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POTENTIAL OF USE THE MODIFIED POLYMERIC SULFUR BASED ON THE BY- PRODUCT PETROLEUM SULFUR IN THE RUBBER PRODUCTION

Abstract. Technological methods have been developed for the production of new polymer sulfur composites based on activated by-product sulfur and polystyrene for their use as a vulcanizing agent with improved binding and astringent properties. Optimum process conditions have been worked out, allowing to vary the sulfur content in the obtained materials. An experimental laboratory batch of new sulfur-polymer composites for testing in extended laboratory conditions as a vulcanizing agent has been gained.

Formulations, optimal conditions for mixing and vulcanization of rubber compounds have been developed. Tests of physical- mechanical and operational properties of rubbers on their basis showed the effectiveness and prospects of their application in the production of tires and rubber products.

The developed technology for the production of new sulfur-based vulcanizing agents based on activated by-product sulfur and polystyrene is promising and can be recommended for use in the production of rubber products with improved performance properties.

Key words: modified polymeric sulfur, polystyrene, rubber, caoutchouc, vulcanization.

Introduction. Vulcanization plays an important role on rubber industry by offering the rubber products containing three-dimensional net work of rubber molecules. By this mean, the significant improvement innumerous properties including tensile and tear properties, set, resilience and abrasion of rubber vulcanizates is resulted. The vulcanization could generally be divided into 3 main systems, i.e., sulfur, peroxide, and metal oxide systems [1-4]. The sulfur vulcanization system is generally preferential because of its superiority in mechanical properties and ease of cure behavior adjustment [5, 6]. Typically, the sulfur used in rubber industry originates from 2 main resources, i.e., natural resource and petroleum refinery. Basically, the sulfur from natural resource is more prefer able because of its certain chemical structure in conjunction with its high sulfur content (99 %). The petroleum-based sulfur is taken as a by-product from petroleum refinery. The annual growth in hydrocarbon production in Kazakhstan and the environmental requirements for the quality of petroleum products resulted in the accumulation of more than 10 million tons of sulfur in the Tengiz field at the sulfur storage site. Our main goal of this work is to make full use of such sulfur by investigating the modification technique for enhancing the petroleum-based sulfur to match the requirement of rubber industry. Thus, the most promising direction for the creation of large-scale production of associated sulfur utilization is the production of polymer compositions of modified sulfur with improved properties for use as vulcanizers and hardeners, as well as a plasticizer of rubber compounds and bases for soft rubbers and elastomers.

This article presents the results of studies on the production of high-sulfur polymers based on the by-produced Tengiz sulfur and polystyrene (PS) and the use of the polymers obtained as the vulcanizing agent of rubber compounds.

Results and discussion. Studies of the using possibility a by-product of oil processing-by-sulfur as a vulcanizing agent of unsaturated rubbers compared to commercially available rhombic sulfur offer several advantages. In contrast to conventional polymeric sulfur has a complex of unique properties: high resistance to aggressive media, high impact strength, the absence of thermal shrinkage deformations in the compositions, insolubility in organic solvents and rubbers, does not "bloom" on the surface of rubbers and vulcanizates, which stabilizes the properties of the product in for long periods of storage and can be widely used as a vulcanizing agent in the tire and rubber industries [7-10].

At this study, the production of polymer sulfur was carried out by direct catalytic sulphurization of polystyrene (PS) using by-product sulfur. In order to obtain high-sulfur polymers, deep sulfurization of granular polystyrene by Tengiz sulfur was carried out, and the physical-chemical properties of the products obtained were studied. In the synthesis, activated colloidal nanosized sulfur was used, obtained by acid decomposition of calcium polysulphides [8].

The reaction was studied in the temperature range 240-330 °C at a molar ratio of PS and sulfur (16 grams of sulfur atoms per unit PC), calculated on partial or exhaustive sulfurization. The synthesized samples are powders of dark gray and black color with metallic sheen, insoluble in water and organic solvents.

The synthesized samples were analyzed for the content of S (C, H). According to the thermogravimetric analysis, the polymers obtained are heat-resistant up to 220-240 °C.

Copolymer sulfur modified with polystyrene (SPSM-PS) is formed by the catalytic copolymerization of colloidal sulfur, obtained on the basis of by-product sulfur (by using diphenylguanidine, DPHG, as a catalyst). It was expected that the reaction would proceed according to figure 1 [11-13].

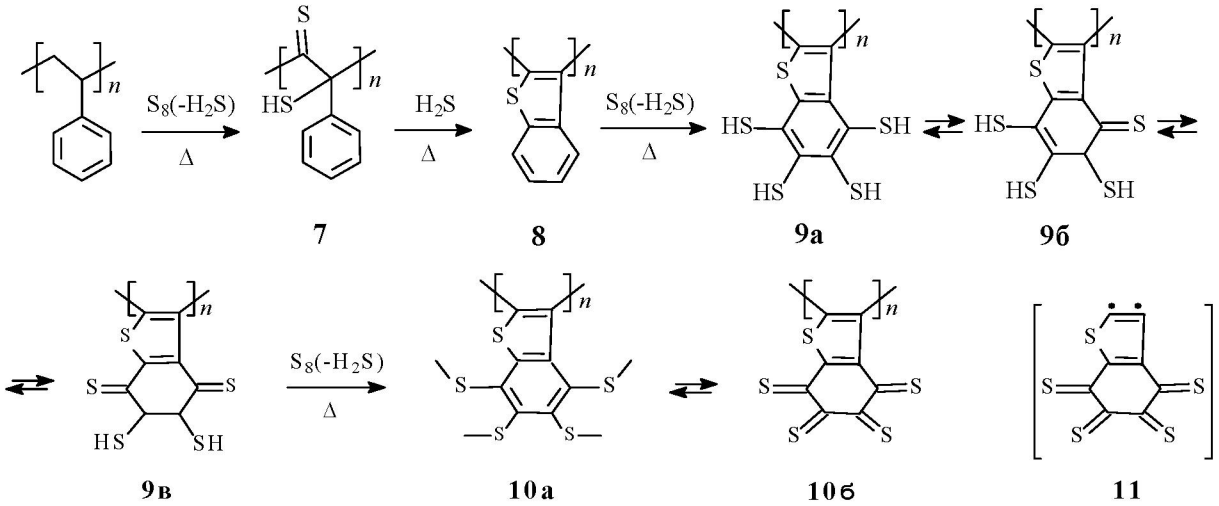

Figure 1 – Reaction scheme of copolymer sulfur modified with polystyrene

As can be seen from the scheme, in the copolymerization products there are condensed benzothiophenes linear and partially cross linked polymers with sulfide units. Under the studied conditions, high-sulfur polymers are formed from PS and colloidal sulfur (content S = 65.7-73.0%) (table 1).

Table 1 - Results of catalytic sedimentation of PS by elemental sulfur

Experi-ence	PS:S, mol	T_a, °C	Time, h	Catalyst, wt. %	Yield	S, %
1	1:8	240	2	DPHG(1)	47.0	42.1
2	1:16	240	2	DPHG (1)	78.1	66.5
3	1:16	240	3	DPHG (1)	98.1	73
4	1:16	300	3	no	96.5	65.7

Analysis of the data given in table 1 shows that the molar ratio of polystyrene to sulfur of 1:16 is optimal, because the molar ratio of PS:S = 1:8 shows a low yield of the product and a low sulfur content in it (runs 1-4). It should be noted that the catalytic synthesis of the sulfurized polystyrene with activated colloidal by-product sulfur shows the best yields (98.1 %) and sulfur content (73 %, experiment 3) compared to elemental sulfur (experiments 1, 2).

In the IR spectra of the compounds obtained (figure 2), the absorption peak with a maximum at 471 cm^{-1} refers to the ν (S-S). Absorption in the 1700-1000 cm^{-1} region (maxima of 1639-1403 cm^{-1}) is apparently due to the vibrations of the skeleton of the exhausted sulfurized benzothiophene skeleton 10a (figure 1). The peak of 1108 cm^{-1} can be attributed to the oscillations of ν(C = S) in structures 9 b, c and 10 b. The triplet 757, 729, 707 cm^{-1} may be due to the mixed vibrations of the aromatic bonds C-C and C-S, in this case in the structure 10 a.

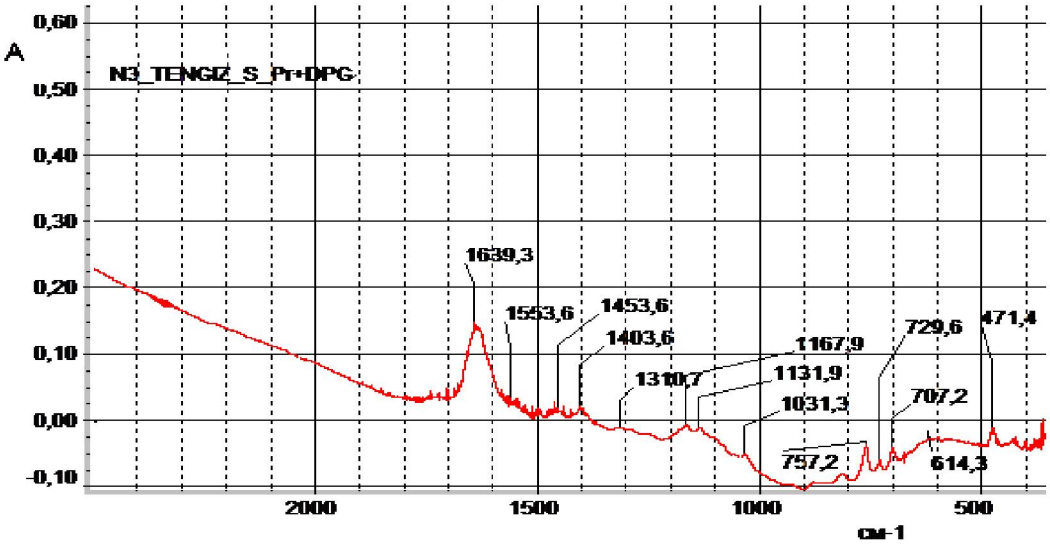

Figure 2 – IR spectrum of sulfurized polystyrene

Development of formulations, optimal conditions for mixing and vulcanization of rubber compounds. The resulting high-sulfur polymers on the basis of associated sulfur and polystyrene were tested during vulcanization of rubbers.

The tests were carried out in the enlarged laboratory conditions on the serial formulations of rubber compounds for the insulation of the bead wire of truck tires containing various amounts of high-sulfur polymer.

The necessary amount of colloidal sulfur preparation depends to a large extent on the compounding formula. As a rule, with an increase in its content for the same composition in the rest of the mixture, the degree of vulcanization increases to a certain optimum. With a further increase in the sulfur dosage, hardness continuously increases, but the overall technological properties deteriorate. For the production of rubber products, 0.2-5.0 wt. h. sulfur (based on 100 parts by weight of rubber); Conversely, for ebonite mixtures, the sulfur content must be increased to 25-40 wt.h. The dosage sulfur in rubber mixtures depends on the rubber type and the number of vulcanization accelerators taken. In mixtures based on sodium-divinyl rubbers, sulfur is taken in an amount of up to 2.5 %, in mixtures with divinyl-styrene rubbers up to 2 %. Rubber is a complex multicomponent system, consisting of 10-15 or more ingredients.

SKMS-30 ARKM-15 (GOST 11138-78 E) - synthetic methylstyrene rubber with a methylstyrene content of 30 %. This rubber refers to the "oil" with an average content of highly aromatic oil. Properties of butadiene-methylstyrene rubbers SKMS largely depend on the content of α-methylstyrene in them.

To establish the curing activity of the obtained SPSM-PS, laboratory samples of copolymer sulfur were tested on model filled rubber compounds based on SKMS-30 ARK rubber of insulation of the bead wire in comparison with the standard (table 2), where a different content of the modified polymer sulfur SPSM- PS (2, 3, 4, 6 mph).