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Review

A CRITIQUE OF LIFETIME PREDICTION OF POLYMERS BY THERMAL ANALYSIS[*]

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Abstract

Attempts are made to use kinetics parameters from thermal decomposition experiments at high temperatures to predict service lifetimes of polymeric materials at lower temperatures. However, besides the obvious measurement and extrapolation errors (which can be considerable), there are two fundamental reasons why quantitative long range extrapolations can not be made for complex condensed phase systems. They are: 1) Arrhenius kinetics parameters can not be extrapolated through phase transitions or softening temperatures; 2) Arrhenius kinetics parameters can not be extrapolated through the ceiling temperature region. Satisfactory lifetime prediction methods can be developed only after a thorough analysis of the causes of service failure. A real method has been taken from literature to illustrate the correct procedures.

Keywords: Arrhenius equation extrapolation, ceiling temperature, kinetics, lifetime prediction, phase change, polyester hydrolysis, polymer degradation, thermal analysis

Introduction

There are two fundamental reasons why Arrhenius parameters obtained at the higher temperatures of thermal analysis experiments usually can not be extrapolated over a broad temperature range to predict service lifetime at a lower

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temperature. One of these reasons is based upon considerations of the reaction kinetics and the other is based upon thermodynamic considerations. They are both discussed in this paper. However, first, the usual development of a typical lifetime prediction method from thermal analysis is described.

Lifetime prediction methods

Methods by which the degradation of a polymer is measured under conditions which accelerate its rate and from which the resulting kinetics parameters are extrapolated to predict accurate service lifetimes would have great commercial importance. They could be used not only for planning economic replacement before catastrophic failure occurs or avoiding premature replacement, but also for developing specifications for quality assurance and control tests and formulations for materials with superior properties and performance characteristics.

Application of the methods of thermal analysis to the prediction of long-term properties is particularly tempting as these techniques are rapid and instruments are readily available. In a typical lifetime prediction routine, an activation energy is calculated from the degradation kinetics by utilizing a form of the Arrhenius equation:

$$\ln k(t) = \ln A - \frac{E}{RT}$$

where k is the rate constant, t, the time, A, the preexponential factor, E, the activation energy, R, the gas constant, and T, the absolute temperature. A failure criterion is posited such as for example, a 5% weight loss from a Thermogravimetric Analysis (TGA) experiment. Then the logarithm of the times to reach failure are calculated for temperatures of interest. Thus plots of logarithm of time *vs.* reciprocal temperature may be used to predict times to failure at service temperatures that are outside the time range of experimental temperature measurement. Such predictions clearly depend on the reaction mechanism remaining unchanged over the range of extrapolation. However, predictions from these artificial aging experiments often are found to be inaccurate.

There are many causes for the poor performance of these aging predictions. Many of these have been discussed in detail elsewhere [2–8]. Briefly, they include:

1) using too drastic degradation criteria (as, for example, many polymeric materials lose their useful properties before any significant weight-loss),

2) using the wrong criteria – the cause of failure may not be thermal, but oxidative, hydrolytic or mechanical breakdown, or merely change in colour, elastic modulus, etc.,

3) using imprecise values of *E*/*R* obtained from the Arrhenius equation as the imprecision in rates calculated from *E*/*R* values increases exponentially during the extrapolation of temperature.

However, even when the above problems are taken into account satisfactorily, there are still two fundamental reasons why many lifetime predictions are flawed. These two reasons are discussed in the following sections.

Extrapolation of temperature through physical property and phase changes

The Arrhenius parameters, *E*/*R* and ln *A*, calculated from kinetics data are used for the extrapolation of reaction rates. For this extrapolation to be valid, the values for these parameters must not change over the extrapolation interval. Most polymeric materials are above their glass and/or melting transition temperatures when their rate of deterioration is fast enough to be measured in a conveniently short time. On the other hand, the temperature range for their service use is usually well below these transition temperatures.

For reactions to take place in polymeric materials there must be movement of reactant and product species [9]. Thus, even for the simplest cases, the rates for the chemical reactions must be coupled with the rates of diffusion of reactant, intermediate, or product species into, through, and out of rigid polymer matrices if one is to obtain the overall rate expression for the kinetics. The rates of these diffusion reactions are often quite slow. Such a reaction may be the rate controlling step of the series of complex reactions which usually take place in most of these condensed phase systems. Therefore, a change in the physical character of the material will have a drastic effect on the measured reaction kinetics. It is, of course, obvious that the rates of diffusion of these species will depend on the physical state and viscosity of the matrix through which they are diffusing [9]. Examples of the catastrophic effect of a phase or physical property change upon the parameters obtained from polymerization and depolymerization reaction kinetics data are found throughout the literature. Some of these have been presented in previous publications [6, 7].

Therefore, only one such example will suffice here, viz., the effect of glass transition temperature (T_g) on cure and degradation reactions of vinyl polymers. First, we will discuss the isothermal cure reaction of vinyl resins which may be measured quantitatively by DSC. Rate data for these reactions have been found to be consistent with equations for free radical chain kinetics reaction mechanisms [10–14]. However, during the cure of a resin, the glass transition temperature of the substrate rises as the molecular weight of the resin increases. Eventually the T_g reaches the isothermal reaction temperature. At this point the rate of cure becomes dependent upon the very slow diffusion of the reacting species through the glassy matrix, and the reaction rate constant will decrease by orders of magnitude. If the partially cured resin is heated to a higher temperature (that is, above its current T_g), then the system will begin to polymerize further until its increasing glass transition temperature reaches the new isothermal cure temperature. At this point the reaction again will practically cease. These stepwise accelerations of the cure by increasing the isothermal cure temperature can be continued until the resin is completely cured or the polymerized resin begins to degrade.

Since the same reactant, intermediate and product species and the same physical states are involved for the reverse of the above reaction, the thermal decomposition of a vinyl polymer, we find that the same sort of catastrophic decrease in rate takes place in the glass transition temperature region. For example, the rate of the isothermal decomposition for poly(methylmethacrylate) suddenly decreases to an unmeasurably low value at isothermal temperatures just below its glass transition temperature [6, 7].

It is obvious from this example that no extrapolation of reaction rates should be attempted over a temperature range within which a viscosity (softening point) change or a melting or glass transition takes place in the substrate. The magnitude of the kinetics parameters will be so drastically altered as to render such extrapolations meaningless. This large change in the values of the kinetics parameters will occur even though the reaction mechanism itself may remain unchanged through the transition temperature range.

Extrapolation of temperature through a ceiling temperature (dissociation equilibrium)

When polymers are degraded, they are in a high temperature region where they are thermodynamically unstable. On the other hand, when polymers are utilized, they are in a lower temperature region where they are thermodynamically stable. This stability–instability reversibility with respect to temperature for polymers has been formalized by the concept of ceiling temperature (T_c) which was developed by Dainton and Ivin [15] and was reviewed extensively by Busfield [16]. The equations defining the ceiling temperature were developed from the thermodynamic equilibrium between the propagation and depropagation reactions for a free radical chain vinyl polymer degradation mechanism. For this case, the depropagation step is

$$-\mathrm{CH_2CHXCH_2CHX}\cdot \xrightarrow{k_2} -\mathrm{CH_2CHX}\cdot + \mathrm{CH_2CHX} \qquad (1)$$

and the reverse propagation step is

$$-CH_2CHX\cdot + CH_2CHX \xrightarrow{k_{-2}} -CH_2CHXCH_2CHX\cdot \tag{2}$$

so when these two opposing rates are equal, the resulting equilibrium is

$$k_2[R\cdot] = k_{-2}[R\cdot][M] \tag{3}$$

where $[R\cdot]$ and $[M]$ are the radical and CH_2CHX (monomer) concentrations, respectively. Thus for equilibrium,

$$[M] = \frac{k_2[R\cdot]}{k_{-2}[R\cdot]} = \frac{k_2}{k_{-2}} = K \tag{4}$$

where K has the character of an equilibrium constant for the polymerization/depolymerization reaction and can be described in terms of the change of free energy ΔF°, enthalpy ΔH°, and entropy ΔS° during the polymerization reaction, that is,

$$K = \exp\left(-\frac{\Delta F^{\circ}}{RT}\right) = \exp\left(\frac{\Delta S^{\circ}}{R}\right)\exp\left(-\frac{\Delta H^{\circ}}{RT}\right) \tag{5}$$

If we add the condition that $[M]$ is unity in some convenient units, for example, one torr pressure, then, when $K = [M] = 1$, $\ln K = 0 = \Delta S^{\circ}/R - \Delta H^{\circ}/RT_c$ and this temperature, T_c, is defined as the ceiling temperature and is given by

$$T_c = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} \tag{6}$$

The ceiling temperature, being a thermodynamic quantity, will depend only on initial and final states, monomer and polymer, respectively, and not on the reaction mechanism. Therefore the ceiling temperature applies equally well to a polymerization equilibrium brought about by anionic or cationic initiators [17]. (Obviously similar thermodynamic developments can be applied to any reversible association – dissociation chemical reaction, be it organic or inorganic.)

Also, as the ceiling temperature is a thermodynamic quantity, it will tell us only whether a polymerization or depolymerization reaction is possible under specified conditions, not whether it will actually take place in finite time. Therefore nothing can be learned from the ceiling temperature, itself, about the rates of the polymerization or depolymerization reactions. Monomers may exist indefinitely in a metastable state at temperatures below their T_c, and many polymers do not degrade at an appreciable rate at temperatures well above their T_c in the absence of proper catalysts. On the other hand, for some other systems, this monomer–polymer equilibrium is almost instantaneously reversible. (Such a rapid reversibility appears to apply to the polyurethane link in many polyurethanes [18].) However, the important conclusion from the T_c concept in this discussion is that if one simply measures the rate constant for the degradation reaction direction at high temperatures where the degradation is dominant, then the resultant calculated rate parameters have no validity whatever when extrapolated to low temperatures where the rate constant of the reverse synthesis reaction is the important factor. Factors which catalyse the dissociation reaction at high temperatures may also catalyse the synthesis reaction at lower temperatures; however, the net effect merely will be the more rapid establishment of equilibrium.

Since the ceiling temperature is a function of an equilibrium constant, its value will depend on concentrations or partial pressures of reactants and products. When a gas such as monomer, water, carbon dioxide, etc., is a product of the dissociation reaction, K will be proportional to the pressure (activity) of that gas. Therefore T_c often can be lowered by decreasing the partial pressure of a stoichiometric product of the depolymerization reaction. For example, many polymers degrade at temperatures as much as fifty degrees lower in vacuum than they do in an inert gas at one atmosphere pressure. On the other hand, at temperatures below T_c, not only will the polymerization reaction be favoured but the equilibrium will be forced further in that direction by the build-up of the partial pressure of the dissociated monomer resulting from its restricted diffusion through the substrate.

An example of this is found in the thermal decomposition of polyurethanes where the decomposition temperatures appear to be proportional to the ease of diffusivity of depolycondensed diisocyanate groups from the interior to the surface of the polymer [18]. Chemical blockage of the surface of polyurethanes prevents this diffusion and the evaporation of the depolycondensed diisocyanate moieties. This macroscopic "cage effect" shifts the equilibrium for these surface blocked polyurethanes in the direction of repolycondensation, and, as a result, they show an enhanced thermal stability [18]. Stoch [19] has developed a "Sealed Box" model for this phenomenon when it occurs during the dehydration of inorganic solids.

A less obvious case of a polymerization–depolymerization equilibrium is the oxygen-induced cure of unsaturated resins *vs.* the oxygen-induced degradation of polyolefins. This is a much more appropriate reversible system to be discussed in connection with lifetime prediction methods than are purely thermally-induced degradation reaction systems because this oxygen-induced degradation reaction is much more likely to be the prime cause of deterioration during service use of many polymeric materials. The initial and often rate controlling step both in the oxygen-induced cure and in the degradation reactions for these vinyl systems is thought to be the formation of hydroperoxide groups at labile positions in the molecules [20]. These hydroperoxide groups decompose to form free radicals which initiate free radical chain reactions such as those described in Eqs (1) and (2). Above the ceiling temperature, where the polymer is in a metastable state, degradation will occur when these radical chains are initiated. Below the ceiling temperature, the monomer is metastable and the resin will cure when the reaction is initiated. However, since the rate controlling step in both directions is often the decomposition of the hydroperoxide groups to form free radicals, it is not surprising that both the oxidative cure and the oxidative degradation reactions yield similar activation energies in the twenty kilocalories per mole (85 kJ/mole) range. Oxidative degradation reactions for many polymers yield similar activation energies which suggests that all these polymers should possess approximately equal stabilities in oxidative atmospheres. However, it is often the side reactions, the presence of oxygen labile groups (ether linkages, hydrogens in the beta position to residual conjugated double bonds, etc.), that determine the oxidative stability of a specific polymeric material. Thus oxidative induction times [8], measured by either TGA or DSC, may be a more appropriate gauge of thermal stability, not because these methods are measuring kinetics constants for the degradative oxidation process, but because they are measuring the amount of antioxidant remaining in the material, that is, the remaining capability for neutralizing the hydroperoxide radicals which initiate the oxidative reaction.

Both the ceiling temperature concept and phase change effects predict that service life estimates should err in the direction of predicting much more rapid low temperature deterioration and underestimation of service life. Why then do polymers degrade when maintained at service temperatures where they should be thermodynamically stable? In many cases, the answer appears to be that other (often surface) reactions take place, and they are the cause of service failure. Nonreversible oxidative, hydrolytic, photochemical, etc. reactions occur which are independent of the polymerization–depolymerization equilibrium system. These "side reactions" include not only chemical reaction systems, but also physical and mechanical processes – crazing, stress fracture, crystallization, etc. Thus often they are the cause of the deterioration of a material's properties.

It is a fact that service life extrapolations using these "irrelevant" Arrhenius parameters from thermoanalytical data often do give "reasonable" predictions, that is, usually somewhere in the range from 3 to 300 years service life. A plausible explanation of this fortuitous result is that the range of carbon–carbon, carbon–hydrogen, carbon–oxygen, etc., bond energies in organic polymers is such that (as to be expected from the compensation effect [9]), both "correct" and "incorrect" energies of activation will produce lifetime predictions that fall into such a broad time range of "reasonable" values.

Factors to take into account in the development of lifetime prediction methods

It is evident from the discussions above that a simple analysis of the kinetics obtained from a thermoanalytical technique is seldom sufficient to develop a satisfactory lifetime prediction method. It is necessary to have a broad understanding of the factors involved in the failure mechanism if such a method is to be developed. Guidelines for setting up such methods are discussed in this final section.

Definition of the problem

The first and most important consideration is that of defining the problem. A method and the kinetics treatment of its data may be scientifically correct, but they may be worthless for predictive purposes if the technique is measuring a property which is irrelevant to the deterioration reaction at service conditions. Therefore certain preliminary considerations must be taken into account in the design of aging tests.

1) The properties of the material whose deterioration is responsible for failure should be determined.

2) The chemical functional groups or morphological characteristics of the material which are most susceptible to attack should be determined.

3) The agents in the service environment or in the material itself which are likely to be responsible for the attack of the above critical groups or phases should be determined.

4) The factors most likely to accelerate the deterioration of the critical property should be determined from a consideration of the above properties, functional groups, characteristics and factors.

Sensitivity of the measurement technique

Often material failure occurs after the appropriate degradation process has proceeded to only a relatively slight degree. Therefore it is important to select a measurement technique which yields quantitative and detailed data for the initial phases of the degradation. In any event, the more sensitive the technique is to the degradation process, the less drastic are the accelerating conditions needed to speed up the reaction to a conveniently measurable rate.

Relevancy of the method

Many factors may render an accelerated test method irrelevant to the prediction of service lifetimes. Several of these factors are what we have been discussing in the bulk of this paper – the temperature extrapolation passing through a ceiling temperature, a phase transition, or other drastic changes in a rheological or mechanical property. Diffusion reactions in solids tend to have low activation energies while chemical reactions involving chain scission have high activation energies. Thus, as the temperature is lowered, a low activation energy diffusion reaction can become the rate controlling step when there is competition between several kinetic paths, while, on the other hand, a high activation energy chain scission reaction can become rate controlling for kinetics involving consecutive or kinetic chain reactions. Due consideration should be given to which reaction should be expected to be rate controlling at service conditions.

Reliability of measurements

The reliability of the data is an important consideration. Some commercial instruments may yield impressive and reproducible curves which are unfit for determining true kinetics parameters. Polymers have low thermal and material diffusivities which may become rate limiting at accelerated conditions. Investigation of the effects of sample weight and geometry on the rate is one way to uncover the presence of 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 [21].

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., temperature, pressure, gaseous atmosphere, catalysts, etc.). For example, the Arrhenius and the WLF (Williams, Landel and Ferry) equations are two functions often found to be applicable for fitting the temperature dependence of the reaction rate. If other factors, for example, oxygen pressure or partial pressure of water vapour are intensified in the accelerated tests, then equations must be developed for the dependence of the rate on their partial pressures (activities).

2) The relationships (equations) mentioned in 1) should be tested over a wide range of values. For example, the applicability of the Arrhenius equation should be obtained over a broad temperatures range (at least fifty degrees, when possible) for thermally accelerated reactions [9]. (This is important for both obtaining precise values for its parameters, ln A and E/R, and for uncovering deviations from the assumed kinetics function. For example, if the kinetics

parameters are not constant, different experimental conditions or a different model for temperature dependence must be chosen and tested.)

3) The precision of the measurements must be maximized. For example, an error in the activation energy calculated from the Arrhenius equation will result in an error in the extrapolated reaction rate which will increase exponentially upon increasing temperature range of the extrapolation. (This problem is discussed in detail in Ref. [3].)

4) As a result of the above, the extrapolation range should be minimized. (However a trade-off usually is made between time of experiment and length of extrapolation.) An important way to decrease the extrapolation range, which is not utilized as frequently as it could be, is to simultaneously intensify several rate-accelerating factors. For example, if one is interested in the stability of a polyether in air, both the partial pressure of oxygen and the temperature can be intensified (for example, in an autoclave). Thus, by decreasing the necessary range of temperature extrapolation, passage through a kinetics-altering phase or physical property change may be avoided. Another example of simultaneously intensifying several degradation factors is illustrated in the example given in the final section.

Tests for reliability

In some rare cases, one can compare the lifetime predictions with actual failure data from service use. This is the only true way for testing the reliability of a service life prediction method. However, this is not often a practical possibility. It is possible only for materials whose service life is comparatively short or whose formulation remains unchanged over many years. There are only a few cases where scientists have had the foresight to set aside well characterized specimens to be stored under controlled conditions so that they could be tested periodically and the data compared with data on specimens subjected to accelerated aging.

It has been suggested that predictions from an accelerated aging method should be compared with those obtained from another prediction technique based upon the measurement of a different physical property. This aspect of testing aging methods is discussed by Toop [22] in articles on predicting thermal ratings of wire enamels. Such an agreement in predictions is an encouraging indication that the two methods are measuring the kinetics of the same reactions but it is not a sufficient condition to establish the validity of either method. The extrapolations may be flawed in the same way in both of the methods. For example, the extrapolations in both cases may pass through a phase change or ceiling temperature region.

An example of a properly developed lifetime prediction method

A short review of the development of a lifetime prediction method for magnetic recording tapes is presented in this final section to illustrate the application of many of the factors discussed above. This work was performed by Brown, Lowry and Smith for the USA National Archives [23].

Information storage on microfilm and magnetic tape has become an important part of libraries and archives, therefore, the expected useful lifetime of these materials is necessary for efficient planning of their periodic replacement.

Magnetic tapes consist of various active coatings attached to the surface of a film of poly(ethylene terephthalate) (PET). These coatings may be composed of ferromagnetic material (small particles of gamma ferric oxide) suspended in crosslinked polyester polyurethane (PEPU) which serves to bind particles to the supporting film. Other materials such as lubricants, adhesives, or stabilizers are frequently added to this layer.

The above authors [23] concluded that the stability of both the tape base (PET) and the coating (PEPU) were susceptible to the acid hydrolysis of their ester groups so preliminary investigations of the hydrolysis of each of these components were made at various temperatures and relative humidities. Changes in acid content and molecular weight were measured. These studies suggested that the PET might retain its useful properties for over 500 years at 20°C and 50% relative humidity (*RH*). On the other hand, for the PEPU, which is susceptible to autocatalytic hydrolysis, the scission of one ester linkage of the 10–20 in each polyurethane molecule will reduce its molecular weight to about 1000–2000 where the polymer will no longer be an elastomer. Thus severe degradation of mechanical properties can occur without an appreciable fraction of the ester groups being consumed. Urethane links were stable under the conditions studied so it was assumed that only the acid catalysed hydrolysis of the ester linkage in the PU coating was the chemical factor to be considered. Some tapes also contain chromium oxide particles which affect the chemical degradation mechanism.

Mechanical properties and acid content were measured for magnetic tapes aged between 55 and 115°C at 100% relative humidity. It became apparent that a method more sensitive than titration was needed to measure change in acid content at low temperatures. Therefore changes in acid and alcohol content were also measured by IR spectroscopy. The rate constants calculated from data from these experiments agreed with those calculated at higher temperatures for acid content by titration.

(We should note in this work, that, by increasing two accelerating factors, both temperature and relative humidity, the measurements were made at temperatures below the phase change temperatures of both the substrate and water, thus avoiding the extrapolation of kinetics parameters through such regions.)

Once the degradation mechanism was established, other means of monitoring degradation were investigated. Differential Scanning Calorimetry, Thermogravimetric Analysis, and Gel Permeation Chromatography did not prove to be good degradation monitors. The tape lifetimes were limited, in many cases, by detachment of binder. Model binder kept at 85°C and 100% *RH* eventually became brittle. Due to its degradation, the tapes failed either cohesively or adhesively at the binder-support interface. Adhesion appeared to be a more valuable indicator of tape condition than sol content*. Therefore various mechanical tests were performed on the aging tapes to measure adhesion or extensibility of the binder layer. Water content and weight change also were monitored. Quantities measured included:

1) the force required to peel binder from support,

2) elongation of the tape at which the binder separates from the support,

3) the number of rolling translations of a crease required to separate the binder from the support,

4) the water content of the tape at 45% *RH* and

5) the change in weight of the tape during aging. All five were found to change during aging. However, although some of these measures may be useful indicators of risk, none of them correlated quantitatively with the ability of the tape transport to read data previously written on the tapes.

Agings at 35°C and several humidities were started early in the investigation. Tests performed over the coming years on such tapes at these slightly accelerated conditions should signal when their replacement is desirable. Therefore the approach to estimate tape lifetimes was to write on the tapes, age them, read the data on tape after aging and continue alternate aging–reading attempts until they became unreadable. Thus lifetimes were determined which were extrapolated to estimate a value under typical storage conditions. Based on this criterion, an estimate of a useful tape lifetime was at least 20 years at ambient conditions.

This summary includes only part of the work which went into the development of these accelerated aging tests. The reader is referred to the original papers [23] for a full description. However, this work of Brown, Lowry and Smith [23] presents an excellent illustration of the type and extent of research which is necessary to develop a satisfactory lifetime prediction method. Such methods require extensive research and analysis. Simplistic methods in which changes in a single property are measured with respect to temperature seldom yield data upon which dependable lifetime predictions can be developed.

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* The fraction which remains soluble and can be extracted from the gel.

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Zusammenfassung — Es wurden Bemühungen angestellt, um kinetische Parameter aus thermischen Zersetzungsexperimenten bei hohen Temperaturen zur Vorhersage der Lebensdauer von polymeren Werkstoffen bei niedrigen Temperaturen zu treffen. Neben den eindeutigen Meß- und Extrapolationsfehlern (die sehr beachtlich sein können), gibt es zwei grundlegende Gründe, warum für komplexe kondensierte Phasensysteme keine quantitativen weitreichenden Extrapolationen erstellt werden können. Dies sind: 1) Arrhenius'sche kinetische Parameter können nicht über Phasenumwandlungen oder Erweichungstemperaturen hinweg extrapoliert werden; 2) Arrhenius'sche kinetische Parameter können nicht über den Hochtemperaturbereich hinweg extrapoliert werden. Zufriedenstellende Lebensdauervorhersagen können erst nach einer gründlichen Analyse der Gründe für Einsatzfehler entwickelt werden.