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Protection of rubbers against ageing using diffusion, kinetic and structural effects

Processes of rubber ageing in the different kinetic modes and mathematical models of the processes including ageing and destruction processes under extreme conditions are studied. The ageing process for rubbers as thermodynamically open nonlinear systems is considered. It was revealed that the ageing process can be controlled by means of the internal physical and chemical processes organization and by creation of external influences (by the organization of thermodynamic forces and streams). According to the Onsager principle, in certain conditions of ageing the conjugation of thermodynamic forces and streams is possible. The diffusion and structural aspects of ageing of elastomeric compositions and articles thereof are considered.

Key words: *rubber aging, thermodynamic mechanism of ageing process*

Ochrona kauczuków przed starzeniem jako wynik dyfuzji, kinetyki i oddziaływań strukturalnych

Procesy starzenia się gumy są badane z wykorzystaniem różnych metod kinetycznych i modeli matematycznych tych procesów, w tym starzenia i destrukcji w ekstremalnych warunkach. Proces starzenia się kauczuków jest zaliczany do termodynamicznie otwartych systemów nieliniowych. Okazało się, że proces starzenia może być sterowany za pomocą wewnętrznej organizacji procesów fizycznych i chemicznych oraz przez tworzenie oddziaływań zewnętrznych (przez organizację sił i strumieni termodynamicznych). Zgodnie z zasadą Onsagera, w pewnych warunkach starzenia możliwe jest sprzężenie sił termodynamicznych i strumieni. Rozpatrywane są dyfuzja i aspekty strukturalne starzenia kompozycji elastomerowych oraz wytworzonych z nich artykułów.

Słowa kluczowe; *starzenie kompozycji elastomerowych, mechanizm termodynamiczny procesu starzenia*

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1. Preview

Rubber ageing is a complicated physical and chemical process running in the non equilibrium open hetero-

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Prof. Kablov is a member of the Russian Academy of Natural Sciences, the Russian Academy of Engineering and Chairman of the Volgograd Regional Branch of Y.A. Ovchinnikov's Russian Society of Biotechnologists. He has also authored over 150 inventions, more than 300 research publications, 6 textbooks and 3 monographs.

In 2000, he was appointed Director of Volzhsky Polytechnical Institute (branch) of VSTU – VPI (branch) of VSTU, and in 2002, was elected Head of Department of Polymer Chemical Technology and Industrial Ecology.

Prof. Kablov's area of research relates to developing a scientific basis for obtaining elastomer materials operating in extreme conditions (heat, fire and corrosion resistant materials, antifriction composite materials); developing nano- and microheterogeneous technological, modifying and operational additives to improve adhesive, thermal oxidation, and processing properties of polymer materials as well as research in other areas of technology.

He has established an Educational Innovation Center where scientific-based products have been manufactured, laboratories of industrial hygiene, environmental safety and biotechnology, Center of Energy Saving, and a number of other laboratories.

Prof. Kablov's inventions have been implemented in more 20 enterprises and, based on them, polymer materials of higher efficiency and modifiers for tire and rubber technical products industries have been produced in the institute.

geneous system. Ageing leads to destruction and/or macromolecules structuring, changes in physical structure, running diffusion processes, and other structure and chemical changes in a material.

The problem of polymers ageing and their stabilization consists a large chapter of polymer material engineering – a science about creation of polymer materials, their processing, preserving, and regulating their performance characteristics [1-2].

Nowadays, more than 120 million tons of synthetic polymers and almost the same amount of natural polymers (natural rubber, polymers based on polysaccharides) are produced in the world. The production dynamics is also important: the rates of growing polymer production are ahead of the rates of metals production by 25-30 %.

If it is possible to prolong the lifetime of polymeric articles, e.g. two times as large, then it will be equivalent to an equal increase of their production.

The other objective is a quantitative prediction of resistance of polymeric products. If the time of reliable operation is underestimated, the polymeric articles will be excluded of operation earlier than their resources are depleted, and it is not of economic benefit. Given the overestimated working lifespan, a polymeric product will fail during operation, which may lead to an accident or even more serious consequences.

One more goal is to apply the destruction process as a method for modification of polymeric articles.

The next objective is related to reuse of worked out (aged) polymeric products. Today, when the amount of worned out polymeric wastes is large, the problems of polymer reuse, regeneration of monomers, and pyrolysis of polymeric wastes to obtain the gaseous fuel become urgent.

The environmental issues and economic considerations are important as well: petroleum (the raw material for polymers) goes up in price, therefore, polymers will be more expensive. Waste plastics have not to be burned at dumps, since in this case a large number of toxic substances, including hydrogen cyanide and dioxin, are formed.

The following problem can be named as creation and search for ways of application self-degrading disposable polymers. The idea is to design polymers made of units connected with swivel groups. In plus, units have to be stable constantly, and swivel groups have to be stable in one cases (while operating) and unstable in other cases (after operating). As a rule, such swivel groups are not resistant to light and hydrolytic processes. That is why, once such polymers get to wastes after use, they easily degrade upon the groups to units-oligomers that dissolve in soil and then eaten by bacteria.

Kinetics is powerful and fine instrument in investigations of chemical, biochemical and biological processes, as well as in medicine, agriculture, etc.

In this paper we shall consider the problem of developing the system technology as a new scientific approach to producing elastomer materials. This technology combines general and special theory of systems, thermodynamics, kinetics, physics and chemistry of polymers, and computer methods of data processing.

2. A system approach to the problem of rubber ageing

Rubber ageing [3-4] is a complicated physical and chemical process running in the non-equilibrium open heterogeneous system. Ageing leads to destruction and/or macromolecules structuring, changes in physical structure, running diffusion processes, and other structure and chemical changes in a material.

A large variety of operating environments, a wide range of effects on polymer materials and the related multitude of technical materials (TM) requires a common conceptual approach to development of new efficient materials. Such a common conceptual approach is a system approach. The system technology combines various complementary methods and approaches to creation of elastomeric materials. The development strategy based on complementary approaches is seen as the most effective. The main theoretical approaches that underlie development of materials based on elastomeric systems are given below.

The task of the system description is a record of all diversity of problems facing both the design and TM as well as finding an optimal pair TM – product. The system description has to be based on the fundamental objective of Materials Science which is to establish relationships between composition, technology, structure and properties of materials.

The basis of the system approach is representation of an object as a system, i.e. as an integral set of interrelated elements of any nature. The main criterion for establishing the need for this element in the system is its participation in the system operation resulting in obtaining the desired result. The system approach allows for functionally supported dissection of any system into subsystems which volume and number are determined by the composition of the system and the consideration scope. One might add that the same object can be represented as different systems while the number of ways to view an object using the system approach has no limitations.

Representing an object as a system, we only get the opportunity to approach the structure of the object; a further step is to search for patterns of whole object relations in a system.

One of the system approach methods is also functional and physical analysis, in which a multi-component material is considered as a technical system carrying out operations to convert some of the input actions on the output ones. At that, the main attention is paid not to the material structure of the object, but to functional transformations of matter and energy flows [2-4].

External flows of matter and energy through functional systems affect a TM and cause its various physical

and chemical transformations (PCT). They lead to a change in the molecular, supramolecular, phase micro- and macrostructure of the TM. Since PCT and structural changes occur at different rates, it is necessary to consider the heterochronic behaviour of system changes. As a result of all the processes occurring in the TM during operation change, their structural and functional characteristics, so we can talk about a system change in the TM or TM system genesis.

3. A thermodynamic approach

Modern thermodynamic methods [5-7] can be applied not only to identify the possibility or impossibility of the running processes, but also as methods to find new technical solutions.

Ageing of elastomeric materials from a thermodynamic point of view can be seen as processes of self-organization and disorganization in open nonlinear systems. Processes occurring in such systems can be operated as an organization of chains of physical and chemical transformations in the systems themselves, highlighting the various functional subsystems as well as by controlled external exposures (thermodynamic forces and flows). In case of exposures, in accordance with the Onsager principle, pairing of thermodynamic forces and flows may take place. This allows for additional opportunities to influence the ageing process.

A polymer operated at high temperatures, in reactive environments, under intense friction, and other intensive effects can be regarded as a non-equilibrium open system, i.e. a system exchanging the medium substance (or energy). Energy and substance exchange is carried out by heat conduction, diffusion of the medium in the material, low molecular additives and products of thermal and chemical destruction of the polymer matrix. Under these conditions, the material as a system is not in equilibrium state, and the further it from equilibrium, the greater the intensity of exposure to the material and, consequently, the more intensive mass and energy exchange with the medium is. The presence of reactive components in a material increases an equilibrium deviation and leads to greater intensification of mass and energy exchange.

For an open system total entropy change dS is given by:
$$dS = d_iS + d_eS \qquad (1)$$
where d_iS – a change (production) in entropy in a system due to irreversible processes, d_eS – entropy flow due to energy and matter exchange with the medium.

It is important that the entropy of an open system can decrease due to the entropy output in the medium ($d_eS < 0$), and provided that $|d_eS| <> |d_iS|$. Then, despite the fact that $d_iS > 0$ (in accordance with the second law of thermodynamics), $dS < 0$.

The decrease in entropy of an open system means that in such system self-organization processes start as

well as forming specific spatio-temporal dissipative structures supporting sustainable state of the system.

To ensure the flow of negative external entropy can be implemented as a specially organized by external influences such as the artificially created concentration gradient, temperature, potential, and due to the chemical reactions that lead to high entropy products output of the system and its enrich with low-entropy products (an example is polycondensation system with by-product output).

The main conditions that lead to ordering in an open system are as follows:
1. A system is thermodynamically open.
2. Dynamic equations are nonlinear.
3. A deviation from equilibrium exceeds a critical value.
4. Microscopic processes are coordinated.

Analysis of behaviour of polymers and processes flowing in them shows the ability to perform these conditions, and, hence, the occurrence of ordered spatial or temporal structures that stabilize a system. It is only necessary to provide special external and internal conditions for this.

When in a non-equilibrium system several irreversible processes run, they are superimposed on one another and cause a new effect. Irreversible effects may occur due to a gradient of temperature, concentration, the electrical or chemical potential, etc. In thermodynamics all these quantities are called „thermodynamic" or „summarized forces", and denoted by X. These forces cause irreversible phenomena: heat flow, diffusion current, chemical reactions, and other flows, called summarized and denoted by J.

Generally, any force can cause any flow that is reflected in the famous Onsager equation:
$$J_i = \sum_{k=1}^{n} L_{ik} X_k \quad (i = 1, 2, \ldots n) \qquad (2)$$
Coefficients L_{ik} are called phenomenological coefficients.

If the system deviates from the stationary state, then, due to the desire of the entropy production to the minimum according to Prigogine's theorem (extreme principle) about the minimum speed of the entropy production in a stationary state, there come such internal changes that will tend to bring the system to that state. Such auto-stabilization phenomenon represents an extension to stationary non-equilibrium systems on Le Chatelier's principle applicable to chemical equilibrium.

A technical task for a developer of physical and chemical systems is to ensure the maximum deviation dA_ρ (the work of changes in a system) from zero in the negative direction, if his purpose is to use the external influences to put the system in a stationary state.

Theoretical analysis of capabilities to apply principles of the non-equilibrium thermodynamics and theory of open systems for production of elastomeric materials with physical and chemical transformations under ope-

rational exposures represents the prospects of the direction.

4. Kinetics of ageing

The ageing kinetics [8-11] is rather complicated. The Fig. 1 represents different types of kinetic curves and their models.

As it is seen from Fig. 1, ageing of polymers runs on various kinetic curves. It is connected with different processes running at ageing including simultaneous running of destruction and structuring, ageing by the mechanisms of auto-acceleration and autobraking, etc.

In some cases it is possible to use kinetic effects to prolong a working period of elastomeric materials.

With ageing materials near the degradation temperature, the mechanism of ageing can vary significantly and, thus, methods of protection.

The processes are especially difficult while intensive thermal destruction – ageing can shift to a „thermal explosion" at that.

When exposed to operational factors on a polymer material, we can distinguish two modes of operation: a normal mode and operation in extreme conditions. A normal mode is characterized by a relatively slow and gradual change of parameters during operation. Such changes in the parameters are usually described by linear dependencies, linear sections of nonlinear dependencies or Arrhenius equations. During normal operation, the effective values of the parameters (temperature, concentration of a corrosive environment, etc.) are far
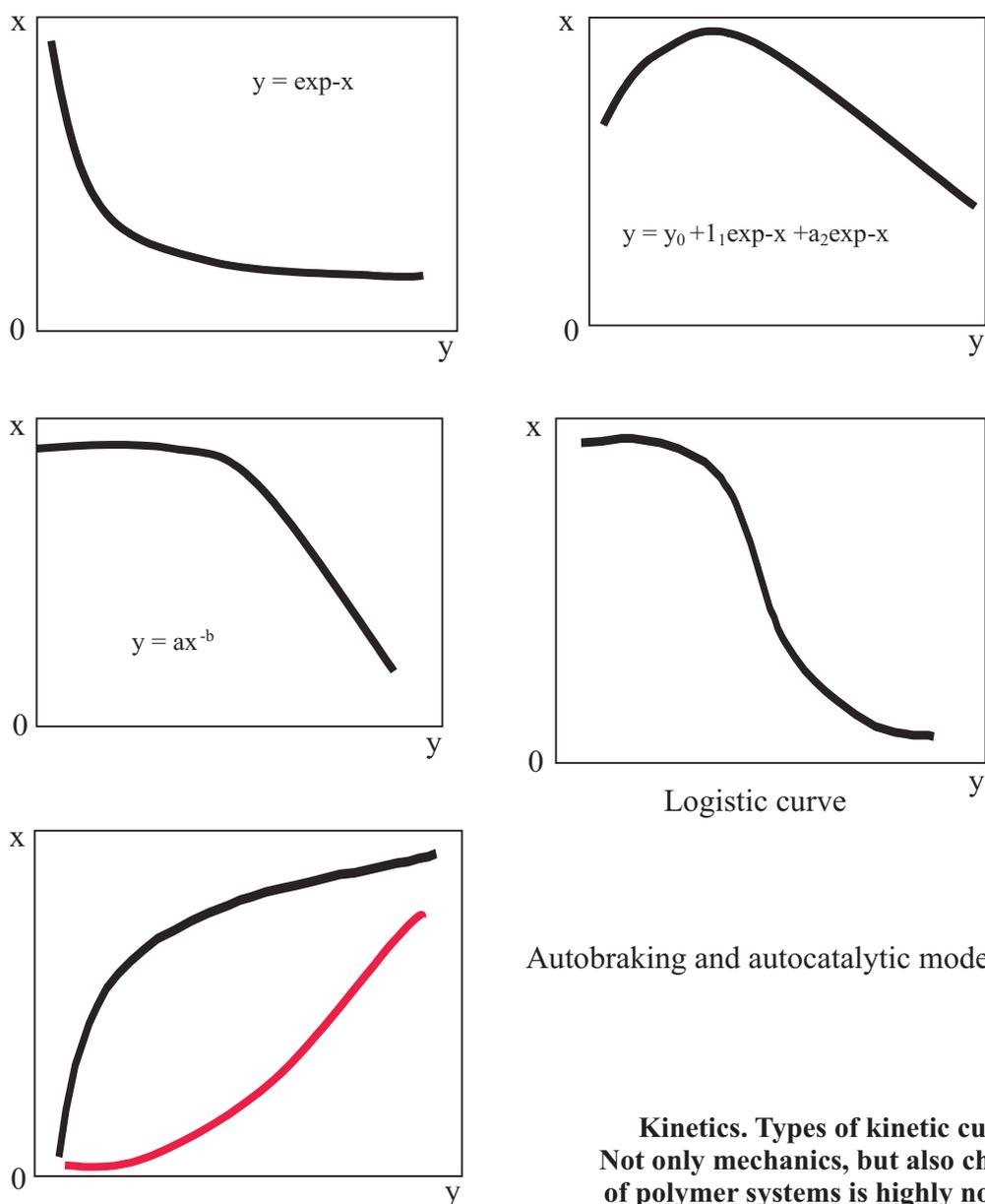

$y = exp-x$

$y = y_0 + 1_1 exp-x + a_2 exp-x$

$y = ax^{-b}$

Logistic curve

Autobraking and autocatalytic modes

Kinetics. Types of kinetic curves.
Not only mechanics, but also chemistry
of polymer systems is highly nonlinear

Fig. 1. *Types of kinetic curves*
Rys. 1. *Rodzaje krzywych kinetycznych*

from the limits of the material performance. Under extreme conditions, the effective values approach the limits of performance, or even fall in the "nonoperation" area. In this mode a material fails dramatically. A change in parameters is described, as a rule, by nonlinear dependencies including extreme ones or dependencies described by equations of the catastrophe theory. Fig. 2 shows an example of ageing in time-temperature coordinates. Under certain conditions – in the area of instability or bifurcation – the investigated parameter of a polymer x_1 can abruptly change its values.
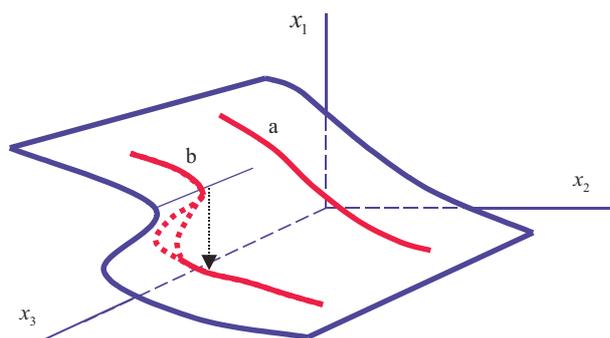
Fig. 2. *Behaviour of a nonlinear system in normal (a) and extreme (b) modes*
Rys. 2. *Zachowanie się systemu nieliniowego w warunkach normalnych (a) i ekstremalnych (b)*

Durability, however, may be sufficient in some cases – at disposable use, large stocks in thickness (mass, volume, etc.), as well as in the case of constructive features of an assembly, the application of protective coatings and other protection methods. Finally, durability of a material may be significantly increased by introduction of functionally active components in its composition that provide the material protection while exploitation. Nonlinear behaviour of polymeric materials increases with the approximation of operational parameters to the critical ones. Concurrently, instability of materials increases as well, in particular, structural stability and dynamic stability (according to Lyapunov). At the same time, nonlinear systems may also have the stability areas under certain values of the parameters. So, a system with autocatalysis or autoinhibition can be described by the following equation:

$$\dot{X} = -kX - k_1X \qquad (3)$$

where $\dot{X}$ – a change in a certain characteristic, k and k_1 – parameters typical for the system.

When $k > 0$, the system has the only real root $X = 0$ corresponding to the stable state, and when $k < 0$ it has three real roots, from which $X = 0$ becomes instable, and two last roots $X_{2,3} = \pm\sqrt{-k / k_1}$ turn out stable. It is seen that when the parameter passes through 0 to the negative side, resistance of the initial state is lost, but instead two new stable states arise: there is a complication (differentiation) of the system by bifurcation (splitting) of the

initial stable state. Mathematical analysis indicates that for sufficiently strong nonlinearity a complication of the structure with the formation of stable states may occur. Complexity of the system structure is even more multivariate in systems with two or more variables.

Systems in a state of instability are particularly sensitive to small external influences that can lead not only to the destruction of the system, but, on the contrary, transfer it to a new steady state which, in spite of its non-equilibrium, has sufficient stability. A typical example is the effect of ultra-low friction manifested at relatively low irradiation of rubbing pair «polymer-metal». Another example is rubber hardening on the initial stages of ageing, when the rubber composition contains polymer forming or structuring additives (see below). Thus, the polymer systems which are in the nonlinear area typical for extreme conditions can be stabilized by internal or external „control" effects [2, 5]. Extreme conditions for heat protective materials are working conditions in high temperature gas streams, operation of rubber products in a dynamic mode in combination with other exposures, etc.

The work [8] demonstrates the occurrence of nonlinearity and instability of the ageing process in ozone and oil environments.

So, when materials are aged near the destruction temperature, the ageing mechanism and, respectively, protection methods can vary considerably [3].

5. A structured approach

Since elastomeric materials are microheterogeneous multiphase materials, the great influence on ageing have diffusion processes including migration of components. By increasing the operating temperature, volatility of components, including the volatility of anti-agers, enhances. Therefore, the urgent problem is reducing the volatility of anti-agers while keeping them sufficient lability (ability to „hit" the zones on destructing macromolecules where free radicals appear). The problem is solved effectively enough by the use of composite anti-ageing systems. We propose the anti-ageing systems capable of continuous „release" of active labile anti-agers of micro- and nanoparticles. Anti-agers are located in the particles matrix in the supersaturated state. When operating, they continuously migrate into the dispersion medium of an elastomer. Various implementations of this method have been considered.

Structure of elastomeric materials at different levels (supramolecular structures, the structure in filled systems, the presence of several polymer phases, polymer-filler, polymer-fiber and polymer-polymer interfaces) largely determines the kinetics of ageing. In particular, the optimal solution is to provide a continuous phase of ageing resistant polymer in the dispersion medium of another one, creating a barrier layers of fillers and protective surface layers and coatings able to withstand static and dynamic loads.

6. Conclusion

Rubber ageing processes, including ageing in extreme conditions, run in different kinetic modes that are described with mathematical models. From the thermodynamic point of view, processes of rubber ageing flows as processes in open nonlinear systems. Ageing can be controlled by targeted organization of internal physical and chemical processes as well as by creating external influences (organization of thermodynamic forces and flows). Under certain ageing conditions, conjugation of thermodynamic forces and flows may take place. Rubber ageing essentially depends on diffusion of components along with phase and supramolecular structures of elastomeric compositions.

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