Kablov Victor Fedorovich[1], Zaikov Gennady Efremovich[2]

Application of polycondensation capable monomers for production of elastomeric materials working in extreme conditions

The research is devoted to creation of elastomeric compositions based on systems with functionally active components for extreme conditions. The use of polycondensation capable monomers (PCCM) and other compounds with reactive groups was proposed for generating the stabilizing physical and chemical transformations. Thermodynamic analysis of open polycondensation systems and substantiation of various PCCM application as functionally active components of elastomeric materials have been conducted; research results of polycondensation in an elastomeric matrix have been represented and a possibility of improving heat and corrosion resistance of elastomeric materials with introduction PCCM has been shown; different ways of applying PCCM have been proposed and experimentally proved.

***Key words**: polycondensation capable monomers, elastomeric composition, extreme conditions*

Zastosowanie monomerów zdolnych do polikondensacji do wytwarzania materiałów elastomerowych pracujących w warunkach ekstremalnych

Przedstawione badania dotyczą tworzenia kompozycji elastomerowych opartych na systemach zawierających funkcjonalnie aktywne składniki, przeznaczonych do ekstremalnych warunków. Do generowania stabilizujących przemian fizycznych i chemicznych zaproponowano wykorzystanie monomerów zdolnych do polikondensacji (PCCM) i innych związków z reaktywnymi grupami. W pracy dokonano analizy termodynamicznej otwartych układów polikondensacji i uzasadnienia różnych aplikacji PCCM jako funkcjonalnie aktywnych składników materiałów elastomerowych; przedstawiono wyniki badań polikondensacji w matrycy elastomerowej oraz wykazano możliwość poprawy odporności cieplnej i odporności na korozję materiałów elastomerowych przez wprowadzenie PCCM; zaproponowano różne sposoby wykorzystania PCCM i sprawdzono je doświadczalnie.

***Słowa kluczowe**: monomery zdolne do polikondensacji, kompozycje elastomerowe, warunki ekstremalne*

[1] Volzhsky Polytechnical Institute (branch) Volgograd State Technical University; e-mail: kablov@volpi.ru, www.volpi.ru

[2] N.M. Emanuel Institute of Biochemical Physics Russian Academy of Sciences; e-mail: chembio@sky.chph.ras.ru, www.ibcp.chph.ras.ru

Victor Fedorovich Kablov was born 27 October, 1948. In 1971, he graduated from the Chemical Engineering Faculty of Volgograd State Technical University (VSTU) and started his working activity as a plant engineer at Volzhsky Plant of Rubber Technical Products.

In 1972, he began working at VSTU. In 1976, he defended his Candidate of Sciences dissertation at Saint-Petersburg University of Technology. In 1991, he defended his Doctor of Sciences dissertation at Lomonosov Moscow Technological University of Fine Chemical Technology. In 1992, he was awarded the academic title of Full Professor.

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 – 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, among others, developing a scientific basis for obtaining elastomer materials operating in extreme conditions; developing nano- and microheterogeneous technology, additives to improve adhesive, thermal oxidation, and processing properties of polymer materials.

He has established an Educational Innovation Center, 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.

1. Introduction

A polymer operated at high temperatures, in reactive environments, under intense friction, and other intensive effects can be regarded as a nonequilibrium 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.

Obtaining of elastomeric materials based on systems with functionally active components aimed to work in high temperatures, pressure and reactive environments is essential when rubber technical products are produced for oil drilling equipment, geophysical instruments and articles for chemical industry.

Theoretical analysis of capabilities to apply principles of the nonequillibrium thermodynamics and theory of open systems for production of elastomeric materials with physical and chemical transformations under operational exposures represents the prospects of the direction [1–3].

In the research the use of polycondensation capable monomers (PCCM) for surface modification and obtainment of gradient nonequilibrium systems with optimal organized spatial structure when the concentration of functionally active components is increased toward the surface of the article have been proposed and experimentally substantiated.

The method for producing gradient systems is that the first condensation monomer is introduced in rubber, then the rubber is cured, and, finally, processing in the second monomer at a temperature providing polycondensation is carried out. Herewith, due to the diffusion of the second monomer into the product the generation of a gradient structure is provided. An important advantage of the gradient systems of is the absence of the phase boundary, and, thus, the layering during operation.

2. Experimental results and discussion

Functionally active components include the components capable of chemical reactions and physical and chemical transformations in bulk or on a surface of a material under external exposures (heat, mechanical, reactive environments). In addition, either protective agents are formed or physical effects are realized that allow for increasing service durability of rubbers.

For generating the stabilizing physical and chemical transformations, it was proposed in the work to use polycondensation capable monomers (PCCM) and other compounds with reactive groups. PCCM in an elastomeric matrix can react with formation of a new polymeric phase and heat absorption.

Thermodynamic analysis of open polycondensation systems and substantiation of various PCCM application as functionally active components of elastomeric materials have been conducted in the work; research results of polycondensation in an elastomeric matrix have been presented and a possibility of improving heat and corrosion resistance of elastomeric materials with introduction PCCM has been shown; different ways of applying PCCM have been proposed and experimentally proved [4–6].

Polycondensation processes allow for obtaining a large variety of chemical structures and, consequently, a possible wide range of properties when PCCM are applied as modifying agents. A distinctive feature of the developing direction is the thermodynamic nonequilibrium of polycondensation systems. In this case, nonequilibrium means that polycondensation systems have functionally active groups capable of further transformations (both the growth of macromolecules and a reversible reaction) nearly at any stage of a transformation. Low molecular product recovery, exo- and endothermic effects enable to classify polycondensation systems as open systems. Since the heat effects of the polycondensation are not too large, and the obtained low molecular product (usually water) takes much heat away, then, when an open system is considered, the process runs as endothermic. Besides, when the low molecular product is removed, an additional negative entropy flow arises resulting in thermodynamic assumptions of self-organization within the system.

According to Le Chatelier's principle, an increase in temperature shifts endothermic reactions towards heat absorption, i.e. towards the polymer formation. In this regard, PCCM introduction to rubbers is of interest in terms of creating a kind of self-cooling rubbers for heat protective materials.

The following reactions have been studied in the research: polyetherification, polytransesterification, polyamidation, the formation of polyhydrazides and their polycyclization into polyoxidiazoles, polyurethane formation and production of poly-1-acylhydrazides, three-dimensional polymerization, and catalytic polycondensation.

Diffusive and kinetic features of polycondensation in the high viscosity rubber matrix are very specific because of the difficult removal of the obtained product, thermodynamic incompatibility of a rubber to monomers and the formed polymer. All this required a study of polycondensation kinetics in a matrix of different elastomers.

One of the most interesting phenomena found at polycondensation in elastomeric matrices is acceleration

of the reaction compared to the reaction in a melt. Kinetic constants of reactions running in rubbers exceed greatly the rates of reactions running in a melt, and the rates of reactions in rubbers of different nature are very different. It has been shown that such dependence of the reaction rate on the rubber nature is connected with a type of the phase structure in systems "rubber – monomer" and "rubber – reaction products". Electron-microscopic analysis has revealed that the reaction rate is maximum, if system "rubber – monomer" is a system with emulsion of one monomer in a rubber with the second monomer dissolved in the rubber. In this case, polycondensation runs on the interfacial mechanism with the product recovery into an individual phase. The rate of the interfacial polycondensation goes up with an increase in the interfacial surface and increase in activating effect of free surface energy, respectively.

The essential thing is that polycondensation runs also in vulcanizates at time-temperature ageing modes.

That allows for realizing the proposed concept concerned to the production of materials with physical and chemical structure which is nonequilibrium in operating conditions. Before the certain values of conversion degree of a polycondensation system, the stabilization of rubber characteristics takes place, which is related to inhibition of residual functional groups and endothermic effects of polycondensation. The results of differential thermal analysis represent a flowing of polycondensation and a slow-down of thermal-oxidative processes in rubbers modified with PCCM.

The features of flowing polycondensation in bulk and surface layers have been investigated while application of mechanical loads and high pressure.

The observed activation of polycondensation under mechanical loading of the elastomeric matrix is an occurrence of coupling chemical and mechanical processes in accordance with the Onsager principle. The possibility of using high pressure (up to 1000 MPa) to selectively target polycondensation in an elastomeric matrix has been shown.

The opportunity to improve heat and corrosion elastomeric materials by using physical and chemical effects running at operational exposures into monomer containing nonequillibrium and open elastomeric systems has been displayed (Table 1). PCCM application is especially effective for some rubbers exploited in extreme conditions (high temperatures, aggressive oxidative environments based on mixes of inorganic and organic acids). It has been demonstrated that PCCM and polycondensation products form some unique buffer system inside a rubber.

An increase in corrosion resistance of rubbers is also possible in elastomeric compositions based on PVC. In the designed compositions for work in nitrating environments a number of proposed concepts are implemented, in particular the use of aggressive nitrating mixture to

Table 1. *Coefficients of properties variation for monomer containing rubbers at ageing*
Tabela 1. *Współczynniki zmian właściwości wulkanizatów zawierających monomer – po starzeniu*

PCCM	Δfp	ΔEp	PCCM	Δfp	ΔEp
Vulcanized rubbers based on nitrile-butadiene rubber SKN-40					
ageing at 398 K × 72 hrs			ageing at 423 K × 72 hrs		
without PCCM	0.30	0.44	without PCCM	0.29	0.07
PA–Glyc.	0.45	0.30	HFDP–AA	0.69	0.59
PA–Glyc.–DEG	0.70	0.40	PFAA–AA	0.88	0.82
PA–DEG	0.60	0.30	ageing at 473 K × 60 min		
AA–DEG	0.51	0.35	without PCM	0.52	0.44
DHAA–AA	0.64	0.68	PA–Glyc.	0.84	0.78
unfilled PA–Glyc.	1.20	0.70	PA–Glyc.–DEG	1.50	0.83
unfilled PA–Glyc.–DEG	0.90	0.80	PA–DEG	1.70	0.66
unfilled PA–DEG	1.25	0.80			
Vulcanized rubbers based on ethylene-propylene rubber SKEP					
ageing at 423 K × 72 hrs			ageing at 443 K × 72 hrs		
without PCCM	0.70	0.62	without PCCM	0.15	0.13
AA–DEG	0.87	0.88	DCA–MPDA	0.52	0.40
1,3 ADA–DAA	1.40	1.50			

where: HFDP – hexafluorodiphenylolpropane; Glyc. – glycerin; PA – phthalic anhydride; AA – adipic acid, DHAA – dihydrazine of adipic acid, 1,3 ADA – 1,3-adamantanedicarboxylic acid, PFAA – bis(monoethanolamide)-perfluoroadipic acid, DCA – 1,3-dimethyl-5,7-dicarboxyladamantane, MPDA – *m*-phenylenediamine, f – the ageing coefficient on strength, E – the ageing coefficient on elongation.

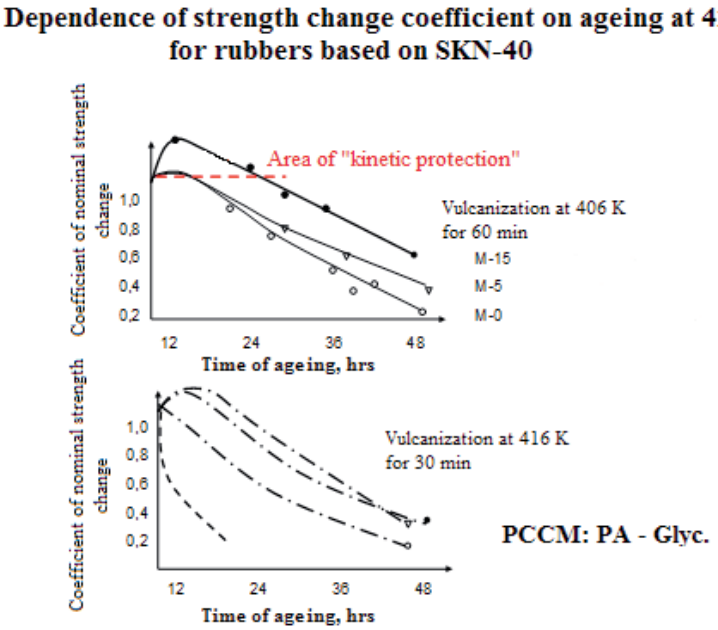

Fig. 1. *Dependence of a change in properties of rubbers containing PCCM at ageing*
Rys. 1. *Zależność zmian właściwości wulkanizatów zawierających PCCM podczas starzenia*

seal and structure a surface layer and creation of internal functional subsystems of physical and chemical transformations based PCCM and other components. All this avoids surface gumming.

Fig. 1 demonstrates the efficiency of PCCM application.

3. Conclusion

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). Application of polycondensation capable monomers containing functional groups on any stage of a chemical transformation creates thermodynamic opportunities for system self-organizing by means of the endothermic reaction of the low-molecular product release.

The conducted research has shown that there is a possibility to create heat and aggressive resistant elastomeric materials based on systems with functionally active ingredients for different operating conditions.

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