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Experiment Design

Evolutionary design of experiment for accelerated aging tests

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Abstract

The article is devoted to a special procedure that was developed by the authors and is used to design experiments for accelerated aging of rubber materials. The procedure involves correction of the final design with the help of short term preliminary tests and therefore it is called evolutionary design of experiment. The procedure was tested on seven rubber materials with different recipes and at different temperatures.

1. Introduction

The accelerated aging tests (AT) are ordinarily used to investigate the properties of rubber compounds. AT means the aging at constant temperature(s) and measuring mechanic properties (such as elongation at break, tensile strength, etc.). This data set may be used for an estimation of rubber stability to thermal aging, for forecasting its behavior at less severe conditions and for comparison of different recipes and different additives. The quality of such analysis depends on the completeness of the data set. The completeness means that the necessary aging degree during AT has been achieved. Such duration of test supplies us with full information about the whole life-cycle of the compound up to its failure and gives a possibility to obtain proper estimation of rubber stability to thermal aging and to build the aging model for prediction of reliability of products. Usually this aging degree is determined by service conditions as some critical value

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which makes the limit of satisfactory behavior for the rubber article. Accelerated aging tests may require much time and therefore correct planning for them is very important.

In this article we describe the procedure of evolutionary design of experiment (EDOE), which assists the researcher to avoid extra expenditure of time and labour and to obtain reliable data rapidly. The main idea is as follows. First of all, preliminary tests are conducted at the highest possible aging temperature T_{max} and at two minimum time terms. Using the results of such tests the procedure allows us to calculate the time to achieve the necessary degree of aging for any given temperature that is lower than T_{max}.

This procedure was realized as a Spreadsheet Solution for Microsoft Excel and was tested on seven tire materials with different recipes. Elongation at break was chosen to characterize aging.

2. Experiment

Elongation at break (ELB) $\epsilon(t)$ is the most sensitive property among those that are usually measured during AT. The change of this parameter first of all reflects modification of structural uniformity or defectiveness of a material. Therefore we chose this property as the base parameter for our procedure and as aging degree indicator. ELB was determined according ASTM D412-87.

We have investigated seven different rubber compounds. All of them were materials for different parts of passenger or truck tires and were provided by Uniroyal Chemical Company, Inc. All samples were rectangular plaques of thickness 0.19–0.22 cm. Five standard specimens (ASTM D412-87) were prepared from each plaque for one test. In Table 1 one can see their curing modes, and initial values of ELB. Thermo-aging of the specimens was conducted in ovens at temperatures from 95 to 140°C. Temperature variance did not exceed 0.5°C.

3. Evolutionary design procedure

The procedure of EDOE consists of three stages: preliminary designing, correction step (steps) and final designing.

Table 1
Curing modes, initial properties of rubber compounds, results of preliminary tests

Sample	Curing temperature, T (°C)	Curing time, t_{cur} (min)	Mean initial ELB value, ϵ_0 (%)	Prior test temperature, T_{max} (°C)	Prior test time 1, t_1 (h)	Prior test time 2, t_2 (h)	Achieved aging degree, $D(t_2)$
1	160	15	584	140	1	2	0.33
2	160	10	557	130	1	2	0.30
3	160	10	510	130	1	2	0.25
4	165	12	380	135	1.1	2.2	0.29
5	165	9	572	135	1	2	0.41
6	150	17	496	130	1	2	0.21
7	174	12	740	140	1.1	2.2	0.50

3.1. The first stage: determination of the conditions of preliminary tests

We chose the temperature and period for the two first measurements of ELB $\epsilon(t)$. The maximum testing temperature $T_{\max}$ we chose as 15–30°C lower than curing temperature T_{cur} (as it is usually accepted for thermo-aging of rubbers). Two measurements of ELB should be carried out at $T_{\max}$ and at two periods of time t_1 and $t_2 = 2t_1$. The period t_1 is calculated using the curing time and the Arrhenius law.

$$t_1 = t_{\mathrm{cur}}\exp[(E/R)(1/T_{\max} - 1/T_{\mathrm{cur}})],$$

where t_{cur} is curing time. Activation energy E is chosen taking into account the rubber recipe ($E/R = 10\,000$°C for sulfur curing agents and 12 500°C for compounds that do not have free sulfur). We tried to choose conditions of AT that provide the necessary aging degree (AD). In referring to AD, we mean relative variation of ELB, i.e. $D(t) = [\epsilon(0) - \epsilon(t)]/\epsilon(0)$, where $\epsilon(0)$ is elongation at break before aging. Using such a method we obtain AD lying in the interval $0.2 < D(t_2) < 0.5$ (see Table 1).

Starting AT at designed conditions, one should put in the oven sufficient quantity of rubber specimens to perform not less than five measurements of $\epsilon(t)$ each time and have a stock of samples for the next stage, where corrections may be required. When this prior AT has been performed, the second stage of EDOE may be conducted.

3.2. The second stage

The results of measurements (including values of $\epsilon(0)$ for unaged samples) are used for construction of the whole plan of AT at any desired temperature. First of all we analyse measurement results $\epsilon(0)$, $\epsilon(t_1)$ and $\epsilon(t_2)$.

3.2.1. Test for decreasing of ELB

Insofar as we use heuristic formulas for determination of t_1 and t_2 there is a chance that we will not achieve sufficient AD during preliminary tests for reliable definition of parameters in Eq. (1) afterwards. Numerous computer experiments have shown that AD during preliminary tests should be about 0.25 taking into account that usual measurement error is about 20–30%. Otherwise, the result of extrapolation through time may be strongly overestimated. Besides, in thermo-aging of rubbers a small increase of ELB is sometimes observed during the initial period of time. This circumstance also may distort the results. To avoid such errors we included in our procedure a test for decreasing of ELB during preliminary tests. To control this hypothesis we use the Student t-test. If values of ELB do not fall we need to conduct additional tests at time $t_3 = 3t_1$, and etc. Our procedure assumes not more than three such corrections. In a common case the value of t_m is calculated as $t_m = mt_1$. Finishing this procedure we obtain values of $\epsilon(t)$ at three last points t_{m-2}, t_{m-1}, t_m.

3.2.2. Extrapolation through the time

To analyse the received data and to define the term of aging we used the simple model for elongation at break:

$$\epsilon(t) = \epsilon_0 \exp(-kt), \quad (1)$$

where ϵ_0 is the initial value and k is the kinetic parameter. To estimate these parameters the Least Squares Method is applied to the logarithmic transformed model:

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

where $y(t) = \ln\epsilon(t)$ and $b = \ln(\epsilon_0)$. This transformation is valid because we use only the initial part of the ELB curve, where error distortion is not important. The quality of estimation may be characterized by variance–covariance matrix $C = \mathrm{Cov}(b,k)$ calculated in the usual way.

Afterwards we evaluate the term t_{max} of aging at temperature T_{max}, meaning that definite aging degree D_{max} would be achieved. The value of D_{max} corresponds to the designed value of ELB ϵ_{des} fixed by the user. Actually the materials conform with more complicated dependencies than Eq. (1). In particular, the let-up in the process of ELB fall is notable for tire rubber at large degrees of aging. To take into account such possibility, we determine the necessary period of time for achievement of D_{max} as the upper bound of the confidence interval. To warrant this term it is necessary to consider all errors of estimation and to construct its confidence valuation. Introducing confidence probability $P = 0.99$, the term t_{max} may be calculated as the solution of a quadratic equation:

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

where $z = \ln(\epsilon_{des})$, x_p is normal P-quantile, C_{xy} are components of variance–covariance matrix C. The example of estimation is given in Fig. 1. It is evident that the exponential curve turns away

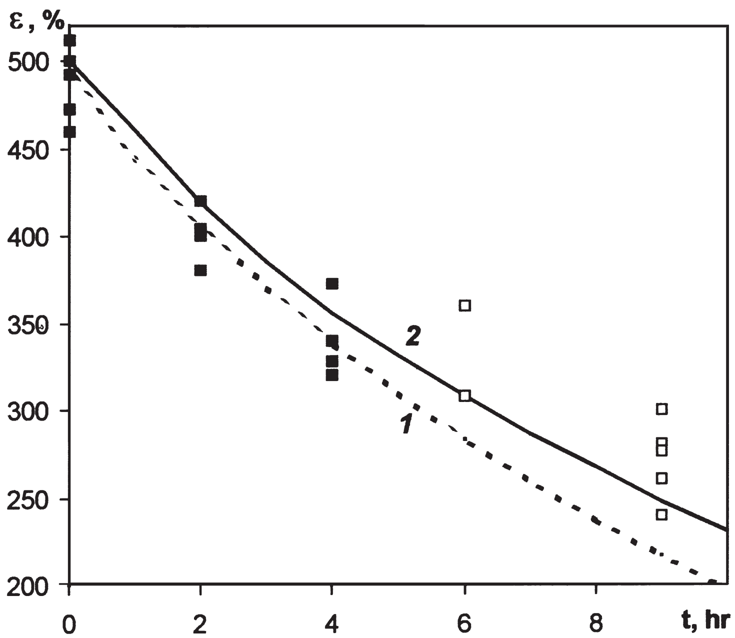

Fig. 1. Extrapolation through time for Sample 4. (■) Data for design; (□) control data. (1) Mean fitting values curve; (2) upper 0.99 confidence curve.

from the results of measurements, but calculation of the one-side upper confidence interval allows correction of these deviations.

3.3. Third stage

3.3.1. Extrapolation through the temperature

Usually, it is supposed that rubber thermo-aging complies with the Arrhenius law. However, activation energy may be different for different materials (E/R is varied from 10 000 to 12 500°C). Therefore, for extrapolation through temperature we used the modified expression, in which activation energy depends on an extrapolation interval $\Delta T = T_{max} - T$

$$E(T) = 10^3[1 + \alpha(1 - \exp(-\beta\Delta T))]. \tag{2}$$

Parameters $\alpha = 0.3$, $\beta = 0.06$ we chose heuristically in order to achieve the given AD, i.e. overestimation of time was considered preferable to understatement.

Now we can compose the plan of experiments for any definite temperature T as

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

where $E(T)$ is calculated by Eq. (2). The term of aging $t_{max}(T)$ is divided by periods in such a way that the first period is a little longer than the term of possible increasing of ELB

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

and t_i for $i = 2,..,n$ (n = desired number of tests) is calculated as $t_i = t_1 + i(t_{max} - t_1)/n$.

4. EDOE validation

To prove the EDOE procedure we used seven rubber materials described in Table 1. For some samples we slightly changed the regimes of preliminary tests in the ranges that are allowed by the EDOE procedure.

The designed values of ϵ_{des} were set from 85 to 580% (for different samples). The maximum value of AD was $D = 0.85$. For each rubber material we carried out tests at three different temperatures: T_{max} (prior test temperature), $T_{max} - 15$ and $T_{max} - 30$. The values of temperatures covered the interval from 95 to 140°C.

The experiment results for T_{max} (extrapolation only through time) are shown in Fig. 2. For different fixed values of ELB ϵ_{des}, the necessary time of aging t_{max} was predicted and the standard test on a series of five samples was carried out. Maximum (●) and minimum (○) experiment values of $\epsilon(t)$ for each series are plotted in Fig. 2. The solid line corresponds to an ideal situation, when the measured ELB ϵ is equal to a designed ELB ϵ_{des} exactly.

We consider the result of the EDOE procedure correct if (●) lies above this line and (○) below. If (●) lies below the bisector it means that the procedure has given an overestimated time of aging and received ϵ is more than the designed ϵ_{des}, but if ϵ is not greatly different from ϵ_{des}, we consider the result to be satisfactory, taking into account that overestimation is preferable than underestimation. If (○) lies above the bisector it means that the procedure has predicted an underestimate of time and the necessary ELB ϵ_{des} is not achieved. Such a result we consider to

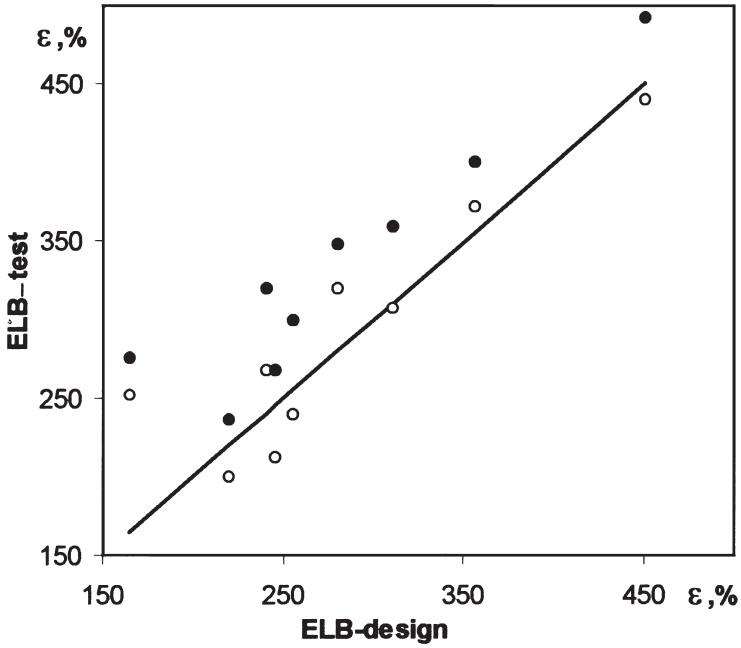

Fig. 2. EDOE validation at $T = T_{max}$. Tested ELB vs designed ELB. (○) Minimum of test values; (●) maximum of test values.

be wrong. From nine tests carried out at the maximum temperatures two were wrong and both of them correspond to rather large aging degrees (0.72 and 0.52). In the other seven experiments, taking into account the measurement errors, we may consider the results as correct.

The similar results for temperature that is equal $T_{max} - 15$ are shown in Fig. 3. Twenty four control tests were carried out, and 16 of them gave a correct result. In six experiments the time of tests appeared to be underestimated, but four of them concern AD that was greater than 0.5. In three tests the overestimated time was predicted, but from our point of view that was not significant enough to consider the result as wrong.

For temperatures that are equal to $T_{max} - 30$ 25 control tests were made (Fig. 4). Correct results were achieved in 19 experiments. One test has shown essential underestimation of testing time, in five tests the time appeared overestimated, and in two of them is rather significant.

The general picture for the whole range of temperatures appears as follows. From 58 control tests on seven materials correct results were achieved in 42 tests, i.e. the chance to obtain the correct result is 7 to 3. If we limit AD as $D_{max} \leq 0.5$, the chances will increase to 8 to 2. The chances to obtain essentially underestimate of time of aging is about 15 in 100 and if we limit AD as $D_{max} \leq 0.5$ the chances will decrease to 8 in 100. The chances to obtain essentially overestimated time of aging is approximately 14 in 100 and it obviously increases with lowering the temperature of tests. Only in two of 58 tests has the procedure given times that are overestimated more than twice and we consider them as wrong results. It is necessary to note, that the cases of wrong design coincide with different materials, i.e. it is impossible to allocate any special material 'with wrong behavior'.

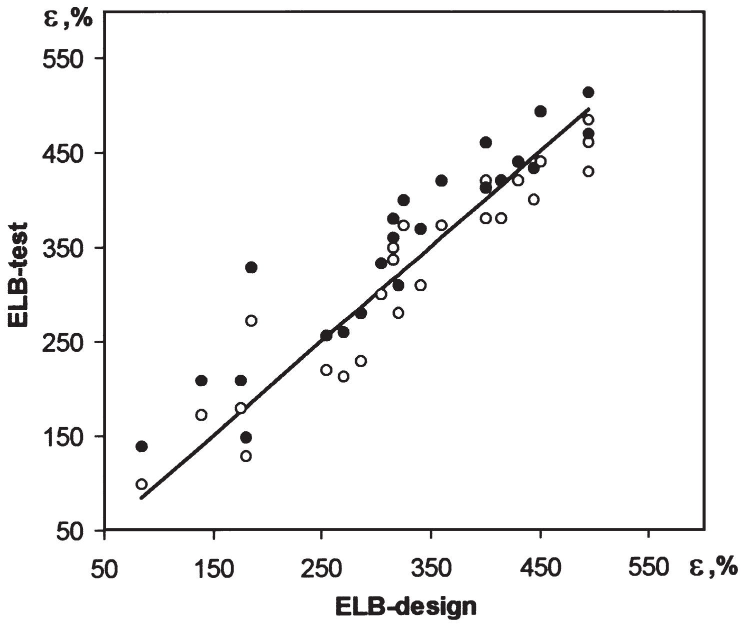

Fig. 3. EDOE validation at $T = T_{max} - 15$. Tested ELB vs designed ELB. (○) Minimum of test values; (●) maximum of test values.

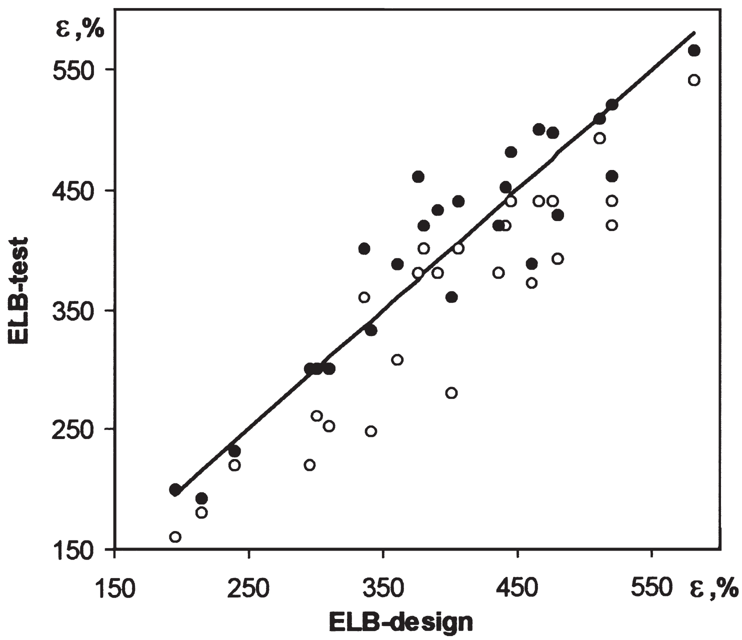

Fig. 4. EDOE validation at $T = T_{max} - 30$. Tested ELB vs designed ELB. (○) Minimum of test values; (●) maximum of test values.

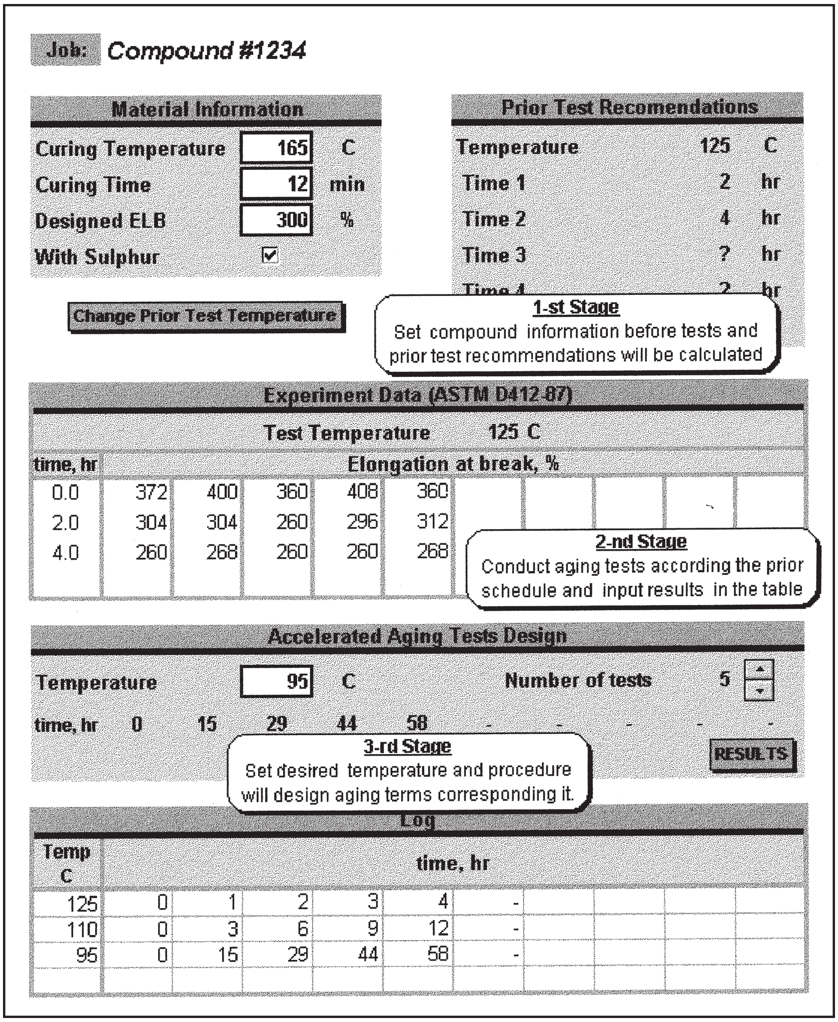

Fig. 5. Design spreadsheet solution.

5. Conclusions

The EDOE procedure uses information about curing time and it is based on half-empirical models, so the AT design is of course rather approximate. The results discussed above show good conformity between those calculated and those achieved in real tests.

In an interval of temperature from T_{max} up to $T_{max}-30$ and for aging degree $D_{max}\leq 0.5$ the procedure gives the exact or insignificantly overestimated time of tests in 89 cases out of 100. The increase of AD augments the risk of obtaining underestimate of testing time. With lowering of the testing temperature, the probability of time overestimate increases.

For further investigation of the EDOE procedure we recommend the following:

- to define the designed value of ELB as $\epsilon_{des}\geq 0.5\epsilon(0)$;

- the closer the aging temperature to the highest testing temperature the more accurate the plan one can achieve;
- in every test use not less than five specimens.

EDOE is a convenient and easy-to-use procedure that may help to design the experiment before testing and to estimate aging time for different temperatures and aging degree. It is realized as a Spreadsheet Solution (Fig. 5) for Microsoft Excel 7.0. The demo version can be found at http://polycert.chph.ras.ru/pcedoe.htm. It is very easy to apply even for the inexperienced user who is familiar only with Excel.

We presume that it is possible to apply a similar approach for designing accelerated tests based on an evolutionary principle to other classes of polymer materials, though the details of a procedure would differ.