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STRUCTURE AND TRIBOGICAL PROPERTIES OF SURFACE FLUORINATED RUBBERS

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Abstract

These studies concern the theoretical approaches to the improvement of antifriction properties of rubbers due to the optimum combination of methods of their surface modification. The model involves formation of a net related system of ingredients in the form of spherical particles with reduced friction coefficients, which is imbedded in the surface layer (including the modified one) of elastomer. There is shown, that in this case the areas of reduced and increased friction are initiated under a normal load, and these areas result in a significant change of a sliding friction overall coefficient of a surface-modified elastomer even under a low concentration of spherical particles. As an example was viewed a variant of realization of this model parallel with friction reduction by the surface fluorination of rubbers, such as rubber on the base of fluorine.

Key words: *antifriction properties, friction coefficient, mathematic simulation, elastomer, metal*

Reduction of the friction coefficient and rubber wear is an important problem in application of indus trial rubber goods for the sealing of sliding friction assemblies in an elastomer–metal couple. Tradition ally, these problems are solved by means of addition of antifriction ingredients to the rubber composition or by modifications of the rubber surface. In the first approach, the most popular are various fluorine compounds, such as polytetrafluorethylene [1], fluorinated oligomers [2, 3], and various fluorine monomer compounds [4]. In the second approach, the rubber surface is modified by means of treatment in a glow discharge plasma in the presence of fluorinecontaining compounds [5] or, for example, by means of fluorination [6]. Combined treatment of rubbers by means of surface (fluorination) and spatial modification is very promising [7]. However, both of these methods have several disadvantages. Thus, in the first variant, a modifying agent is introduced into the rubber bulk, whereas this substance is functionally required mainly in the surface layers; that is, the added amount is significantly higher than the required level, and this is not cost efficient and in certain situations can impair other rubber properties. In surface modification of rubber, there is a problem of long lifetime of the modified layer; its thickness, as a rule, is not higher than several microns. In this respect, it would be very interesting to consider theoretical models that optimally combine the methods of spatial and surface modifications with a structure construction approach. This approach can consist not only in selection of optimal elastomer counterbody structures but also in nano, micro, and macroformation of structures in the elastomer, pro moting positive properties in combination with modifying approaches [8]. As a case study of the structure construction approach, let us consider a model involving the formation of an interconnected network system of ingredients in the form of spherical particles *4* with

a low friction coefficient imbedded in the surface layer (including the modified one) of elastomer *1* (Fig. 1). Under impact of normal load *N* and tangential load σ, the mechanism of action of such a network structure in the surface layer can be illustrated with the model of elastic springs with various elastic constants. More elastic springs *3* (spring constant g_{net}) correspond to a formed network structure containing spherical particles. Such particles can be, for instance, PTFE, graphite, and MoS_2 and be characterized by the positive property of reduction of sliding friction. We assume that the springs of lower elasticity *2* (spring constant $g_E < g_{net}$) simulate the response of the elastomer crosslinked structure to normal load and have no effect on variations of sliding friction coefficients in terms of counterbody *5*. The overall volume of the elastomer sample is affected by deformation; Fig. 1 illustrates only the surface layer where the interconnected network structure is located.

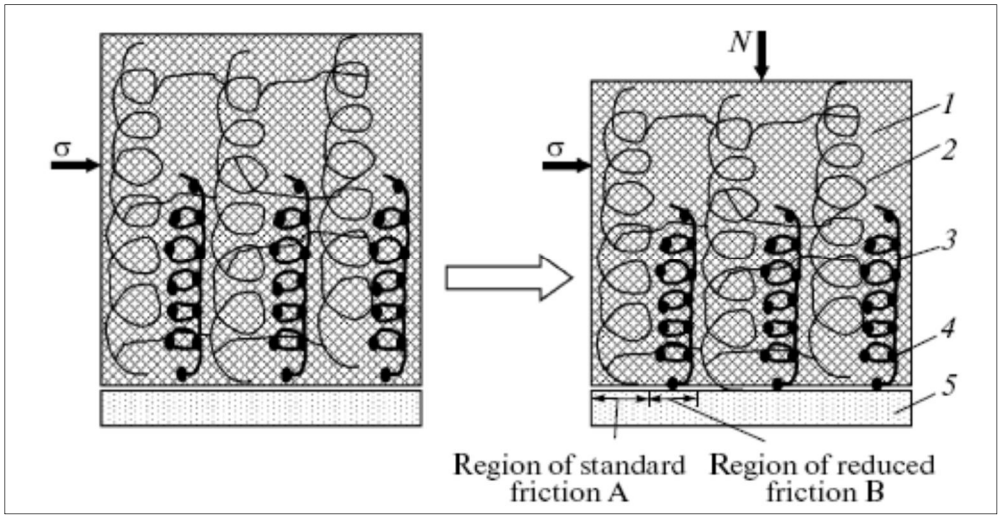


Fig. 1. Spring model of sliding friction in elastomer–metal couple

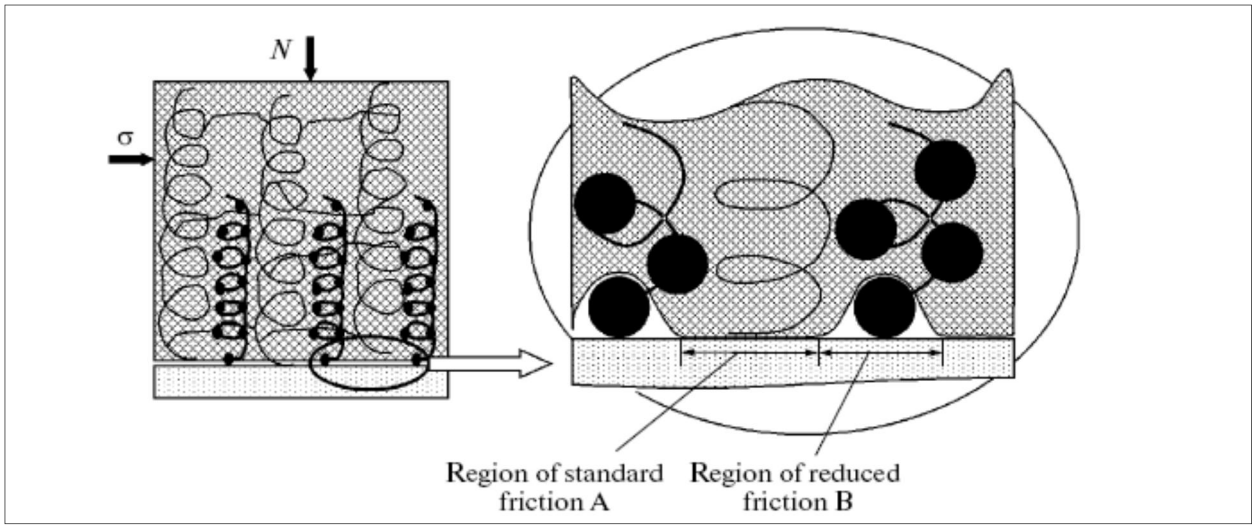


Fig. 2. Schematic diagram of a possible mechanism of reduction of sliding friction in the vicinity of spherical particles

When a normal load occurs owing to higher rigidity of the network structure, the spherical particles "exit" to the surface of contact with the counterbody, and at the points of exit, there are formed regions with reduced friction owing to positive properties of spherical particles (Fig. 2). In this case, the modified (fluorinated) elastomer surface layer is protected against increased wear, while maintaining the contact with the counterbody for sealing the friction assembly. Let us denote the portion of the reduced friction region corresponding to the interconnected network structure with spherical particles in the overall sample area as α_{net} and the sliding friction coefficients of elastomer and spherical particles as k_E and k_{net}, respectively ($k_E > k_{net}$).

Let us assume that the network structure has such links with the crosslinked structure of the elastomer that allow the springs to be considered independently of one another. In addition, let us assume that the counterbody surface and the sample itself are deformed slightly, so that there are no additional tan gential forces preventing the sample motion across the counterbody. Taking into consideration the aforementioned assumptions, the total coefficient of sliding friction of the overall modified elastomer sample under occurrence of a normal load can be estimated as follows:

$$k_{tot} = \frac{k_E g_E (1-\alpha_{net}) + k_{net} g_{net} \alpha_{net}}{g_E (1-\alpha_{net}) + g_{net} \alpha_{net}}, \quad (1)$$

Let us convert Eq. (1) to a form more convenient for analysis:

$$\overline{k_{tot}} = \frac{\alpha_{net}(\overline{k_{net}}\,\overline{g_{net}} - 1) + 1}{\alpha_{net}(\overline{g_{net}} - 1) + 1}, \quad (2)$$

where $\overline{k_{tot}} = \frac{k_{tot}}{k_E}$ is the normalized friction coefficient of a modified sample;

$\overline{k_{net}} = \frac{k_{net}}{k_E}$ - the normalized friction coefficient in the "outcome" areas of spherical particles;

$\overline{g_{net}} = \frac{g_{net}}{g_E}$ - the normalized stiffness coefficient of a network structure.

The total sliding friction coefficient of the elastomer sample obtained on the basis of the aforementioned assumptions does not depend on normal load N or on tangential load σ (Fig. 1).

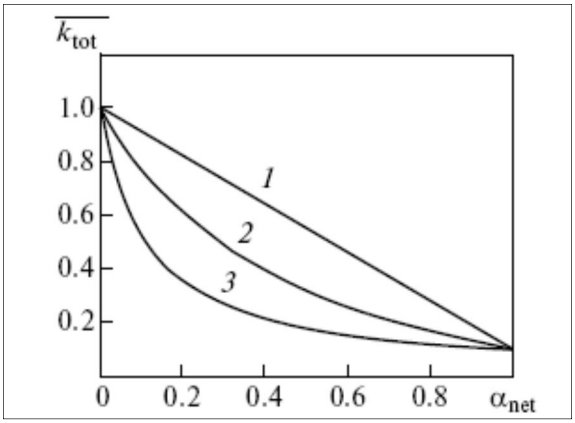


Fig. 3. Normalized friction coefficient of a sample k_{tot} as a function of the fraction of reduced friction zone α_{net} for values of g_{net} equal to (*1*) 1, (*2*) 3, and (*3*) 10.

The dependences $k_{tot}=f(\alpha_{net})$ for various values of the normalized rigidity coefficient of the elastomer interconnected network structure at k_{net}= 0.1 are illustrated in Fig. 3. As can be seen in Fig. 3, for sufficiently rigid inter connected network structures ($g_{net}\geq 5$), significant reduction of the total sliding friction coefficient of as urface modified polymer is possible even at moderate values of α_{net}, which corresponds to low surface concentrations of spherical particles. Fabrication of an interconnected network structure with rigidity many times higher than that of an elastomer cross linked structure is probably a very complicated task. In this case, the required reduction of the total sliding friction coefficient can be obtained by means of increasing the portion of reduced friction area α_{net}. The limit of reduction of the friction coefficient depends on the properties of spherical particles and is equal to k_{net} . The sections of dependence for moderate values of α_{net} are more interesting from the practical point of view, that is, when constructional modification of the elastomer does not result in significant modifications of its main properties (wear resistance, elasticity, permeability, sealing ability, and the like).

Much more interesting is the variant when the couple of network structures begin to work asynchronous under a change of the load volume. The imitation of this dependence effect of overall friction coefficient on the load volume (depending on the load range the friction coefficient is reduced or increased) will be realized later on, but as for now the complexity of the practical realization of this model is obvious. The combination of "spring" models and surface modification, especially critical parts, e.g. of fluorine rubber, seems to be interesting. The investigation of the surface fluorination of rubber on the basis of fluorine rubber was realized on the samples as shown in the table 1. The fluorination was realized under standard conditions [7], under the temperature 20°C, modification time was 3 hours.

Table 1. The investigated samples of rubber and degree of its fluorination

No.	Sample key (type of elastomer and filling material), manufacturer	Fluorination degree $C_A^F \cdot 10^3$, kg/m^2	No.	Sample key (type of elastomer and filling material), manufacturer	Fluorination degree $C_A^F \cdot 10^3$, kg/m^2
1	VA-13 DB (SKF-26, TU) Hydrosoft Company	1,2	4	FER-70 (fluorine rubber), Ena-Holding	0,4
2	D-928 (fluorine rubber with addition of PTFE) Hydrosoft Company	1,1	5	Aflas-70 (copolymer TFE/VF), Ena-Holding	0,2
3	VT 17423 (Viton Gf-600S – copolymer VF/TFE/PFMVE) Dupont	0,9	6	PC-66 (modified Aflas), Reamt-RTI Company, Russia	0,3

On the table 1 we can see that under the action of fluorhelium composition on the stated samples of rubber there is noticeable fluorination of surface layers in residual C-H link (fluorination degree is from 0,2 to 1,2·10^{-3} kg/m^2 respectively) and in other hydrogenous ingredients; at the same time, as the photography of the surface shows (under the enlargement up to 10000-times) made with an electron focused beam microscope Stereoscan-360, producing company is Cambridge Instrument, there are no changes of the surface morphology of the samples in contrast to the carbochain rubber of other rubbers type [7]. It is natural to assume that the nearer is the structure of the original rubber to its structure after the fluorination, the smaller are the changes of surface morphology after the fluorination of rubber.

For the estimation of the effect of surface fluorination on the friction properties of fluorine rubber there are realized the tests according to the shifting circuit of plane rubber samples relative to the horizontal metal surface under a low standard load. As is well known the friction force of two contacting surfaces in general case is determined by deformation and adhesive components. It was expected that the dominant role in the definable sliding friction coefficient will act in our case its adhesive component. The tests were conducted on the serial friction machine Masplast "Delta" under a standard load 2 H and a conveying speed of rubber samples 200 mm/min (contact area: 9·10^{-4} m^2) relative to the plates of stainless steel, duralumin or bronze with the 9th cleanliness level of the surface as well as the plates of tool steel with the 14th cleanliness level of the surface (Johansen plate) (Table 2).

As the received data indicate, the surface fluorination of rubber results in a evident reduction of the friction coefficient on the metal surfaces. It is significant that the distinctions of the received values of K_{fc} for the steel surfaces with the 9th and 14th cleanliness level of the surfaces are small. It is caused probably by low values of standard load on the counterbody, and is as a sequent an insignificant contribution of the deformation component to the friction force. Thus the observed reduction of the friction coefficient

Table 2. The values of the kinetic friction coefficient of the check samples and the fluorine rubber samples

No.	Brand mark of the sample (rubber type)	Type of the sample	Kinetic friction coefficient, K_{fc}			
			Stainless steel	Duralumin	Bronze	Steel (Johansen plate)
1	BA-13 (SRF-26)	Check sample	0,90	0,80	0,90	0,60
		Fluorine sample	0,31	0,40	0,60	0,18
2	FER-70 (Fluorine rubber)	Check sample	1,50	1,40	1,80	2,10
		Fluorine sample	0,54	0,34	0,74	0,55
3	D-928 (Fluorine rubber+PTFE)	Check sample	1,25	1,10	1,40	1,00
		Fluorine sample	0,50	0,56	0,57	0,40
4	Aflas-70 (copolymer TFE/VF)	Check sample	2,43	1,70	3,11	2,80
		Fluorine sample	0,16	0,24	0,23	0,08
5	RC-66 (Modified Aflas)	Check sample	2,84	3,38	4,06	2,03
		Fluorine sample	0,18	0,15	0,30	0,20
6	VT 17423 (copolymer VF/TFE/ PFMVE)	Check sample	2,84	2,45	4,33	2,43
		Fluorine sample	0,31	0,30	0,36	0,40

should be referred obviously to the significant reduction of the interaction in the rubber – metal couple.

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REFERENCES

1. Petrova, N.N., Portnygina, V.V., and Biklibaeva, R.F., RF Patent no. 2294346, 2007.

2. Ovchinnikov, E.V., Tribological Properties of Industrial Rubber Articles Modified by Fluorine–Containing Oligomers, *Trenie Iznos*, 2004, vol. 25, no. 5, pp. 542–549.

3. Krasnov, A.P. and Afonicheva, O.V., Friction of the Rubbers with Fluorine–Organic Modifier, *Trenie Iznos*, 2000, vol. 21, no. 3, pp. 333–340.

4. Krylova, S.N., Ural'skii, M.L., and Gorelik, R.A., Industry of SK, Tyres, *Rezinotekhn. Izd.*, 1985, no. 6, pp. 12–15.

5. Abdrashitov, E.F., Tikhomirov, L.A., and Ponomarev, A.N., Plasmochemical Modification of the Elastomers, *1 Vseros. konf. Prikladnye aspekty khimii vysokikh energii* (Proc. 1st All–Russian Conf. Applied Aspects of High–Energy Chemistry), Moscow: RKhTU, Oct. 30–Nov. 2, 2001, pp. 85–86.

6. Nazarov, V.G., *Poverkhnostnaya modifikatsiya polimerov* (Polymers Surface Modification), Moscow: MGUP, 2008, 474 p.

7. Pyatov, I.S., Vasil'eva, S.N., Tikhonova, S.V., Stolyarov, V.P., and Nazarov, V.G., Combined Method for Modifying the Friction Properties of Elastomers, *Kauchuk Rezina*, 1999, no. 5, pp. 28-33.

8. Nazarov, V.G., Stolyarov, V.P., Gagarin, M.V., Baranov, V.A., Evlampieva, L.A. Inorganic Materials: Applied Research. 2010, vol.1, no.2, pp.162-166