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Influence of glass fibers on the physico-mechanical and performance properties of rubber based on general and special purpose caoutchoucs

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ABSTRACT

The effect of glass fibers (GF) on the rheometric (vulcanization) characteristics of the rubber compound, physico-mechanical, performance and dynamic properties of vulcanized rubber based on general and special purpose caoutchoucs for rail fastenings has been studied. It is shown that with the introduction of GF into the rubber compound, an increase in the minimum torque and the time of the onset of vulcanization is observed. An increase in the content of GF in the rubber compound leads to an increase in elastic-strength properties, hardness, a decrease in tear resistance and changes in physico-mechanical parameters, hardness of vulcanizates after daily thermal aging in air and after exposure to standard SZhR-1 liquid. GF contribute to an increase in the mechanical loss factor and the storage modulus of vulcanizates. It was found that the rubber compound containing 12.0 phr, has improved technological properties, and vulcanizates based on it are characterized by increased physico-mechanical, performance and dynamic parameters.

KEYWORDS

glass fibers • caoutchoucs • rubber • rheometric, physico-mechanical, performance and dynamic properties

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Introduction

It is known [1–4] that fibrous fillers are used to improve the physical, mechanical and operational properties of rubbers. One of these fillers are glass fibers (GF) [5–10], which can increase the strength, incombustibility, heat resistance, and aggressive resistance of various materials [11–21]. The influence of GF on the physico-mechanical properties of rubbers based on siloxane [22], chloroprene [23], natural [24], and nitrile butadiene [25] caoutchoucs was studied in [22–25]. It was shown in [22] that adding 10.0 wt. % of GF in the composition of silicone rubber resulted in an increase in tensile strength by more than 26 % compared to a vulcanizate containing no GF. In [23–25] an increase in strength parameters is also shown when GF are introduced into rubber. It was found in [26] that the maximum results for testing mechanical properties were obtained from a sample of natural rubber vulcanizate with 8 wt. % GF, whose tensile strength and hardness were 57 and 32 % higher than rubber without GF. It was shown in [27] that the addition of GF modified with the capping agent Si69 (bis-[γ-(triethoxysilyl)propyl]tetrasulfide) in an amount of 5.0 wt. % in the rubber composition based on styrene butadiene rubber led to a significant increase in tensile strength by 37 %. In this regard, it is of interest to study the influence of GF on the rheometric characteristics of the rubber compound, physico-mechanical, performance and dynamic properties of vulcanized rubber based on general and special purpose caoutchoucs used for the manufacture of rail fastening gaskets.

Materials and Methods

The combination of isoprene SKI-3, α-methylstyrene-butadiene SKMS-30ARK, and nitrile-butadiene SKN-2655 caoutchoucs served as the polymer base of the studied rubber compound. In addition to rubbers, the rubber compound contained the following ingredients: vulcanizing agents - sulfur, N,N'-dithiodimorpholine, tetramethylthiuram disulfide; vulcanization accelerator - N-cyclohexyl-2-benzothiazolesulfenamide; vulcanization activators - zinc oxide, stearic acid; antioxidants - acetonanil N, protective wax ZV-P, N-isopropyl-N'-phenyl-para-phenylenediamine; softeners - rosin, industrial oil I-12A; fillers - kaolin, carbons black N 220 and P 514, silicon dioxide Zeosil 1165 MP and trans-polynorbornene; scorch retarder - N-nitrosodiphenylamine.

The rubber compound was made on laboratory rolls LB 320 160/160 at a temperature of the surface of the rolls of 60–70 °C with a mixing cycle of 25 min. The vulcanization (curing) characteristics of the rubber compound were studied on a Mon Tech MDR 3000 Basic rheometer at 143 °C for 40 min in accordance with ASTM D2084-79. Rubber compound samples for determination of physico-mechanical properties were vulcanized at a temperature of 143 °C for 20 min in a P-V-100-3RT-2-PCD type vulcanizing press. Elastic-strength properties were determined according to GOST 270-75; hardness - according to GOST 263-75; tear resistance - according to GOST 262-93; change in tensile strength, elongation at break and hardness after thermal aging in air - according to GOST 9.024-74; change in tensile strength, elongation at break and hardness after exposure to standard oil liquid SZhR-1 - according to GOST 9.030-74 (method B); change in mass after exposure to aggressive media (water, industrial oil I-20A, standard oil liquid SZhR-3) - according to GOST 9.030-74 (method A). The dynamic characteristics (mechanical loss factor and storage modulus) of the rubber compound vulcanizates were studied on a Metravib VHF 104 dynamo-mechanical analyzer. The GF of Limited Liability Company Glassteks were staples with a cutting length of 4.5 mm, an elementary fiber diameter of 11 μm, a density of 2.66 g/cm^3, a refractive index of 1.566, and an elastic modulus of 80 GPa.

Results and Discussion

First, the rheometric (vulcanization) characteristics of a rubber compound containing GF in an amount from 3.0 to 20.0 phr (parts per hundred parts of rubber) were studied at 143 °C, the results of which are given in Table 1.

As can be seen from Table 1, with an increase in the content of GF to 12.0 phr the maximum torque of the rubber compound remains practically unchanged. However, with a further increase in the content of GF, the maximum torque, as well as the minimum torque, of the rubber compound increases, leading to a deterioration in its technological properties and poor processability by extrusion and calendering methods. Thus, the optimal content of GF is 12.0 phr.

Table 1. Variants and rheometric properties of the rubber compound

Ingredient, indicators	Variants of the rubber compound							
	1	2	3	4	5	6	7	8
GF, phr	–	3.0	6.0	9.0	12.0	15.0	18.0	20.0
Rheometric properties of the rubber compound								
M_H, dN·m	18.20	18.24	18.26	18.18	18.30	18.41	19.37	20.94
M_L. dN·m	2.95	3.07	3.16	3.24	3.33	3.48	3.75	4.03
t_s. min	4.47	4.82	4.92	4.96	4.99	5.17	5.34	5.58
t_{90}. min	15.33	15.32	15.34	15.31	15.33	15.48	15.69	15.97
Note: M_H is the maximum torque; M_L is the minimum torque; t_s is the curing scorch time; t_{90} is the optimum curing time.								

Table 2. Physico-mechanical properties of vulcanizates

Indicators	Variants of the rubber mixture				
	1	2	3	4	5
f_{100}, MPa	5.4±0.2	6.2±0.2	6.4±0.2	6.5±0.3	7.2±0.3
f_p, MPa	13.4±0.5	13.5±0.5	13.5±0.5	13.7±0.5	13.9±0.6
ε_p, %	340±13	410±16	380±15	390±15	350±14
H, units Shore A	74±1	72±1	73±1	74±1	76±1
B, kN/m	50±2	53±2	48±2	47±2	46±2
Note: f_{100} is the modulus stress at 100% elongation; f_p is the tensile strength; ε_p is the elongation at break; *H* is the hardness; *B* is the tear resistance.					

Subsequently, we investigated the physico-mechanical, performance and dynamic properties of vulcanizates containing up to 12.0 phr GF. The results of studying the physico-mechanical properties of vulcanizates (modulus stress at 100 % elongation, tensile strength, elongation at break, hardness and tear resistance) are presented in Table 2.

From the data in Table 2 it follows that an increase in the content of GF in the composition of the rubber compound contributes to an increase in the tensile strength, elongation at break, hardness and a decrease in the tear resistance of vulcanizates. These indicators increase to a GF content of 12.0 phr, the excess of which, as noted above, leads to a deterioration in the technological properties of the rubber compound and the associated physico-mechanical properties of the vulcanizates.

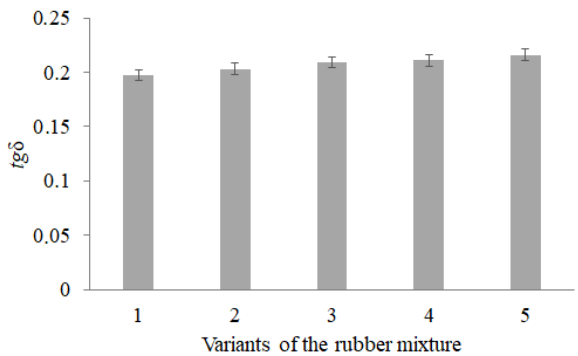
The results of studying the performance properties (changes in physico-mechanical parameters) of vulcanizates after thermal aging in air and exposure to standard hydrocarbon liquid SZhR-1 at a temperature of 100 °C for 24 hours are given in Table 3.

From the data in Table 3 shows that with an increase in the content of GF, there is a decrease in changes in the physico-mechanical parameters of vulcanizates after daily aging in air and in SZhR-1. The least changes in these indicators has vulcanizate, including 12.0 phr GF.

Table 3 also shows the results of a study of the change in the mass of vulcanized rubbers after soaking in water, industrial oil I-20A and SZhR-3 at 23 °C for 24 hours. As can be seen, an increase in the content of GF leads to a decrease in the change in the mass of vulcanizates. The smallest changes in the mass of vulcanizates in the studied aggressive environments are characterized by vulcanizate containing also 12.0 phr including GF.

Table 3. Performance properties of rubber mixture vulcanizates

Indicators	Variants of the rubber mixture				
	1	2	3	4	5
Change in physico-mechanical properties of vulcanizates after air aging					
Δf_p, %	-21.5±0.8	-23.9±0.9	-35.6±1.4	-20.9±0.8	-15.2±0.6
$\Delta \varepsilon_p$, %	-35.3±1.4	-31.2±1.2	-32.1±1.3	-33.3±1.3	-28.6±1.1
ΔH, units Shore A	+2.0±1.0	+2±1	+4±1	+4±1	+4±1
Change in physico-mechanical properties of vulcanizates after exposure to SZhR-1					
Δf_p, %	-45.9±1.8	-41.5±1.7	-38.9±1.6	-35.2±1.4	-30.4±1.2
$\Delta \varepsilon_p$, %	-29.5±1.2	-30.5±1.2	-27.8±1.1	-23.9±0.9	-18.6±0.7
ΔH, units Shore A	-16±1	-12±1	-12±1	-12±1	-10±1
Change in the mass of vulcanizates in various environments					
Δm (water), %	0.64±0.01	0.59±0.01	0.51±0.01	0.46±0.01	0.41±0.01
Δm (I-20A), %	6.97±0.10	6.31±0.09	5.97±0.08	5.11±0.07	4.89±0.07
Δm (SZhR-3), %	12.10±0.18	11.76±0.17	10.71±0.16	9.83±0.15	8.65±0.13
Note: Δf_p, $\Delta \varepsilon_p$, Δm – relative changes in tensile strength, elongation at break and mass; ΔH is the difference in hardness after and before holding in an aggressive environment.					



Figs. 1. The mechanical loss factor of vulcanizates

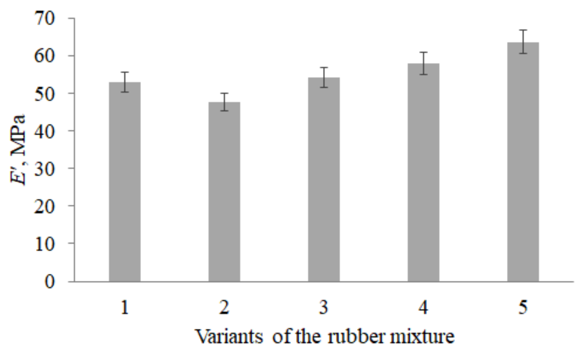


Fig. 2. Storage modulus of vulcanizates

A quantitative measure for assessing the dynamic (vibration-damping) properties of polymer materials, including vulcanized rubber, are the values of the mechanical loss tangent (tgδ) and the storage modulus (E') [28–30]. For the resulting vulcanizates, the dynamic properties were studied: the mechanical loss factor *tg*δ (Fig. 1) and the storage modulus E' (Fig. 2) in the "tension-compression" mode at a frequency of 1000 Hz, a degree of deformation of 0.01 % and a temperature of 30 °C.

From Figs. 1 and 2, it can be seen that the introduction of GF into the rubber compound contributes to an increase in both dynamic parameters. It is known [30–34] that as the mechanical loss factor of polymers (vulcanized rubbers) increases, their vibration-damping properties increase.

The highest value of tgδ, and, consequently, good dynamic properties is characterized by the vulcanizate of the fifth variant containing 12.0 phr GF.

Conclusions

The influence of GF on the properties of vulcanized rubber based on general and special purpose caoutchoucs has been studied. It has been shown that with a GF content of up to 12.0 phr, the rubber compound has satisfactory technological properties and can be well processed by injection and calendering methods. The physico-mechanical properties of vulcanizates increase to the same content of GF in the rubber compound, the excess of which leads to their reduction due to deteriorating technological properties. The best performance properties are characterized by a vulcanizate that has the greatest physico-mechanical properties, i.e. vulcanizate containing 12.0 phr of GF. This is consistent with the well-known statement that most rubbers with high physico-mechanical properties are also characterized by increased performance properties. The same vulcanizate has improved dynamic properties, which is associated with the previously noted good processability (manufacturability) and the resulting homogeneous structure of the rubber compound used to produce it. Thus, for the manufacture of gaskets for rail fastenings, rubber containing 12.0 phr of GF can be recommended.

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