Prediction of Rubber Stability by Accelerated Aging Test Modeling

Oxana Y. Rodionova, Alexey L. Pomerantsev

Institute of Chemical Physics, Russian Academy of Sciences, Kosygina Street 4, 119991 Moscow, Russia

ABSTRACT: This study was devoted to the prediction of polymer material aging. The prediction of the shelf time of tire rubber is used as an example in this article. The main steps of the whole procedure are described. They are the design of the experiment, accelerated aging testing, the construction of a multiresponse mathematical model and parameter estimation, and the extrapolation of the model in real-life settings. The main pitfalls were deduced, and techniques to overcome these pitfalls are described. Novel methods of data modeling, such as evolutionary design of experiment and successive Bayesian estimation, were used. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1275–1284, 2005

Key words: rubber; mechanical properties; ageing; modeling

INTRODUCTION

The prediction of the operation and the shelf stability of polymer materials is one of the most difficult modeling problems. Very often, the shelf (operation) time of these materials is greater than 10 years, and statistics of failures for this period are absent. Ordinary accelerated aging testing (AT) is used for prediction purposes. During these tests, samples are exposed to conditions (aging factors) that are more severe than in real life, and these factors lead to accelerated aging. The AT results are used for mathematical modeling that describes changes in the material properties (y; responses) in time t regarding aging factors (X values):

$$y = f(t, X, a)$$

The model depends on unknown parameters (a values), which are estimated with the help of a data set obtained in the course of AT. As a rule, the least squares method (or the maximum likelihood method) is used, and parameter estimates for a are determined as values that minimize the objective function, Q

$$Q(a) = \sum [f(t_i, X_i, a) - y_i]^2$$

With the values of these estimated parameters, one can extrapolate the material properties on shelf (operation) conditions. For known critical levels of investigated properties, it is possible to calculate the time when these levels are attained. This is the main scheme of the prediction procedure, but there are several difficult issues that merit special attention.

Multidimensional response

Aging is characterized by simultaneous changes in various properties, and several characteristics are controlled in the course of AT. Each of them is described by its own model. So, in modeling procedures, one deals with not one but several objective functions. However, the same aging process affords the basis of these changes. Therefore, common parameters are used in the mathematical descriptions of various properties. Such parameters as activation energy and the pre-exponential factor of the reaction rate constants of chemical and physical processes should be common and belong simultaneously to different models. Thus, one cannot estimate unknown parameters by minimizing each objective function separately, and one encounters an interesting mathematical problem when one searches for parameter estimates on dissimilar data sets. The classical approach offers to build common multiresponse regression for simultaneous analysis of the whole array of experimental data and to use each model with a specified weight value because different responses are measured with different errors. As a rule, one does not know the measurement error variances, and elaboration of the common model leads to a complicated iteration procedure.

To overcome this problem, successive Bayesian estimation (SBE) was developed;[1] it allows the data to be processed successively for every response. The SBE method is widely used for experimental data process-

ing.[2–6] In this study, the SBE method was used for rubber shelf-time prediction.

Multicollinearity

In practice, very often it is difficult to determine the minimum of the objective function. From a geometrical point of view, it can be explained as a degradation of the surface when it looks like a ravine without an explicit minimum point. Such a situation is called *multicollinearity*. To understand the reasons, we have to distinguish two different cases: strict multicollinearity, or the nonidentification case, and nonstrict multicollinearity, or the ill-posed case.[7] In the first variant, there are some intrinsic dependences (maybe implicit) between the parameters in the model that forbid the estimation of all of the parameters. The simplest example is

$$y = a_1 a_2 t$$

It is obvious that for any experimental plan, one cannot estimate parameters a_1 and a_2. In the second variant, multicollinearity is caused by the poor design of the experiment and may be overpassed by another experimental data set. The simplest example is

$$y = a_1(1 - e^{-a_2 t}) \approx a_1 a_2 t \quad \text{when } a_2 t \ll 1$$

For small t values, the model becomes singular. However, with a good plan, there is no problem for parameter estimation. Unfortunately, there is no strict definition for a good experimental design. This depends on measurement errors and computational accuracy and may be improved by data scaling and model modification.

Strict multicollinearity is often found in the hard modeling of the kinetics of chemical reactions, and the second variant ordinarily occurs in soft modeling. The prediction of the operation and the shelf stability of polymer materials and products is just this case, and later, we show scaling techniques applied to the Arrhenius equation.

Extrapolation

All of the aforementioned difficulties are nothing in comparison with the prediction problem; that is, extrapolation of the model at settings that are far from the observed area. How can one guarantee that the results are reasonable? How can one confirm that he or she used a good model for a formal description of the aging process? Standard validation methods, such as test validation or cross-validation, do not work here because they are suitable only for interpolation problems. Strictly speaking, there are no mathematical methods that can answer the posed questions. How-

ever, hard physicochemical modeling that uses complicated kinetic schemes to describe the degradation process cannot guarantee the results either. Any complication of the model in the framework of the experiment that is limited in time and content leads not only to unreliability of the forecast but also to overestimation of the model and, as a result, to strict multicollinearity of the whole problem.[8] Polymer aging is a complex physicochemical process that is characterized by numerous parameters. However, we can arrange them in the degree of each parameter's impact on the aging process. In very many practical cases, aging is determined by one or two, rarely by three, main parameters. To make the right choice, it is necessary to fulfill two main conditions:

- Parameters under consideration should be common for all individual models.
- In the course of AT, one should observe and identify the influence of these parameters on the aging process; that is, the AT settings should not be far from real life.

Here, we can draw an analogy with projection methods, which are used for multivariate linear modeling, that is, the choice of principal components.[8] The main difference between these two approaches is in the validation method. In our case, validation was realized by consistent model construction. Next, we illustrate it.

Software

All of the procedures described in this article demanded mathematically complicated data and model processing. For this purposes, we used a special software called FITTER,[3,9] an add-in for the popular Microsoft Excel program. All of the necessary data were placed on a worksheet of a standard workbook and then registered by wizards. FITTER is used for parameter estimation of complicated mathematical models. These models may be in the form of explicit or implicit functions or differential equations, and they are accepted by the program when written in ordinary algebraic notation. In addition to experimental data, *a priori* parameter information also may be input into the program. FITTER provides vast statistical information regarding the input data and fitting results.

EXPERIMENTAL

Samples and data set

We demonstrated the capabilities of the advocate approach on the forecasting of the thermooxidation aging of tire rubber. All of the rubber samples were rectangular plaques $200 \times 200 \times 2$ mm in size, which

TABLE I
Measurements Characteristics at Accelerated Aging

No.	Property	Notation	Unit
1–5	MOD at ELN = 1, 2, 3, 4, and 5	MOD(ELN, t, T)	KPa
6	TEN	TEN(t, T)	KPa
7	ELB	ELB(t, T)	1

were produced especially for this experiment. The material characteristics were as follows: the tread tire rubber was formulated from natural rubber, butadiene–styrene rubber, and sulfur; the curing temperature (T_{cur}) was 160°C; and the curing time (t_{cur}) was 16 min. Five standard specimens (ASTM D 412-87) were prepared from each plaque for one test. The properties were measured in the course of testing (Table I).

An Instron tensile testing machine was used for the measurements. Time was measured in hours, and temperature was measured in degrees centigrade.

AT design

In our case, AT meant artificial material aging at several (three) constant temperatures. Testing design is essential for obtaining a reliable forecast. It was also important to solve two main problems. First, we had to achieve the necessary aging depth in a short time. Obviously, the change in a property should not have been less than its critical level value that characterized the failure of the material. This results in an increase in the testing temperature. Second, we wanted to simulate the mechanisms of natural aging, and this forced us to decrease the testing temperature. Therefore, this AT required much time, and correct planning was very important. We considered elongation at break [ELB; $\varepsilon(t)$] to be the most sensitive property among those that are usually controlled during the AT of rubbers. This parameter first reflects changes in the structural homogeneity and defectiveness of the material. Therefore, we used this characteristic as the basic parameter in the special procedure for the evolutionary design of experiment (EDOE).[10] EDOE helps the researcher avoid the extra expenditure of time and labor and obtain reliable data in reasonable terms. The idea of the EDOE procedure is as follows. First, we conducted preliminary testing at the highest possible temperature (T_{max}) during two minimal time periods. With the help of these preliminary results, we calculated the time that is necessary for achievement the predefined aging depth for any given temperature, that is, the whole plan of AT. EDOE consists of three stages: preliminary design, a correction step (or steps), and final design. For a detailed description, see Appendix A.

Table II shows the results of EDOE and the testing conditions used in the experiments for the investigated material (Samples and Data Set section). The experimental data are shown in Figure 1. Some comments are necessary here:

1. The EDOE procedure is based on half-empirical models, and the AT design is, of course, rather approximate. The investigator should consider the results assistance but not as strict instruction.
2. The aging terms calculated by EDOE turned out less than we planed before the experiment, so we decided to keep our original plan of the experiment. The EDOE results confirmed that we reached the predefined aging depth.
3. The results of AT (see Fig. 1) show that the EDOE procedure worked well, at least in this case.

Deformation curves

Apparently, the deformation curve, that is a diagram of strain (STR) versus elongation (ELN), obtained for each specimen is the best data set for forecasting the mechanical properties of rubbers. The advantages of this approach are evident as we reconstructed the aging trajectory that reflects the dependence between changes in different properties in the course of aging in the uniform compact form.[5] The existence of a uniform trajectory that does not depend on testing temperature revealed that all of the changes are caused by the total aging process.

At first, we constructed a model for the deformation curve [STR(ELN, f, T)] that was correct for any ELN, time t, and temperature T. After that, we derived a model for every modulus (MOD), for example
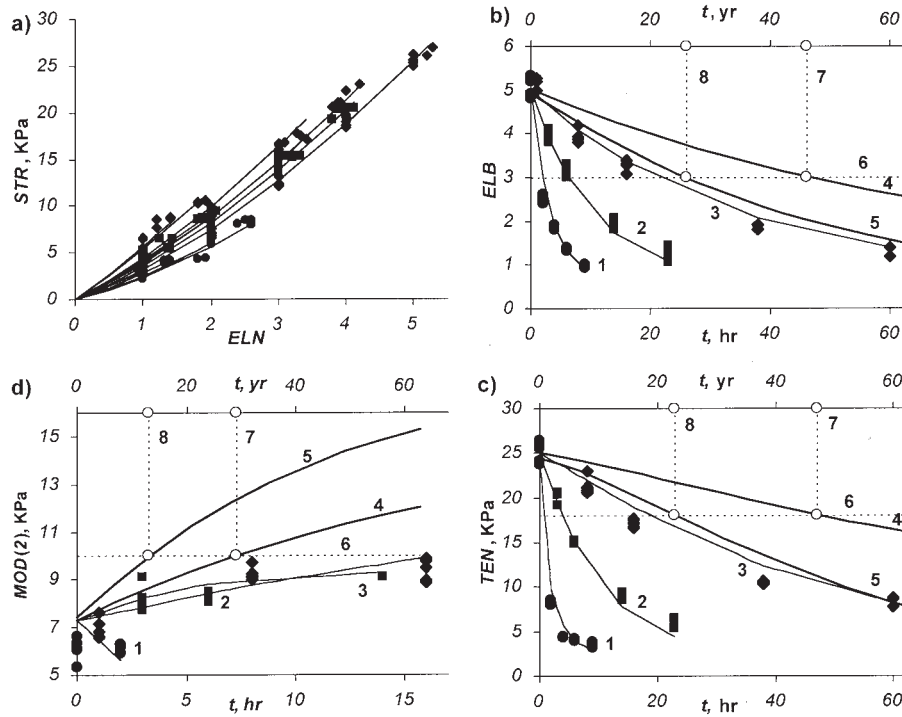
$$MOD(1, t, T) = STR(1, t, T) \tag{1}$$

When we constructed a model for elongation at break [ELB(t, T)], we could derive a model for tensile strength (TEN) from two models as

$$TEN(t, T) = STR[ELB(t, T), t, T] \tag{2}$$

TABLE II
Design of the AT

	T (°C)	Times (h)			
EDOE	140	0.9	1.7	2.8	3.9
	125	2.1	4.1	7.7	12.0
	110	5.5	11.0	27.0	42.0
Experiment	140	2.0	4.0	6.0	9.0
	125	3.0	6.0	14.0	23.0
	110	8.0	16.0	38.0	60.0

Figure 1 AT data and results of the extrapolation to $T = 20°C$: (a) deformation curve, (b) ELB, (c) TEN, and (d) MOD. (1, ●) $T = 140°C$, (2, ■) $T = 125°C$, (3, ◆) $T = 110°C$, (4) mean values, (5) 0.95 confidence value, (6) critical level, (7) mean time, and (8) confidence time.

Moreover, with deformation curves for each specimen, we could have determined the differences between specimens and, as a result, separated the measurement error and the sample heterogeneity.[11] However, such measurements were not conducted, and we had to reconstruct deformation curves with the experimental data set.

MODELING

Models

To describe the AT data, the following base models were used. For the deformation curve

$$STR(ELN, t, T)$$
$$= [b_0 + b_1 e^{-K_1 t} + b_2 e^{-K_2 t}]ELN$$
$$+ b_3(1 - e^{-ELN b_4}) \quad (3)$$

For ELB

$$ELB(t, T) = a_0 + a_1 e^{-K_1 t} + a_2 e^{-K_2 t} \quad (4)$$

Auxiliary models [eqs. (l) and (2)] were derived from the base models as it described previously. For TEN

$$TEN(t, T) = [b_0 + b_1 e^{-K_1 t} + b_2 e^{-K_2 t}]ELB(t, T)$$
$$+ b_3[1 - e^{-ELB(t,T) b_4}] \quad (5)$$

For MOD

$$MOD(ELN, t, T) = [b_0 + b_1 e^{-K_1 t} + b_2 e^{-K_2 t})ELN$$
$$+ b_3(1 - e^{-ELN b_4}) \quad (6)$$

The models in eqs.(3)–(6) depend on two common (kinetic) parameters, K_1 and K_2, and several partial (formal) parameters a_0, a_1, b_0, b_1, b_2. The common parameters depend on temperature by the Arrhenius law, which we write as follows:

$$K_i = e^{-k_i - E_i X} \quad \text{where } i = 1, 2$$

where

$$X = \frac{1000}{T + 273} - X_0, \quad X_0 = \frac{1}{3} \sum_{i=1}^{3} \left(\frac{1000}{T_i + 273} \right),$$

$$T_1 = 140, T_2 = 125, T_3 = 110$$

This form is very convenient from a computational point of view in comparison with a traditional one:

$$K = g \exp\left[-\frac{F}{R(T + 273)}\right], \quad F = 1000RE, g = e^{-k + EX_0}$$

TABLE III
Scheme of Successive Parameter Estimation

Parameter	ELB-1	STR-1	ELB-2	STR-2	Physical values	
Partial						
a_0	0.97		**0.64**			
a_1	4.19		**4.31**			
a_2			**0.06**			
b_0		11.56		**11.41**		
b_1		−4.22		**−4.14**		
b_2		3.95		**3.87**		
b_3		−62.20		**−59.71**		
b_4		0.14		**0.14**		
Common						
k_1	1.40	**1.65**			$2.70 \times 10^{+12}$	g_1
E_1	12.53	**12.32**			102.32	F_1
k_2		1.51		**1.50**	$1.96 \times 10^{+27}$	g_2
E_2		25.78		**26.16**	217.44	F_2

where R is the gas constant. It is evident that values E (activation energy) and k (pre-exponential) are closer to 1 than natural parameters g (traditional pre-exponential) and F (traditional activation energy) (see Table III). Such a simple model transformation helped us to improve model structure and to overcome the problem of multicollinearity.[13] As a result, for data processing, we obtained four models with eight partial and four common parameters.

Data processing

We used the SBE method[1] for estimation of all of these parameters. The idea of this method is the following. A regression model for each response (the series) is analyzed separately but with regard to the information about the common parameters estimate (from the previous series). As a result, posterior Bayesian information is formed after each model fitting. Then, this information is used as *a priori* information for processing the next series. For a mathematical description of SBE in application to the given method, see Appendix B. Figure 2 shows an example of the posterior and prior information matrices.

Here, the AT data were processed in the following order

$$ELB \xrightarrow{1} STR \xrightarrow{2} ELB \xrightarrow{3} STR$$

The procedure started from the ELB, and we used a simplified model for the first step

Posterior Information after ELB+STR											
Name	**Value**					**Matrix**					**Exclude**
b0	11.6	3007.5	2162	2487.2	341.04	-1E+05	-2452	-194.4	1276.6	62.36	
b1	-4.2	2162	1714.9	1921.7	240.67	-82409	-1460	-129.3	685.17	36.247	
b2	3.95	2487.2	1921.7	2234.3	278.2	-95803	-1797	-180.7	801.34	55.857	
b3	-62	341.04	240.67	278.2	38.908	-13717	-286.5	-22.33	151.18	7.261	
b4	0.14	-1E+05	-82409	-95803	-13717	5E+06	103699	7926.9	-55517	-2618	
k1	1.65	-2452	-1460	-1797	-286.5	103699	2974.8	210.73	-1568	-68.45	
E1	12.3	-194.4	-129.3	-180.7	-22.33	7926.9	210.73	34.78	-68.45	-8.83	
k2	1.51	1276.6	685.17	801.34	151.18	-55517	-1568	-68.45	1132.7	32.383	
E2	25.8	62.36	36.247	55.857	7.261	-2618	-68.45	-8.83	32.383	4.1908	

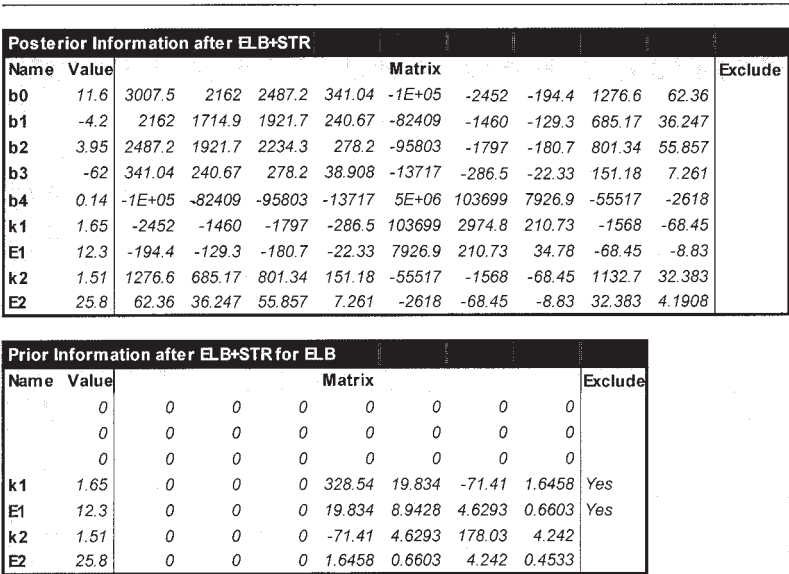| Prior Information after ELB+STR for ELB | | | | | | | | | | |
|------|-------|---|---|---|--------|--------|--------|--------|-----|
| **Name** | **Value** | | | | **Matrix** | | | | **Exclude** |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| k1 | 1.65 | 0 | 0 | 0 | 328.54 | 19.834 | -71.41 | 1.6458 | Yes |
| E1 | 12.3 | 0 | 0 | 0 | 19.834 | 8.9428 | 4.6293 | 0.6603 | Yes |
| k2 | 1.51 | 0 | 0 | 0 | -71.41 | 4.6293 | 178.03 | 4.242 | |
| E2 | 25.8 | 0 | 0 | 0 | 1.6458 | 0.6603 | 4.242 | 0.4533 | |

Figure 2 Examples of the posterior and prior information matrices.

TABLE IV
Model Extrapolation to a Temperature of 20°C

Property	ELB	TEN	MOD(1)	MOD(2)	MOD(3)	MOD(4)	MOD(5)
Initial value	5.01	25.05	3.10	7.29	12.40	18.33	24.95
Limiting value	0.71	2.04	7.25	15.57	24.83	34.89	45.66
Critical value	3.00	18.00	5.00	10.00	17.00	25.00	32.00
Property variation	47%	31%	46%	33%	37%	40%	34%
Confidence time (year)	25.00	23.00	20.00	14.00	16.00	18.00	15.00
Mean time (year)	46.00	47.00	45.00	29.00	34.00	38.00	31.00

$$\mathrm{ELB}(t, T) = a_0 + a_1 e^{-K_1 t}$$

as it is impossible to estimate the complete model [eq. 4]. At the end of the first step, we constructed the posterior information and recalculated it into prior information (with regard to k_1 and E_1). This new prior information was used for the deformation curve fitting. On the second step, it is possible to estimate four common parameters and pass them in the form of prior information to the next step. On the third step, we returned to the ELB model to specify parameters a_0, a_1, k_2, and E_2 and to estimate a_2. On this step, parameters k_1 and E_1 were excluded from the estimation procedure; that is, we kept their values constant. As the result of the third step, we estimated values of all of common (kinetic) parameters, and we only needed to specify values of the partial parameters $(b_0, \ldots b_4)$. For this purpose, on the fourth step, we fit the deformation curve with all common parameters kept constant.

In the application of such a technique, when the same data set is used several times, it is very important to closely watch that on the second and further fittings, the common parameters remain constant and that the estimation is made only for the partial parameters. Table III presents the scheme of such an estimation. The final parameter values are indicated in boldface type. The final values of the kinetic parameters were obtained on the second step (STR-1), and these values did not changes afterward. On the third step (ELB-2), we estimated the final values for the partial parameters a_0, a_1, and a_2. Moreover, in the two last columns of Table III, we present the physical values of the kinetic parameters: the pre-exponential parameters (h^{-1}) and activation energy (kJ). Finally, we determined all of the values of the unknown parameters in the models in eqs. (3)–(6). The details of data processing and the initial data set are located in the file rubber.xls online in ref. 12.

RESULTS

The forecast was built as model extrapolation to $T = 20°C$ for the given critical levels (y_{crit}) for all of the properties (see Table IV). The values of these critical

levels (Table IV, row 2) were defined by the producer. For each property, we determined the mean value and the confidence value. The mean value was calculated as the time required for achievement the critical level with the parameter estimates (Table IV, row 6). The confidence value (Table IV, row 5) was calculated with respect to uncertainty in the parameter estimates. For this purpose, we evaluated the 0.95 one-side confidence interval [the upper interval for MOD(n) and the lower interval for the other characteristics] for each model. The shelf time was determined as the interception point of such an interval and the critical level.

All of these results are also presented in Figure 1(b–d); there are the prosperities' mean values (curve 4), the confidence intervals (curve 5) and the correspondent shelf times (points 7 and 8). All of the confidence values were less than mean values. Moreover, there were the initial and the limiting values of all of the properties (Table IV, rows 1 and 2). The initial value was equal to the regarding property at $t = 0$:

$$y_0 = y \, (T = 20°C, t = 0)$$

The limiting values (y_{lim}'s) were calculated by the formula

$$y_{lim} = y \, (T = 20°C, t = 1000 \text{ years})$$

We defined this limiting point with the following considerations. ELB goes down monotonically, and its limiting value is $\mathrm{ELB}(\infty) \approx \mathrm{ELB}(1000 \text{ years})$. The MOD($n$) values reaches their maximum and TEN(t) had an inflection at this point. Table IV (row 4) presents variations of all of values calculated as

$$\left| \frac{y_0 - y_{crit}}{y_{lim} - y_{crit}} \right|$$

It was interesting to compare the shelf-time values (Table IV, rows 5 and 6) with the variation values (Table IV, row 4). Apparently, the longer shelf life values (ELB and TEN) were related to the more essential changes in properties. We supposed that mismatch in the estimated terms of the shelf life was due
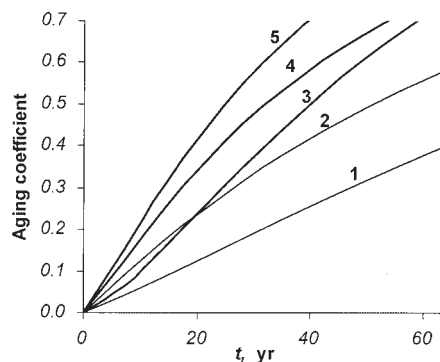
Figure 3 ACs for different properties, mean characteristics, and confidence characteristics: (1) TEN mean characteristics, (2) ELB and all MODs (mean characteristics), (3) TEN confidence characteristics, (4) ELB confidence characteristics, and (5) all MOD confidence characteristics.

to incorrect critical limits that were defined by the producer. To test this assumption, we plotted changes in properties with the aging coefficient (AC) as a function of time:

$$AC = \left| \frac{y(t) - y_{crit}}{y_{lim} - y_{crit}} \right|$$

Figure 3 shows the correspondent curves for all of the characteristics (the means and confidence values) calculated on the practically important time interval. All of the curves begin at the zero point and tended toward 1 as t tended toward infinity. On the interval in question, the ACs for all of the MODs overlap (Fig. 3, curve 2). This fact evidently follows from eq. (6). Much more interesting is the fact that the mean value of AC for ELB overlaps with the mean value of AC for all of the MODs (Fig. 3, curve 2). This fact does not follow from the mathematical models, but this is an inherent characteristic of the whole system. The ACs for TEN (Fig. 3, curves 1 and 3) settle lower than the other curves. This means that in the course of aging, changes in TEN were less than the changes in the other characteristics.

DISCUSSION AND CONCLUSIONS

The application of the SBE method manifested advantages in parameter estimation and in the prediction of the operation and shelf stability. This method allowed us to construct a complicated harmonious model with common parameters. We suppose that the availability of such a model and its adequacy to the experimental data prove the possibility and validity of extrapolation. Discussed next are the main issues of the advocated approach.

The critical point in the construction of a thermooxidation aging model is the question about the number of common parameters depending on temperature. Why did we use only two such parameters in the given example? Parameter K_2 is necessary in the deformation curve model and is redundant in the ELB model. At the same time, the introduction of the third parameter, K_3, did not improve the description of the STR/ELN relationship but only led to overfitting, that is, to the strict multicollinearity. It is well known,[8] that overfitting results in instability and some slips in prediction. The redundant parameter K_2 in the ELB model did not contradict this principle, as K_2 was estimated from the deformation curve. As a matter of fact, eqs. (3)-(6) give the general multiresponse model, and the parameter estimates belonged to all of these responses. Also, the overlap of ACs for all of MODs with AC for ELB is connected with the lack of necessity of K_2 for the prediction of these properties. At the same time, it is necessary to add parameter K_2 in the ELB model. If it was not done, the estimates of k_1 and E_1 were equal to the values obtained at the first step of the SBE procedure (Table III, column 1). In this case, we obtained inflated shelf times: the mean was 52 years, and the confidence was 36 years.

The second issue was the form of the aging models and their dependence on the partial parameters. This seemed for us less important than the choice of common parameters. If we used the proper design of AT and all of the properties crossed their critical levels, we did not have to do time extrapolation, and therefore, the form of the models, that is, their dependence on time, was not essential. For example, in the ELB model [eq. (4)], we could use a hyperbola instead of an exponential, and this did not change the prediction results essentially: the confidence time was 25 years instead of 23 and the mean time was 46 years instead of 43. The simplest way to construct the proper design of experiment is to do it evolutionary, consequently specifying the next measurement point with regard to the previous measurements. It was done with the help of the FITTER software and the EDOE procedure designed for these purposes.

Therefore, we concluded that the true number of common kinetic parameters could be defined with principles of model adequacy and identifiability. These parameters carry physical meaning; they reflect the process of thermooxidizing destruction in the material. Partial parameters do not carry any physical sense and may depend on the selected mathematical description; they are not essential for prediction results. Analyzing the numerical results of the forecast, we concluded that apparently, these values were close to the empirical estimates of the shelf time. The common aging processes differently influence different material properties, and therefore, we had a disagreement in the estimates of the ACs (Fig. 3), which was expected.

In conclusion, we emphasize that such an analysis of an aging model was possible only because of the application of the SBE method. Other methods do not allow one to estimate the parameters of a multiresponse model with a heteroscedastic data set.

APPENDIX A: EDOE PROCEDURE

Here we present a special procedure, which was used to design the experiments for the accelerated aging of rubber. To characterize the investigated material, we used T_{cur} and t_{cur} as input data. We used ELB to characterize the aging process (Fig. 4).

First stage: Preliminary testing

First, we performed testing at T_{max} for two minimal time periods. T_{max} was chosen as less than T_{cur} at 15–30° because it is usually taken for the thermoaging of rubbers. Two measurements of ELB were performed at T_{max} and for two time periods: t_1 and $t_2 = 2t_1$. The term t_1 was calculated with the curing mode and the Arrhenius law

$$t_1 = t_{cur} \exp\left[\frac{E}{R}\left(\frac{1}{T_{max}} - \frac{1}{T_{cur}}\right)\right] \qquad (A.1)$$

where t_{cur} is the curing time. E was chosen with regard to the rubber recipe ($E/R = 10,000$ for sulfur curing agents and 12,500 for compounds that do not have free sulfur). Our goal was to select the AT conditions that provided the achievement of a given aging depth (AD). When we write about AD, we the mean relative change of ELB, that is, $D(t) = [\varepsilon(0) - \varepsilon(t)]/\varepsilon(0)$, where Dis AD, $\varepsilon(t)$ is ELB, $\varepsilon(0)$ is ELB before aging.

Second stage: Time extrapolation

The results of the measurements [including values of $\varepsilon(0)$ for the unaged samples] were used for the construction of the whole plan of AT at each desired temperature. First, we analyzed the data for $\varepsilon(0)$, $\varepsilon(t_1)$, and $\varepsilon(t_1)$ to be certain that ELB essentially decreased. Our computer experiments showed that AD should not have been less then 0.25 at the end of the preliminary tests. Otherwise, the result of extrapolation through time could be strongly overestimated. We also had to consider that sometimes a small increase in ELB could be seen during the initial stage of rubber thermo-aging. This circumstance also may have distorted the results. To confirm the decrease in ELB, we used the Student's test. If ELB did not fall enough, we conducted an additional test at time $t_3 = 3t_1$. The procedure permitted not more than three such corrections. Any value of t_m (m = 2, 3, 4, . . .) was calculated

as $t_m = mt_1$. At the end of the procedure we obtained values of $\varepsilon(t)$ at three last points, t_{m-2}, t_{m-1}, and t_m.

To analyze the data and to define the term of aging, we used a simplified model for ELB:

$$\varepsilon(t) = \varepsilon_0 \exp(-kt) \qquad (A.2)$$

where ε_0 is the initial value of elongation at break and k is a kinetic parameter. These parameters were estimated by the least squares method, which was applied to the logarithmic transformed model

$$y(t) = b - kt$$

where $y(t) = \ln \varepsilon(t)$ and $b = \ln(\varepsilon_0)$. This transformation was valid because we used only the initial part of the ELB curve, where error distortion was not important. The quality of estimation may have been characterized by the variance–covariance matrix $\mathbf{C} = \mathrm{cov}(b, K)$, as calculated in the usual way.

Afterward, we evaluated t_{max} at T_{max}, meaning that a given aging depth, D_{max} should have been achieved. The value of D_{max} corresponded to the designed value of ELB ε_{des} fixed by the user. Actually, the description of the material aging behavior was more complicated than shown in eq. (A.2). For example, the ELB curve went down more slowly for a large AD in comparison with the initial period [see eq. (4)]. To consider such a possibility, we determined t_{max} as the upper confidence bound. For confidence probability, $P = 0.99$, t_{max} was calculated as the solution to a quadratic equation:

$$(k^2 - x_P^2 C_{kk})^2 t^2 + 2(bk + zk + x_P^2 C_{kb})t$$
$$+ (z^2 + b^2 - 2zb - x_P^2 C_{bb}) = 0$$

where $z = \ln \varepsilon_{des}$, x_P is the normal P quantile (inverse normal distribution), and the C_{xy} values are the components of the variance–covariance matrix $\mathbf{C}$.

Third stage: Temperature extrapolation

Usually, it is supposed that rubber thermoaging complies with the Arrhenius law. However, E may be different for different materials (E/R varies from 10,000 to 12,500). Therefore, for the temperature extrapolation, we used an expression in which E depended on extrapolation interval $\Delta T = T_{max} - T$:

$$E(T) = 10^{+3}[1 + \alpha(1 - \exp(-\beta\Delta T)] \qquad (A.3)$$

The parameters $\alpha = 0.3$ and $\beta = 0.06$ were chosen heuristically to achieve the given AD; that is, overestimation was considered more preferable than underestimation.

Figure 4   EDOE spreadsheet solution.

Then, we composed the plan of experiments for any given T as

$$t_{max} = t_{max}(T_{max})\exp\left[\frac{E(T)}{R}\left(\frac{1}{T} - \frac{1}{T_{max}}\right)\right]$$

where $E(T)$ was calculated by eq. (A.3). The aging interval $t_{max}(T)$ was divided by the time points (e.g., the points where ELB was measured) in the following way. The first period was a little longer than the term of a possible ELB increase:

$$t_1 = t_{cur}\exp\left[\frac{E(T)}{R}\left(\frac{1}{T} - \frac{1}{T_{cur}}\right)\right]$$

and other time points, t_k, for $k = 1,\ldots,n$ (where n is the number of points), were calculated as $t_k = t_1 + k(t_{max} - t_1)/n$.

The EDOE procedure uses information about the curing mode, and it is based on half-empirical models. The AT design was, of course, rather approximate. Validation of EDOE was performed on seven different rubber componds.[10] There was good conformity between the predicted results and those received in the real tests. In the temperature interval from T_{max} up to $T_{max} - 30°C$ and for the aging depth $D_{max} \leq 0.5$, the procedure gave the exact time or an insignificantly overestimated time of the tests in 90 cases of 100. The increase in the aging depth augmented the risk of obtaining underestimated testing times. When we lowered the testing temperature, the probability of time overestimation increased.

APPENDIX B: SBE

The idea of SBE applied to our example was the following. The whole data set was divided into parts (the series) so that each part was related to some response (ELB, STR). The estimation of common parameters was made successively series by series. After processing each series, we obtained the estimates that formed posterior Bayesian information. This information consisted of the vector of parameter values and the covariance matrix, and it was used as prior information for the next series. The first series was processed without prior information, and the last series gave the ultimate results of the procedure. To form prior information, it is necessary to separate common parameters

from the partial ones and to recalculate the Fisher information matrix.

A priori information was taken into account by modification of the objective function. In our case, the objective function $Q(a)$ is the product of two terms, the sum of squares $S(a)$ and the Bayesian term $B(a)$:

$$Q(a) = S(a)B(a)$$

$S(a)$ (may be weighted with w_i) is calculated as

$$S(a) = \sum_{i=1}^{N} w_i^2 (y_i - f_i)^2 \tag{A.4}$$

The Bayesian term has the form

$$B(a) = \exp\left[\frac{R(a)}{N}\right] \tag{A.5}$$

where $R(a)$ is a quadratic form

$$R(a) = (a - b)^t H(a - b)$$

and where vector $\mathbf{b}$ consists of the prior parameter values

$$b = (b_1, \ldots, b_p)^t \tag{A.6}$$

The matrix $\mathbf{H}$ is the prior information matrix: .0

$$H = \{h_{ij}, I = 1, \ldots, p, j = 1, \ldots, p\} \tag{A.7}$$

The Bayesian information matrix $\mathbf{H}$ is constructed from the posterior Fisher's matrix $\mathbf{A}$

$$\mathbf{A} = B(\hat{a})\left(\frac{N}{S(\hat{a})} V^t V + H\right)$$

which was obtained on the previous step. $\mathbf{V}$ is the $p \times N$ matrix whose elements are weighted derivatives of the fitting function

$$\mathbf{V}_{ij} = w_j \frac{\partial f(x_j, \hat{a})}{\partial a_i}, \quad i = 1, \ldots, p; j = 1, \ldots, N \tag{A.8}$$

where $S(a)$ and $B(a)$ are defined in eqs. (A.4)–(A.5), N is the number of observations, and the vector $\hat{a}$ consists of estimates of the a parameters. All of the elements in eq. (A.8) are related to the previous step (series), and they should not be confused with the elements of the same name but related to the current step.

When *a priori* information is constructed from *a posteriori* information, it is essential to separate data relating to the common and partial parameters. Common information is kept for further use, and partial information is removed because it does not conform with the next portion of data. The posterior Fisher matrix $\mathbf{A}$ can be represented by a block matrix

$$\mathbf{A} = \left[\begin{array}{cc} \mathbf{A}_{00} & \mathbf{A}_{01} \\ \mathbf{A}_{01}^t & \mathbf{A}_{11} \end{array} \right]$$

where $\mathbf{A}_{00}$ is the $(r \times r)$ square matrix corresponding to the common parameters, $\mathbf{A}_{11}$ is the $(p - r) \times (p - r)$ square matrix corresponding to the partial parameters, and $\mathbf{A}_{01}$ is the $r \times (p - r)$ matrix. The prior information matrix $\mathbf{H}$ is recalculated from matrix $\mathbf{A}$ by the following formula:

$$H = \frac{1}{s^2} \left[\begin{array}{cc} \mathbf{A}_{00} - \mathbf{A}_{01}\mathbf{A}_{11}^{-1}\mathbf{A}_{01}^t & 0 \\ 0 & 0 \end{array} \right] \tag{A.9}$$

where s^2 is the posterior value of the error variance. The matrix dimension should correspond to the number of parameters in the next portion of data, so the matrix is completed with zero values. The prior parameter values are transformed in parallel

$$b_\alpha = \left\{ \begin{array}{ll} \hat{a}_\alpha, & 0 < \alpha \leq r \\ 0, & r < \alpha \leq p \end{array} \right. \tag{A.10}$$

Equations (A.9) and (A.10) present the prior information that is applied on the next step of the SBE procedure.

References

1. Maksimova, G. A.; Pomerantsev, A. L. Zavod Lab 1995, 61, 432.
2. Bystritskaya, E. V.; Pornerantsev, A. L.; Rodionova, O. Y. Chemom Intell Lab Syst 1999, 47, 175.
3. Bystritskaya, E. V.; Pornerantsev, A. L.; Rodionova, O. Y. J Chemom 2000, 14, 667.
4. Pomerantsev, A. L. Chemom Intell Lab Syst 2003, 66, 127.
5. Bystritskaya, E. V.; Karpukhin, O. N.; Maksimova, G. A. In Proc of Conference Rubber-94, Moscow, USSR, 1994; Vol. 4, p 605.
6. Bystritskaya, E. V.; Pomerantsev, A. L. Presented at II Conference on Experimental Methods in Physics of Heterogeneous Condensed Media, Barnaul, Russia, 2001.
7. Gorski, V. G. Design of Kinetic Experiments; Nauka: Moscow, 1984 (in Russian).
8. Hosskuldsson, A. Prediction Methods in Science and Technology: Thor: Cöpenhagen, Denmark, 1996.
9. FITTER Add-In. http://polycert.chph.ras.ru/fitter.htm (accessed 2004).
10. Bystritskaya, E. V.; Rodionova, O. Y.; Pomerantsev, A. L. Polym Test 1999, 19, 221.
11. Pomerantsev, A. L.; Brin, E. F.; Karpukhin, O. N. Zavod Lab 1986, 5, 48.
12. FITTER Applications. http://polycert.chph.ras.ru/applicat.htm (accessed 2004).
13. Rodionova, O. Y.; Pomerantsev, A. L. Kinet Catal, 2004, accepted.