Yu.O. Andriasyan, I.A. Mikhaylov, A.L. Belousova*, G.E. Zaikov, A.E. Kornev*, A.A. Popov

Properties of fluorine-containing natural rubber and butyl rubber, obtained by method mechanochemical halide modification

Taking into account modern requirements a new alternative technology of obtaining fluorine-containing elastomers based on solid-phase (mechanochemical) halide modification was created. New fluorine-containing rubbers produced by this technology proved themselves in the conditions of the rubber production. The new alternative technology of obtaining fluorine-containing elastomers, based on mechanochemical halide modification was created taking into account current requirements. New fluorine-containing cauotchoucs, obtained by given technology, showed yourself to good advantage in condition of rubber's production.

***Key words**: halide modification, cauotchouc, technology, mechanical chemistry, fluorine-containing natural rubber, fluorine-containing butyl rubber, elastomer, halide-containing, rubber compound, rubber*

Właściwości kauczuków naturalnego i butylowego zawierających fluor, otrzymywanych metodą mechanochemicznej modyfikacji z udziałem chlorowców

Uwzględniając obecne wymagania, stworzono nową alternatywną technologię otrzymywania elastomerów zawierających fluor, opartą na metodzie modyfikacji w fazie stałej z udziałem chlorowców (mechanochemicznej). Uzyskane za pomocą omówionej technologii nowe kauczuki zawierające fluor okazały się dobrym rozwiązaniem w warunkach produkcyjnych.

***Słowa kluczowe**: modyfikacja chlorowcami, kauczuk, technologia, mechanochemia, kauczuk naturalny fluorowany, kauczuk butylowy fluorowany, zawartość chlorowca, mieszanka kauczukowa, guma*

1. Aims and background

Based on historical data halide modification (HM) of high-molecular compound which was carried out in 1859, natural rubber (NR) was exposed to modification and to NR was dissolved in perchloromethane, through which chlorine gas was run through. Modified NR is powder product with content of fixed chlorine not over 62-68% m., which doesn't have properties of elastomer [1, 2]. Halide modification of NR may be referred to one of the first attempt of commitment a new properties to polymer with help of carrying out of chemical modification.

Nowadays HM of polymers together with obtaining of halogen-containing polymers with help of synthesis is one of intensively developing direction in the field of obtaining chlorine-containing polymers. In result of carrying out of halide modification of polymers, which have technologically smoothly, large capacity industrial production, elastomer materials and composites are managed to obtain with wide complex of a new specific properties: high adhesion, fire-, oil-, gasoline-, heat resistance, ozone resistance, incombustibility, resistance to influence of corrosive environments and microorganisms, high strength, gas permeability, etc.

In the article we consider questions, concerning with obtaining and properties of halide modified fluorine-containing cauotchoucs as natural rubber (NR) and butyl rubber (BR), which are prospective in terms of application in rubber industry as corrosion preventing coatings. Perspectivity of their production and application consists in specific properties of these cauotchoucs (high gas permeability of FBR and accessibility, high strength of FNR). These properties are caused by structure of both initial (BR and NR) and fluorine-containing cauotchoucs (FBR and FNR). Also fluorine containing NR and BR has high rate sulfuric vulcanization in comparison with initial NR and BR.

2. Results and discussion

As a result of the conducted work samples of fluorine-containing natural rubber's using technology of

N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin str., 119334 Moscow, Russia; Chembio@sky.chph.ras.ru, igmi85@mail.ru

* M.V. Lomonosov Moscow State University of Fine Chemical Technologies, 110 Vernadskii prospect, 119571 Moscow, Russia

solid phase mechanical-chemical haloid modification (FNR-2, FNR-4, FNR-6 and FNR-8) were obtained. The ciphers in notation of caoutchouc point at quantity of added fluorine-containing modificator in weight fraction (w.f.). Modification of natural rubber (NR) was carried out, when study mechanical-chemical conversions of NR was in optimal conditions on lab rubber mixer in self-heating mode. To determine presence and content of fluorine in modified elastomeric samples, the method of mass-spectrometric analysis was used. To define the presence of fixed fluorine in macromolecule of NR infrared of extracted samples FNR was used. Extraction was carried out in Soxhlet's apparatus by adding acetone during 20 hours and by adding dimethyl formamide during 20 hours.

To determine the reaction activity (RA) of a natural rubber samples relatively fluorine-containing modificator in the process of mechano-chemical haloid modification, was used the ratio of content fixed fluorine in caoutchouc (F_f) to its common content (F_{com}). F_f determined using samples FNR after extraction, but F_{com} – using FNR, which were not exposed to extraction.

$$RA = (F_f/F_{com}) \cdot 100\%.$$

The results of investigations are showed in Table 1.

Table 1. *Reaction activity and fluorine content in patterns FNR*
Tabela 1. *Wydajność reakcji i zawartość fluoru w próbkach FNR*

	FNR-2	FNR-4	FNR-6	FNR-8
Common fluorine content, %	1.16	2.31	3.21	4.44
Content of fixed fluorine, %	0.92	1.50	1.73	2.53
Reaction activity, %	79	65	54	57

Obtained results showes, that the fraction of chemically fixed fluorine with caoutchouc also increased with increasing of quantity of added fluorine-containing modificator.

However it is necessary to note, that reaction activity of NR slightly decreased with increased fraction of adding modificator and hence it refers to increase of content unreacted modificator fraction in FNR.

The highest RA is noted in FNR-2 (79%) and slightly decreased in range of FNR-4 (65%), FNR-6 (54%), FNR-8 (57%).

In similar, with NR were obtained samples of fluorine-containing butyl rubber (FBR-2, FBR-4, FBR-6 and FBR-8) and determined their reaction activity. The results of investigations are presented in Table 2.

Table 2. *Reaction activity and fluorine content in patterns FBR*
Tabela 2. *Wydajność reakcji i zawartość fluoru w probkach FBR*

	FBR-2	FBR-4	FBR-6	FBR-8
Common fluorine content, %	1.17	2.3	3.23	4.43
Content of fixed fluorine, %	1.11	2.25	2.78	4.12
Reaction activity, %	95	98	86	93

Obtained data point to high reaction activity of butyl caoutchouc relatively fluorine-containing modificator in process of mechano-chemical haloid modification (~95%). Moreover when content of modificator is changed, reaction activity practically keeps on one level.

Then we studied vulcanized characteristics of rubber mixes and physical-chemical properties of rubbers, prepared by using standard formula for NR and BR on the basis of NR (BR) and FNR (FBR). Results are presented in Table 3 for NR and Table 4 for BR respectively.

Vulcanized characteristics showes, that mechanical-chemical modification of NR by fluorine-containing organic compound refers to increase the vulcanization rate almost in two times in comparison with vulcanization rate of rubber, based on initial NR (21%/min for NR and 40%/min for all FNR). Other characteristics practically don't change.

Vulcanizing characteristics show, that mechanical-chemical modification of BR by fluorine-containing organic compound refers to increase of vulcanization rate almost in two times in comparison with rate of vulcanization of rubbers, which based on initial BR

Table 3. *Vulcanized characteristics rubber compounds based on fluorine-containing natural rubber*
Tabela 3. *Charakterystyka wulkanizacji mieszanek kauczukowych opartych na kauczuku naturalnym zawierającym fluor*

Rubber compound based on:	Vulcanized characteristics						
	M_{st}, dN·m	M_{min}, dN·m	M_{max}, dN·m	M_{opt}, dN·m	t_s, min	t_c, min	V_c, %/min
NR	9.2	7.9	35	32.3	2	6.7	21
FNR-2	7	5	33	29.7	1.5	4	40
FNR-4	7	5	33	29.7	1.5	4	40
FNR-6	7	5	30	27	1.7	4,5	36
FNR-8	7	5	33	29.7	1.5	4	40

Table 4. *Vulcanized characteristics rubber compounds based on fluorine-containing butyl rubber*
Tabela 4. *Charakterystyka wulkanizacji mieszanek kauczukowych opartych na kauczuku butylowym zawierającym fluor*

Rubber compound based on:	Vulcanized characteristics						
	M_{st}, dN·m	M_{min}, dN·m	M_{max}, dN·m	M_{opt}, dN·m	t_s, min	t_c, min	V_c, %/min
BR	13	10	23	20.7	8	45	2.7
FBR-2	12	9	20	18.0	5	25	5
FBR-4	12	9	18,5	16.7	5	25	5
FBR-6	12	9	19	17.1	5	25	5
FBR-8	12	9	19	17.1	5	25	5

Table 5. *Physical-mechanical properties of rubbers based on fluorine-containing natural rubber*
Tabela 5. *Właściwości mechaniczne wulkanizatów kauczuku naturalnego zawierającego fluor*

Properties	Rubber based on:				
	NR	FNR-2	FNR-4	FNR-6	FNR-8
Conventional strength at elongation, MPa					
at 200%	2.2	1.8	1.9	2.0	2.4
at destruction	21.9	24.3	24.8	26.1	23.6
Tensile strain, %	644	690	700	700	660
Elongation set after destruction, %	29	32	38	38	43
Tear resistance, kN/m	110.9	102.4	96.2	111.6	113.6
Shore hardness number	57	60	56	56	60
Rebound elasticity, %	38	29	30	32	28

(2.7%/min for BR and 5%/min for all FBR). Other characteristics don't change practically.

Also we studied physical-mechanical properties of rubbers based on fluorine-containing natural rubber and butyl rubber. Results are presented in table 5 for NR and table 6 for BR respectively.

The results of carried out investigations show, that the adding of fluorine in macromolecular structure refers to some increase of tensile strain (650% for NR and -700% for FNR) and conventional stress (21.9 MPa for NR, 34.3 MPa for FNR-2, 24.8 MPa for FNR-4, 26.1 MPa for FNR-6 and 23.6 MPa for FNR-8).

Obtained experimental data show, that in the process of adding modificator is observed by some kind of degradation rubbers strength properties (18.3 MPa for BR, 15.5 MPa for FBR-2, 14.8 MPa for FBR-4, 16.5 MPA for FBR-6 and 14.8 MPa for FBR-8), which can be associated with decrease of molecular mass of butyl caou-

Table 6. *Physical-mechanical properties of rubbers based on fluorine-containing butyl rubber*
Tabela 6. *Właściwości mechaniczne wulkanizatów kauczuku butylowego zawierającego fluor*

Properties	Rubber based on:				
	BR	FBR-2	FBR-4	FBR-6	FBR-8
Conventional strength at elongation, MPa					
at 100%	0.48	0.17	0.12	0.20	0.12
at 200%	0.87	0.33	0.34	0.39	0.34
at 300%	2.0	0.72	0.58	0.85	0.58
at destruction	18.3	17.4	17.8	18.5	17.6
Tensile strain, %	881	1150	1075	1060	1075
Elongation set after destruction, %	27	40	35	36	34
Tear resistance, kN/m	64.6	59.6	59.4	55.6	59.4
Shore hardness number	45	46	46	48	50
Rebound elasticity, %	7	5	5	5	4

tchouc because of destruction of macromolecular under mechanical influence in rubber mixer, when modificator is added in quantity 6 w.f. is achieved optimal content of fixed fluorine (2.78%). Also the presence of fluorine in macromolecular structure of caoutchouc refers to increase of tensile strain (880% for BR and -1100% for FBR) and permanent elongation (25% for BR and -40% for FBR). At the same time nominal rupture resistance, tear resistance, hardness and rebound elasticity practically don't change [3-7].

3. Conclusions

So, was learned of new obtained fluorine-containing natural rubber and butyl rubber by method of mechanical-chemical halide modification. Were studied some structural characteristics of caoutchoucs, vulcanized and physical-mechanical properties of rubber mixes and rubbers, which are based on them.

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