

Investigation of surface halide modification of nitrile butadiene rubber

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Abstract. The investigation is devoted to the novel technology of surface halide modification of rubber samples based on nitrile butadiene rubber (NBR). 1,1,2-trifluoro-1,2,2-trichlorethane was used as halide modifier. The developed technology is characterized by production stages reduction to one by means of treating the rubber compound with a halide modifier. The surface halide modification of compounds based on nitrile butadiene rubber (NBR) was determined to result in increase of resistance to thermal oxidation and aggressive media. The conducted research revealed the influence of modification time on chemical resistance and physical-mechanical properties of rubbers under investigation.

1. Introduction

Nowadays obtaining of halogen-containing polymers including synthesis and halide modification is one of intensively developing direction in rubber industry. Due to halide modification of polymers having technological flexibility and effectiveness in production, elastomer materials and composites are managed to obtain with a wide complex of required specific properties: high adhesion, incombustibility, high strength, gas permeability, resistance to fire and heat, corrosive media (oil, gasoline, ozone) and microorganisms, etc. [1-4].

Among the various methods of polymers modification, the surface modification is most promising in the area of polymers practical application. Different methods have been developed to obtain the required surface properties of polymer composites. The most-used method of polymer solution halogenation comprising a heterogeneous reaction of gaseous F₂ or Cl₂ and their mixtures with a polymer surface [5]. One of the main disadvantage of this method is high aggressiveness of initial fluorinating and chlorinating reagents. The method is also characterized by a high labor input, undesirable presence of toxic by-products and complex technical design of production process.

The proposed novel technology of surface mechanochemical modification is one of the new approach of scientific direction “Mechanochemical halide modification of elastomers” [6, 7]. The developed technology is characterized by production stages reduction by treating the rubber compound with a halide modifier.

2. Materials and Methods

In this work, nitrile butadiene rubber (NBR) supplied by SIBUR Holding was used as a basic raw



material. Rubber compounds based on NBR were prepared according to the requirements of GOST 54554-2011. 1,1,2-trifluoro-1,2,2-trichloroethane was used as a halide modifier [8]. The modification of rubber was carried out by treating the surface with a modifying compound for different periods of time (24h, 72h, 144h).

Modified rubber compounds based on NBR were oxidized by a temperature of 150°C at an oxygen pressure of 300 mmHg. The kinetics of oxygen absorption was studied using a manometric unit with the absorption of volatile reaction products by solid KOH according to GOST ISO 188-2013. As a result, kinetic curves of oxygen absorption for samples with different modification time (24h, 72h, 144h) and initial NBR rubber compound sample without modification were obtained.

Rubber resistance to aggressive media was determined by a change in mass of samples at relaxed state in accordance with GOST 9.030-74. As aggressive media a set of different compounds were used including industrial mineral oil, “Nefras” gasoline, sulfuric acid, hydrochloric acid, and nitric acid.

Physical and mechanical properties of the vulcanizates were determined by tensile testing machine (DEVOTRANS, Turkey) [9] according to GOST 270–75 (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 by a Schob instrument according to GOST 27110-86.

3. Results and Discussions

For the purpose of oxidative stability study, the kinetics of thermal oxidation of untreated and modified rubbers depending on modification time was analysed. The oxygen absorption by the samples was fixed within certain time intervals followed by plotting kinetic curves (Figure 1). According to study results, the influence of modification time on the oxidation resistance of modified rubbers was determined.

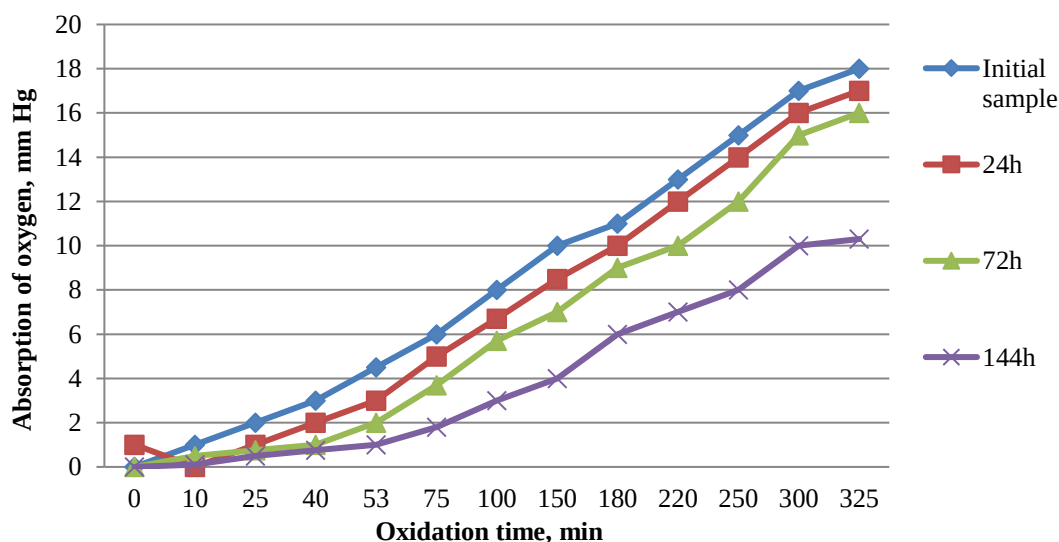


Figure 1. Kinetic curves of oxidation of rubbers based on NBR obtained by mechanochemical surface halide modification.

Figure 1 shows the surface halide modification within 24h–72h has no significant effect on the resistance to thermal oxidation compared to the oxidation resistance of initial untreated sample. In case of surface halide modification for 144h the resistance to thermal oxidation was increased by a factor of 1.5.

The influence of modification time on the resistance of modified rubbers to different aggressive media was investigated with the application of standard test solutions. Results are presented in Table 1.

Table 1. Resistance of modified NBR-rubbers to aggressive media depending on modification time.

Modification time	Swelling degree (%) ($\Delta \pm 15\%$)								
	Initial sample			48h			72h		
Time of exposure, h	24	48	168	24	48	168	24	48	168
Industrial oil	2.7	2.7	2.7	-1.4	-4.1	-4.1	-3.8	-6.0	-6.0
Gasoline	2.7	4.0	5.3	1.3	2.6	2.6	-3.7	-3.7	-3.7
Sulfuric acid	139.0	251.0	251.0	118.0	160.0	170.0	100.0	150.0	152.0
Hydrochloric acid	8.0	9.5	16.0	0.0	0.0	5.9	-3.6	-9.0	-12.0
Nitric acid	48.0	-	-	29.3	32.0	37.0	20.5	26.0	34.0

According to results illustrated in Table 1, the surface haloid modification leads to reduction of swelling in industrial oil and gasoline, as well as in sulfuric and hydrochloric acids. After modification for 3 days in nitric acid swelling of rubber samples completely stopped revealing that the samples have acquired the increased acid resistance [10]. It was suggested that the samples of modified NBR during more than 3 days would also be resistant to acids and oils.

Physical-mechanical properties of modified compounds based on NBR rubbers obtained by surface halide mechanochemical modification and serial rubber mixtures were determined by tensile testing machine. In the course of the experimental studies, the following parameters were determined: tensile strength (σ_b , MPa), relative elongation at break (ε_b , %), elongation set after destruction during 1 min (%), Shore hardness number (c.u.), and rebound elasticity (%) (Table 2).

Table 2. Physical-mechanical properties of initial sample of NBR rubber and rubbers based on modified NBR.

		σ_b (MPa) ($\Delta \pm 0.5$ MPa)	ε_b (%) ($\Delta \pm 10$ %)	Elongation set after destruction (%) ($\Delta \pm 0.5$ %)	Rebound elasticity (%) ($\Delta \pm 2$ %)	Shore hardness number (c.u.) ($\Delta \pm 2$ c.u.)
Initial sample of NBR rubber		9.7	590	8	32	62
Rubbers based on NBR	24h	12.3	480	8	31	63
	72h	13.1	440	7	31	63
modified during:	144h	13.6	460	7	31	64

As shown in Table 2, the properties of all the modified NBR rubbers have higher values than the initial untreated sample of NBR rubber. Summing up the investigation results, the modification induce some increase of such physical-mechanical properties as tear resistance (from 9.7 MPa to 13.6 MPa) and to some decrease of tensile strain (from 590% to 460%). Hardness and elasticity of modified NBR rubbers remained virtually unchanged [11].

4. Conclusion

The optimized technique for the surface modification of rubber products of various types and form using 1,1,2-trifluoro-1,2,2-trichloroethane as a modifier was developed. The increase in duration of halogenation of samples under investigation apparently leads to a proportional increase in degree of samples modification (fluorination and chlorination). The presence of halogen atoms (fluorine, chlorine) in the surface layer of rubber sample are responsible for a complex of enhanced properties, such as chemical resistance to oxidants and aggressive solutions, high tensile strength without a loss of continuity of the halogenated surface layer, and a number of other characteristics. In addition, an increase in the resistance to aggressive media of surface-modified rubbers could be related to a decrease of reaction centres on the rubber surface.

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