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Properties and application of polyolefin chlorine-containing rubbers, obtained by mechanochemical halide modification method

The new alternative technology of obtaining chlorine-containing elastomers, based on solid phase (mechanochemical) halide modification was created taking into account current requirements. New chlorine-containing polyolefin cauotchoucs, obtained by given technology, showed yourself to good advantage in condition of rubber's production.

***Key words**: halide modification, mechanical chemistry, chlorine-containing ethylene-propylene-diene cauotchouc (CEPDC), chlorine-containing butyl rubber (CBR), rubber mixture, rubber, unsaturation, covulcanization*

Właściwości oraz zastosowanie kauczuków poliolefinowych zawierających chlor, uzyskanych metodą modyfikacji mechanochemicznej halogenkami

Nowa, alternatywna metoda uzyskiwania elastomerów zawierających chlor, polegająca na ich modyfikacji w fazie stałej (mechanochemicznej) halogenkami, została opracowana z uwzględnieniem aktualnych wymagań. Nowe kauczuki poliolefinowe zawierające chlor, otrzymane z wykorzystaniem wspomnianej technologii, wykazywały istotne zalety podczas przetwórstwa.

***Słowa kluczowe**: modyfikacja chlorem, mechanochemia, kauczuk etylenowo-propylenowo-dienowy zawierający chlor (CEPDC), kauczuk butylowy zawierający chlor (CBR), mieszanka kauczukowa, elastomer nienasycony, kowulkanizacja*

1. Aims and background

Based on historical data halide modification (HM) of high-molecular compound was carried out in 1859, natural rubber (NR) was exposed to modification and, in addition to that, 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 didn't have properties of elastomer [1, 2]. Halide modification of NR may be referred to one of the first attempt of commitment of 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 new specific pro-

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perties: high adhesion, fire-, oil-, gasoline-, heat resistance, ozone resistance, incombustibility, resistance to influence of corrosive environments and microorganisms, high strength, gas permeability, etc.

Nowadays by world polymer industry was developed manufacture of those widespread polymers of halide modification, which has properties of elastomers such as: chlorosulfonated polyethylene (CSP), chlorinated polyethylene (CP), chlorinated and brominated butyl rubber (CBR, BBR) and chlorinated ethylene-propylene (CEP) and ethylene-propylene-diene cauotchoucs (EPDC) in small amount.

In the article we consider questions, concerning with obtaining and processing of halide modified chlorine-containing cauotchoucs as CBR and CEPC, which are prospective in terms of application in rubber industry. Perspectivity of their production and application consists in specific properties of these cauotchoucs (high gas permeability of CBR and high heat, ozone resistance of CEPDC). These properties are caused by structure of both initial (BR and EPDC) and chlorine-containing cauotchoucs (CBR and CEPDC).

Originally, before carrying out of halide modification of cauotchoucs BR and EPDC, attempts of rubber application based on these cauotchoucs were undertaken for purpose of items creation from elastomer materials, differing in high gas permeability and high heat-ozone resistance. In the process of properties study of rubber mixtures and rubbers from these cauotchoucs was found, that rubber mixtures had unsatisfactory characteristics by manufacturability of obtaining and processing. For the purpose of improvement of technological characteristics of rubber mixtures, attempts of combination of cauotchoucs BR and EPDC with diene cauotchoucs (natural rubbers, synthetic isoprene rubbers SIR-3, etc) was undertaken. However, this combination didn't result in positive decision of given problem. If production and processing of rubber mixtures based on combined system of cauotchoucs with technological point of view didn't provoke difficulties, that creation of rubber items, which are able to use, is impossible. The reason is that if we combinate cauotchoucs, which differ in its unsaturation in case of application of sulfur vulcanization, that resulted in absence of covulcanization between phases of combined cauotchoucs [3]. Thus, there were no unified, spatial, vulcanized network in rubbers based on combined system. In process of vulcanization took place redistribution of catalyst with help of diffusion and vulcanizing agent from the phase of cauotchouc with less unsaturation (BR, EPDC) to the cauotchouc's phase with high unsaturation (NR, SIR-3). Obtained rubbers are not satisfied with its strength and dynamic characteristics.

Many decisions of this problem were suggested, but the most effective was decision to add trace amount of halogen in macromolecular structure of cauotchouc with low unsaturation [4, 5]. It gave additional functionality to cauotchouc and therefore higher vulcanization rate. The optimum halogen content was when deterioration of initial cauotchoucs specific properties was not observed, and additionally capability of halide-containing cauotchouc to be covulcanized with high unsaturated elastomers was gathered.

Historically, the most popular in tire industry was chlorine-butyl rubber (CBR). CEPDC cauotchouc had limited application, because required level of rubbers ozone resistance in rubber technology, traditionally, created by adding of chemical age resistors and antioxidants. Rubber ozone resistance and service time of the rubber item had the same duration. It's necessary to note, that this protect is inefficient for items with long period of service, because of exudation of age resistors and antioxidants from rubber. It is important to note, that the fraction of this items in common amount of output rubber products is very insignificant.

There were no problems on the first industrial production stage of halide modification of chlorine-containing cauotchoucs, the requirement in this cauotchoucs was growing, that was promoting to open new factories for production these cauotchoucs. However it's necessary to note, that since realization of halide modification of natural rubber in 1859 almost nothing was changed in technology of obtaining of chlorine-containing cauotchoucs. This technology was preserved with some small changes until the present time. The meaning of given technology [6] or as it called by specialists "dissolved technology" is that, on the first stage, the polymer, which we want to modify, is dissolved in organic solvent. The concentration of solution should not exceed 10% from technological consideration. Then gaseous halogen, it's chlorine or bromine, is leaked through obtained solution, then when planned content of halogen in polymer is reached, the process is suspended. Then are following the stages: detrainment of obtained chlorine-containing polymer, its washing and neutralization, then the stage of drying, packing and storage. As secondary process we can consider recuperation of solvent. All developments of this technology consisted in replacement of gaseous halogen with halogen-containing organic compounds, that did not promote simplification of both technology and ecology of production process. Dissolved technology of obtaining of chlorine-containing cauotchoucs is multistage process, which in terms of current, strict ecology requirements doesn't stand up to scrunity.

Taking into account the above disadvantages of dissolved technology of obtaining of chlorine-containing cauotchoucs, alternative technology of obtaining of chlorine-containing cauotchoucs was developed and was offered in the end of ninetieth of past century by scientists' community and specialists of Moscow Academy of Fine Chemical Technology, Institute of biochemical physics, research and manufacturing association of firms "Polikrov" and The Moscow tire factory [7]. The differential characteristic of new technology is technological simplicity of carrying out obtaining process of chlorine-containing cauotchouc and its ecological safety.

The developed technology is based on solid phase (mechanochemical) halide modification of initial cauotchoucs by chlorine-containing organic compounds, which are environmentally safe in process of carrying out of halide modification. The developed technology has patent protection and opportunity to obtain both CBR and CEPDC, and others (saturate and unsaturated) cauotchoucs. Within the framework of newly developed technology is assimilated experimental-industrial output of cauotchoucs CBR-2,5 and CEPDC-2,0 (the number shows content of fixed chlorine in cauotchouc).

2. Results and discussion

Research-industrial testing of cauotchouc CBR-2,5 in rubber formula of radial tires inner lining, tubeless construction, was carried out on the Moscow tire factory. The point of carrying out of investigations was to substitute serially used rubbers of inner lining of chlorine-containing cauotchouc HT-1066 (produced by USA) for cauotchouc CBR-2,5. Conducted investigations showed, that production and processing of rubber mixtures with new cauotchouc CBR-2,5 on technological equipment created no problems. Plasto-elastic, physical-mechanical and some specific properties of serial and experiment rubber mixtures and their vulcanizates, containing cauotchouc CBR-2,5 were studied. The results of investigations are showed in Table 1.

We can see from the Table 1, that experimental and serial rubbers almost didn't differ in plasticity, Mooney viscosity, and cohesion strength.

Test of rubber mixtures on plastometer "Faerston" found higher fluidity of experimental rubber with cauotchouc CDR-2,5.

Study of vulcanized characteristics of the rubber mixtures on Monsanto rheometer showed, that experimental mixtures with cauotchouc CDR-2,5 excel serial mixtures almost in two times in the initial vulcanization time and have higher vulcanization rate in basic period, that is very important with technological point of view.

Study of physical-mechanical characteristics of the rubbers showed, that experimental rubber much excel serial in tensile strength 300%, but there are no differences between experimental and serial rubbers in strength, conventional breaking elongation and tear strength.

The values of gas permeability (to hydrogen) of experimental and serial rubbers are the similar.

Thus, in the Table 2 we showed, that new chlorine-containing butyl cauotchouc CBR-2,5 satisfies the requirements by their characteristics, demanded on halogen-containing butyl cauotchoucs, used in rubber production of inner lining.

The next stage of our investigations was to study opportunities of application of new chlorine-containing cauotchouc CEPDC-2 in the formulas of rubbers for sidewall of radial tires and rubbers for production of diaphragm press.

Table 1. *Properties of rubber mixtures and rubbers for radial tires' inner lining with application of serial chlorine-butyl rubber CBR HT-1066 and CBR-2,5*
Tabela 1. *Właściwości mieszanek gumowych oraz kauczuków przeznaczonych na wykładziny wewnętrzne opon radialnych z zastosowaniem seryjnego chlorowanego kauczuku butylowego CBR HT-1066 oraz CBR-2,5*

Index	HT-1066	CBR-2,5
Plasticity	0.37	0.40
Cohesion strength, MPa	3.49	3.45
Mooney viscosity (100°C)	58.5	66.0
Plastometer "Faerston" tests		
Flow time of rubber mixture, s	25.8	16.2
Shrinkage, %	62.0	58.5
Monsanto rheometer tests		
Rotational moment, N·m		
Min	9.0	9.8
Max	16.0	24.5
Initial time of vulcanization, min	4.4	9.3
Vulcanization rate, %/min	7.9	9.4
Optimum vulcanization time, min	17.0	20.0
Physical-mechanical indexes		
Conventional tensile strength 300%, MPa	4.2	6.9
Conventional tensile strength, MPa	10.5	10.0
Conventional breaking elongation, %	650	550
Tear resistance, kN/m	31	39
Gas permeability (to hydrogen), $l/(m^2 \cdot d)$	0.49	0.52

As we know, sidewalls' rubber is exposed deformations in process of service, that is the reason of intensive heat emission. Increased temperature promotes premature heat and ozone ageing of rubbers of tire sidewalls. Traditionally chemically synthesized antioxidants and age resistors are mixed in rubber formula for protection of sidewall rubber from heat and ozone ageing [8]. The "bleeding" of protectors takes place in process of service, because they don't bind chemically with elastomer matrix; all this reasons promote premature ageing and destruction of sidewalls. Considering that part of tires can be reconstructed after service period, it will be very practically advantageous to increase heat and ozone resistance of sidewalls by adding of protection component, which can build into elastomer matrix with help of chemical links. The function of that component can make new chlorine-containing cauotchouc CEPDC-2, because we know, that it has capability to covulcanize with high unsaturated cauotchoucs, composing on rubber formula for sidewalls. It is well-known, that adding 20-30 mass part of cauotchouc CEPDC-2 is enough for increase of ozone resistance of rubber from diene cauotchoucs [9].

In this case we studied the opportunity of application of cauotchouc CEPDC-2 in rubber formula for sidewalls of radial tires, elastomeric part of which has diene cauotchoucs SIR-3 and CDR in ratio (50:50). The ratio of cauotchoucs SIR-3:CDR:CEPDC-2 was 50:20:30 and 50:30:20 in experimental rubber. Chemical antioxidants weren't added in experimental rubber mixtures.

We established, that production and processing of rubber mixtures with cauotchouc CEPDC didn't have difficulties on technological equipments. We studied plasto-elastic, physical-mechanical and some specific properties of serial and experiment rubbers. Experimental data are showed in Table 2.

Table 2. *Properties of studied serial and experimental rubber mixtures and rubbers, based on cauotchoucs SIR-3, CDR, CEPDC-2*
Tabela 2. *Właściwości badanych kauczuków i mieszanek gumowych, seryjnych i eksperymentalnych, bazujących na kauczukach SIR-3, CDR, CEPDC-2*

Index	Serial rubber*	Experimental rubber	
		1**	2***
Mooney viscosity(120°C)	43	45	47
Plasticity	0.44	0.44	0.36
Conventional modulus at 300%, MPa	3.7	7.2	6.0
Conventional tensile strength, MPa	15.7	20.5	18.4
Conventional breaking elongation, %	770	600	610
Conventional permanent tension elongation, %	14	15	13
Coefficient of heat ageing (100°C, 72h)			
- at strength	0.56	0.85	0.82
- at conventional elongation	0.63	0.92	0.91
Coefficient of ozone resistance of dynamic tests (ε=20%)	0.52	0.95	0.92
TM-2 hardness	56	60	62
Rebound elasticity, %			
under 20°C	41	42	44
under 100°C	47	50	52
Crazing strength, th. cycle	>252	>252	>252
Dynamic repeated tension durability, th. cycle	>50	>50	>50

*Based on cauotchoucs SIR-3 – CDR (50:50),

**Based on cauotchoucs SIR-3 – CDR – CEPDC-2 (50:30:20),

***Based on cauotchoucs SIR-3 – CDR – CEPDC-2 (50:20:30).

We can see from the Table 2, that plasto-elastic characteristics of serial and experimental rubbers have close values, serial rubbers have conventional modulus at 300% twice higher as experimental ones and have higher conventional tensile strength and hardness. The value of rebound elasticity, crazing strength and dynamic repeated tension durability of experimental and serial rubbers are very similar. It should be noted, that serial rubbers have heat resistance and ozone resistance doubles that serial rubbers, containing antioxidants.

Thus, the investigations showed, that new chlorine-containing cauotchouc CEPDC-2 in rubber formulas for tires sidewalls can be used as polymer antioxidant.

The practice states that the main reasons of break-down of diaphragm press are the low capacity to elastic recovery of rubbers based on butyl cauotchoucs, leading to "treading out" of diaphragm, and high extent of "tar value" of diaphragm work surface. To eliminate these disadvantages we studied opportunity of substitution of cauotchouc SEPC-60 in formulas of serial rubbers (resin curing) for diaphragm for new chlorine-containing ethylene-propylene-diene cauotchoucs CEPDC-2.

Table 3. *Properties of serial and experimental rubber mixtures and rubbers for production of shaper-vulcanization*
Tabela 3. *Właściwości seryjnych i eksperymentalnych mieszanek gumowych oraz kauczuków do produkcji elementów formowanych*

Index	Serial rubber	Experimental rubber
Plasticity	0.41	0.42
Mooney viscosity(140°C)	37	36
Conventional modulus at 300%, MPa	5.0	6.0
Conventional tensile strength, MPa	10.2	12.6
Conventional breaking elongation, %	620	600
Conventional permanent tension elongation, %	34	20
Tear resistance, kN/m	60	63
Coefficient of strength heat ageing (180°C, 24h)	0.6	0.6
Coefficient of strength temperature resistance under 100°C	0.7	0.62
TM-2 hardness	74	78
Dynamic repeated tension durability (ε_{dyn}=50%; ε_{stat}=37,5%), th. cycle	42	>50
Creep (160°C, 24h, 0,3MPa), mm	119	53
Rebound elasticity*, %	13/18	18/32
Rebound elasticity*, after ageing, %	16/28	18/30
Tar value, %	1.2	0.6

*In numerator under 20°C, in denominator under 100°C

Cauotchoucs BR-1675 and SEPC-60 in ratio (85:15) compose formula of serial rubbers for diaphragm production, in experimental rubber SEPC-60 was substituted for similar amount of CEPDC-2. It is well-known, that chlorine-containing compounds have the ability to activate resin curing of butyl cauotchouc, which is the

main elastomer component of membraneous rubbers [1].

The investigations showed, that there were no difficulties in production and processing of rubber mixtures with cauotchouc CEPDC-2 on technological equipments.

We studied plasto-elastic, physical-mechanical and some specific characteristics of serial and experiment rubber mixtures and rubbers. Experimental data are showed in Table 3.

We can see from the Table 3, that plasticity and Mooney viscosity of experimental and serial rubber mixtures have close values. The values of conventional modulus at 300%, conventional tensile strength, tear resistance, hardness, rebound elasticity and dynamic durability of experimental rubbers are higher than serial ones.

It should be noted, that experimental rubber has lower by half conventional permanent tension elongation in comparison with serial rubber, although the values of conventional tensile elongation are the similar; "tar value" and creep under 160°C are lower (in two times and more, than in two times respectively).

3. Conclusions

Thus, we can make conclusion, based on obtained results, that application of new chlorine-containing cauotchouc CEPDC-2 in rubber formula for production of press diaphragm will permit to increase the diaphragm service time.

It should be noted, that developed new technology of obtaining of chlorine-containing cauotchoucs permits to manufacture competitive chlorine-containing polyolefine cauotchoucs CBR-2,5 and CEPDC-2. As showed the investigations of cauotchouc CBR-2,5, well recommended yourself in conditions of rubber production and cauotchouc CEPDC-2, which didn't have analogues on synthetic cauotchoucs market, can be used as polymeric antioxidant in rubbers based on diene cauotchoucs.

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