DEVICE AND METHOD FOR EVALUATION OF THE RUBBERS PROPERTIES AND DEGRADATION

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The possibility of using of the methods of static and dynamic indentation for the evaluation of the service life of rubber is discussed. It was founded that the effectiveness of testing of rubber products using dynamic modulus of elasticity, is comparable with the main destructive testing methods. The possibility of using dynamic indentation parameters for prediction of service life of rubber products using the standard method of calculating and using the Zhurkov equation is shown.

Introduction

At present the estimation of service life and durability of the mechanical rubber goods is extremely important problem in practice. The most sharply this problem is for the articles such as sealants, gaskets, shock absorbers and others, which work in the conditions of aggressive temperature and chemical action. Traditionally for predicting the change of the properties of polymeric materials are used procedures according to ISO 11346:2004, IEC-216. In accordance with the given normative documents the tests must be carried out on the specially prepared control samples. However, practice shows that the samples and real articles can considerably differ in their properties. In the same time for the consumers of rubbers it is very complicated to prove the fact of the poor quality manufacture of article, for that reason, that the properties should be determined on the samples, which are made separately and they can correspond to all requirements. In this connection for the objective evaluation of the service life of rubber goods it is necessary to perform two basic conditions:

- the method of control should give the possibility of measuring the properties directly of the material of article
- for establishing the periods of the safe operation of the material tested it is necessary to determine the characteristic of material (aging characteristic), which will be sensitive to the change of the sample properties during degradation. In this case the service life will be determined by the limit values of the aging characteristic, established by the practice of the application of the article.

These terms define the purpose of this work to explore possibility of the indentation methods for the evaluation of the service life of rubber. The method of dynamic indentation and measurement of the Shore A hardness are the main testing methods used in this work.

Materials and testing methods

In order to conduct research two rubber mixtures based on natural rubber with different resistant to temperature exposure were taken.

According to ISO relative residual compressive strains (80%), stress relaxation (20%), the static module (50%), conditional equilibrium modulus (50%), tear resistance (50%) can be taken in account as a characteristic indicators of aging. Here and further allowable limit of changes of parameters of the aging are indicated. The most frequently conventional tensile strength σ(50%) and the elongation at fracture, δ(50 %) are used to predict changes in the properties. At the same time, ISO makes it possible to establish indicators of aging, and these characteristics can be measured by any means and the main task is to choose the parameter that will be sufficiently sensitive to changes in properties during degradation. Therefore, the: static and dynamic indentation methods were proposed to use for estimation of material degradation. The static indentation was carried out by well-known instrument for measuring the hardness of Shore A. The method of dynamic indentation (MDI) [1, 2] is based on the mechanical impact of the hard indenter on the material and the registration of the penetration process of indenter into material tested. In such manner it can be obtained not only finite impact parameters (the maximum displacement of the indenter into the material, the rate of rebound, etc.), but also can be recorded the contact force versus displacement depending, which is analogous to the stress-strain diagram. It was shown to describe the process of a hard indenter intrusion in a viscoelastic half-space (rubber), it can use a nonlinear model [3], consisting of two main parameters: the dynamic modulus E_d and the coefficient of viscosity η. For objective estimation of possibility of indentation methods it is necessary to evaluate the sensitivity of recorded parameters in comparison with to the sensitivity of standard methods. Therefore, for the experiments samples in the form of blades according to ISO (2 mm thick) were made. The number of the blades to obtain values of the aging parameters was 10. Indentation measurements were made at different points in each sample and calculated the average values. The aging was carried out in a heat chamber in air at temperature T = 70, 80, 90 and 100 º C. For testing the samples was taken out cameras and air-conditioned for two hours at 20 º C.

Theory and experiment

The exact value of service life of rubber or polymer is determined by the individual conditions in which degradation occurs. This may be ozone, chemical, mechanical, thermal effects. The rate and mechanism of their combined effects are very different. Therefore, as a rule, tests are conducted under the influence of any single factor, which has the greatest effect. The most important and widely distributed factor is the thermal effect. Method of estimation of the service life in this way is based on the assumption that the degradation of the material can be described as a process whose rate is determined by some constant depending on the temperature according to the Arrhenius law:

$$K(T) = Ae^{-\frac{U}{RT}}, \tag{1}$$

where: *K (T)* – change in time of the characteristic property of the aging; *A* - constant depending on material properties; *U* - activation energy of thermal degradation; *R* - universal gas constant (8.617 J /(mol K)); T-temperature (º K).

This rapid methods of predicting the conservation properties of rubber is based on extrapolation and conversion rates of change of aging parameters on the operating temperature. A known method of calculation service life consists in replacement rate of change of material properties by the ratio of time to reach a threshold rate of aging at different temperatures, the construction of schedule of the selected pameter versus the duration of thermal exposure at different temperatures and determining service life. It is known another method of estimation of service life on the basis of the Zhurkov equation linking the durability τ with the effective tensile stress σ at a test temperature:

$$\tau = \tau_0 e^{\frac{U-\gamma\sigma}{RT}}, \tag{2}$$

where γ, τ_0 – are empirical constants.

In the absence of external stress it can be written:

$$\tau_w = \tau\left\{\frac{U}{R}\left(\frac{T-T_w}{TT_w}\right)\right\}, \tag{3}$$

where: T_w and *T*– are working and aging temperatures in degrees Kelvin.

τ_w and τ - durability at temperatures T_w and T respectively. Value of τ associated with the change in material properties up some specified limit. Therefore, for accurate determination of τ it is necessary to carry out monitoring of change of the parameter of aging.

Expression (3) is the base for the calculation of service life according to ISO. Unknown in (3) is the ratio of U/R, but it can easily be determined by results of tests at two different temperatures T_1 and T_2.

$$\frac{U}{R}=\frac{\ln\left(\tau_2/\tau_1\right)}{\frac{T_1-T_2}{T_1T_2}} \tag{4}$$

For the most objective information about the properties of materials under investigation was carried out the multiparameter testing. The measurements were made using dynamic indentation on the device IMPULSE-1R [2], Shore A hardness and on tensile machine. Dynamic indentation according to the specially developed algorithms [3] allowed to determine such parameters as the dynamic modulus E_d, the coefficient of viscosity η, the restitution coefficient *e,* the loss tangent *tg* θ, the value of residual strain after removal of the load α_r. With the help of Shore A hardness it was measured hardness H_A. The tensile machine allowed to determine elastic modulus E at 5%, 10%, 50% strains, tensile strength σ_t, the relative elongation δ_b. The experiment showed that the most sensitive to changes in the properties were characteristics: E_d, σ_b, δ_b, $E_{5\%}$. The change of average values of these parameters, as well as H_A during thermal aging for a mixture # 2 it is shown in Fig.

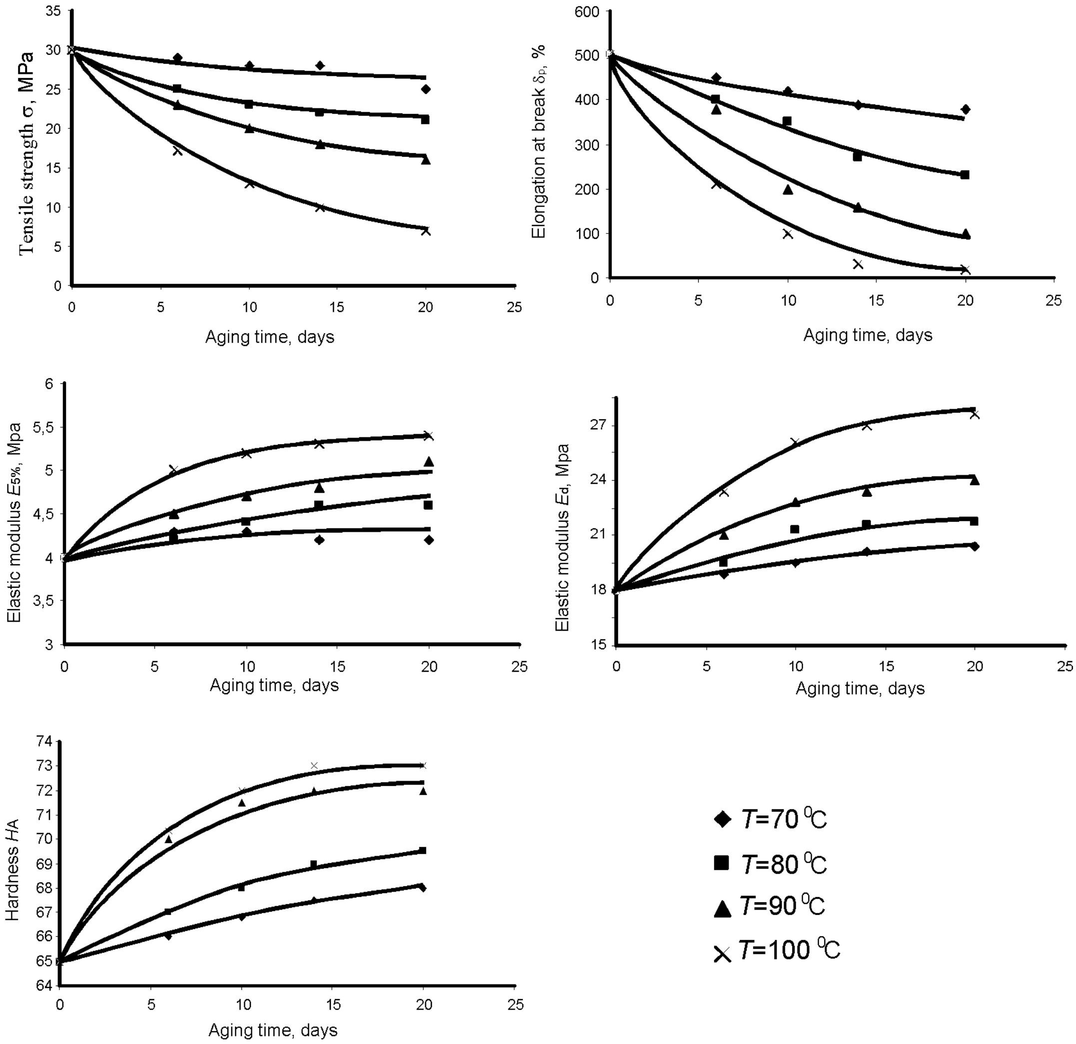

Fig. 1. Change of the physical and mechanical characteristics of the mixture 2 in the process of thermal degradation.

Similar results were obtained also for a mixture of # 1. It should be noted the difference in the magnitude and nature of deformation in determining characteristics. The modulus is determined at sufficiently small values of strain, but the σ_b and δ_b in the region of large strain. The nature of deformation determines the sensitivity of parameters. Measurement of σ_b and δ is carried out under tension, which is upon the most effect of the structure of rubber. When indentation is taken a tensile deformation is only in selected areas of contact. Thus reduction of strength by 50% does not mean the loss of efficiency. For example, for products such as seals, are not experiencing tensile stresses, service life will be determined by the ability to maintain the necessary pressure determined by the modulus of elasticity. At the same time for pressure hoses basic design characteristics of the design is the tensile strength. This suggests that the aging parameters should be set individually based on the purpose and practice of product. Also noteworthy is the fact that E_d determined by indentation has a smaller spread of data: the maximum coefficient of variation of χ for the E_d was 0.11, despite the fact that for δ_b χ was substantially higher - 0.24. These values of χ were determined at the end of aging, when the spread in date of measured characteristics was the maximum value. In the intermediate time moments values χ were less significant: up to 0.04 for E_d and 0,12 for δ_b.

An important parameter for estimation of aging, is its relative sensitivity, which was determined by the following formula:

$$Z = \frac{dH}{dt} \Big/ S, \qquad (5)$$

where H - the measured characteristic, S - standard deviation of the measured value, t - time of aging.

As seen from Fig. 2 relative sensitivity of the MDI is above its for the hardness of Shore A and $E_{5\%}$, but much smaller for tensile strength. This fact indicates a preference for dynamic indentation in comparison with static diagnosis of rubber when you want to test directly product.

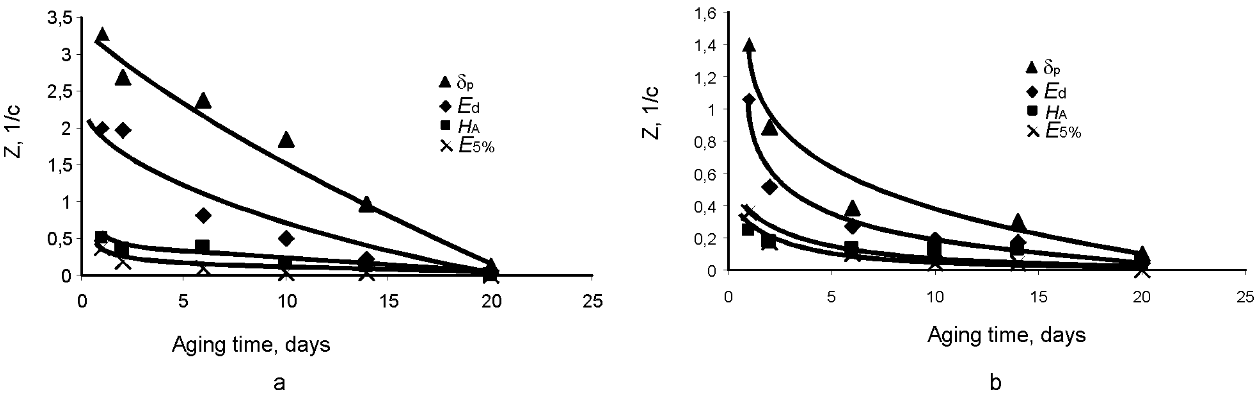

Fig. 2. Relative sensitivity of aging parameters during thermal degradation for mixture # 2. a - aging conducted at 100 º C, b - at 80 º C.

In this regard Fig. 3 shows a more accurate estimation of characteristics for testing, taking into account random errors. As an indicator of the effectiveness it was proposed to use of the ratio S at the time corresponding to the maximum permissible change to the corresponding maximum permissible change in material properties. As follows from Fig. 3 the effectiveness of the use of dynamic modulus of elasticity is comparable with the basic destructive tensile method. In addition, the simplicity of the of dynamic indentation method makes it the only acceptable for estimation of the service life of real products.

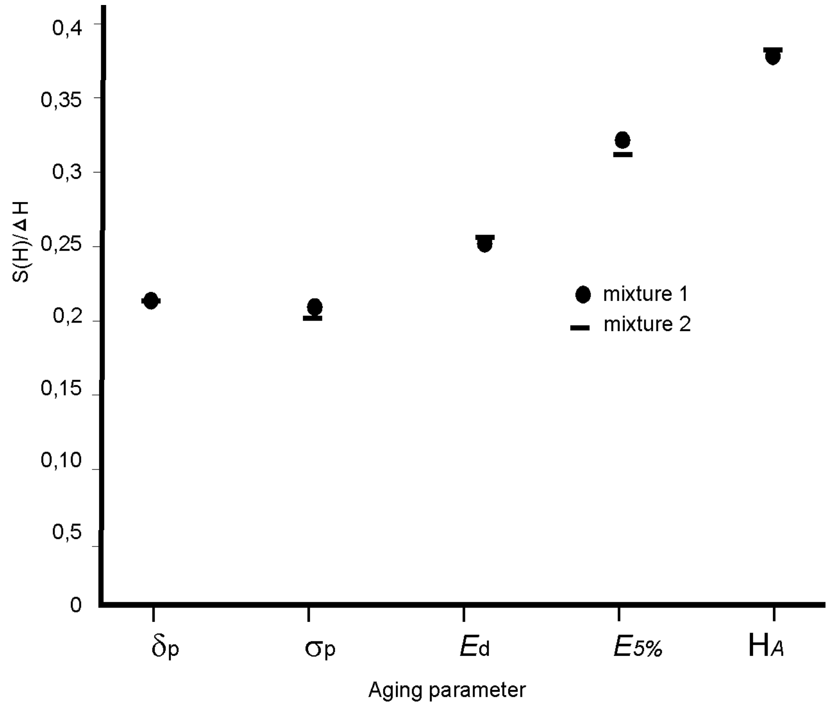

Fig. 3. Comparative evaluation of the sensitivity of the aging characteristics, taking into account random errors.

It will consider equivalence methods of calculations of service life based on the standard methodology and using equation (2). Fig. 4 shows a combined graph of change of E_d and σ_b for a mixtures of 1 and 2, constructed in accordance with ISO.

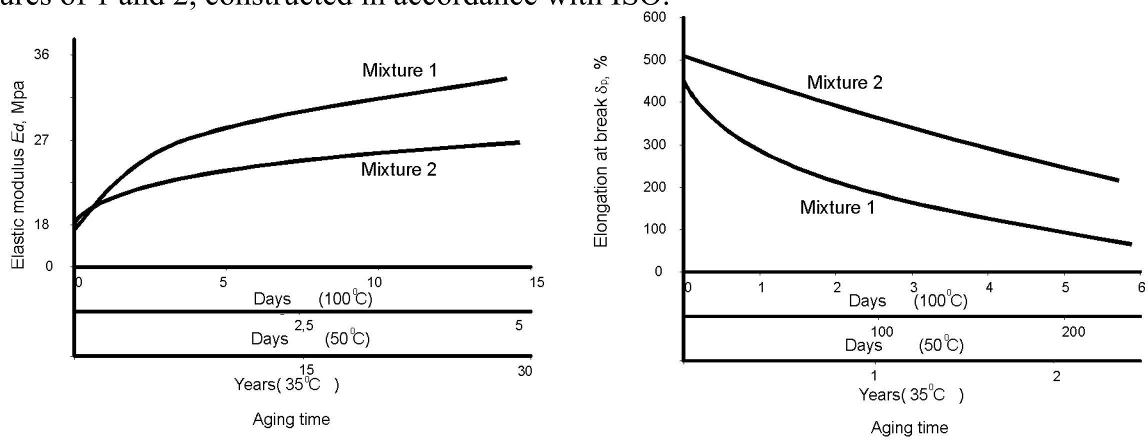

Fig.4. The combined plot of δ_b and E_d versus the duration of aging at different temperatures.

As can see from Fig. 4. mixture of 1 was less persistent in comparison with a mixture of 2. According to the graph is also easy to determine that the decrease in E_d at 50% for mixture 1 at 50 º C will be achieved through 1.1 years, at 35 ºC - after 7,1 years. Calculation by formula (2) using for the calculation of characteristics at 100 and 50 ºC and recalculating to the temperature of 35 º C gives a value of 1.1 and 8.6 years, respectively.

Analyzing the results we can say that the calculation procedures are equivalent, and the difference in these values can be explained by the different amount of calculations and procedures for statistical processing. Therefore, they both may be applied successfully in practice. Calculations for other characteristics are given in Table 1.

Table 1.

characteristics	Relative change of characteristics, %	Calculated characteristics (equation 1), years		Calculated characteristics (equation 2), years	
		35 ºC	50 ºC	35 ºC	50 ºC
mixture1					
δ_b	50	0,74	0,19	0,8	0,2
σ_b		9,3	1,5	7,76	1,4
$E_{5\%}$		11,2	1,8	11,1	1,8
E_d		7,1	1,1	8,6	1,1
mixture 2					
δ_b	50	2,13	0,55	2,41	0,59
σ_b		18	3,2	12,6	2,35
$E_{5\%}$		55	9,7	52,3	9,07
E_d		29	5,1	34,9	5,6

Conclusions

Thus, we have demonstrated the possibility of using indentation methods for predicting of the service life of industrial rubber products. It was analyzed the relative sensitivity of the methods with respect to the standard testing methods. . It was established that the characteristics of dynamic indentation are more sensitive in comparison with the characteristics defined by static indentation. Thus, the relative sensitivity of the dynamic elastic modulus exceeds this value for the hardness of Shore A 1,5-3 times. It was also found that the effectiveness of testing of rubber products on dynamic modulus of elasticity, taking into account random error is comparable to the basic destructive tensile testing methods. The possibility of using dynamic indentation parameters for prediction service life of rubber products using the standard method of calculating in accordance with ISO, and on the basis of the equation Zhurkova was shown. It was established of limiting allowable values of change of aging characteristics (tensile strength, elongation at break, modulus, hardness Shore A).

Literature

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