IGNACY JAKUBOWICZ

SP Swedish National Testing and Research Institute Polymer Technology
Box 857, SE-501 15 BORÅS, Sweden
e-mail: ignacy.jakubowicz@sp.se

Research, standardization and practice in accelerated ageing tests

Summary — The increasing use of polymers in various technological environments requires understanding of the degradation phenomena and ultimately controlling them. Questions associated with performance, cost, durability and environmental effects are closely related to each other and must be answered before the industry and the consumers can adopt new materials. Often, the use of accelerated ageing tests constitutes the only possibility to produce measurable degradation and the desired materials assessment. However, prediction of service life, especially for materials expected to perform reliably for many decades, is a continuing challenge, which contains many pitfalls. In this paper, examples of the many years' work with accelerated ageing tests and lifetime predictions carried out at SP Swedish National Testing and Research Institute are used to demonstrate some problems and pitfalls that can be met with in practice. Some examples are also given on insufficient information in international standards for ageing tests. Special attention is given to prediction of service life with one data point only as well as the influence of different previous history, different environments and different evaluation methods on lifetime prediction. Other examples concern the use of high stress levels and physical depletion of stabilizers.
Key words: accelerated ageing tests, mathematical modelling, durability of materials, Arrhenius relation, service life prediction.

BACKGROUND

The constantly increasing use of polymers in various technological environments presents an important challenge to the polymer technologists concerning development of new materials and products, and to scientists in providing a scientific basis for understanding the degradation phenomena and ultimately to controlling them. Questions associated with performance, cost, durability and environmental effects are closely related to each other and must be answered before the industry and the consumers can adopt new materials.

Long-term performance or durability is defined as "Ability of a product and its parts to perform its required function over a period of time and under the influence of technological environments". There are two fundamentally different approaches to modelling the durability of materials: empirical approach that attempts to describe mathematically "what has happened" and predictive approach which is based on a mathematical assessment of the effects of dependent and independent variables and the subsequent refinement of the prediction based on experimental data.

The natural (normal) tests are a basic reference for any approach to the durability of polymeric materials. Conception "normal" is used to include conditions, which occur in a specific technological environment while "simulated" environmental conditions indicate that the simulated environment is as close as possible to the practical conditions. In these cases it is implicit that the tests and the practical applications have the same time scales. However, the use of accelerated tests is sometimes necessary as tests may take many years to produce measurable degradation and the desired materials assessment.

Accelerated ageing tests and extrapolation of test results constitute the predictive approach. Acceleration is achieved using higher stress levels of one or more degradation factors relative to the service life conditions. However, the viability of the method requires some information on deterioration rate constants for various properties as the functions of structure, composition and stresses. The lack of information makes the development of expressions that completely predict performance *a priori* of actual exposure data difficult and sometimes impossible.

MATHEMATICAL MODELLING OF DURABILITY

Rates of deterioration of many important properties of polymeric materials may be described by S-shaped curves in which the retention of property is plotted in form of dependent variable as a function of independent variable. Induction is a descriptor of the value "i" that represents quantitatively the magnitude of the independent variable necessary to initiate the rate controlled property change. Induction then describes both the reaction rates specific to initiation and the quantity of stress required for the production of a sufficient number of defects, or "observable" changes, that are necessary in order to be detected by the diagnostic tools. The rate-controlling step is that part of the degradation reaction that is easiest represented by a single rate equation. Writing a slope intercept equation we obtain:

$$\Delta P = m \cdot S - b \qquad (1)$$

where: S — *exposure or stress, m — slope, b — intercept on the ΔP ordinate, representing property change.*

We can write:

$$\Delta P = m \cdot (S - i) \qquad (2)$$

where: $i = b/m$ *the intercept on the abscissa which is the induction measured in terms of the independent variable.*

Equation (2) permits prediction of the durability of the property "P" in terms of the exposure in the rate-controlling portion. The independent variable, which acts as the driving force for the degradation reaction, may be light (UV, X-ray...), temperature, chemicals or physical stresses. In most cases, the independent variable is a combination of two or more variables sometimes leading to synergistic effects. If it assumes that ageing process consists of several chemical or physical reactions, or both, then the rates of these reactions can be presented in general form with N equations

$$\frac{dc_i}{dt} = -k_i(T) \cdot G_i(g_1, g_2, \dots g_m) \cdot C_i(c_1, c_2, \dots c_N) \qquad (3)$$

where: $i = 1 \dots N$, $k_i(T)$ — *function of T and may be of Arrhenius form, T — absolute temperature, G_i — simplified function of chemical reactions expressed as $\prod_{i=1}^{m} g_i^{n_{im}}$ (where n_{mi} represents the reaction order due to chemical m, in reaction i), C_i — function of the concentration of characteristic group (c_i) in reaction i (assumed to be independent on temperature).*

For a simple case of N homogenous equations and time transformation $t' = A \cdot t$, the acceleration factor (A) may be calculated at two different temperatures T_1 and T_2, if reaction rates at both temperatures are known (see Table 1):

$$A = \frac{(dc_{i2}/dt)}{(dc_{i1}/dt)} = \frac{k_i(T_2) \cdot g_{i2}^{ni2}}{k_i(T_1) \cdot g_{i1}^{ni1}} \qquad (4)$$

where: $i = 1 \dots m$.

However, degradation by its very nature involves non-equilibrium processes, so even with some practical utility this model may not be completely self consistent in a long term thermodynamic sense.

ARRHENIUS RELATION FOR THERMAL EXPOSURE

Relations of the Arrhenius form may apply to some properties of some materials over limited temperature ranges. They neither apply to all materials, nor to all properties and may be different in different temperature ranges. Furthermore, degradation is caused by a number of different mechanisms for a given case, where some or all may follow the Arrhenius relation, but there is no guarantee that overall behaviour is of Arrhenius form. Despite of that, the Arrhenius representation is probably the only procedure currently available for extrapolation of accelerated ageing tests to in-use conditions.

In order to allow extrapolation of short-time data to predict long-term performance, an appropriate curve must be drown through the short-term values obtained at elevated temperatures. Integration of the rate equation for the chemical reaction and taking logarithm gives an equation in the form:

$$\ln t = (E/R) \cdot 1/T + B \qquad (5)$$

A plot of $\ln t$ *vs.* $1/T$ then gives a straight line with slope E/R and is known as Arrhenius plot. The short-time points are obtained by selecting an appropriate end-point criterion of a critical property. At least four such points are recommended in order to draw a best straight line. The slope of the line is a measure of the activation energy of the degradation process. Extrapolation of the line to lower temperature can be drawn to extremely long times, but consideration must be given to the risk of other factors which might cause deviation from the projected straight line. It is of course essential, when choosing elevated temperature not to induce any degradation mechanisms other than those occurring under in-use conditions. An important condition in the use of this technique is a reasonable knowledge of both the underlying chemistry and the importance of various physical effects.

The procedure described above is valid for the simplest (ideal) situation, which occurs when the relative rate of change of all important degradation processes remains constant at each of the accelerated stress levels. This means that all chemical or physical changes are speeded up equally, as the temperature is changed. Another controversy involves the assumption that the effective activation energy of the degradation process is independent of temperature and ageing time.

PREDICTION OF SERVICE LIFE
WITH ONE DATA POINT ONLY

Prediction of service life, especially for materials expected to perform reliably for many decades, is a con-

tinuing challenge, which contains many pitfalls. One of them is use of accelerated ageing tests at one stress level for ranking or for pass/fail decision on different materials without consideration of activation energy. In place of establishing the Arrhenius diagram from ageing experiments at different temperatures, it is often practised to use one experimental point only and an assumed slope (activation energy). If the slope is selected conservatively (low activation energy) the risk that the true activation energy is lower is minimal and the expected lifetime is a conservative value.
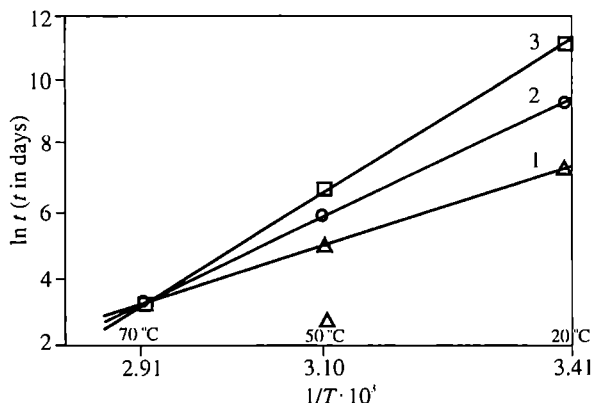
Fig. 1. Lifetime evaluation using one data point — the consequence of various activation energies (1 — 70 kJ/mole, 2 — 100 kJ/mole, 3 — 130 kJ/mole); life time at 20 °C: 1 — 5.5 years, 2 — 33 years, 3 — 198 years

Figure 1 shows the consequence of various activation energies (E_a) on lifetime prediction. Using time transformation function, the calculation gives that one month at 70 °C corresponds to the lifetime of 5.5 years at 20 °C for the material with E_a = 70 kJ/mole, it corresponds to 33 years for the material with E_a = 100 kJ/mole and to 198 years for a material with E_a = 130 kJ/mole.
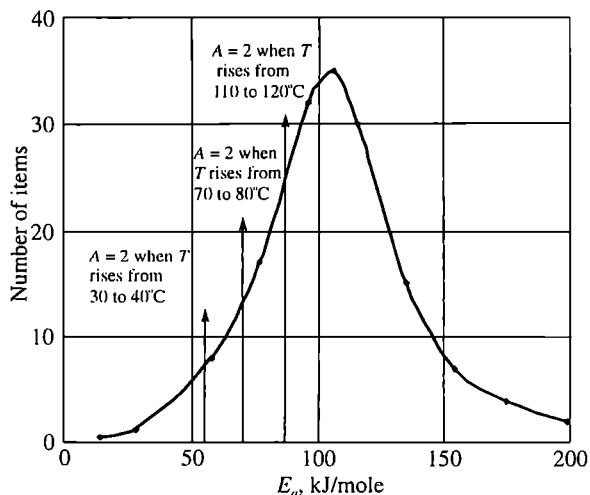

Fig. 2. Frequency distribution of activation energies (E_a) of 225 different polymeric materials; A — acceleration factor

The key to select an activation energy that can be regarded as conservative is a knowledge about the distribution of activation energies of the specified type of materials. In Figure 2 the frequency distribution of activation energies of 225 different materials is presented [1]. It is evident that the most frequent values are in the range 90—120 kJ/mole but the whole range includes values from 20 to 200 kJ/mole. Many engineers and scientists are using a "rule of thumb" in selection of time and temperature for accelerated ageing tests. This rule tells that if the temperature is increased by 10 K, the rate of degradation reactions is doubled (the time is halved). It is indicated in Fig. 2 when this assumption is true. Of course the acceleration factor (A) depends on activation energy and on the temperature range as shown by the time transformation functions (Table 1).

Table 1. Examples of time transformation functions

Degradation process	Time transformation function*)	Comments
Chemical reaction	$a_T = \exp[-E/R(1/T_t - 1/T_s)]$	Arrhenius equation temperature dependence of rate constants
Diffusion	$a_D = \exp[-E_D/R(1/T_t - 1/T_s)]$	Arrhenius equation for diffusion
Irradiation	$a_I = (I_t/I_s)^p$	p = 1 when pure photo-chemical degradation
Mechanical stress	$a_\sigma = \exp[b(\sigma_{f,t} - \sigma_{f,s})]$	amorphous polymers under glass transition temperature (T_g)
Mechanical stress	$a_\sigma = \dfrac{\sigma_{f,t} - \sigma_f(\infty)}{\sigma_{f,s} - \sigma_f(\infty)}$	amorphous polymers above T_g

*) E — activation energy, E_D — activation energy (diffusion), R — gas constant, t — test conditions, s — in use conditions, I — light intensity, p — material constant, σ_f — applied mechanical stress, $\sigma_f(\infty)$ — the highest value for infinite lifetime.

ILLUSTRATIVE EXAMPLES

It is generally recognized that the service lifetime prediction is valid for a given polymeric system under given service conditions only. In the following examples the various results, which also are of significance, are presented.

The same material, different previous history

New indoor profiles made of rigid PVC have been studied after various numbers of repeated extrusions (mechanical recycling) in order to gain knowledge about the changes of properties and durability after conventional processing [2]. The profiles were re-extruded, from one to five times without adding new additives. The activation energies of the thermal degradation process in dark were determined for the material after each
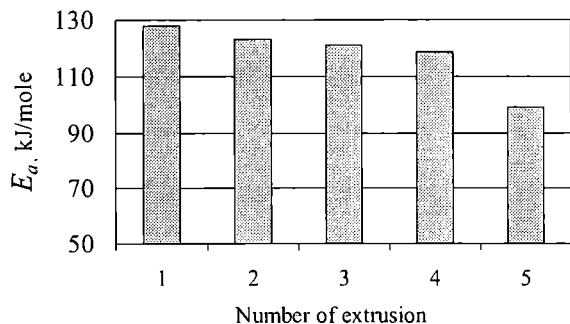
Fig. 3. Effect of repeated extrusion of rigid PVC on activation energy (E_a) of thermal degradation

re-extrusion and were found to decrease with increasing number of extrusions (see Fig. 3). The activation energy of the material after one extrusion was 128 kJ/mole but after five extrusions the corresponding value was 99 kJ/mole. This involves the overestimation of the lifetime by a factor up to 3.6 if we assume that the first value is valid independent of the number of extrusions.

The same material, different environments

PE films are commonly used in buildings as vapour barriers. In certain constructions, these products are in contact with wet concrete during their service life. The alkaline environment created by wet concrete may accelerate the degradation of these products. PE-LD films were investigated with respect to their durability by accelerated ageing at 70, 80, and 90 °C in contact with wet concrete and in moist air. The rate of degradation in the environment of fresh wet concrete at ambient temperature was much higher than in moist air [3]. But also the activation energy was higher in wet concrete environment (136 kJ/mole compared to 118 kJ/mole). In spite of
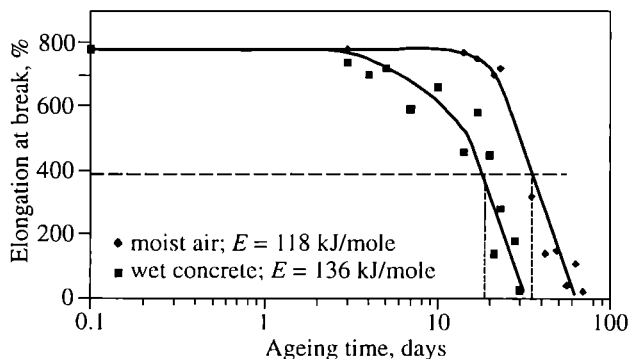

Fig. 4. Effects of wet concrete and moist air on durability (elongation at break) of PE at 90 °C

the fact that the lifetime (elongation at break ≥400 %) of the film at 90 °C in wet concrete environment was half of the lifetime in moist air (Fig. 4), the extrapolation to 40 °C gives a lifetime of 66 years in contact with wet concrete but 51 years in moist air.

The same material, different evaluation methods

The oxidative degradation of PE is often followed using IR spectroscopy measurements. A quantitative method depends on measurements of the intensity of the carbonyl absorption band at 1710—1720 cm^{-2} in the IR-spectrum. The carbonyl absorbance is related to the absorbance of a reference band at 2019 cm^{-2} and is re-
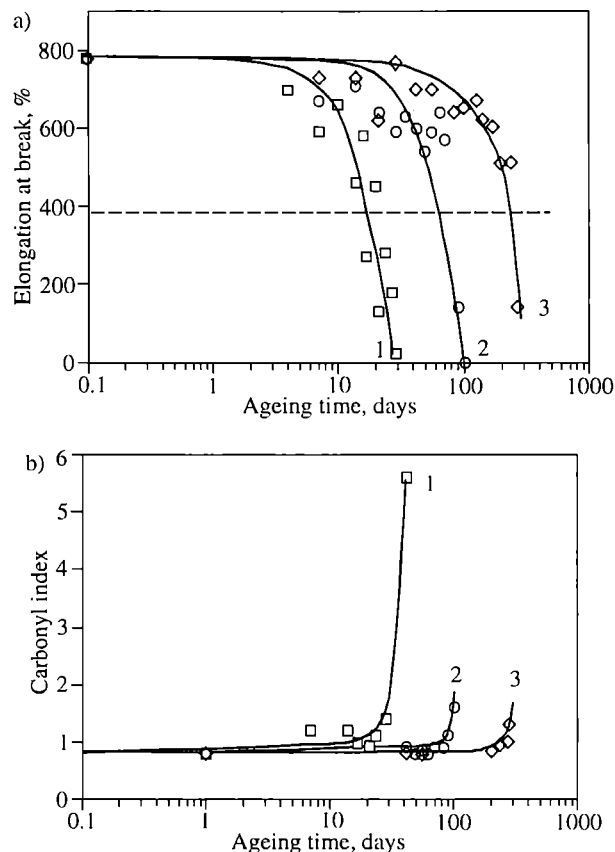

Fig. 5. Effects of heat ageing of PE-LD film on elongation at break (a) and on carbonyl index (b); temperature: 1 — 90 °C, 2 — 80 °C, 3 — 70 °C

ferred to as carbonyl index. Figure 5 shows that monitoring of the degree of degradation by measuring the carbonyl oxidation products does not correspond to the results of the elongation at break measurements [4]. This accentuates the importance of the correct choice of critical property for the evaluation of ageing.

High stress levels

Prediction of rubbers lifetimes is important for the rubber industry, particularly for the materials expected to perform reliably for many years. It is dependent on accelerated ageing tests and extrapolation of test results. Acceleration is achieved using higher stress levels of one or more degradation factors relative to the service life conditions. When choosing
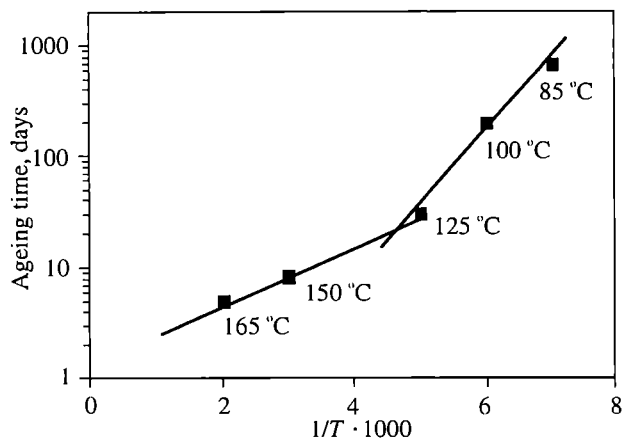
Fig. 6. Compression set of ethylene/propylene/diene terpolymer (EPDM) in the Arrhenius plot

higher stress levels in accelerated ageing tests it is important not to cross certain critical levels. Physical and chemical processes occur simultaneously when a constant stress is imposed on rubber. Generally, physical effects are dominant at short times and low temperatures and chemical effects are more apparent at long times and high temperatures. If accelerated conditions, such as elevated temperature, are used it follows that results could be misleading. In Figure 6, a deviation from a straight line is demonstrated as a result of too high temperature (>125 °C) [5].

Depletion of stabilizers

One of the most frequently used accelerated tests is oven ageing at selected temperatures with periodical examination of the materials. Changes in mechanical properties are often used to follow the course of degra-
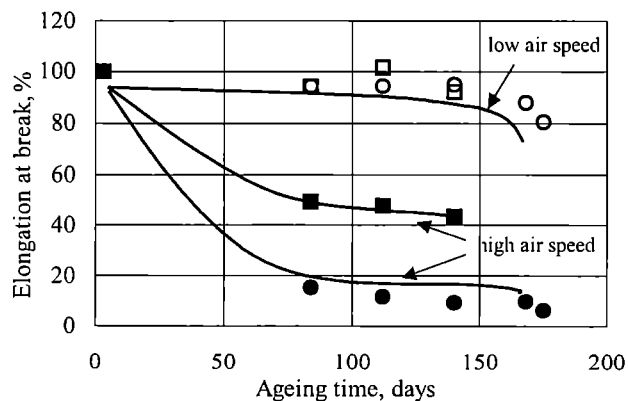

Fig. 7. Oven ageing of PE-based non-woven materials at 80 °C in cabinets with low (0.2 m/min) and high (100 m/min) air speed

dation. The importance of a proper selection of the most significant factors causing degradation is demonstrated in Fig. 7, where the air speed in the oven-ageing test was

of vital importance [6]. After periods of ageing, the elongation at break was measured. The results clearly demonstrate that forced-air ovens (the type used predominantly) can cause a significant antioxidant loss by evaporation.

Another important physical transport process that can influence lifetime prediction of polymeric materials
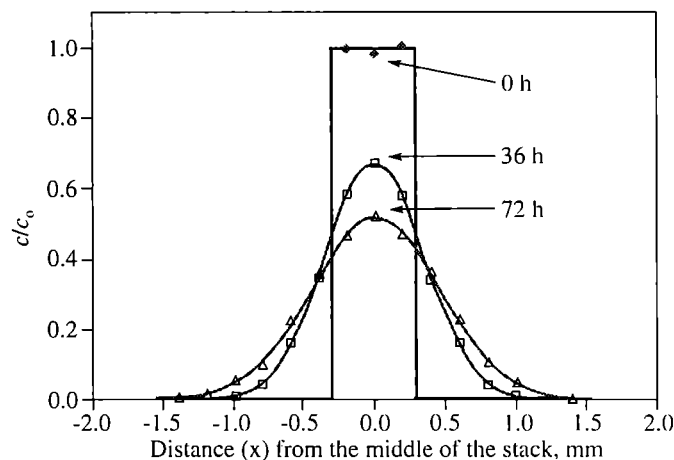

Fig. 8. Migration of an antioxidant (Irganox 1076) in PE at 50 °C. The figures stand for the experimental values while the solid curves represent theoretical solutions of Fick's second low of diffusion

is depletion of stabilizers by migration or diffusion. In Figure 8 the concentration profiles of an antioxidant in a film stack are shown. The antioxidant, which was octadecyl ester (Irganox 1076) was present in three films in the middle of the stack at the concentration of 0.1 %. The film stack was then heated at 50 °C and the concentration of the antioxidant in each film in the stack was measured after various periods [7]. It is demonstrated that the concentration in the doped films is reduced to half of the original value after 72 hours only showing the crucial importance of this process for the lifetime predictions.

DESIGN OF LIFETIME TESTING

In the design of lifetime testing, following critical steps should be included:

— Consideration of all the factors which might contribute to the degradation of the product in the intended end use environment.

— Description of the mechanism of the degradation.

— Accelerated testing in order to define the most significant factors causing degradation and evaluation of the activation energy or acceleration coefficient.

— Construction of models and failure functions for the response of the material to the environment, based on the accelerated test results and the environmental measurements.

REFERENCES

1. Dixon R.: "Constructing an Arrhenius Plot with Only One Data Point", Westinghouse Electric Corporation, 1985.
2. Yarahmadi N., Jakubowicz I., Gevert T.: *Polym. Degrad. Stab.* 2001, **73**, 93.
3. Jakubowicz I.: "Influence of Moist Concrete on the Durability of Polymers", Seminar at Chalmers University of Technology, Gothenburg (Sweden), March 15—16, 1993.
4. Jakubowicz I.: "Influence of Wet Concrete on the Durability of Polymer Films", VIII International Congress on Polymers in Concrete, Oostende (Belgium), 4th July 1995.
5. Jakubowicz I., Lindgren A.: "Time-temperature Limits of Rubbers in Compression", Poster presentation, Rubbercon 95, Gothenburg (Sweden), 11th May 1995.
6. Jakubowicz I., Johansson U.: "Thermal Ageing of Wind Protection Layers", SP Technical Report (97M76109), 1998.
7. Möller K., Gevert T.: *J. Appl. Polym. Sci.* 1994, **51**, 895.