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LIFETIME PREDICTION FOR POLYMERS FROM THERMAL ANALYTICAL EXPERIMENTS -- PROBLEMS AND HOW TO DEAL WITH SOME OF THEM

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ABSTRACT

Heating polymeric materials to accelerate their deterioration often alters their physical and rheological properties. As a result, kinetics parameters and even the degradation mechanism may change in the extrapolation range from accelerated to use conditions. Therefore, predictions based on such extrapolations are invalid. Examples of change in kinetics with changing temperature are given for poly(methylmethacrylate), polystyrene, polyurethane and poly(ether-ether-ketone). Error propagation during extrapolation is discussed. Some guidelines for successful extrapolation and prediction are presented.

INTRODUCTION

The concept of measuring degradation of a polymer under conditions designed to accelerate its rate and extrapolating the resulting kinetics parameters to milder conditions to predict service lifetime has great appeal. Successful development of such methods would have great practical use and commercial importance. These could be used not only for planning economic replacement before catastrophic failure occurs or avoiding premature replacement, but also in developing specifications for quality assurance and control tests and formulations for polymeric materials with superior fabrication properties and performance characteristics.

Applications of the methods of thermal analysis -- TG, DSC, TMA, etc., -- to the prediction of long term properties is particularly tempting as these techniques are rapid and instruments are readily available. However, predictions from these artificial aging experiments often are found to be inaccurate which has led to considerable well-warranted skepticism. Indeed, it is presumptuous to expect simple kinetics models to describe the complex events taking place in these condensed phase systems.

However, the development of adequate accelerated tests is possible sometimes if selection of the method and conditions takes into account (1) the nature of the aging process, (2) the factors which cause this process to occur, and (3) the ways to intensify these factors to bring about more rapid aging without altering its

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mechanism. After examples of how long extrapolations give false predictions, we will discuss some of the questions to ask, criteria to meet, and maxims to follow in the development of an accelerated aging method.

TEMPERATURE DEPENDENCE OF POLYMER DEGRADATION MECHANISM

Rates and mechanisms of heterogeneous reactions depend upon physical factors and some of these such as phase change take place over a sharp temperature range. Collision rates of reacting species are limited by viscosity and diffusion, and often reversibility and cage effects contribute to the reaction mechanism. Thus changes in the rate limiting step can occur as the reaction temperature is changed so that not only the values for kinetics parameters change but even the forms of kinetics equations may differ in different temperature regions. Obviously, extrapolation of a kinetics parameter through such regions will give false predictions. Some examples of where sudden changes in weight loss kinetics of polymers are caused by such effects are given below.

a) Oxidative Degradation of Poly(methylmethacrylate): PMMA was investigated by Hirati (1) in air at 0.5 to 5 deg/min and weight loss occurred in the 200 to 250C range. The same sample of PMMA lost weight at 0.0320 and 0.0733 %/day at 111.9 and 121.3C during a study of the solubility and diffusion of oxygen in it by Flynn and Levin (2). The two sets of experiments gave an activation energy of 111.9 kJ/mol which suggested that this 140 degree temperature range might be extrapolated to make lifetime predictions at lower temperatures. It was found, however, that, in the latter study, no weight change due to oxidation could be detected at 105C, the glass transition temperature of PMMA, or below. The diffusion of oxygen through glassy polymers is very slow. Vitrification also suppresses the reverse reaction -- the oxidative cure of resins. Thus the glass transition serves as a cutoff for the oxidative degradation and extrapolation of rates for PMMA to temperatures below the glass transition temperature will be in error.

b) Oxidative Degradation of Polystyrene: The degradation of polystyrene (PS) in air has been investigated by weight-loss measurement over a thousand fold range of heating rates of 0.1, 0.01, 0.001 and 0.0001 deg/sec (3). The rate of fractional weight-loss is plotted against fractional weight loss in figure 1. If the mechanism for the oxidative degradation was the same at each of the four heating rates, then the four curves would have similar shapes. This is more or less true for the curves at the slow heating rates of 0.0001 and 0.001 deg/sec which leave a char at 90% conversion. However, the rate in the experiment at 0.01 deg/sec shows an acceleration at 70% conversion, and the rate at 0.1 deg/sec shows a radical autocatalytic change at 15% conversion. These changes in the kinetics both occur at 270C. The viscosity of molten polystyrene decreases dramatically at about 250C so it appears that this permits greater mobility of the reacting species and thus alters the reaction mechanism. The fastest heating rate for these experiments, 0.1 deg/sec (= 6 deg/min), is in the range commonly used for lifetime prediction software in commercial instruments. Kinetics parameters such as activation energy which were obtained from this heating rate range would give erroneous extrapolations to service lifetimes at lower temperatures.

c) Oxidative Degradation of Polyurethane: The weight-loss kinetics of MDI and TDI polyether and polyester soft segment 1,4-butanediols have been investigated over a thousand-fold range of heating rates in vacuum, nitrogen, air and with and without water vapor (4). Some results for a polyester soft segment polymer are seen in figure 2 where rate is plotted against temperature. In this experiment at 6 deg/min, the reaction occurs more rapidly in vacuum and is almost explosive at 300C. A char is formed in all other cases. Water suppresses the effect of air at low conversion but catalyzes the burning of the residue. Slowing the heating rate to 9 deg/day (fig. 3) shifts the reactions to the 150-300C range and better separates their components. In the presence of dry oxygen, a weight gain occurs at 130 - 145C. The sudden weight loss at 150C must represent the dissociation of this oxygen-containing moiety. Water vapor suppresses these reactions and hydrolysis occurs at 240C. The char-burning temperature has been lowered to the 300C range. It is obvious from the drastic change the structure of these curves by this reduction in the heating rate that experiments at usual TG heating rates would produce kinetics parameters unrelated to reactions occurring at lower temperatures.

d) Oxidative Degradation of PEEK: The thermal degradation of poly(aryl-ether-ether-ketone) (PEEK) in air by TG was investigated by Day and coworkers (5). They obtain much longer lifetime predictions at the conventional heating rates (1 to 20 deg/min) than for slower heating rates (0.01 to 0.5 deg/min). The latter correlate with isothermal results so that the TG of this high temperature thermoplastic provides another example which may be a rather general case for oxygen induced depolymerization reactions.

PROPAGATION OF ERRORS BY ARRHENIUS EXTRAPOLATION

Flynn and Dickens (6) have pointed out that, in extrapolations over temperature, an error in the activation energy produces exponential promulgation of the uncertainty in the extrapolated reaction rate. Thus an error in E of 4.0 kJ/mol will cause an error of ± 100% at the 95% confidence level in an extrapolation from 225 to 25C. Therefore, even if E remains unchanged over the extrapolation interval, the range should be kept as short as is practical. This means performing experiments at very slow rates or intensifying factors other than temperature which increase the rate.

CONSIDERATIONS FOR SETTING UP ACCELERATED AGING TESTS

The above examples and discussions show that a great degree of caution and restraint must be used in applying data obtained at accelerated conditions to the estimation of service lifetime of plastic materials. The remainder of this paper will discuss ways to ameliorate some of the problems described above and will suggest some guidelines for developing methods to predict long term properties of plastics.

a) Defining the Problem: (Preliminary considerations to be taken into account in the design of accelerated aging tests): 1) Determine which property of the material it is whose deterioration is responsible for failure. 2) Determine the chemical functional groups or morphological characteristics which are most susceptible to attack. 3) Decide which agent in the service environment or the material itself is likely to attack the critical groups or phases. 4) From these facts, determine the factors whose intensification will best accelerate the deterioration of the critical property.

Some factors to consider intensifying are: temperature, mechanical stress (flexure, load, stretching, abrasion, ultrasonic vibration, etc.), oxygen pressure, water vapor pressure, total pressure, gaseous agents, liquid agents (organic solvents, acids, bases, etc.), surface area, film thickness, radiation, particulate beams, amount of solid (catalytic) impurities or other additives in the substrate, concentration of labile functional groups, etc.

b) Sensitivity of Measurement Technique: Failure often occurs after the degradation process has proceeded to only a few percent conversion. Therefore, it is important to select a technique which yields quantitative detailed data for initial phases of the degradation. In any event, the more sensitive the technique is to the degradation process, the less drastic the accelerating conditions need to be to speed up the reaction to a measurable rate.

c) Relevancy of Method: Many factors may render accelerated test data irrelevant to the prediction of service lifetimes. In addition to the cases discussed previously in which the polymer passed through a transition or a change in a rheological or mechanical property, the extrapolation may include a "ceiling" or equilibrium temperature above which depropagation and degradation are favored and below which equilibrium has shifted toward recombination and crosslinking. Diffusion reactions tend to have low activation energies, and chemical reactions involving chain scission have high E's. Thus, at low temperatures, diffusion can be dominant when there is kinetic competition, and chain scission can be rate limiting for consecutive or chain reactions.

c) Reliability of Measurements: The reliability of the data is an important consideration. Commercial instruments may yield impressive and reproducible curves which are unfit for determining true kinetics parameters. Plastics have low thermal and material diffusivities which may become rate limiting at accelerated conditions. Investigation of the effect of sample geometry on the rate is one way to uncover these factors. These and other problems encountered during treatment of thermal analysis kinetics data and solutions for some of them are discussed in another paper (7).

e) Reliability of the Extrapolation: Some factors to be considered in setting up a meaningful extrapolation procedure include: 1) There must be a well-defined functional relationship between the physical property measured in the accelerated experiments and the intensified factors, e.g., the Arrhenius equation is often applied to thermally accelerated reactions. 2) The relationship in 1) should be fitted over a wide range of values. This is important both for obtaining precise values for its parameters and for uncovering deviations from the assumed function. (If the kinetics parameters are not consistent a new model must be tested.) 3) The precision of measurement must be maximized. (The importance of this was shown previously when the propagation of errors was discussed. 4) It is very important to minimize the extrapolation range, but usually a trade-off is made between time of experiment and length of extrapolation.

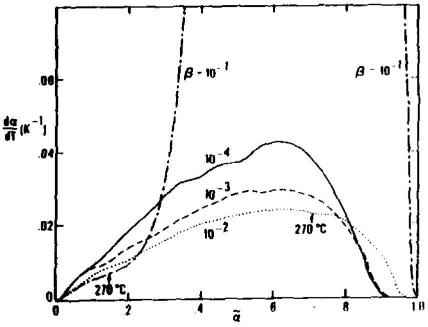

fig 1 Rate vs Degree of Conversion for PS, Air at 0.0001, 0.001, 0.01 and 0.1 deg/s

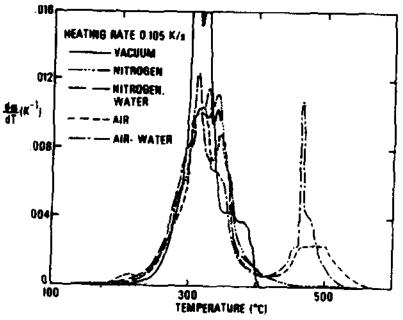

fig 2 Rate vs T for PU in Various atmospheres at 0.105 deg/s

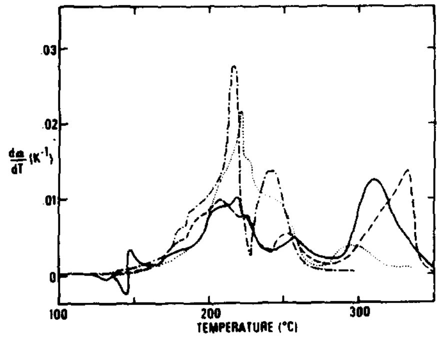

fig 3 Rate vs T for PU in same atmospheres as fig 2 at 0.000110 deg/s

An important way to decrease the extrapolation range, which should be used more often, is to intensify several rate-accelerating factors, e.g., the partial pressure of oxygen or water vapor can be increased as well as temperature in the degradation of polyethers or polyesters, respectively. This will decrease the temperature extrapolation. Such a procedure would not be done just to improve precision as each factor would have its own functional relationship with the rate and its own extrapolation error. However, shortening the extrapolations may avoid the problem of passing through reaction-altering phase or other physical changes which would invalidate the extrapolation.

f) Tests for Reliability: Once a proposed test method has been set up and service lifetime predictions made, there are several ways to test the validity of the procedure: i) Comparison with a Method Measuring a Different Property -- Predictions of an accelerated aging procedure should be compared with those of a technique based on the measurement of a different physical property. This aspect of testing aging methods is discussed by Toop (8) in articles on predicting thermal ratings of wire enamels. ii) Comparison with Failure Data from Service Use - A comparison with actual use data is possible only for a materials whose service life is short or whose formulation has remained unchanged for many years. This is the only true test of an accelerated aging method. iii) Comparison with Long Term Aging - If long term use of a material is likely, well-characterized specimens should be set aside under controlled conditions and periodically tested and compared with data on specimens subjected to accelerated aging.

Concluding note: These discussions should not discourage attempts to apply thermoanalytical techniques to lifetime prediction of polymers which can be accomplished sometimes if proper care is taken in test design and data analysis.

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