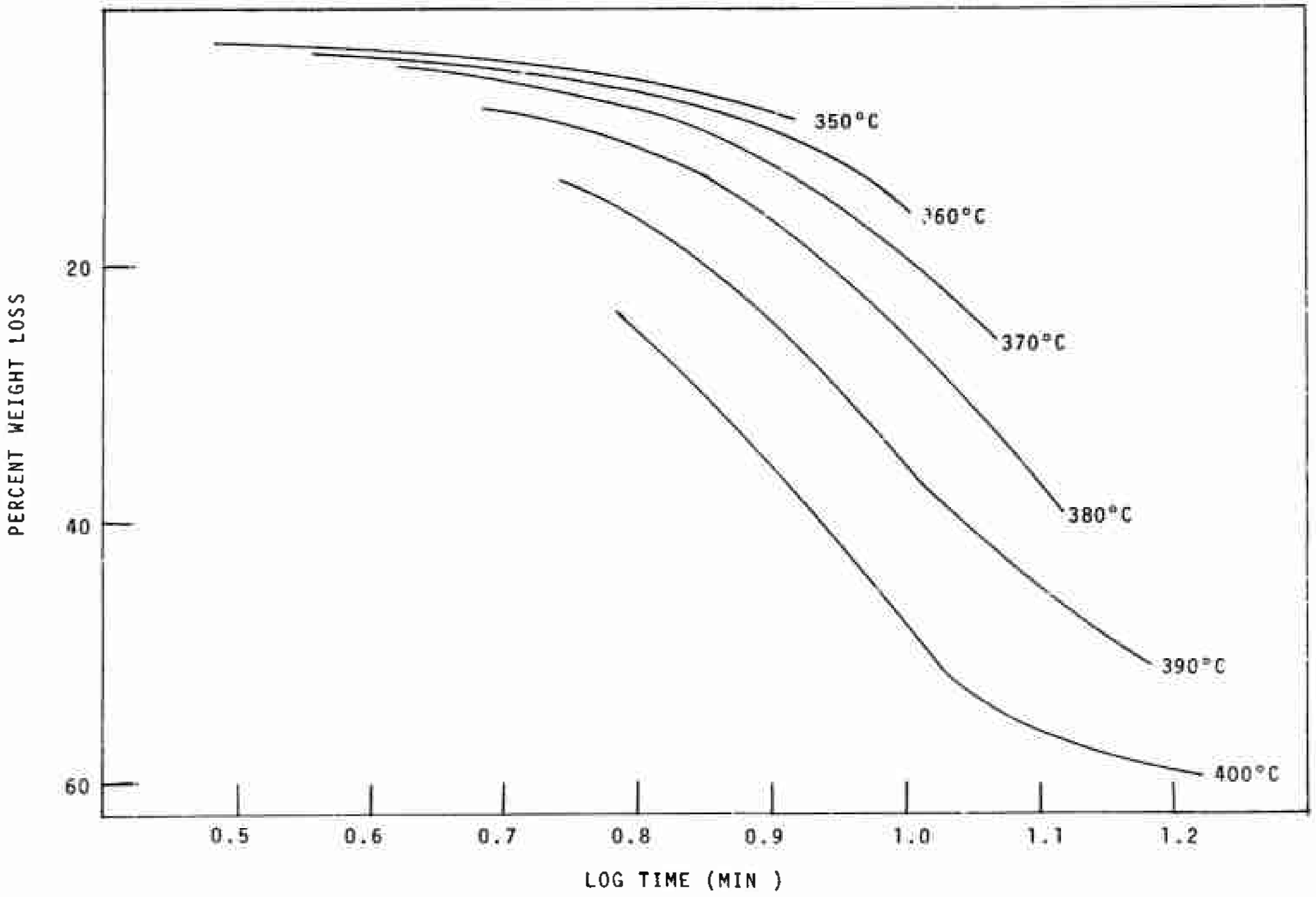


Fig 7 Weight loss of Undecyl as a function of time

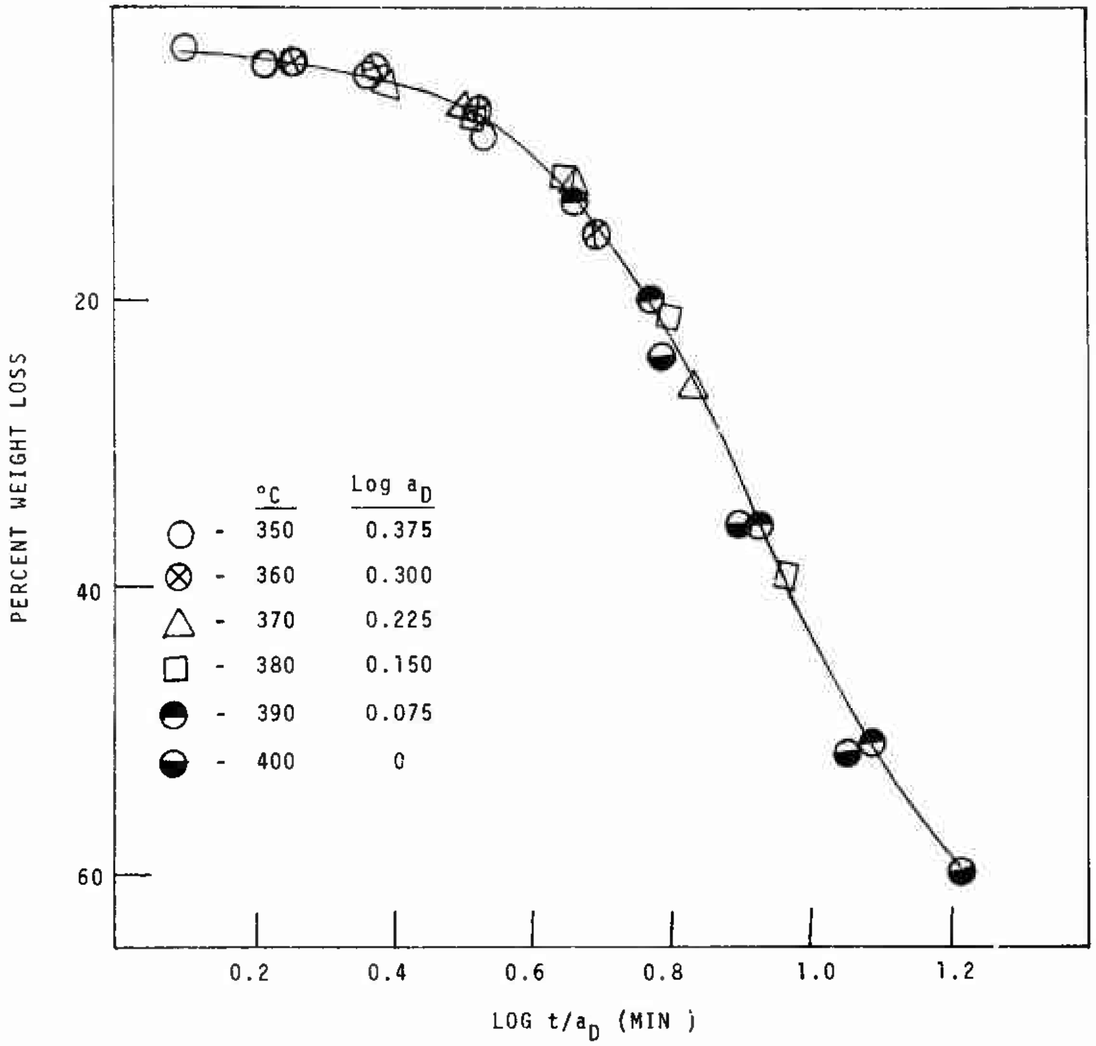


Fig. 8 Master curve of weight loss versus reduced time for Undecyl. Constructed from Fig 7 using the log a_D terms on the graph

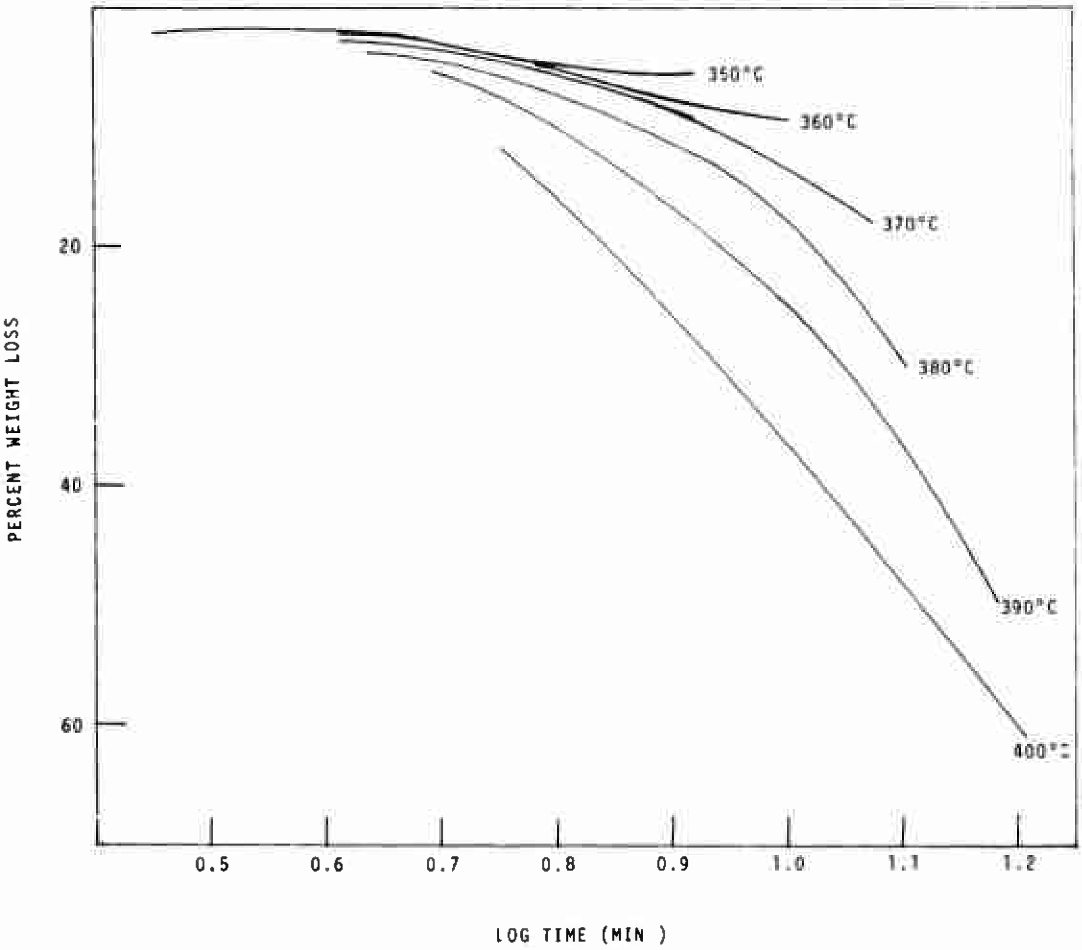


Fig 9 Weight loss of Pentadecyl as a function of time

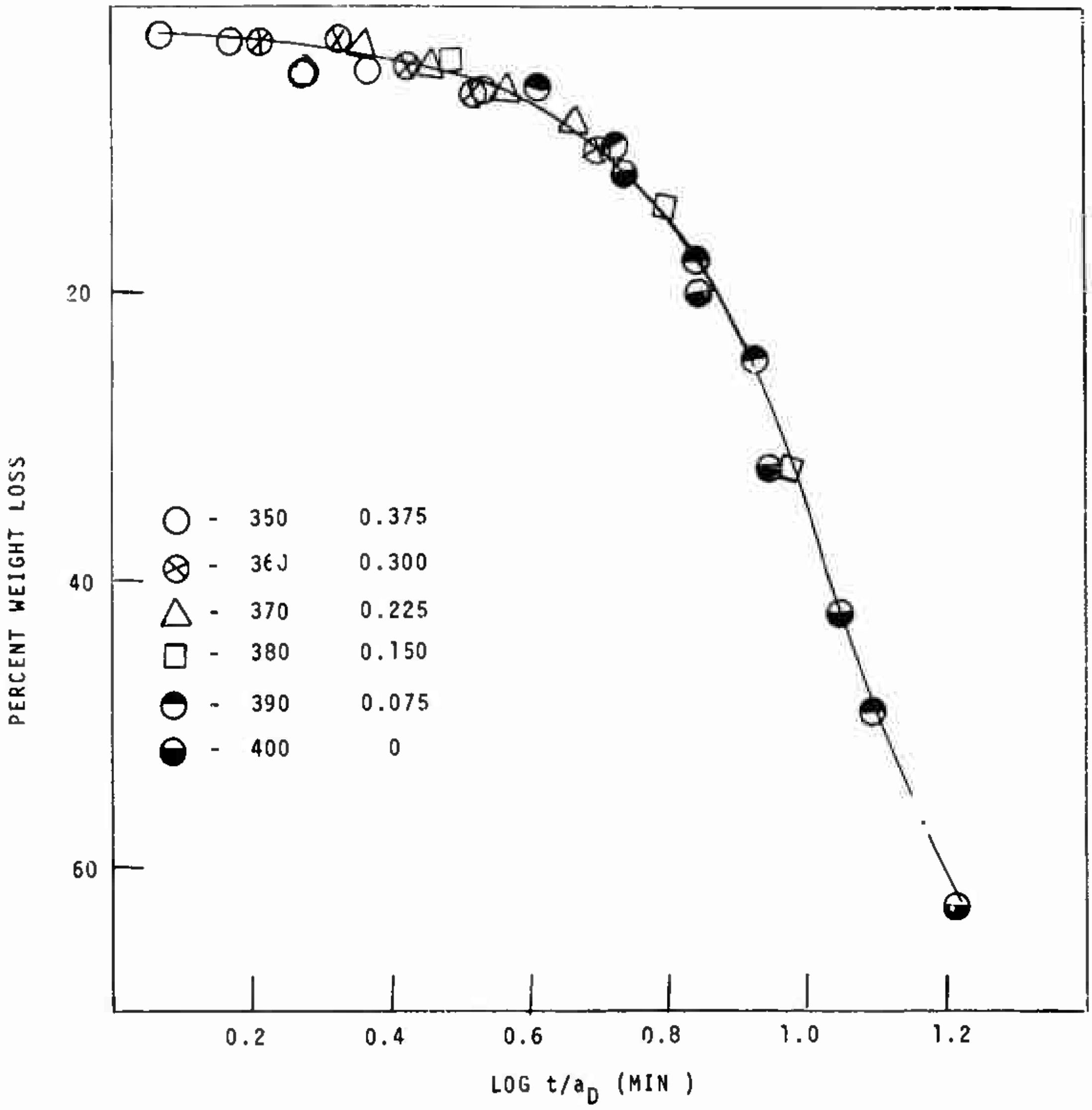


Fig 10 Master curve of weight loss versus reduced time for Pentadecyl. Constructed from Fig 9 using the log a_D terms on the graph

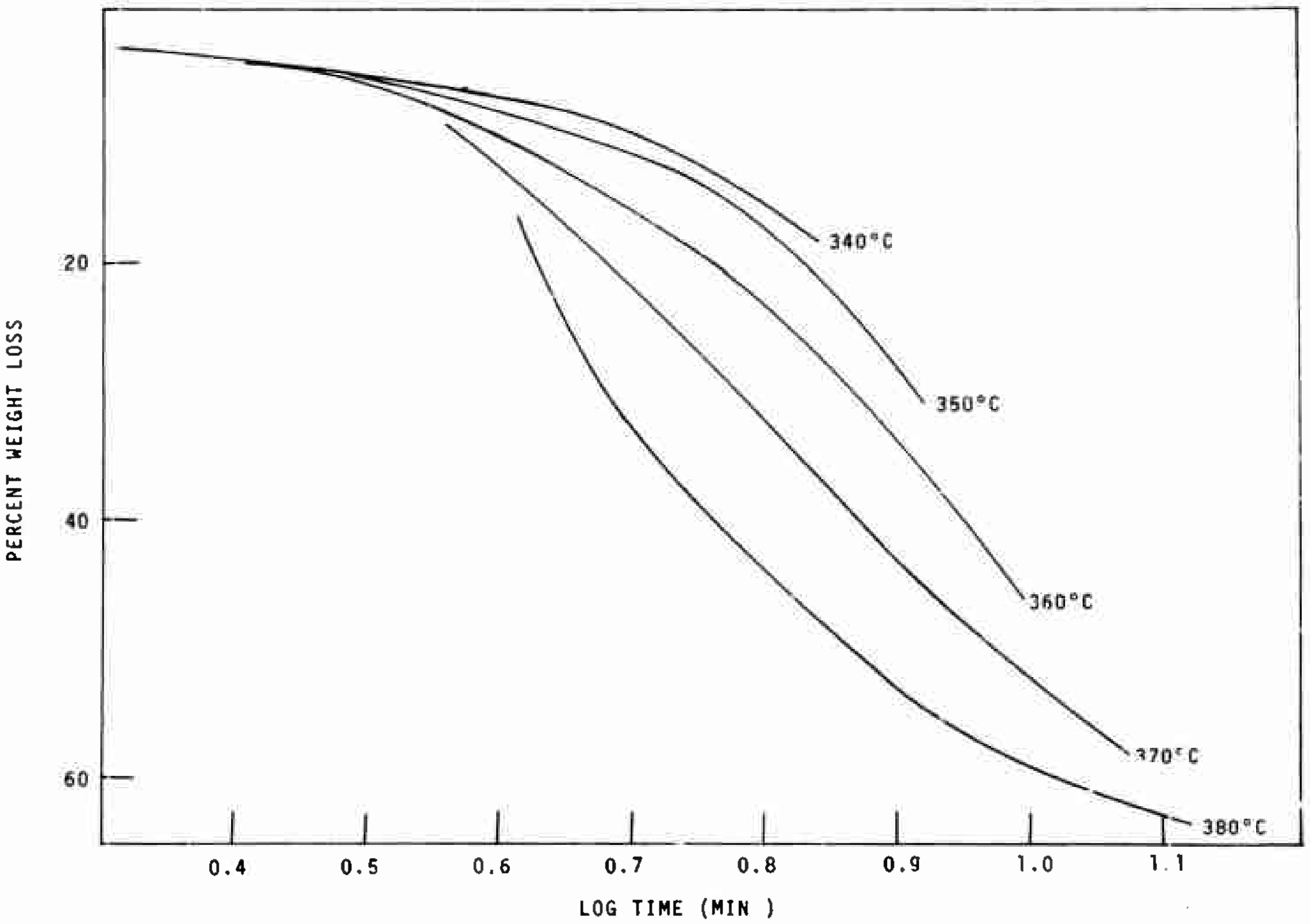


Fig 11 Weight loss of halogenated 6F as a function of time

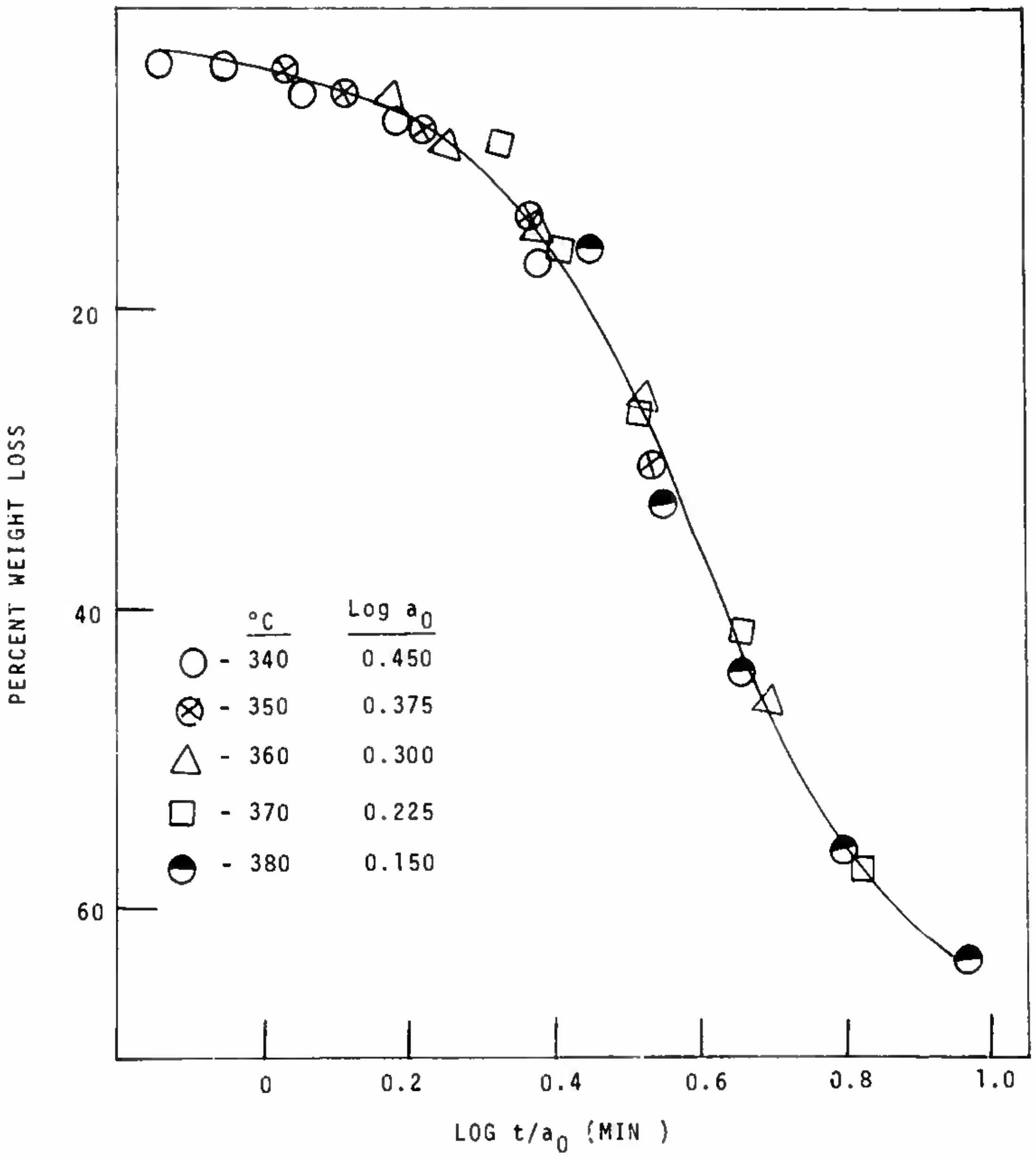


Fig 12 Master curve of weight loss versus reduced time for halogenated 6F. Constructed from Fig 11 using the log a_D Terms on the graph

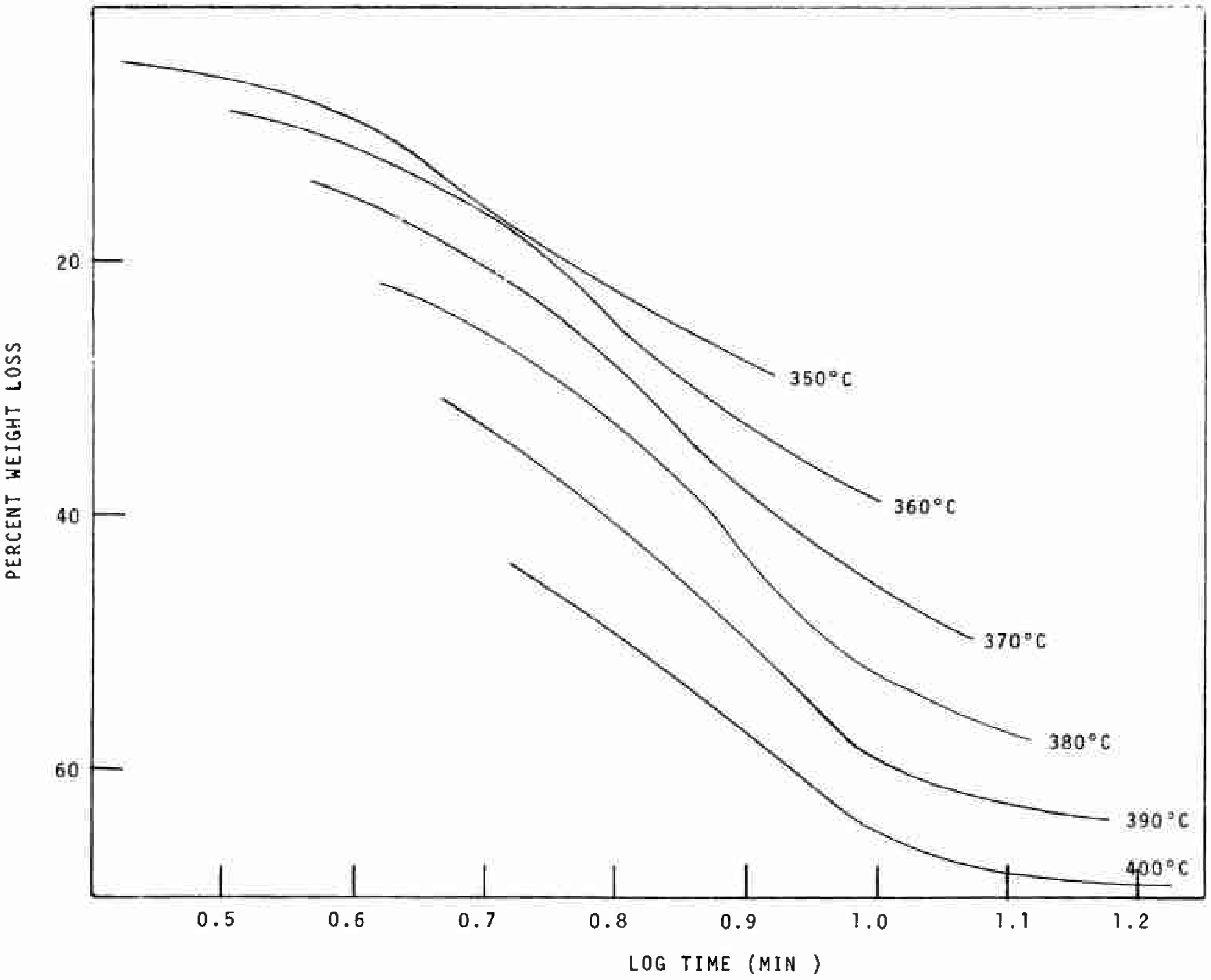


Fig 13 Weight loss of Undecyl (HMDA cured) as a function of time

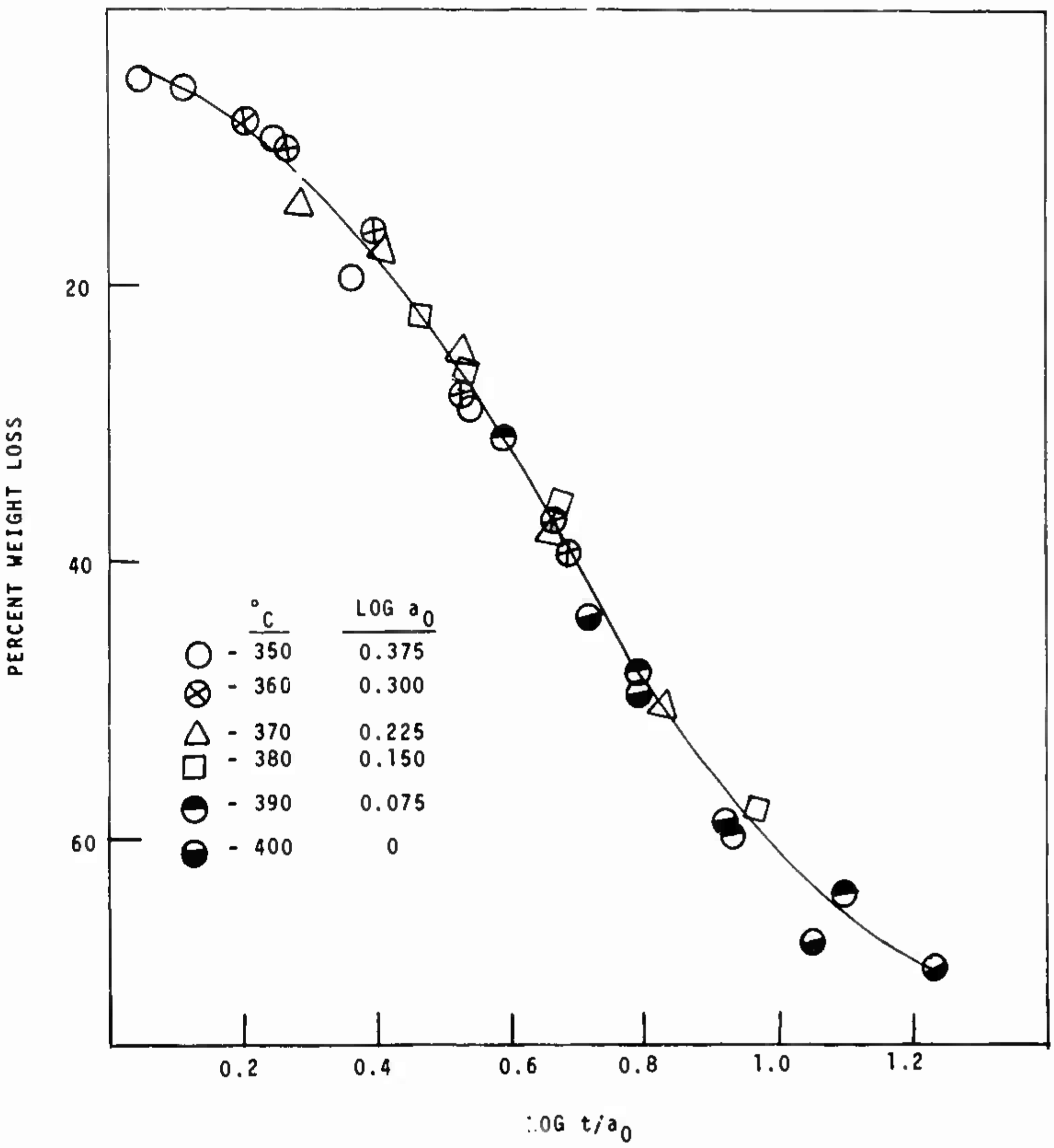


Fig 14 Master curve of weight loss versus reduced time for HMDA cured Undecyl. Constructed from Fig 13 using the log a_D terms on the graph

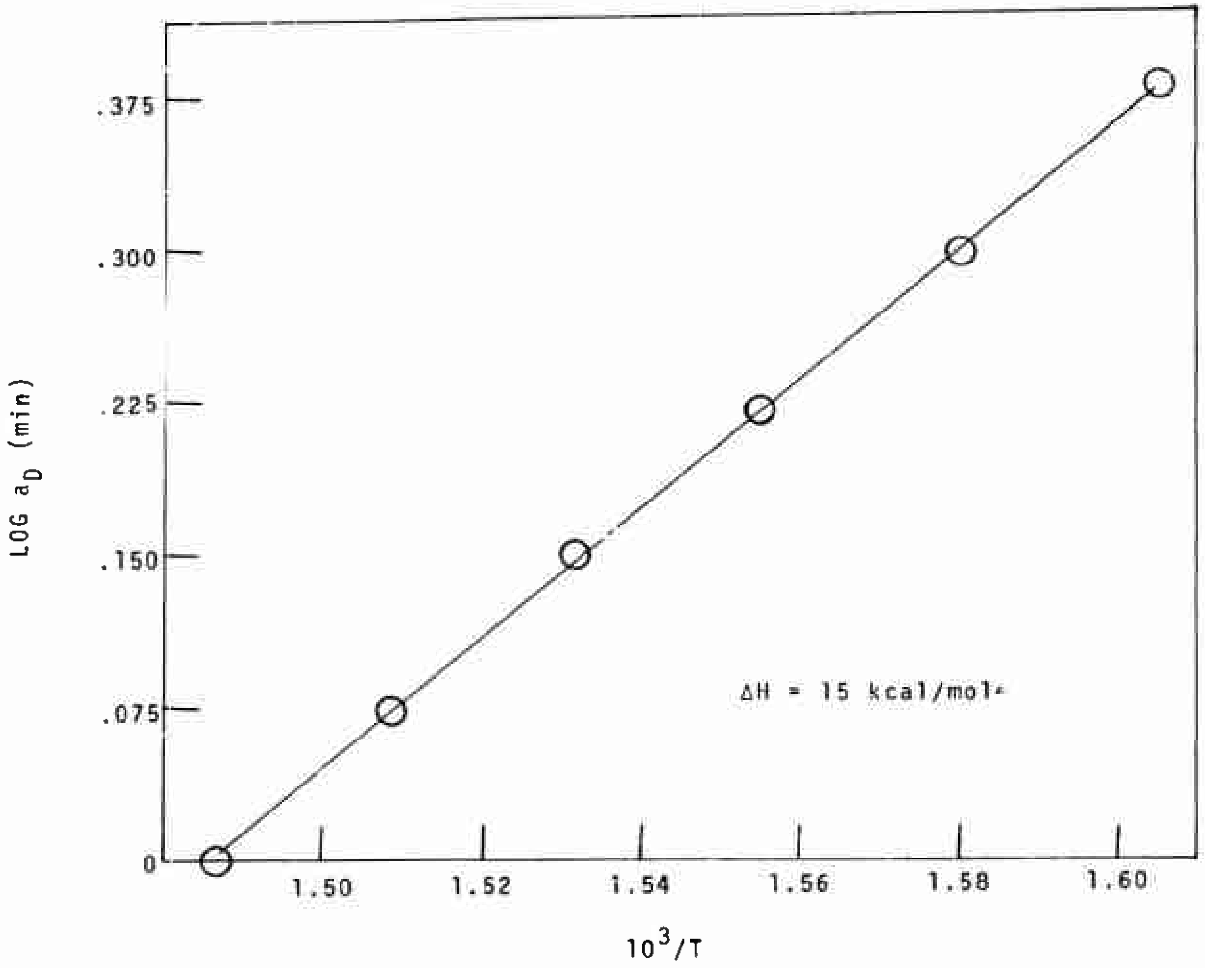


Fig 15 Arrhenius plot of shift factors for determination o. activation energy

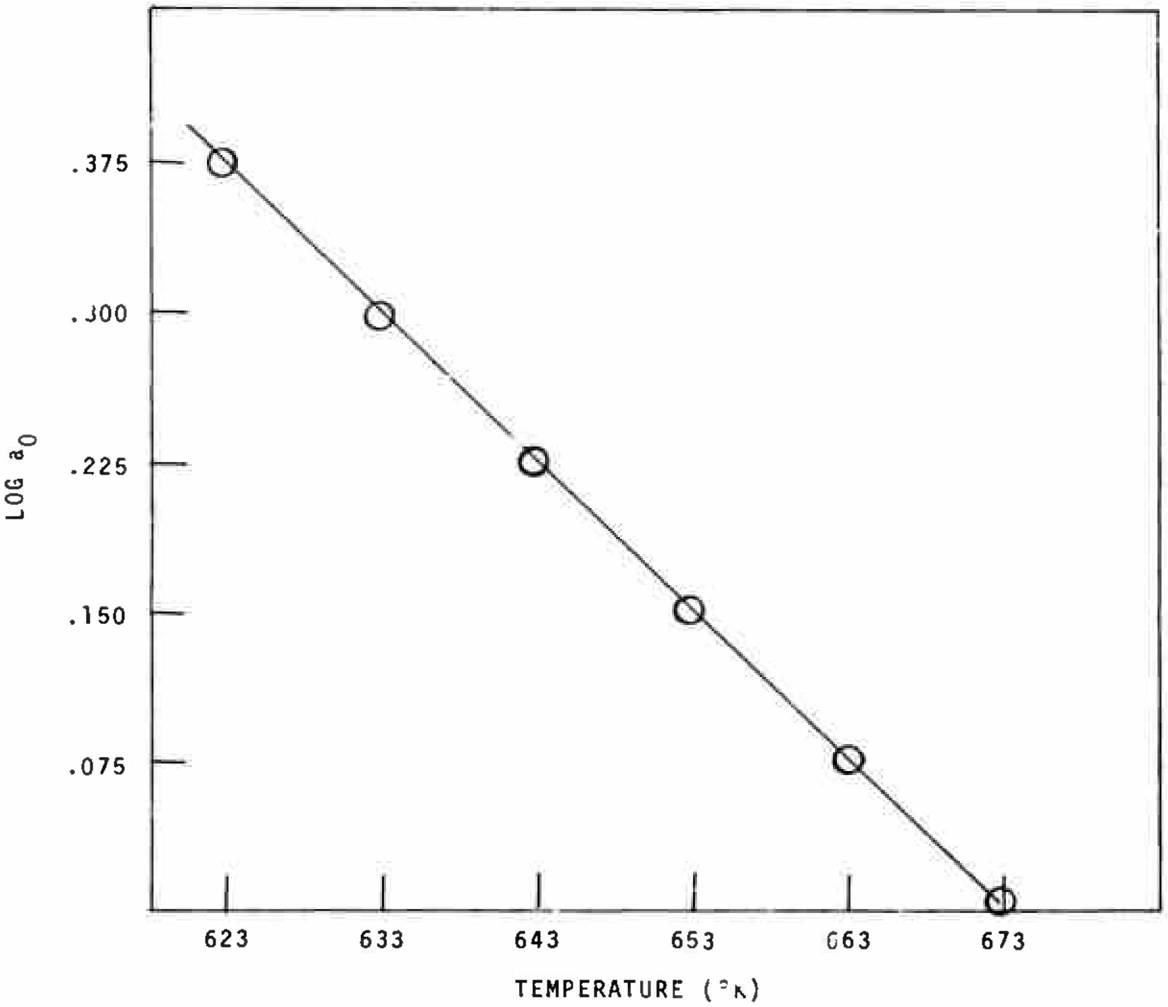


Fig 16 Shift factors versus temperature for the cured epoxide resins

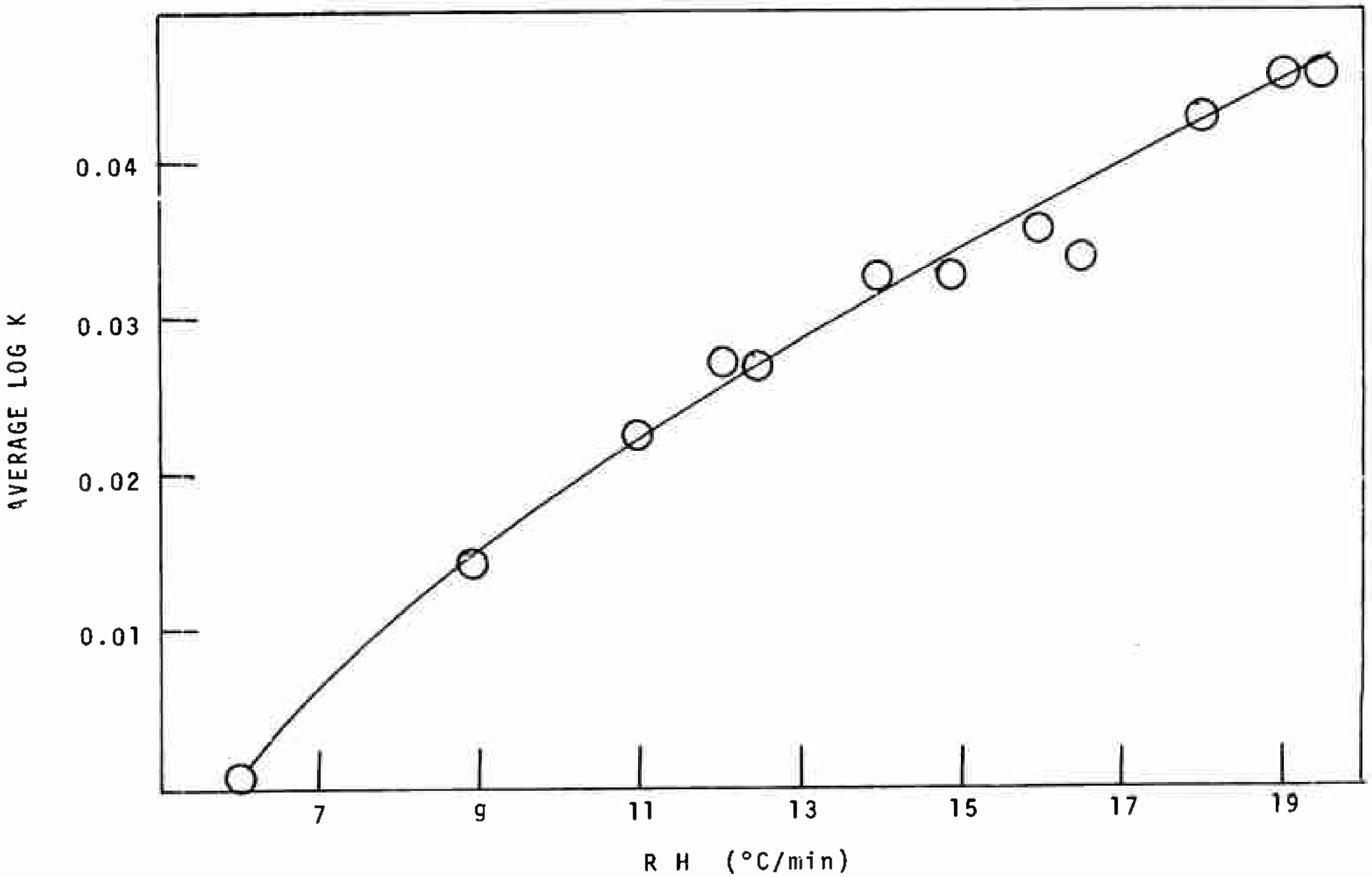


Fig 17 Shift factor versus rate of heating

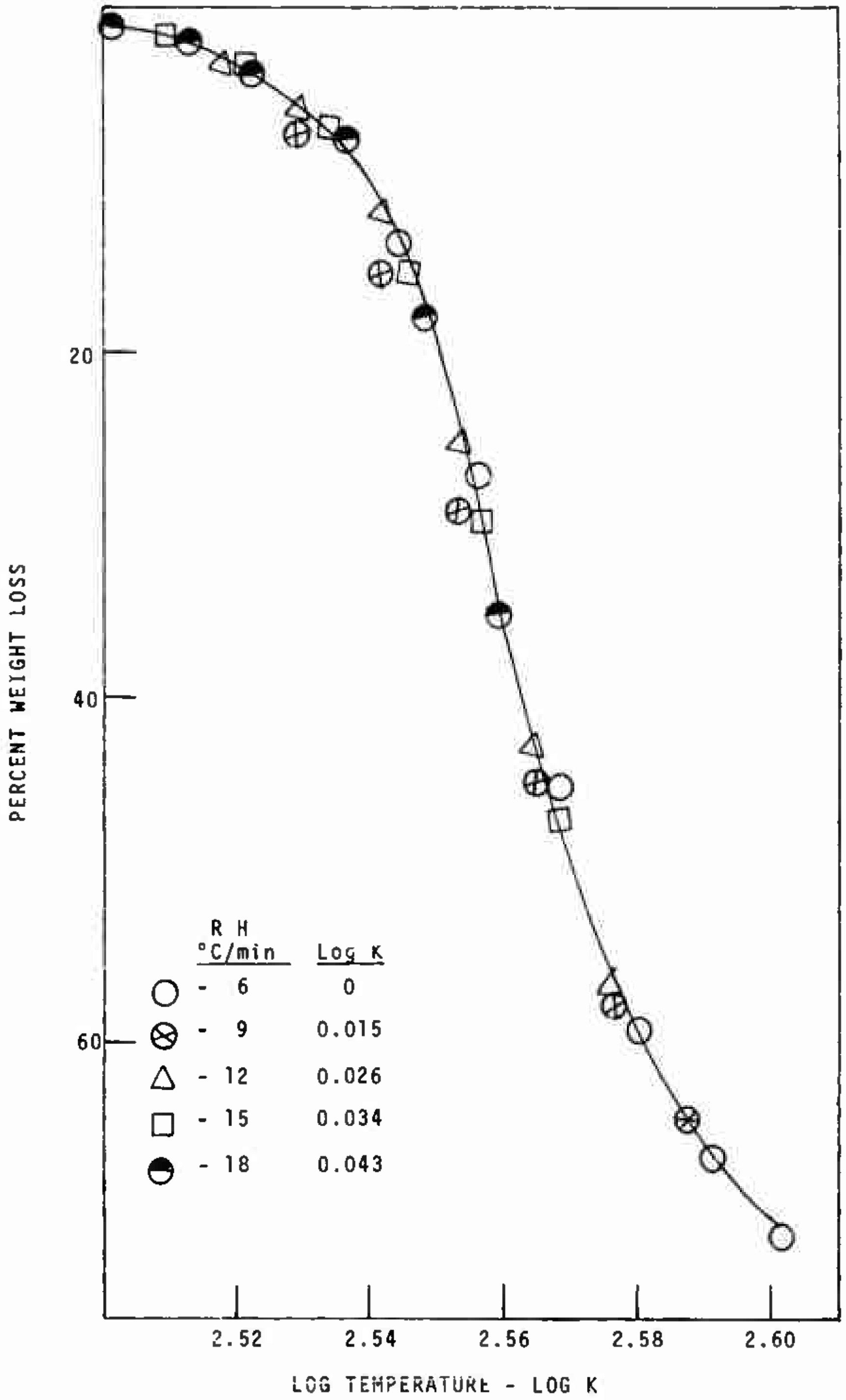


Fig 18 Master curve of weight loss versus temperature for DER 332

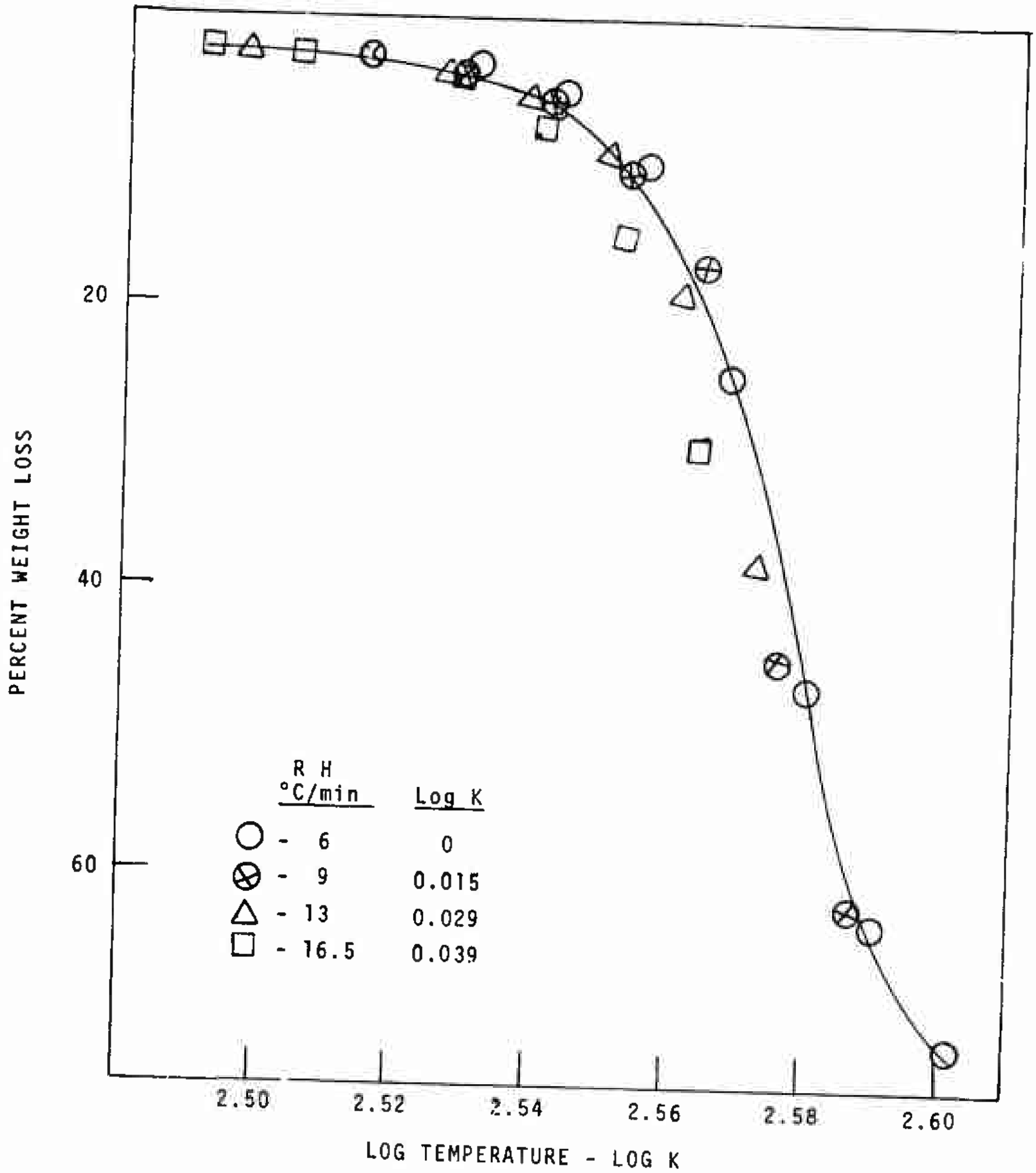


Fig 19 Master curve of weight loss versus temperature for Epon 820

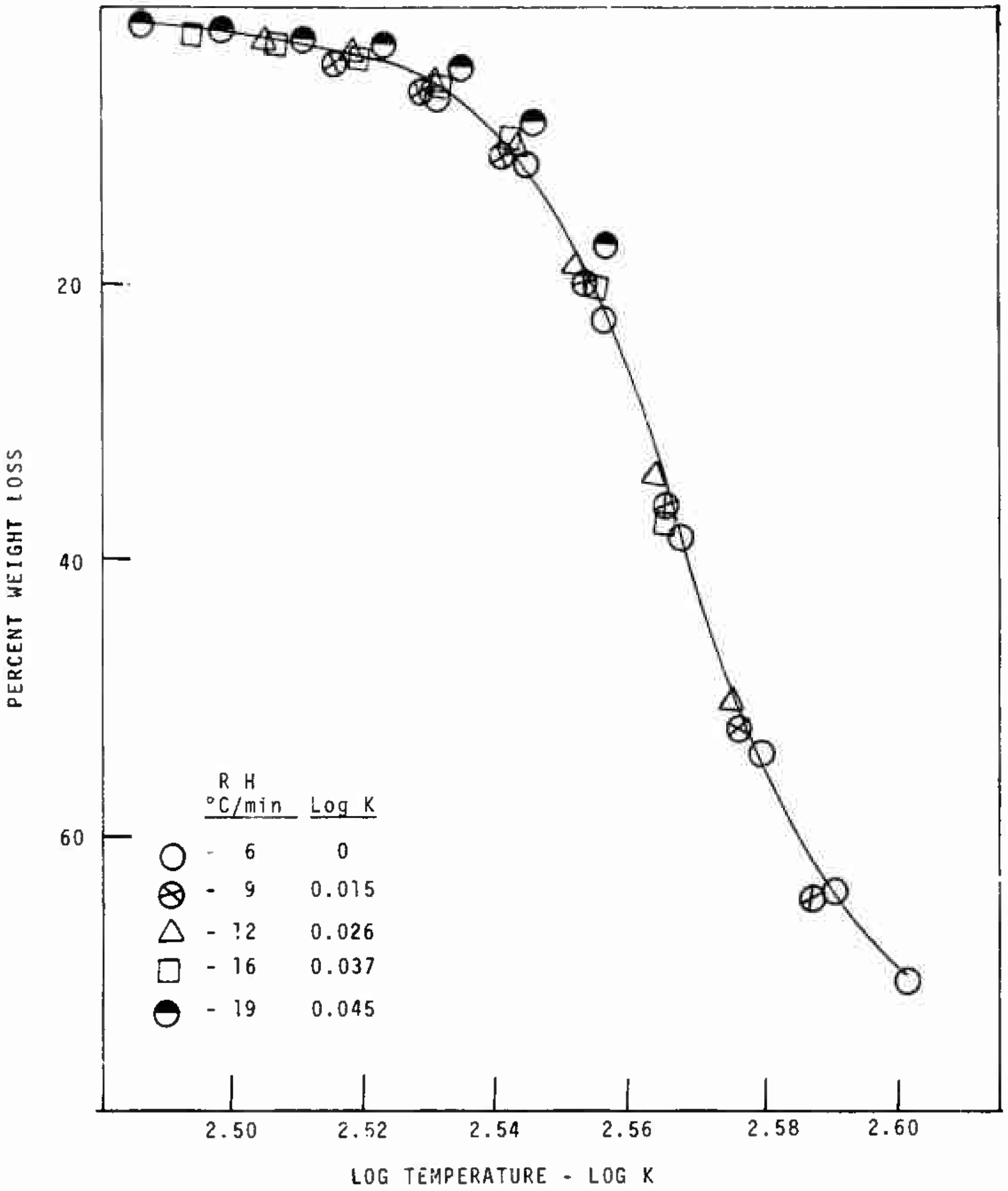


Fig 20 Master curve of weight loss versus temperature for Heptyl

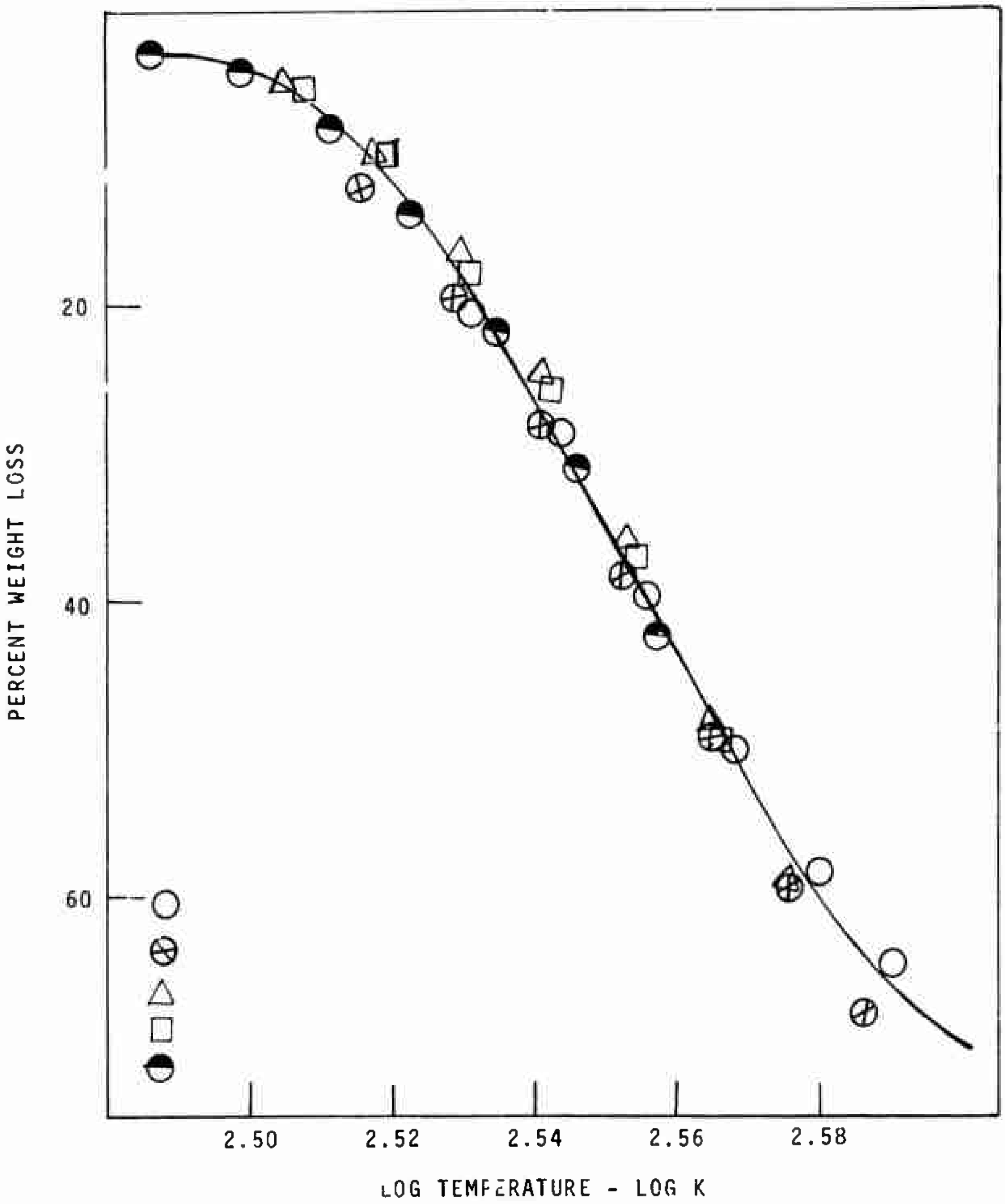


Fig 21 Master curve of weight loss versus temperature for Undecyl

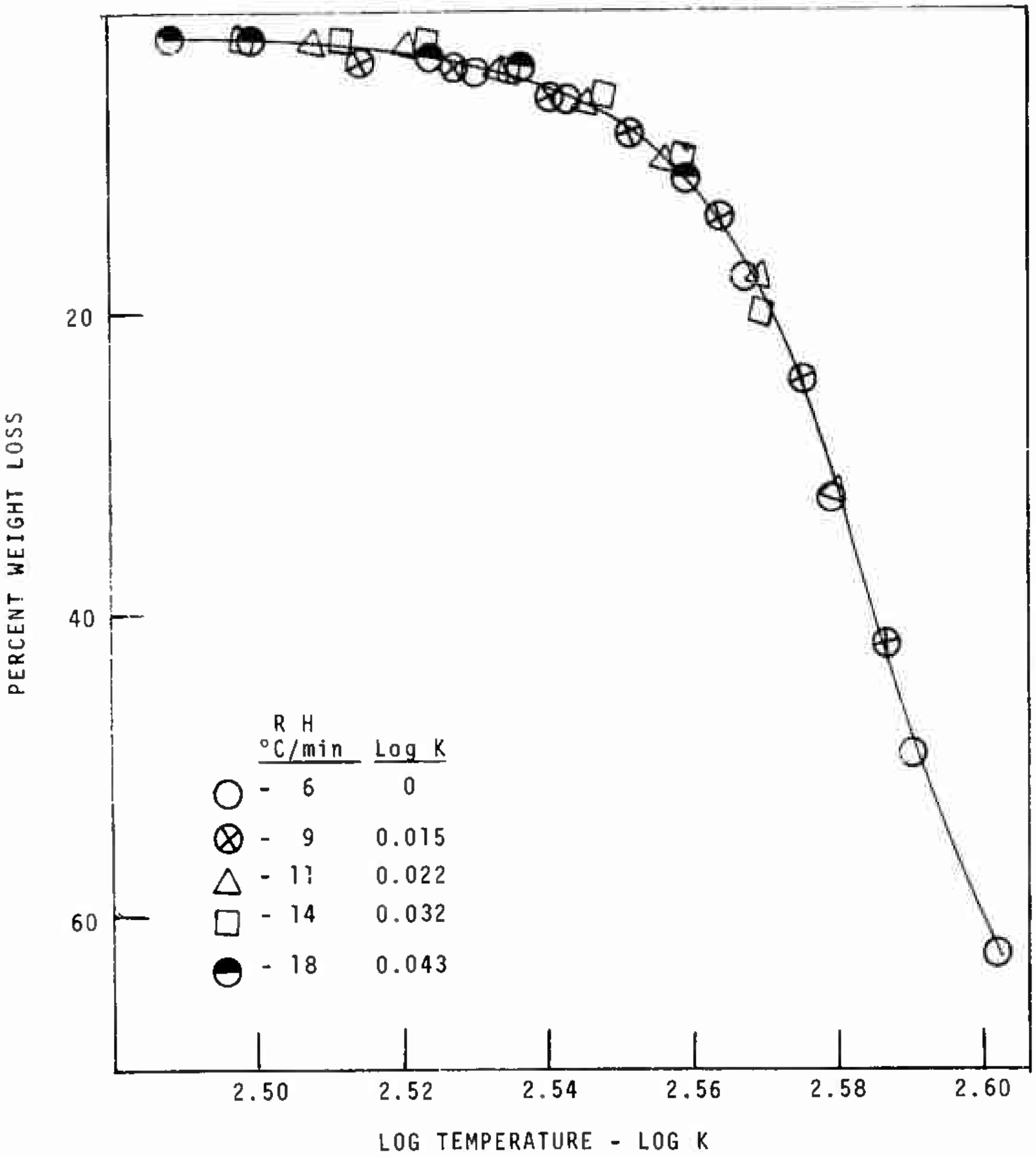


Fig 22 Master curve of weight loss versus temperature for Pentadecyl

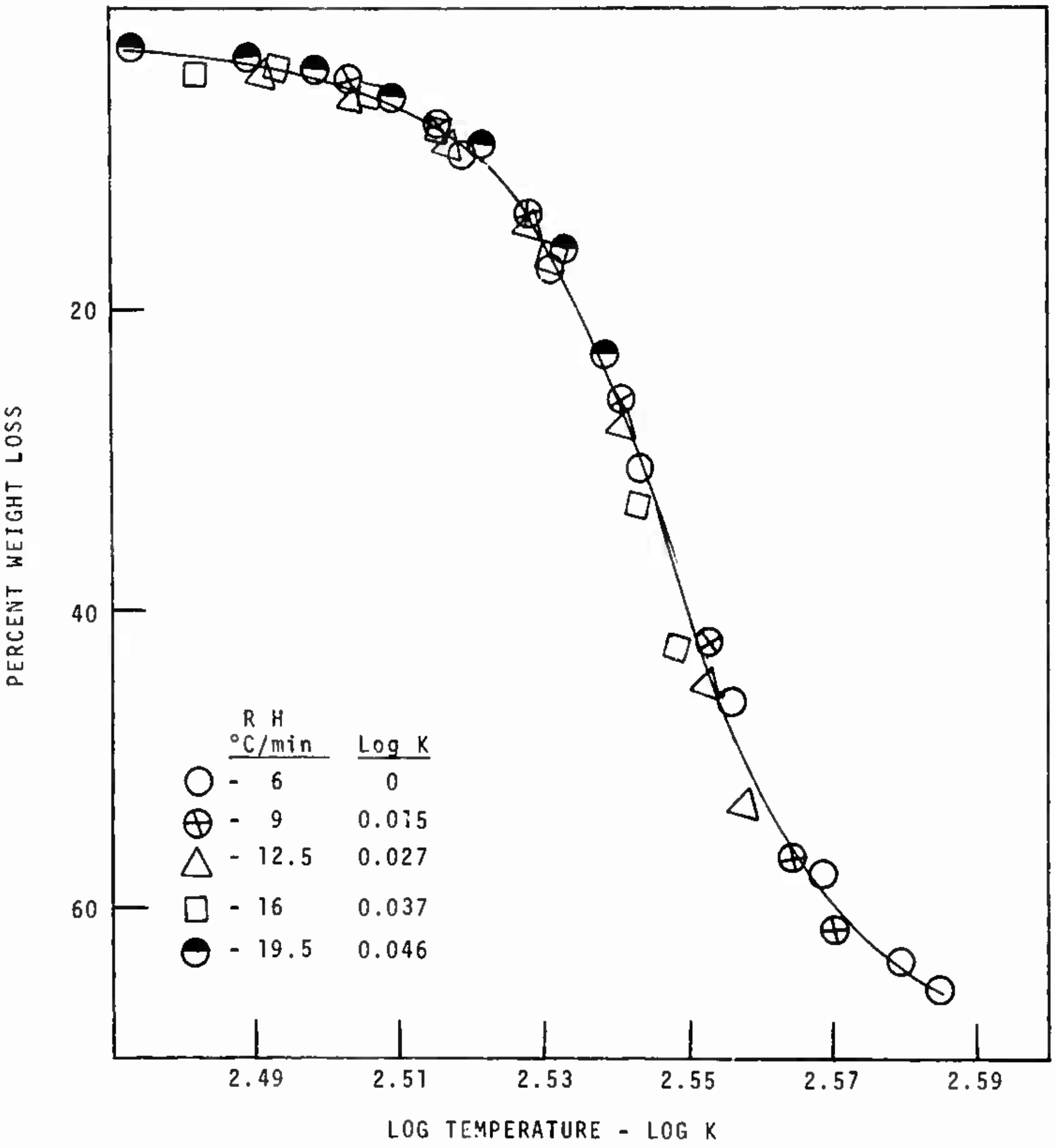


Fig 23 Master curve of weight loss versus temperature for halogenated 6F

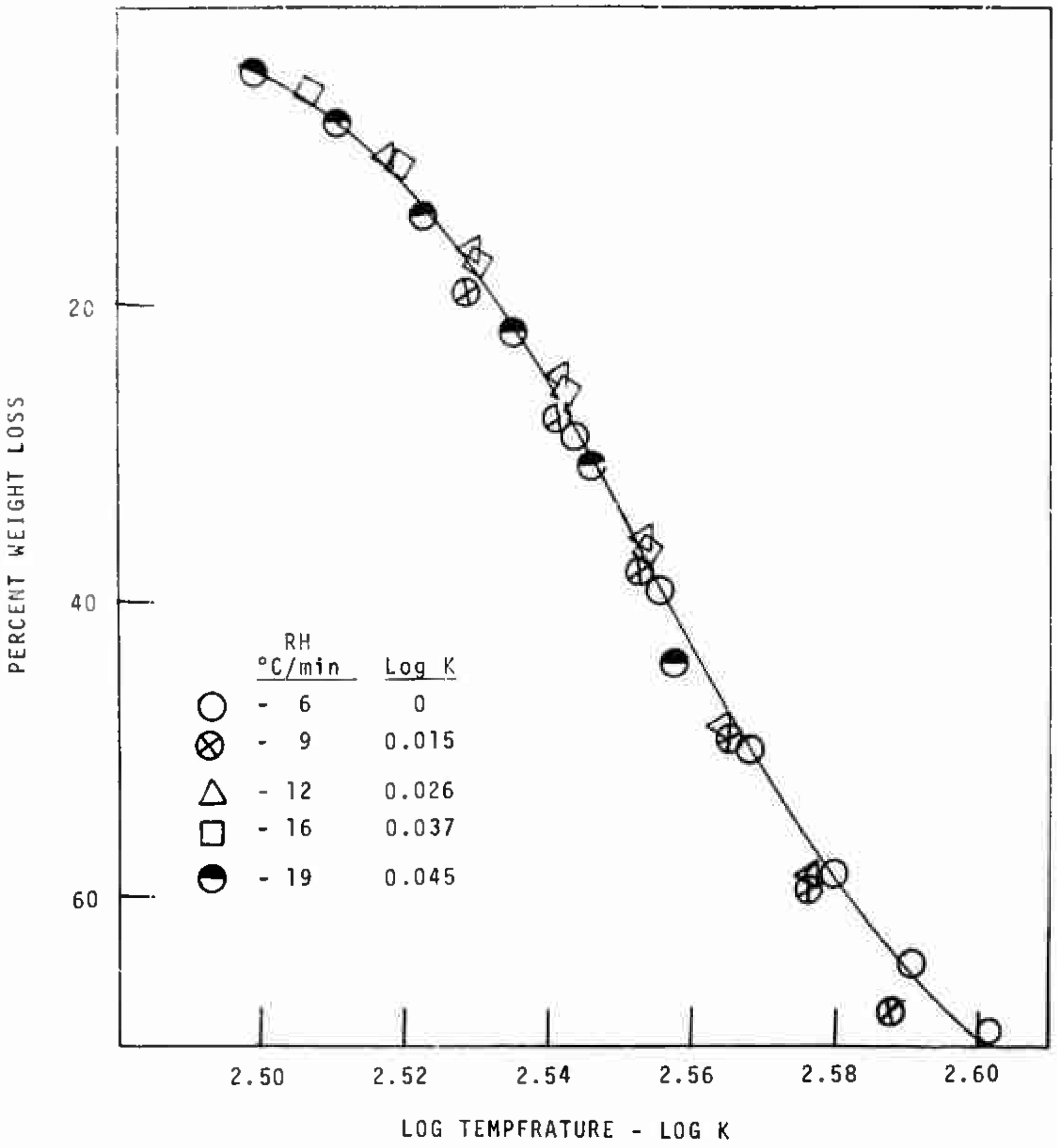


Fig 24 Master curve of weight loss versus temperature for HMDA cured Undecyl