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# Siloxane Rubber Nanocomposites with Increased Thermal and Fire Resistance and Protective Rubberized Materials Based Thereon\*

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## Abstract

Research into the development of siloxane rubbers with increased thermal and fire resistance was carried out. Rubber nanocomposites based on SKTV-1 siloxane rubber that were filled with aluminium trihydrate were obtained using domestic and foreign manufacture organobentonites. It was found that the introduction of organobentonites into siloxane rubbers filled with  $\text{Al}(\text{OH})_3$  contributed to an increase in their thermal and fire resistance. Fire-resistant and heat-protective materials, and also preparation technology of tissues by glue spreading using IVO 3320 and Siltex spreading machines were developed according to the results of experiments using glass, silica, and aramid fabrics as a reinforcing frame. Tests of the resulting materials were carried out and areas of application of protective clothing based thereon were proposed.

**Keywords:** nanocomposites, siloxane rubbers, fire resistance, protective rubberized materials

## INTRODUCTION

Currently, technique development is characterised by toughening of operation conditions of various products and, accordingly, by the elevation of requirements to materials used in their manufacture. This also refers to elastomeric materials. In this regard, rubbers based on special caoutchoucs, including siloxane ones, are of great interest. They are notable for a wide temperature range of operation, good resistance to UV radiation, ozone, thermal

ageing in air and in vacuum, extra electrical properties, and also for physiological inertness [1–3]. Due to their properties, siloxane rubbers are used in electrical engineering, aerospace industry, machine-building and shipbuilding, medicine, and construction. They are used for the manufacture of wires and cables short-time working in fire conditions, the insulating protection seals, coatings for space ships and missiles, as well as for systems where unacceptable failures of the equipment. Extension of the scope of siloxane rubbers, continuous tightening of requirements to them, including on thermal and fire resistance, requires the search for new approaches during their development.

Traditional methods can no longer signifi-

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cantly improve the properties of rubbers, including siloxane ones, so the attention of researchers is increasingly attracted to the methods of chemical and physical modification of caoutchoucs and rubbers. Creating elastomer-based nanocomposites using different nanoscale fillers appears to be one of the most promising trends [4–10]. Analysis of papers using the introduction of nanoscale fillers both during synthesis of caoutchoucs and at the stage of processing in preparation of rubbers demonstrates especial effectiveness of this approach. Its application in case of siloxane rubbers allowed obtaining nanocomposites with elevated thermal and fire resistance.

It is known that organobentonites (OB) have proven themselves good in the development of polymer nanocomposites [11, 12]. Different polymer nanocomposites modified with quaternary ammonium salts of natural layered aluminosilicates have elevated barrier properties, thermal, and fire resistance during preservation or even improvement of their physicochemical properties.

Earlier [13, 14], there had been studied modification of siloxane rubbers of OB of foreign (Southern Clay Company, USA) and domestic manufacture. An opportunity for intercalation and exfoliation of SKTV-1 siloxane rubber in the presence of Cloisite 15A OB or domestic brands was determined using X-ray phase and structural analysis.

It was found that the introduction of OB slowed down processes of peroxide vulcanization and contributed to an increase in tension upon 100 % elongation, strength, and elasticity with some decrease in relative elongation hardness, and in turgescence of modified siloxane rubbers in toluene [15].

Furthermore, OB exhibit properties of efficient thermal stabilizers, which is expressed in a shift of initial temperature of the destruction

of vulcanizates (according to differential scanning calorimetry) and a decrease in mass loss dynamic heating conditions (as reported by thermogravimetric studies). Preservation of strength and elongation of siloxane rubbers after thermal ageing also attests to this [15].

## EXPERIMENTAL

To prepare rubbers, dimethylvinyl rubber SKTV-1 was used. The basic formulation included the following filling agents: aerosil-A-300 (TU 241-321695418-002-2003, 40 mass parts), anti-structuring additive ND-8 (8 mass parts), peroximone F-40 (1.6 mass parts), and Treofil-744-300 VST aluminum trihydrate (120 mass parts). Vulcanizates were also obtained according to the formulation with the addition of OB based on bentonite from the Top-Nurlat field of the Republic of Tatarstan, modified with dimethyldialkylammonium chloride (5 mass parts). Peroxide was not introduced into the composition of radiation vulcanizates.

Rubber compounds were prepared using Brabender plasticorder at a temperature of 70 °C, a rotor frequency of 60 min<sup>-1</sup>, and a total mixing time of 8 min. Vulcanization was performed in a hydraulic press with heat tracing at 160 °C for 20 min; the pressing pressure was 10 MPa. Rubberized fabrics were produced by the technique of spreading of rubber compounds as 25–30 % solutions in nefras S-2 using IVO 3320 and Siltex spreading machines. Radiation vulcanization was carried out by  $\gamma$ -radiation (Co<sup>60</sup>) using RV-1200 setup.

Thermogravimetric analysis was performed in the air using a SDC Q600 thermal analyzer, a heating rate of 10 °C/min. Properties of rubberized materials were analyzed in accordance with regulatory documents.

TABLE 1

Effect of composition on thermal (TG-DTG) properties of siloxane rubbers based on SKTV-1 containing Al(OH)<sub>3</sub>

Samples	Temperature range, °C				Temperature of mass			Total mass loss in 25–600 °C range, mass %
	(Mass loss, mass % )				loss beginning, °C			
Basic formulation	25–150	150–260	260–360	360–560	203	276	379	38.93±0.2
	(0.09)	(2.59)	(12.19)	(23.91)				
The same + OB	25–150	150–260	260–350	350–560	201	274	420	40.58±0.2
	(0.15)	(3.04)	(12.95)	(24.20)				

Fire test was carried out by firing samples in a MEGA 1 type burner with Kovica KS-1005 piezo ignition (Korea). Samples with dimensions of 2–4 cm, a thickness of 1 mm were brought to the burner at an angle of 90 °C, ignited along the centre, were aged in an open flame for different times (5–60 s). Afterwards, the nature of ignition, burning

time after the removal from the open flame, and the ability to self-extinguishing were determined.

## RESULTS AND DISCUSSION

It was found that despite an increase in thermal resistance of siloxane rubbers, OB were inef-

TABLE 2

Technical characteristics of flame-resistant rubberized materials (OTS)

Indicators	Regulatory documents for determinable indicator	GOST R 53264 requirements	Actual value		
			OTS-800	OTS-500	OTSF
Reinforcing frame type			Silica fabric	Стеклоткань Aramid конструкционная	
Surface density of the fabric, g/m <sup>2</sup>			620	390	134
Surface density of the material, g/m <sup>2</sup>	GOST 17073-71	300-750	790 ±20	550± 20	380±20
Breaking load, N,	GOST 30303-95				
– warpwise, not less than		500	1960±30	3528±30	1029±20
– fillingwise, not less than		500	784±20	3234±30	1617±30
Breaking load after exposure to 300 °C (16 min), N,	GOST 30303-95				
– warpwise, not less than		250	1666±30	2401±30	2744±30
– fillingwise, not less than		250	784±20	990±20	1421±30
Tear resistance, N,	GOST 30304-95				
– warpwise, not less than		40	64±5	59±5	392±10
– fillingwise, not less than		40	69±5	54±5	294±10
Tear resistance after exposure 300 °C (16 min), N,	GOST 30304-95				
– warpwise, not less than		20	39±5	29±5	255±10
– fillingwise, not less than		20	49±5	34±5	186±10
Water resistance at a static pressure of 1000 mm water column, min, no less than	GOST R 53264-2009 Section 7.9	1	first water drop at 900 mm water column	first water drop at 700 mm water column	1.5±0.5
Shrinkage after getting wet and drying, %,					
– warpwise, not less than	GOST 30157.0-95	2.5	2.1±0.3	1.8±0.3	<2.5
– fillingwise, not less than	GOST 30157.1-95	2.5	2.0±0.3	1.6±0.3	<2.5
Abrasion resistance, cycles, no less than	GOST R 53264-2009 Section 7.11	1000	1000±30 No cracks, no tearing off	1000±30 No cracks, no tearing off	5000±50 No cracks, no tearing off
Frost resistance, °C, no higher than	GOST 15162-82	-40	-40±2	-40±2	-40±2
Resistance to contact with solid surfaces heated to 400 °C no less than	GOST R 53264-2009 Section 7.13	15	более 15	более 15	более 15
Resistance to open flame, s, no less than не менее	GOST R 53264-2009 Section 7.14	30	более 120	более 120	более 30
Hardness, N, not more than	GOST 8977-74	0.3	0.23±0.05	0.17±0.05	0.1±0.05

fective as antipyrenes and did not improve their fire-resistance. For this reason, the efficiency of OB was assessed in combination with traditional antipyrenes, in particular, with alumina trihydrate. The results of thermogravimetric studies of modified siloxane rubbers containing  $\text{Al}(\text{OH})_3$  attest to increasing in the temperature of the beginning of mass loss due to complicated diffusion of volatile rubber decomposition products, slowing of thermal oxidation processes and coking processes (Table 1).

It was determined that the introduction of OB into siloxane rubbers containing  $\text{Al}(\text{OH})_3$  as antipyrene substantially improved their open flame resistance, moreover, these rubbers have self-extinguishing properties even after long exposure to flame, while their oxygen index reaches 60.

Preservation of properties of siloxane rubbers after open flame impact was assessed. It is found that even after being in open flame for 15 s, modified OB retained residual strength, while reference rubbers decomposed.

Thus, based on the developed rubbers one may obtain rubberized materials with improved properties, flame resistance, and lowered permeability towards aggressive media.

There were developed rubberized materials using reinforcing one-sided fabrics of different nature: OTS-800 (silica fabric), OTS-500 (constructional fiberglass), OTSF (aramid). Rubber coatings of fabrics are made on the basis of SKTV-1 siloxane rubber. Vulcanization of materials was carried out by radiation ( $\gamma$ -radiation dose of 100 kGy). In OTSF material, a fluororubber based coating was applied onto the basic rubber layer.

The information in Table 2 indicates that OTS materials (lightweight silicone fabric) with a rubber coating based on methylvinyl siloxane caoutchouc have high mechanical strength, open flame resistance and the direct contact with a solid surface heated to 400 °C. The materials do not ignite or burn; there are no traces of soot on the surface of the samples of the material even after prolonged open flame impact. Physical and mechanical parameters are reduced slightly after ageing the material for 16 min in a drying oven at 300 °C (GOST R 53264–2009 requirement) [16]. The OTSF material is characterised by higher indicators of tear resistance and abrasion resistance. Coating mass over OTS materials varies within 180–200 g/m<sup>2</sup>. A fire-resistant and heat-protective material

is also resistant to aggressive media, solvents, and oils.

The OTS material ensures protection when exposed to toxic gaseous chemicals with chlorine content in the gas-air mixture of (2890±40) mg/m<sup>3</sup> for 50 min, with ammonia content therein (710±30) mg/m<sup>3</sup> for 45 min. Elastic OTS materials (the stiffness coefficient of less than 0.3 N) and OTSF (01 N) can be used for making protective clothes for firemen, electrical and gas welders, specialists of metallurgical, oil and gas industry working in conditions of exposure to thermal radiation and open flame, during extinguishing fires and carrying out various rescue operations in close proximity to open flame.

## CONCLUSION

Thus, it is found that the use of organobentonites in siloxane rubbers containing aluminium trihydrate as antipyrene allows substantially increasing their both thermal stability and fire-resistance. Their properties, and also resistance towards aggressive media have been improved in the resulting rubberized materials using developed rubbers.

## REFERENCES

- 1 Rejkhshfel'd O. V., Khimiya i Tekhnologiya Kremnij-organicheskikh Elastomerov, Moscow, Khimiya, 1973. 176 p.
- 2 Shetts M., Siloksanovyj Kauchuk, Leningrad, Khimiya, 1975. 192 p.
- 3 Khakimullin Yu. N., Khusainov A. D., Osnovy Tekhnologii Pererabotki Siloksanovykh Elastomerov: Uch. Posobie, Kazan, KNITU Publ., 2014. 164 p.
- 4 Pomogajlo A. D., Rozenberg A. S., Uflyand I. E., Nanochasticy Metallov v Polimerakh, Moscow, Khimiya, 2000. 672 p.
- 5 Pomogajlo A. D., Dzhardinalieva G. I., Metallopolimernye Gibridnye Nanokompozity, Moscow, Nauka, 2015. 494 p.
- 6 Khakimullin Yu. N., Kurbangaleeva A. R., *Vestnik Kazanskogo Tehnologicheskogo Universiteta*, 2011, No. 12, P. 78–81
- 7 Chvalun S. N., Novokshonova L. A., Korobko A. P., Brevnov P. N., *Ros. Khim. Zhurnal*, 2008. Vol. 11, No. 5. P. 52–57.
- 8 Tutorskij I. A., Sklovskij M. D., Mezhfaznye Yavleniya v Polimernykh Kompozitakh, Moscow, CNIITeneftchim, 1994. 100 p.
- 9 Ivanchev S. S., Ozerin A. N., *Vysokomolekulyarnye Soedineniya. Ser. B*, 2006, Vol. 48, No. 8, P. 1531–1544.
- 10 Mikitaev A. K., Kozlov G. V., Zaikov G. E., Polimernye Nanokompozity. Mnogoobrazie Strukturnykh Form i Prilozhenij, Moscow, Nauka, 2009. 278 p.

- 11 Yu-Ving Maj, Zhong-Zhen Yu. M. (Eds.), *Polimernye Nanokompozity*, Moscow, Tehnosfera, 2011. 688 p.
- 12 Antipov E. M., Barannikov A. A., Gerasin V. A. Shklyaruk B. F., Tsamalashvili L. A., Fisher H. R., Rasumovskaya I. V., *Vysokomolekulyarnye Soedineniya. Ser. A*, 2003, Vol. 45, No. 11, P. 1885–1899.
- 13 Khakimullin Yu. N., Gadel'shin R. N., Denezhkin O. I. Tez. dokl. 3 Vseross. Konf. "Kauchuk i Rezina-2013: Tradicii i Novacii", Moskva, 2013, P. 73–74.
- 14 Gadel'shin R. N., Gubaidullina A. M., Lygina T. Z., Naumkina N. I., Trofimova F. E., Khakimullin Yu. N., *Kauchuk i Rezina*, 2014, No. 2, P. 20–22.
- 15 Gadel'shin R. N. *Modificirovannye Siloksanovye Reziny Vysokogo Napolneniya* (Candidate's Dissertation in Technology), Kazan, 2013. 120 p.
- 16 Khakimullin Yu. N., Gadel'shin R. N., Kurbangaleeva A. R., Gimatdinova G. R., *Siloksanovye Reziny s Povyshennoj Termo-, Ognestojkost'yu*, Sb. Dokladov 3 Vseros. NTK FGUP "VIAM", Moskva, 2016. P. 38.