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Kinetic Parameters from Thermogravimetric Analysis

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Introduction

High performance polymeric materials are finding increased use in aerospace applications. Proposed high speed aircraft will require materials to withstand high temperatures in an oxidative atmosphere for long periods of time. It is essential that accurate estimates be made of the performance of these materials at the given conditions of temperature and time. Temperatures of 350° F (177° C) and times of 60,000 to 100,000 hours are anticipated. In order to survey a large number of high performance polymeric materials on a reasonable time scale, some form of accelerated testing must be performed.

A knowledge of the rate of a process can be used to predict the lifetime of that process. Thermogravimetric analysis (TGA) has frequently been used to determine kinetic information for degradation reactions in polymeric materials. Flynn and Wall studied a number of methods for using TGA experiments to determine kinetic information in polymer reactions.[1] Figure 1 shows a typical TGA graph with the mass and the derivative plotted against the temperature. Kinetic parameters, such as the apparent activation energy and the frequency factor, can be determined in such experiments. Recently, researchers at the McDonnell Douglas Research Laboratory suggested that a graph of the logarithm of the frequency factor against the apparent activation energy can be used to predict long-term thermo-oxidative stability for polymeric materials[2]. Such a graph has been called a kinetic map. In this study, thermogravimetric analyses were performed in air to study the thermo-oxidative degradation of several high performance polymers and to plot their kinetic parameters on a kinetic map.

Kinetic Map

The kinetic map, shown in Figure 2, assumes that the reactions involved follow first order kinetics and the Arrhenius reaction model. The solid lines, called aging limits, serve as benchmarks against which the experimental values are compared. For a first order reaction,

$$\frac{dV(t)}{dt} = -kV(t)$$

where V(t) is the concentration of the reacting specie at time, t, and k is the rate

$$k_o = \frac{\ln(\frac{V}{V_o})}{-t} e^{\frac{E}{RT}}$$

where V_o is the initial concentration. Now, one can pick a specific reaction temperature, T, a fraction of conversion or degradation of the polymer, and the time, t, required to reach that conversion. The upper line in Figure 2 assumes a fractional conversion of 0.01, i.e., $V/V_o = 0.99$, a temperature, T, of 450 K (350° F), and a time, t, of 60,000 hours. Values of k_o are calculated for several reasonable values of E, and the line is drawn. The lower line assumes room temperature with the other parameters the same.

Experimental

The kinetic parameters were determined by running dynamic TGA experiments for each material studied at 6 different heating rates, 1, 2, 4, 8, 10, and 15° C/min. It has been shown that the derivative of the mass loss curve as a function of temperature during a TGA experiment with a linear heating rate is[3]

$$\frac{dV}{dT} = \frac{k_o V_o}{m} \exp[-\frac{E}{RT} - \frac{k_o R T^2}{mE} e^{-\frac{E}{RT}}]$$

where m is the linear heating rate, and the other quantities are defined above. The derivative reaches a maximum during the rapid degradation of the material at high temperature, as seen in Figure 1. The temperature at which this occurs, T_{max}, can be determined by setting the second derivative to zero, i.e., $d^2V/dT^2 = 0$. Solving for k_o at this point gives

$$k_o = \frac{mE}{RT^2} e^{\frac{E}{RT}}$$

Plotting $\ln(m/T^2_{max})$ against $1/T_{max}$ yields a straight line with slope = $-E/R$, and intercept = $\ln(k_o R/E)$. Thus, both kinetic parameters are determined for such a graph.

The TGA experiments were performed on a Seiko TG/DTA 200 thermogravimetric analyzer. Several materials were analyzed: LaRC-IA, a polyimide developed in the Polymeric Materials Branch at the Langley Research Center; PETI, the same polyimide with a phenylethynl endcap and a composite, IM7/K3B, made with IM7 carbon fibers and K3B commercial thermoplastic. Two forms of PETI were analyzed, they differed in the number of mass units of oligomer between endcaps. One had 9000, the other had 6000, and they are specified below as PETI-9 and PETI-6. The LaRC-IA and PETI samples were obtained as powders and were used as received. The composite was ground to a powder fine enough to pass through an 80 mesh screen. Dry ice was ground with the composite to prevent heat buildup during the grinding process. The powder was dried overnight in a vacuum oven.

Data from the TG analyzer were transferred to a personal computer for smoothing and analysis. Values of T_{max} for a specific sample were determined for each heating rate. The slope of the line on the ln(heat rate/T^2_{max}) vs $1/T_{max}$ plot was determined by a linear least squares analysis. The results are tabulated in Table 1, and plotted on Figure 2.

In theory, materials whose kinetic parameters fall on or to the right of the upper aging line will suffer no more than 1% degradation during 60,000 hours at 350° F. On this basis, the composite, IM7/K3B, is apparently the best of the materials tested. However, it is the only composite material used. A better comparison with the other materials would be with the pure K3B resin. At best, kinetic mapping can only serve as a preliminary screening for materials. Aging tests must still be done though the kinetic map could eliminate some materials before such tests.

References

1. Flynn, J. H. and Wall, L. A., "General Treatment of the Thermogravimetry of Polymers", *J. Res. NBS-A*, **70A**, 487 (1966).

2. Michael A. Grayson, McDonnell Douglas Research Laboratory, St Louis, MO, private communication.

3. K. H. van Heek, H. Juntgen, and W. Peters, *Berichte der Bunsengesellschaft fur Physikalische Chemie*, **71(1)**, 113, (1967).

Table 1

Kinetic Parameters of Several Materials

Material	E (kJ/mol	k_o (min^{-1})	log k_o
LaRC-IA	131	5.84×10^6	6.77
PETI-9	106	1.66×10^5	5.22
PETI-6	134	6.86×10^6	6.83
IM7/K3B	165	2.84×10^9	9.45

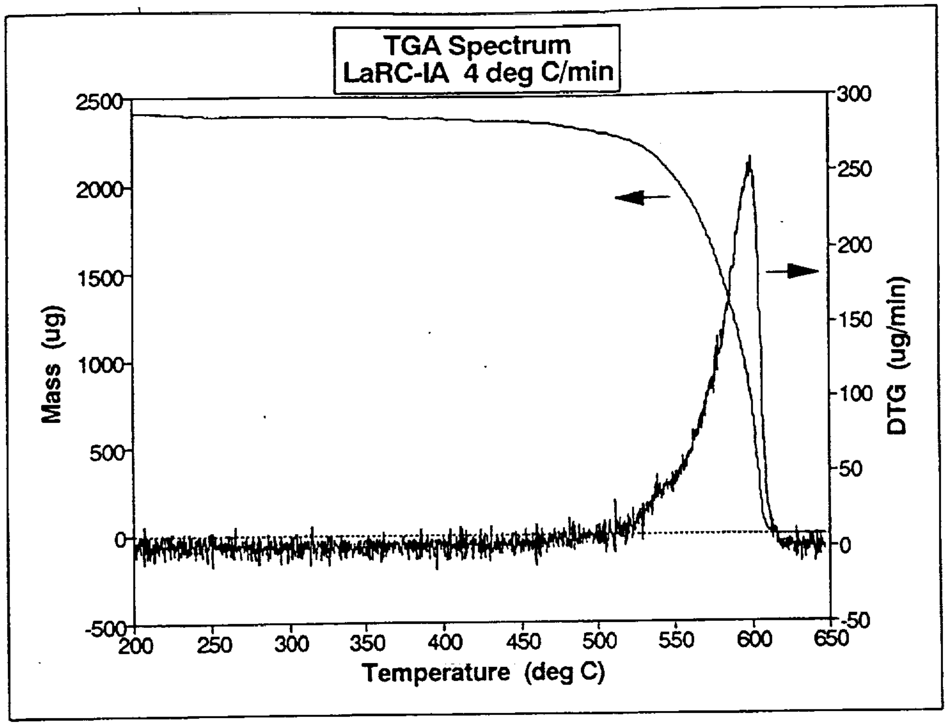

Figure 1. A TGA spectrum for LaRC-IA powder at a heating rate of 4° C/min.

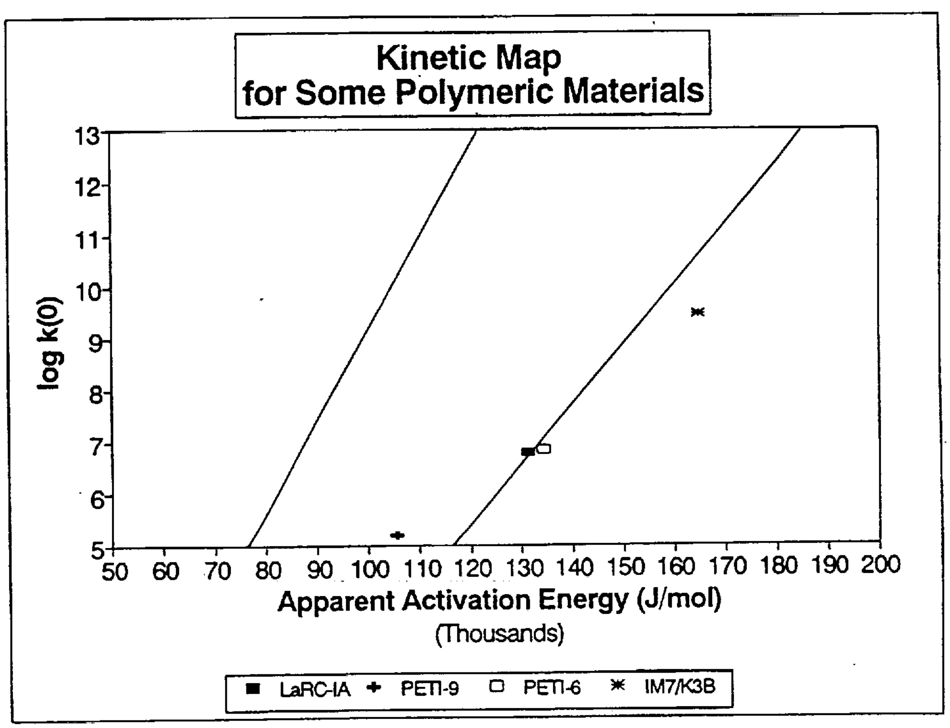

Figure 2. A kinetic map for several polymeric materials.