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Prediction of the aging of polymer materials

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Abstract

The article deals with prediction of aging of multiplex polymer systems under conditions where the direct measurements of required properties are either impossible or difficult. To receive the reliable forecast, it is necessary to use physically reasonable models of processes. Solution of such problem and brief mathematical background is described in the article. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The problem of predicting polymer aging [1] is interesting not only theoretically but it is also very important from a practical point of view. First of all, here should be mentioned application of polymer goods at highly dangerous objects such as nuclear power plants. The control of electric cable isolation is necessary for preventing accidents. The whole procedure of aging investigation is very complicated. It includes chemical (physical) aspects as well as mathematical ones. In this article, we present a brief review of the mathematical side.

The properties of polymer material are not determined only by its composure. Molecules of the most simple (linear) polymer have different lengths, so there is the molecular mass distribution. Besides these molecules can cooperate with each other forming complex structure. It leads to non-reproduction of material properties. The same plastics made in different conditions demonstrate completely different properties. As a result, there is a large variation of properties in measurements. This variance consists of rather small equipment error and random component connected with diversity of the samples. Polymers are out of thermodynamic equilibrium. Their structure and their properties are changing in the course of time even in the absence of external influence. Besides, many polymers are rather sensitive to external environment. Oxygen, light and high temperature affect their behaviour greatly. So, for example, the polyethylene being in darkness keeps the initial mechanical properties for a long time (more than 30 years). The same polyethylene loses them in light in 2 years. The physical–chemical process of change in polymer properties in the course of time is called 'aging' of polymer materials. The prediction of such aging is the problem to be solved.

For its decision, it is necessary to construct physical–chemical model, describing the aging process and to extrapolate it to the conditions of aging. It is well

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known that extrapolation (as against interpolation) is an ill-posed problem. Unfortunately, all 'external', i.e., the mathematical methods of regularization, are not acceptable here. The unique opportunity to come by the correct prediction is to rely on reasonable model. The methods of construction of such models are rather good developed by efforts of many scientists, working in the field of physics–chemistry of polymers and first of all in the works of Semenov's school. We shall not discuss these methods, since it lies beyond the scope of this article. We shall hereafter assume that we have some mathematical model describing aging. It connects the properties of material (responses) with conditions of aging (predictors) and unknown parameters. For the estimation of parameters, it is necessary to carry out an experiment, but aging under natural conditions may requires a rather long time. Therefore, in practice, various ways of acceleration of aging process are used.

2. Accelerated aging

It is known that the rate of chemical reaction changes depending on the conditions in which the reaction proceeds. In particular, the temperature dependence of reaction rate constant k is described by the Arrhenius law:

$$k = k_0 \exp\left(-\frac{E}{RT}\right).$$

where T is temperature (K), k_0 is entropy factor (pre-exponential), E is activation energy, R is gas constant. From this equation, it follows that the process proceeds really faster under increased temperature. There are similar ideas about the influence of other factors of external environment (such as light, loading, etc.) on the process of aging. Founded on these ideas, it is possible to design the experiment in which, during a reasonable time, polymer aging reaches deep degrees of transformation. Such technique of testing is called an accelerated aging test and widely used in practice. However, while planning such tests, it is necessary to keep in mind that conditions of experiment should be such that mechanisms of accelerated and natural aging are similar. (For example, for accelerated thermoaging of polyethylene, temperature should be of course below melting point.) Only under these conditions is extrapolation possible. In this connection, very interesting mathematical problems concerning the optimization of the plan of such accelerated tests are originated.

We have developed and successfully used the Excel spreadsheet solution 'DESIGN' for evolutionary planning of aging tests of tire rubbers. This procedure allows us to make the plan of experiment in such a way that:

1. We may guarantee the necessary depth of aging during accelerated testing;
2. We define the temperature mode that keeps aging mechanism similar to natural conditions;
3. We optimize the time of thermoaging (not to keep samples in the ovens too long).

3. Parameters estimation

Next stage of forecast problem solution is estimation of the unknown parameters of the model. Here, we apply regression methods, in particular, maximum likelihood method. As a rule, we deal with complicated nonlinear dependencies. In addition, these models are often multicolinear. The modification of gradient method offered in the works of Pavlov and Povzner [2] is used to search a minimum of target function. The main idea of this approach is the following. For inversion of the Fisher matrix $\mathbf{A}$ at every step of minimization, the recurrence algorithm is used:

$$\mathbf{C}(2t) = \mathbf{C}(t)\left[2\mathbf{E} + \mathbf{AC}(t)\right].$$

It is easy to see that matrix $\mathbf{C}(t)$ satisfies matrix differential equation:

$$\dot{\mathbf{C}}(t) = \mathbf{E} + \mathbf{AC}; \quad \mathbf{C}(0) = 0;$$

with solution:

$$\mathbf{C}(t) = \int_0^t \exp(\mathbf{A}s)\,\mathrm{d}s.$$

Therefore, as $t \to \infty$, matrix $\mathbf{C}(t) \to -\mathbf{A}^{-1}$. If $\mathbf{A}$ is a singular matrix, then matrix $\mathbf{C}(t)$ does not lose sense and gives quasi-inverted matrix $-\mathbf{A}^{+}$. Application of such method essentially accelerates a procedure of search. Besides that, the stability of recurrent procedure allows the inversion of matrices with large spread in eigenvalues.

4. Bayesian estimation

Aging is characterized by simultaneous changes of various properties. Each of them is described by their own model. However, the same aging process affords the basis of these changes. Therefore, the common parameters are used in the mathematical descriptions of various properties. Such situation causes interesting mathematical problems while we search parameter estimations on dissimilar data sets. The classical approach offers to build common multiresponse regression for simultaneous analysis of the whole array of experimental data. Such approach is difficult to carry out due to the large number of estimated parameters and the necessity to inverse large-dimension matrices. We have developed a method that allows the processing of the data consequently for each response [3]. The idea of this method consists in the following. Regression dependence for each response (the series) is analysed separately, but taking into account the information about common parameters estimated from the previous series. As a result, a posterior Bayesian distribution is formed after every response processing. This information is then used as a priori one for processing the next series.

If the dispersion of measurement error σ^2 is the same for different responses, it is transferred from the previous series of data η to the next and the parameter estimations a is found as a minimum of functional:

$$Q(\eta,a) = [\eta - f(a,x)]^t[\eta - f(a,x)] + (a - \boldsymbol{a}_0)^t\mathbf{H}(a - \boldsymbol{a}_0) + n_0\sigma_0^2.$$

If dispersions are different, than the functional has another form

$$Q(\eta,a) = [\eta - f(a,x)]^t[\eta - f(a,x)] \times \exp\left[\sigma_0^{-2}n^{-1}(a - a_0)^t\mathbf{H}(a - \boldsymbol{a}_0)\right].$$

Here, the vector $\boldsymbol{a}_0$ is a priori parameters estimation, σ_0^2 is a priori dispersion estimation, n_0 is the number of degrees of freedom. All of them are assumed to have been determined at the previous series. For construction of Bayesian matrix $\mathbf{H}$, it is necessary to separate common parameters from partial ones and to transform the regression information matrix:

$$\mathbf{A} = \begin{bmatrix} \mathbf{X} & \mathbf{Z} \\ \mathbf{Z}^t & \mathbf{Y} \end{bmatrix}$$

into the matrix:

$$\mathbf{H} = \begin{bmatrix} \mathbf{G} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix},$$

where $\mathbf{G} = \mathbf{X} - \mathbf{Z}\mathbf{Y}^{-1}\mathbf{Z}^t$.This procedure allows considerably accurate prediction of aging in comparison with traditional methods.

5. Confident forecast

To estimate the accuracy of forecast, it is necessary to build confidence interval. The existing methods do not satisfy us as we deal with complicated nonlinear models. The elementary method of stochastic approximation, where the linearization of model is used, does not give sufficient accuracy. On the other hand, boot-strap with high accuracy requires inadmissible expenses of computer time for its realization (about 10 h in our case). We have developed a new way of constructing the confidence limits. The idea of this method is the following. With the help of a Monte-Carlo procedure we obtain parameter estimation sampling. Unlike boot-strap, we simulate not initial experimental data, but estimations of parameters. To simulate such distribution correctly, we use a special technique guaranteeing us that quantity of realizations getting in the field of indifference $I(C)$ of the target function Q:

$$I(C) = \{a{:}Q(\eta,\alpha) - Q(\eta,a) < C\},$$

is equal to the expected value. Here level C is set as:

$$C = s_0^2\,\chi_p^2(P),$$

where $\chi_p^2(P)$ is P-quantile of χ^2-distribution with p degrees of freedom and s_0^2 is dispersion estimate. It was shown that this method has the same accuracy as boot-strap but about 1000 times faster.

6. Conclusions

All these and some other methods were incorporated in the large computer program ‘Kinetic Trunk’.

This software allows the interpretation of various experimental data and the estimation of model parameters arbitrarily set by the user. Explicit, implicit functions, and also models in the form of the ordinary differential equations are admitted. The program has the special block ‘Forecast’, in which procedure of reception of any of the three components for forecast problem (response, factor, reliability) is automated at given two others.

The above-stated technique of prediction of changes in polymer properties was applied to different polymer systems and some practical methods were developed. With the help of the ‘Kinetic Trunk’ software, the following solutions have been done: (1) Technique of testing of antioxidizing activity of stabilizers in polyolephyne with help of differential scanning calorimetry (DSC) in a dynamic mode; (2) High-sensitivity method for controlling radiating and chemical cross-linking of crystalline polymers based on the results of thermo-mechanical analysis (TMA); (3) Technique of complex processing the results of tire rubber testing in purposes of prediction service life, optimization curing modes and recipes; (4) Method of estimating the resistance of composition materials to thermo-moist aging using the results of cycling tests ‘moistening–drying’; (5) Monitoring and estimation of residual life time of cable insulation used at nuclear power plants.

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