

## Prediction of Polymer Degradation Kinetics at Moderate Temperatures from TGA Measurements

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### Synopsis

Thermal degradation under vacuum, as measured by weight loss of polymer, has been studied for a variety of polymers and composites. Small-sample ( $\sim 10$  mg) TGA studies have been made on polymeric materials. Isothermal studies, at much lower temperatures, have been made on the same materials of much larger size and weight (4-6 g). Comparison of the results shows that TGA can accurately predict the isothermal kinetics.

### INTRODUCTION

In many practical instances it is of importance to know the kinetics of polymer degradation at quite moderate temperatures. Thermal degradation of a polymer, even if very slow at moderate temperatures, can lead to failure, for example, of a structural plastic. Therefore, it is of considerable interest if studies at high temperatures, where kinetics are rapid, can be used to correctly predict kinetics at much lower temperatures. If many materials require investigation, time and money become prohibitive and very short-time test methods are a necessity. One high-temperature, short-time data acquisition method is thermogravimetric analysis (TGA), which requires only an hour or so of testing time. In this method, a small amount of polymer is taken through total decomposition by increasing the temperature on the sample at a predetermined rate (e.g.,  $10^\circ\text{C}/\text{min}$ ). From the data obtained one may determine rate constants and activation energies for the decomposition. The purpose of the present communication is to demonstrate that TGA results can be extrapolated to much lower temperatures in order to obtain thermal degradation (as measured by weight loss) near normal-use temperatures of samples of realistic size and weight.

A preliminary account of this study was presented earlier.<sup>1</sup> Here, the work has been extended to a variety of materials including filled polymers. The analysis method reveals details of decomposition not readily distinguished by isothermal methods.

### EXPERIMENTAL

All measurements were made under vacuum. Thermal degradation or decomposition is measured as weight loss of polymer.

The TGA measurements were made with a Mettler Thermoanalyzer I which had a DTG (TGA derivative) output and a vacuum capability. The system has been described elsewhere.<sup>2</sup> The sample size was always  $\sim 10$  mg obtained by cutting it from a larger piece of material which is then used for the isothermal study. The heating rate was  $10^\circ\text{C}/\text{min}$ , except for Dacron as noted in the text below. Before start of heating, the instrument was evacuated to about  $5 \times 10^{-6}$  torr.

The isothermal weight loss measurements were made in a system designed in this laboratory. It consisted of furnace and controller, ion pump, appropriate valving and vacuum gauges, and a Ainsworth recording semimicro vacuum balance. Two thermocouples were in the vacuum space near the sample under study. One thermocouple was embedded in another piece of the material under study for a sample temperature reference. There was no difference in temperature between thermocouples. Sample weights used in this system were about 4–6 g. Sample sizes were about  $1/16$ – $1/8 \times 1/2$ – $3/4 \times 2$ –4 in. in size, except for Dacron which was a piece of parachute cloth. After the system was evacuated to about  $5 \times 10^{-6}$  torr, the heating was started. The weight loss was recorded for about 12 hr at each temperature.

The simple first-order kinetic equation

$$k_T = \frac{dx/dt}{(a_0 - x)} \quad (1)$$

has been found to be very adequate for describing the weight loss. In this equation,  $k_T$  is the rate constant at temperature  $T$ ,  $dx/dt$  is the rate of weight loss,  $x$  is the weight loss, and  $a_0$  is the initial amount of the "active component." The active component is that portion of the original weight of sample which participates in decomposition. For decompositions with a simple TGA curve, the active component is taken as the total weight loss. For polymers where the TGA curve shows more than one step in the decomposition, the initial weight of an active component ( $a_0$ ) is taken as that portion of sample weight participating in the step. For example, Figure 1 shows the TGA curve for Dow Corning Silicone 6-1106; it is apparent that

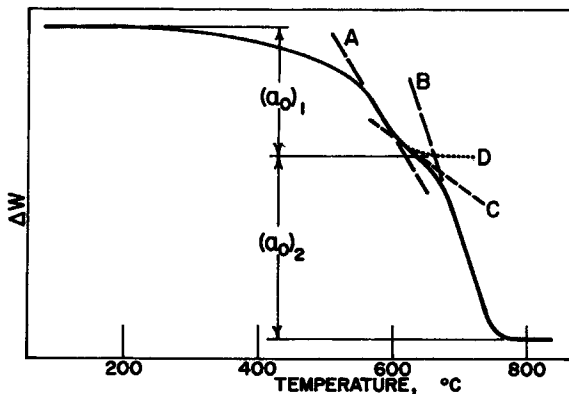


Fig. 1. TGA curve for Dow Corning Silicone 6-1106 showing method of analysis (see text).

the degradation is not simple. In order to obtain  $(a_0)_1$  for the first step, the TGA can be repeated at a much slower heating rate so as to expand the time scale in the region between the two steps. Alternatively, if the slopes A, B, and C are drawn as in Figure 1 and half the length of C, where it intersects A and B, is taken as the decomposition in step 1 (as depicted by the dotted curve D), a very good estimate of  $(a_0)_1$  can be made. Then  $(a_0)_2$ , the active component for step 2, is the difference between the total weight loss and  $(a_0)_1$ . In utilizing eq. (1), the thermoanalyzer yields  $dx/dt$  from the DTG output,  $x$  is obtained from the TGA, and  $a_0$  is as described. For the isothermal measurements,  $dx/dt$  is obtained from the slope of the weight loss curve near the end of a run at temperature,  $x$  is obtained from the weight loss curve, and  $a_0$  is taken as the fraction of original sample weight as determined by the TGA analysis above.

Figure 2 shows the Arrhenius relationship obtained for the first step of decomposition for the silicone depicted in Figure 1. The points in Figure 2 are representative of the very large number of data points available from the TGA-DTG output of the thermoanalyzer. The larger slope is the activation energy for the decomposition of the polymer associated with  $(a_0)_1$ . The smaller slope is the result of degassing of "solvent" such as unreacted monomer, catalyst, etc. This slope appears because at the lower temperatures of the TGA the weight loss,  $x$ , in eq. (1) is predominately "solvent" loss, whereas,  $a_0$  is for the polymer itself since there is no way of obtaining an  $a_0$  for the "solvent" from the TGA curve. The amount of "solvent" is so small with respect to the amount of polymer that it does not affect  $a_0$  for the polymer degradation. Thus, when the "solvent" is degassed during the

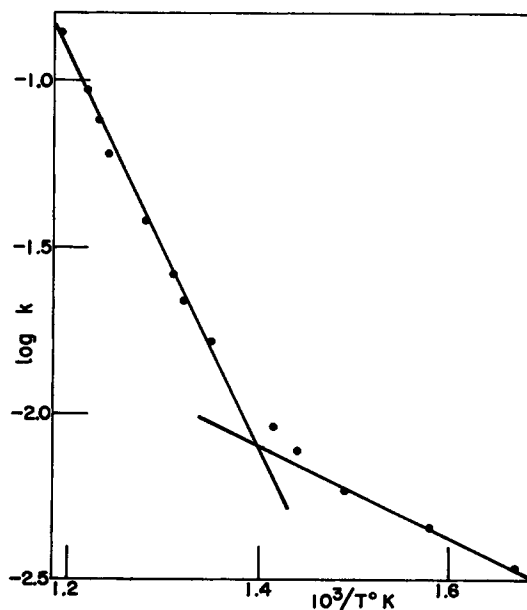


Fig. 2. Arrhenius relationship from TGA curve for decomposition over  $(a_0)_1$  in Fig. 1.

early stages of an experiment, the Arrhenius relationship reverts to the correct one for the polymer itself. This is verified by the results below.

As a check on the TGA method outlined, the activation energy determined for Teflon is 82.5 kcal/mole, and Madorsky<sup>3</sup> gives 80.5 kcal/mole for the thermal decomposition under vacuum.

## RESULTS

Some typical results on a variety of different materials are presented here.

Since it is of importance to predict kinetics at much lower temperatures than those at TGA temperatures, only the first step of a multiple step decomposition is of interest. Figure 3 is a comparison between the TGA

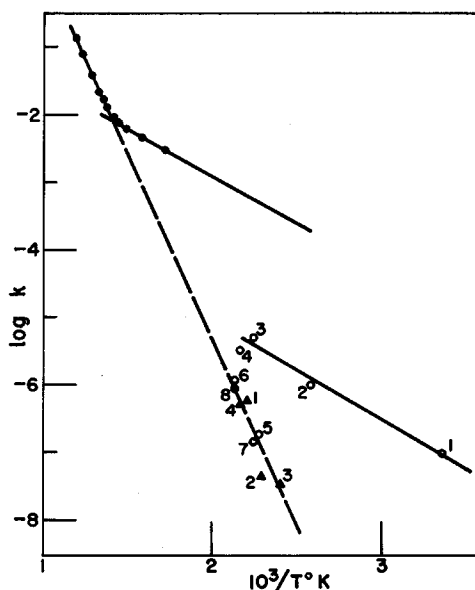


Fig. 3. Arrhenius relationships comparing TGA and isothermal results for Dow Corning Silicone 6-1106. Solid circles: TGA results of Fig. 2; open circles and triangles: isothermal results. See text for numbering sequence.

results of Figure 2 and isothermal measurements at much lower temperatures. The solid circles are the results from Figure 2. The open circles are isothermal results where the temperature of the sample is increased periodically from ambient to about 200°C. The triangles are isothermal results on another sample where the temperature is decreased periodically from about 200°C to ambient. With the increasing temperature sequence, an activation energy type slope is found for the "solvent." However, with the decreasing temperature sequence, the "solvent" is removed rapidly during the initial portion of the weight loss curve for point 1; therefore, no "solvent" points are observed. It can be seen that for the degradation of the silicone itself the rate constant at much lower temperatures is accurately predicted by the TGA results.

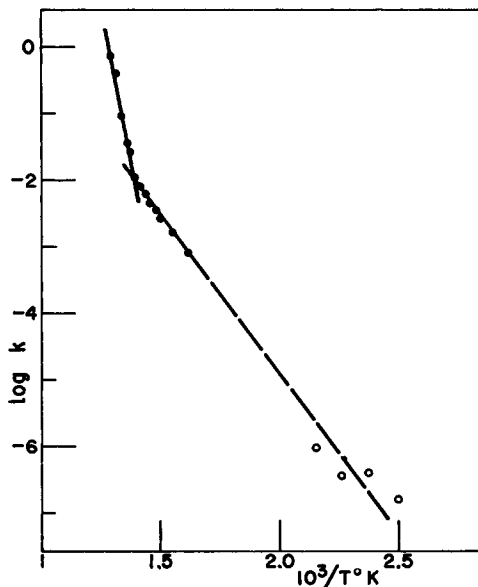


Fig. 4. Arrhenius relationships comparing TGA and isothermal results for Viton A. Solid circles: TGA results; open circles: isothermal results.

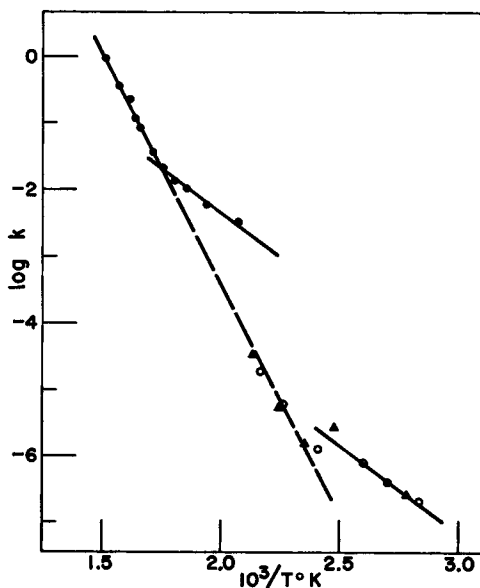


Fig. 5. Arrhenius relationships comparing TGA and isothermal results for an epoxy (Shell Epon 828). Solid circles: TGA results; open circles and triangles: isothermal results.

Figure 4 shows the Arrhenius relationship comparison for Viton A. The TGA yields two activation energies—the higher temperature having a  $\Delta E = 85$  kcal and the lower temperature region, a  $\Delta E = 25.6$  kcal. It can be seen that the rate constants associated with the smaller activation energy

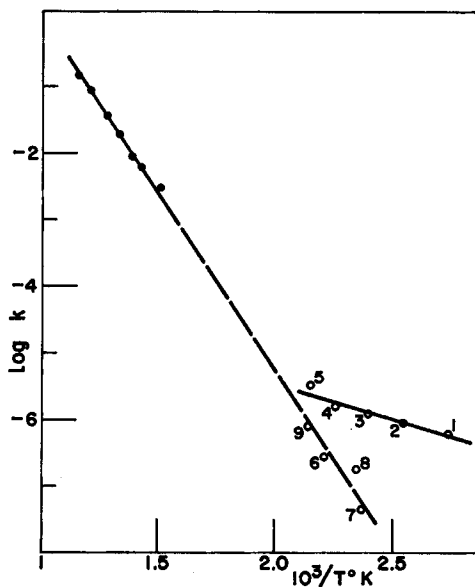


Fig. 6. Arrhenius relationships comparing TGA and isothermal results for a heavily filled silicone (Choseal). Solid circles: TGA results; open circles: isothermal results. Numbering indicates temperature sequence.

obtained from the TGA analysis are accurately extrapolated to those obtained from the isothermal measurements at the lower temperatures.

Figure 5 shows the results for the epoxy Shell Epon 828. The analysis is similar to that for Figure 1;  $(a_0)_1$  is 76% of the total sample weight. The data point at the highest temperature represents 68% decomposition of the total sample weight and 90% of  $(a_0)_1$ . The activation energy for this step is 30.8 kcal. Both isothermal runs depicted in the figure are with an increasing temperature sequence. The excellent prediction by the TGA is evident.

Figure 6 shows the results for a silicone (Choseal) heavily filled with silver. The TGA curve showed a simple one-step decomposition with  $a_0 = 18.8\%$  of the total sample weight. Thus, this silicone is very nearly filled with about 80% silver. For the TGA analysis there is so little silicone ( $\sim 0.19 \times 10 \text{ mg} \approx 1.9 \text{ mg}$ ) that "solvent" evolution is not apparent. However, with the much larger sample weight (6.424 g) for the isothermal study a "solvent" evolution is obtained. The activation energy for the decomposition of the polymer is 24.0 kcal. The figure shows that even with a heavily filled material that there is no difficulty in predicting the kinetics at moderate temperatures from TGA analysis.

Figure 7 shows the results for a glass-filled diallyl phthalate. From the TGA curve the active component  $a_0$  was found to be 43.6% of the total sample weight. The activation energy for decomposition of this diallyl phthalate is 24.1 kcal. Again, for this heavily filled material there is no difficulty in predicting moderate temperature rate constants from TGA analysis.

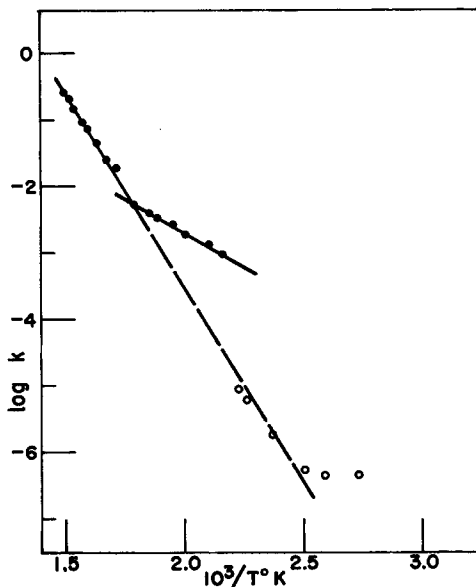


Fig. 7. Arrhenius relationships comparing TGA and isothermal results for a glass-filled diallyl phthalate. Solid circles: TGA results; open circles: isothermal results.

Figure 8 shows the TGA/isothermal comparison for Dacron. As with Viton A, there is no "solvent" evolution either in the TGA or isothermal studies. The activation energy over the higher temperature region is 48.3 kcal, and over the lower temperature region it is 26.5 kcal. Madorsky<sup>3</sup> gives one value of 38 kcal over the range of 336–356°C. This range is delineated by the two vertical lines in the lower left portion of the figure. It can be seen that for this rather small temperature range one would obtain isothermally an intermediate value of the two activation energies. In fact, the average of the two values determined here is 37.4 kcal. Figure 8 shows that an excellent extrapolation from the TGA can be made to the much larger sample (3.940 g) at a much lower temperature.

## DISCUSSION

It is rather remarkable that with an enormous increase in sample weight and size and with temperature extrapolations of over 200°C such accurate predictions of rate constants can be made from TGA measurements. Of course, the TGA has the distinct advantage of yielding the active component  $a_0$  for a decomposition which permits utilization of eq. (1).

With a rate constant for near normal-use temperatures predicted by TGA, the amount of degradation or weight loss may be determined by standard kinetic methods. Integration of eq. (1) yields

$$a_0 - x = a_0 e^{-kt} \quad (2)$$

or

$$\frac{a_0 - x}{a_0} = e^{-kt} = \text{fraction remaining.} \quad (3)$$

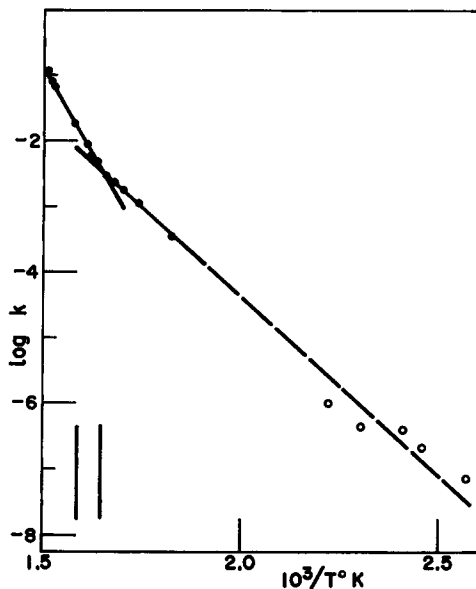


Fig. 8. Arrhenius relationships comparing TGA and isothermal results for Dacron. Solid circles: TGA results; open circles: isothermal results.

Alternatively, if the per cent weight loss is desired,

$$(1 - e^{-kt}) \times 100 = \% \text{ weight loss.}$$

Information obtained from TGA may also be used to make good estimates of degassing time near normal-use temperatures for "solvent." Throughout the course of this study it has been observed that the Arrhenius-type slope associated with the "solvent" measured isothermally is nearly identical with that obtained from TGA, but it is displaced to smaller values of  $k$  by a factor of  $10^{-2}$ . During a TGA, if the temperature rise is arrested where most of the weight loss is "solvent" and an isothermal weight loss is measured, one can estimate  $a_0$  for the "solvent" from the asymptote of the curve. Alternatively, one can apply the usual kinetic method by taking the log of eq. (2) and the intercept will yield  $a_0$  for the "solvent." From this  $a_0$  one can determine the fraction of sample weight in a realistically sized sample. Then multiplying by  $10^{-2}$  the  $k$  determined by TGA, substitution into either eq. (3) or (4) will yield degassing time of "solvent."

Clearly, TGA results may be scaled up to realistically sized samples and may be extrapolated to much lower temperatures.

### References

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3. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Wiley, New York, 1964, Table CLII, p. 303.

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