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Note

Prediction of polymer degradation kinetics at moderate temperatures from high temperature TG measurements

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INTRODUCTION

The time consumed in making isothermal degradation studies below 200 °C can be considerable for materials with moderately large activation energies. Therefore, it is of considerable interest if tests at high temperatures, where kinetics are rapid, can be used to predict the kinetics at much lower temperatures. The purpose of this communication is to present some results comparing isothermal kinetic studies of polymer degradation with thermogravimetric analysis (TG) measurements; both studies being made under vacuum.

EXPERIMENTAL AND RESULTS

The TG measurements were made on a Mettler Thermoanalyzer I which had a DTG (TG derivative) output and a vacuum capability. The system has been described elsewhere[1]. The sample size was about 10 mg and the heating rate was 10 °C/min. Before start of heating, the instrument was pumped to 5×10^{-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 an Ainsworth recording semi-micro vacuum balance. Sample weights used in this system were 5–6 g and 1/6–1/8 × 1/2–3/4 × 2–4 in. in size. The system was maintained at 5×10^{-6} torr.

The simple first order kinetic equation

$$k = \frac{\mathrm{d}x/\mathrm{d}t}{(a-x)}$$

has been found to be very adequate in describing the decompositions. Fig. 1 shows the comparison between TG and isothermal measurements on Dow Corning Silicone 6-1106. The solid circles are TG results and are representative points from the very large number of data points available from the TG–DTG output of the thermoanalyzer. The open circles are isothermal results where the temperature of the sample is varied from ambient to about 200 °C, each point representing about 12 h of test. The triangles are isothermal results on another sample where the temperature is decreased from about 200 °C. The isothermal points are calculated from the slope of

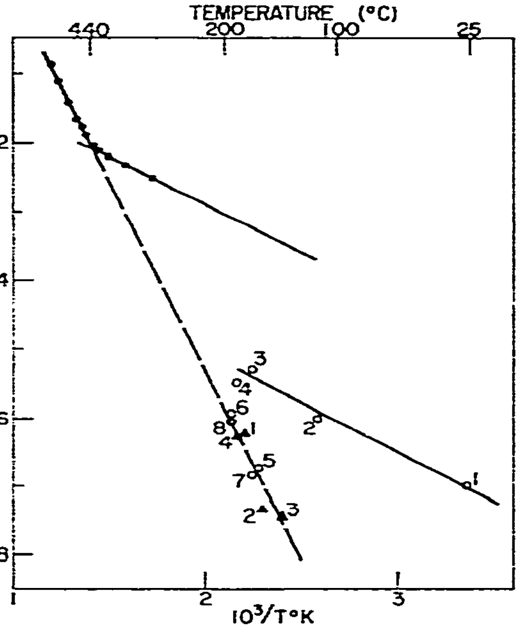

Fig. 1. Arrhenius relationships comparing TG and isothermal results. TG: ●—●; Isothermal: ○—○, increasing temperature on sample; ▲—▲ decreasing temperature on another sample; numbers indicate sequence in temperature increase or decrease. Material, Dow Corning Silicone 6-1106.

the weight loss curve near the end of the run at temperature. The small activation energy (4.3 kcal) is associated with the evolution of "solvent" such as catalyst, monomer, etc., and the larger activation energy (26.4 kcal) is associated with the thermal decomposition of the polymer. It may be seen that both activation energy and frequency factor for the isothermal decomposition of the polymer is given accurately by the TG.

With the increasing temperature sequence (circles in Fig. 1) of the isothermal tests, an activation energy (4.4 kcal) is found for the "solvent". With the decreasing temperature sequence (triangles in Fig. 1), the "solvent" is removed rapidly during the initial portion of the weight loss curve for point 1; therefore, no activation energy for the "solvent" is found. Other materials, including filled polymers, have also been studied. With some there is no relationship between the isothermal and TG results for the "solvent", but in all cases studied to date, the activation energy and frequency factor for the decomposition of the polymer itself are given very accurately by the TG.

It is rather remarkable that with an enormous increase in sample weight and size, and with a temperature extrapolation of over 200 °C, such predictions of the rate constant can be made from TG measurements.

Studies are continuing and will be reported in detail later.

REFERENCE

1 H. A. Papazian, P. J. Pizzolato, and J. A. Patrick, *J. Amer. Ceram. Soc.*, 54 (1971) 250.