Investigation of chlorinated modifier content influence on the physical-mechanical properties and vulcanizing characteristics of rubber and rubber mixture

K V Sukhareva1,2, I A Mikhailov1,2, Yu O Andriasyan2 and A A Popov1,2
1Plekhanov Russian University of Economics, 36 Stremyanny Lane, Moscow, 117997, Russia
2Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygina str., Moscow, 119334, Russia

E-mail: aspirantras@mail.ru

Abstract. Present paper is devoted to the novel solution for the chlorination technology of polyolefin and diene rubbers – mechanochemical halide modification, as a more efficient way to obtain halogenated elastomers with a wide range of halogen content (from 3 to 7 %). The vulcanizing characteristics of elastomeric compounds based on the chlorinated rubber compounds as well as the production conditions of vulcanization process have been studied by the methods of dynamic mechanical rheometry. The performed investigation revealed the influence of chlorine content in different types of rubber compounds on rheological and physical-mechanical properties. New halogen-containing polyolefins rubbers produced by this technology proved themselves in the conditions of the rubber production.

1. Introduction
Today demand for elastomeric materials that have a complex set of specific properties ensuring their operation in the extreme conditions is constantly increasing. In this regard, the necessity to develop novel production technologies for a variety of industrial sectors is growing. Chemical modification of produced elastomers becomes the main trend in the field of producing elastomeric materials with a new complex of properties. One of the most important directions of elastomers modification is halide modification [1]. It is possible to obtain elastomeric materials and composites with a wide range of new specific properties on the basis of halogenated rubbers [2, 3] such as high adhesion, advanced resistance to fire, heat, petrol, oil, ozone, aggressive media and microorganisms, non-flammability, high strength, good gas impermeability, etc. A new method was developed for the halide-containing elastomer production, which is an alternative to the existing method (polymer solution halogenation), namely, the method of mechanochemical halide modification that sufficiently simplifies and cheapens the process of halide-containing rubber production. The developed method is based on the effect of initiation of radical polymer cleavage [4, 5] and participation of produced radicals in the bimolecular reaction with radical scavengers [6–9]; it allows us to halogenate polymers without halogen gases in solution and in the solid phase.
The research is aimed to determine influence of chlorine contain in rubbers on the physical and mechanical properties of rubber compounds based on different chlorinated rubber obtained through thermomechanical halide modification [10,11].

2. Materials and Methods
In this work, styrene-butadiene rubbers SBR-30RP and SKMS-30RP, isobutylene isoprene rubber IIR 1675 and ethylene propylene rubber EPDM-E60 were used as a basic raw material. Chlorine-containing saturated paraffin, which have the length of the carbon chain C30 and contain ~70% of chlorine (wt) was used as modifier. On the base of this rubbers were obtained rubber compounds with a total chlorine content from 5% to 15% by weight.

To determine presence and content of chlorine in modified elastomeric samples, the Schoniger flask combustion method was used.

To determine the bound chlorine in the composition of the rubber macromolecules, the samples of the chlorinated rubber were subjected to extraction to remove the unreacted modifier. Extraction was carried out in Soxhlet’s apparatus by adding acetone during 20 hours. Rubber compounds based on SBR, SKMS, EPDM and IIR were prepared to the standard formulation according to GOST 54554-2011.

The research of the vulcanization kinetics of rubber compounds with different halogen content was carried out in accordance with GOST 12535–84 (Rubber compounds. The method for determining the cure characteristics with vulcametric) through dynamic mechanical rheometry (DMR) (RPA 2000 Monsanto).

Physical and mechanical properties of the vulcanizates were determined by tensile testing machine (DEVOTRANS, Turkey) according to GOST 270–75–75 (Rubber. The method of determining the elastic properties of tensile strength.). The hardness was estimated according to GOST 263–75 (Rubber. Determination of Shore A hardness.) Rebound resilience tests of specimens were conducted on a Schob instrument according to GOST 27110-86.

3. Results and Discussions
The first stage of the work is devoted to the study of vulcanization characteristics of elastomeric compositions based on non-chlorinated rubbers (SBR-30RP, CSKMS-30RP, IIR, EPDM-E60) and chlorinated rubbers (CSBR-30RP, CSKMS-30RP, CIIR and CEPDM) containing different amount on combined chlorine. The number in brackets after the rubber compound (CSBR-30RP (5)) indicates the amount of modifier (mass parts (wt.) in terms of 100 grams of rubber). The research results of viscosity and vulcanization characteristics with the help of a dynamic mechanical rheological tester are given in Table 1.

Vulcanized characteristics shows, that mechanochemical modification of SBR-30RP by chlorine-containing organic compound refers to slight reduces the vulcanization rate (2.70 %/min for SBR-30RP and 2.56 %/min for CSBR-30RP) and to increase optimum time of vulcanization (42 min for SBR-30RP and 46 min for CSBR-30RP). This can be explained by an increase of an unsaturation level resulting from dehydrochlorination reaction, which proceeds by the vulcanization temperature (150°). The same dependence was observed for rubbers CSKMS-30RP. Increase in chlorine content of CEPDM rubbers doesn’t have significant effect on vulcanization characteristics.

The next stage of our investigations was to study physical-mechanical properties of rubber compounds based on chlorine-containing rubbers, obtained by halide mechanochemical modification and properties of serial rubber mixtures. In the course of the experimental studies, the following parameters were determined: conventional strength at 200% elongation (M200 MPa), conventional strength at 300% elongation, (M300 MPa), conventional strength at 500% elongation (M500 MPa), tear resistance (Ϭp, MPa), tensile strain of the material before it breaks, %, elongation set after destruction during 1 min, %, Shore hardness number, c.u. and rebound elasticity, % (Table 2).

We can see from the table 2, that properties of all chlorine containing rubber compounds have higher values that the serial rubber mixture. The results of carried out investigations show, that adding of chlorine in macromolecular structure refers to some increase of physical-mechanical properties of CIIR,
CSBR-30RP and CSKMS-30RP and to some decrease CEPDM-E60. The strength properties of CSBR-30RP decrease (from 13.9 MPa to 11.4 MPa) apparently due to the increase in the rigidity of the polymer chain with an increase in the chlorine content. Hardness and elasticity of CEPDM-E60 rubbers fast does not change, but strength decreases (from 17.2 MPa to 8.1 MPa) which may be due to an increase in the irregular structure. For CSKMS-30RP the strength and elasticity changes are insignificant.

**Table 1.** Rheological and vulcametrical parameters of the rubber mixtures.

| Rubber compound based on: | Amount of combined chlorine (% wt.) | Vulcanized characteristics |
|---------------------------|-------------------------------------|---------------------------|
|                           | $M_{st}$ (dN·m) | $M_{min}$ (dN·m) | $M_{max}$ (dN·m) | $M_{opt}$ (dN·m) | $t_{c}$ (min) | $t_{c}$ (min) | $V_{c}$ (%) |
| SBR-30RP                  | 0                     | 5.5                    | 5.0                  | 19                  | 17.6                  | 5          | 42          | 2.7         |
| CSBR-30RP (5)h            | 2.6                    | 5.0                    | 4.0                  | 19                  | 17.5                  | 10         | 50          | 2.5         |
| CSBR-30RP (10)j           | 5.0                    | 5.8                    | 5.0                  | 22                  | 20.3                  | 7          | 46          | 2.6         |
| CSBR-30RP (15)k           | 7.5                    | 5.8                    | 5.0                  | 21                  | 19.4                  | 7          | 46          | 2.6         |
| SKMS-30 RP                | 0                     | 6.8                    | 6.0                  | 31                  | 28.5                  | 6          | 47          | 2.4         |
| CSKMS-30 RP (5)           | 1.8                    | 5.5                    | 4.8                  | 23                  | 21.2                  | 7          | 54          | 2.1         |
| CSKMS-30 RP (10)          | 3.5                    | 5.8                    | 5.0                  | 26                  | 23.9                  | 7          | 50          | 2.3         |
| CSKMS-30 RP (15)          | 5.4                    | 5.8                    | 5.0                  | 26                  | 23.9                  | 6          | 45          | 2.5         |
| BR                        | 0                     | 10.8                   | 9.8                  | 31                  | 28.5                  | 2          | 40          | 2.6         |
| CBR (5)                   | 2.7                    | 11.3                   | 10.5                 | 32                  | 29.9                  | 2.5        | 41          | 2.6         |
| CBR (10)                  | 5.2                    | 12.5                   | 10.5                 | 34                  | 31.9                  | 2          | 38          | 2.8         |
| CBR (15)                  | 7.5                    | 15.2                   | 13.0                 | 27                  | 25.4                  | 2          | 30          | 3.6         |
| EPDM-E60                  | 0                     | 11.0                   | 9.0                  | 57                  | 52.2                  | 2.5        | 34          | 3.2         |
| CEPDM-E60 (5)             | 2.1                    | 13.0                   | 10.0                 | 60                  | 55.0                  | 2.5        | 30          | 3.6         |
| CEPDM-E60 (10)            | 4.0                    | 14.5                   | 11.5                 | 63                  | 57.9                  | 1          | 28          | 3.7         |
| CEPDM-E60 (15)            | 5.5                    | 13.0                   | 10.2                 | 58                  | 53.2                  | 1          | 33          | 3.1         |

- $M_{st}$ - starting torque value
- $M_{min}$ - minimum torque value
- $M_{max}$ - maximum torque value
- $M_{opt}$ - optimal torque value
- $t_{c}$ - optimum time of vulcanization
- $t_{c}$ - compound scorch time
- $V_{c}$ - vulcanization velocity
- h (5) - amount of the introduced chlor-modificator 5 wt% (mass parts (wt) in terms of 100 grams of rubber).
- j (10) - amount of the introduced chlor-modificator 10 wt% (mass parts (wt) in terms of 100 grams of rubber)
- k (15) - amount of the introduced chlor-modificator 15 wt% (mass parts (wt) in terms of 100 grams of rubber)
Table 2. Physical-mechanical properties of rubbers based on chlorine-containing rubbers.

| Rubber compound based on: | Amount of combined chlorine (% wt.) | Physical-mechanical properties |
|---------------------------|-------------------------------------|--------------------------------|
|                           | M_{200} (MPa) (Δ±0.5 Mpa) | M_{300} (MPa) (Δ±0.5 Mpa) | M_{600} (MPa) (Δ±0.5 Mpa) | 6b, (MPa) (Δ±0.5 Mpa) | Tensile strain (%) (Δ±0.5 %) | Elongation set after destruction (%) (Δ±0.5 %) | Shore hardness number (c.u.) (Δ±2 c.u.) | Rebound elasticity (%) (Δ±2 %) |
| SBR-30RP                  | 0                         | 0.5                         | 1.2                         | 4.4                         | 10.6                         | 720                           | 14                         | 43                         | 37                         |
| CSBR-30RP (5)             | 2.6                       | 1.8                         | 2.7                         | 9.0                         | 13.9                         | 720                           | 14                         | 43                         | 37                         |
| CSBR-30RP (10)            | 5.0                       | 1.8                         | 4.4                         | 11.0                        | 11.9                         | 525                           | 6                          | 52                         | 29                         |
| CSBR-30RP (15)            | 7.5                       | 0.9                         | 2.3                         | 6.6                         | 11.4                         | 680                           | 14                         | 58                         | 23                         |
| SKMS-30RP                 | 0                         | 2.5                         | 5.2                         | 8.8                         | 350                          | 6                             | 60                         | 60                         | 32                         |
| CSKMS-30RP (5)            | 1.8                       | 1.3                         | 3.5                         | 9.9                         | 11.7                         | 550                           | 10                         | 54                         | 31                         |
| CSKMS-30RP (10)           | 3.5                       | 1.3                         | 2.9                         | 7.9                         | 12.2                         | 600                           | 12                         | 58                         | 26                         |
| CSKMS-30RP (15)           | 5.4                       | 1.4                         | 4.0                         | 10.3                        | 13.2                         | 580                           | 11                         | 57                         | 25                         |
| BR                        | 0                         | 2.7                         | 5.4                         | 13.7                        | 16.3                         | 565                           | 28                         | 62                         | 14                         |
| CBR (5)                   | 2.7                       | 1.7                         | 4.0                         | 10.4                        | 15.1                         | 590                           | 40                         | 66                         | 17                         |
| CBR (10)                  | 5.2                       | 2.1                         | 4.0                         | 10.2                        | 14.3                         | 650                           | 47                         | 77                         | 12                         |
| CBR (15)                  | 7.5                       | 1.3                         | 2.6                         | 6.3                         | 13.5                         | 740                           | 53                         | 76                         | 13                         |
| EPDM-E60 (5)              | 0                         | 7.9                         | 15.1                        | -                           | 16.4                         | 330                           | 4                          | 72                         | 32                         |
| EPDM-E60 (10)             | 2.1                       | 6.1                         | 11.2                        | -                           | 17.2                         | 475                           | 24                         | 81                         | 27                         |
| EPDM-E60 (15)             | 4.0                       | 9.5                         | -                           | -                           | 10.3                         | 225                           | 8                          | 82                         | 25                         |
| EPDM-E60 (15)             | 5.5                       | 8.1                         | -                           | -                           | 8.1                          | 200                           | 10                         | 80                         | 25                         |

4. Conclusion
So, a new chlorine-containing rubbers obtained by method of mechanical-chemical halide modification were studied. Some structural characteristics of rubbers, curing kinetics of rubber compounds and vulcanized rubbers physical-mechanical properties, were studied. Thus, it can be seen from the studies carried out that the introduction of chlorine into the structure of the rubber macromolecules somewhat reduces the rate of vulcanization. Also, when the modifier is added to 5 wt. for CSBR-30RP and EPDM-E60, some increase in strength is observed, but when more modifier is introduced, the strength decreases, which is apparently due to the increase in the proportion of unreacted modifier that acts as a plasticizer. In the case of modification of SKMS-30RP, this effect is not observed until the introduction of 15 parts by weight of the modifier. However, when the BR is modified, the strength decreases, since the BR has a highly ordered structure and is broken during mechanical processing, as does the plasticizing effect of the unreacted modifier.

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