Creation of special compositions based on butadiene-nitrile elastomers for diesels

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Abstract. In the article, it was determined that furan oligomer added to the composition causes additional structuring in the process of vulcanization, and as a result, the density and hardness of the vulcanization network in the composite increases, and the value of the relative length decreases. It was shown that the optimal amount of furan oligomers in the composition of rubber compounds is equal to 10 weight units per 100 weight units of rubber.
With the inclusion of the secondary product of acetylene production in the elastomer compositions, it was found that the amount of carbon-rubber gel and the vulcanization network increased, and the level of vulcanizate shrinkage decreased, which was shown to be mainly due to the presence of oligomeric components on the surface of carbon particles. It is shown that the inclusion of this raw material in elastomeric compositions based on butadiene nitrile rubber increases the interaction at the "rubber-filler" boundary and the formation of additional bonds between rubber macromolecules and functional groups of the oligomer, and as a result, the overall technological and technical properties of the compositions are improved.

1 Introduction

Today, in developed countries, rubber engineering products with special properties obtained from composite materials are used in internal combustion engines. For these rubber engineering products to meet the requirements set for internal combustion engines of modern vehicles, special attention [1-3] is paid to composition of composite materials, improvement of technological, physical, and mechanical properties. Others have conducted scientific research on the creation of technologies for obtaining polymer compositions and products with specific properties for internal combustion engines [4-5].

As a result of the increase in the power of modern vehicles, obtaining rubber-metal-textile products with special properties used in internal combustion engines is the current demand.

Therefore, scientific research is being carried out on creating the composition of composite elastomer materials, developing the ingredients to be added to the composition,

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studying their required properties, determining the structure, and developing the technology of making details based on the created material [6-8].

2 Methods

The object of research is synthetic rubber, nitrile butadiene, furan oligomer, secondary source of acetylene production. The composition consists of zinc oxide - 5.0 parts by weight, stearic acid - 2.0 parts by weight, sulfur - 2 parts by weight, O-, N- containing accelerator - 0.4 parts by weight, plasticizer -5, 10, 15 - wt.h, filler -20, 40 wt.h. per 100 wt.h. rubber. The production of rubber compounds was carried out on laboratory mixing rollers RC-WW 150/330 (Rubicon, Germany). The determination of the Mooney viscosity of rubber compounds was carried out on a Mooney viscometer MV 2000 (Alpha Technologies, England). The stress relaxation test is carried out on the same specimens as the Mooney viscosity immediately after the completion of the viscosity measurement by stopping the rotation of the rotor very quickly and measuring the drop in the final Mooney viscosity over time. The vulcanization kinetics of rubber compounds was determined on an ODR 2000 rheometer (Alpha Technologies, UK). Technical indicators were determined according to the relevant GOSTs [9-12].

3 Results and discussion

To improve the hermetic bonding of internal combustion engine parts, and to increase their heat tolerance, it is desirable to create compositions based on butadiene nitrile rubber with the addition of local secondary raw materials and to study their technological properties. It is known that the physic-mechanical and dynamic properties of products based on elastomeric compositions depend on the physic-chemical properties, composition and structure of the ingredients, the sequence and amount of addition during the preparation of the rubber mixture. [13-18]. Therefore, the effect of the amount of ingredients in the mixture, the sequence of their addition to the composition, on the properties of elastomeric compositions was studied. As a result of studies in the standard composition of butadiene-nitrile rubber, the amount of rubber and ingredients and the mixing sequence were selected as follows (Table 1), where the main attention was paid to the uniform distribution of ingredients among the rubber macromolecules.

Table 1. Mixing sequence and amount of rubber and ingredients

Name of rubber and ingredients	**Amount of rubber and ingredients, wt.b.**			
SKN-18	100.0	100.0		
SKN-40	-	-	100.0	100.0
Sulfur	2.0	2.0	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0
Mercaptobenzthiazole	1.5	1.5	0.8	0.8
Carbon P 803	20, 40, 60	-	20, 40, 60	
AIChCh	-	20, 40, 60	-	20, 40, 60
Stearic acid	1.5	1.5	1.5	1.5
DBF	5, 10, 15	-	5, 10, 15	-
FO	-	5, 10, 15	-	5, 10, 15

Studies have shown that furan oligomers, along with improving the technological properties of the rubber mixture, significantly change the kinetic parameters of the elastomeric compositions, regardless of the polarity of the rubbers. At the same time, the viscosity is 2.2; 1.25 kg, and plasticity is 0.55; 0.45, respectively, in similar amounts of dibutyl phthalate, these indicators are: 1.8 and 1.2; 0.52 and 0.43 respectively. With the introduction of furan oligomers into SKN-18-based compositions, the viscosity of the mixture increases, this is explained by the interaction between the functional groups of the oligomer and rubber macromolecules.

The study of the effect of furan oligomers on the vulcanization kinetics of rubber compounds based on SKN-18 rubber made it possible to determine the increase in the vulcanization rate of cis-1,4-polyisoprene in its thiuram vulcanization system, and the time to achieve optimal vulcanization decreased. However, the degree of vulcanization has decreased significantly. The use of a sulfur vulcanization system activates the vulcanization process, which was found to be due to the presence of active functional groups (-ON, -COON, etc.) in its composition. The observed effect was confirmed by IKS studies of furan oligomers and thiuram reaction products at high temperature. A sharp decrease in intensity at 1720 cm-1 associated with the C=O group of the carboxyl group and a slight decrease in its intensity between 360-300 cm-1 (ON group) indicate the formation of furan oligomers. Combined with thiuram, new compounds are formed with the participation of these groups [19-20].

The kinetics of sulfur binding with rubber macromolecules during vulcanization shows that the formation of vulcanization networks in mixtures with the above-selected vulcanizing ingredients is sufficiently intensive (Fig. 1).

It was found that vulcanizing substances and furan oligomers contribute to the maximum absorption of atoms on various surfaces of fillers, and thereby affect the formation of more durable vulcanization structures.

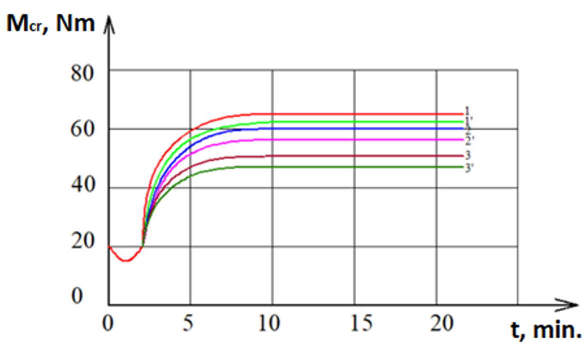

Fig. 1. Kinetics of vulcanization of rubber mixtures based on SKN-40 rubber: 5 (1.11) and 15 (3.31) weight units FO and DBF per 100 weight units of rubber, temperature 428K

This effect shows that the combination of ingredients and different reactivity in the composition not only activates, but also accelerates the process of vulcanization structure formation (Table 2).

Table 2. Effect of furan oligomers on the formation of vulcanization network of elastomer composition

Elastomers	Ingredient	Planted orchards, %			
		$-CS_x-C-$	-CSSC-	-CSC-	-CC-
SKN-18	DBF	32	34	24	10
	FO	30	26	25	19
SNK-40	DBF	29	5	19	17
	FO	20	25	27	28

As can be seen from the table, when furan oligomers are included in the composition, macromolecules are somewhat more active in terms of the rate of sintering during vulcanization, which was shown by the increase in the sintering rate and the decrease in cross-link sulfidity.

As a result of the study of sol-gel fractions of composites, when furan oligomers were added, the intensity of wear and tear processes decreased, and the percentage of vulcanization net active chains increased significantly. It was shown that this situation depends on the structure and chemical properties of furan oligomers of selected resin mixtures. The analysis showed that the furan oligomer added to the composition causes additional structuring in the vulcanizate, and as a result, the density of the vulcanization network in the composite increases, and as a result, its hardness increases and the value of its relative length decreases. This allows for purposeful control of the structure and physical-mechanical properties of composites.

By studying the influence of the amount of furan oligomers on the technological properties of rubber compounds, its optimal amount is equal to 10 weight units per 100 weight units of rubber.

By incorporating the secondary product of acetylene production into elastomeric compositions, the amount of carbon-rubber gel and the vulcanization network increases, while the degree of shrinkage of the sample decreases. This is mainly due to the presence of oligomeric components on the surface of carbon particles.

Studying the influence of the amount of furan oligomers on the technical properties of the composition based on SKN-18 and SKN-40 rubber, it was determined that its optimal amount is 10 weight units per 100 weight units of rubber (Fig. 2).

Such samples have high strength and relative elongation, and elasticity is maintained at a moderate level. All tested rubbers have increased stiffness and tensile and tear resistance at 300% elongation compared to the original compound. This situation can be explained by the increase in the degree of cross-linking due to the cyclization of furan units under the influence of temperature.

Balanced curing of vulcanizates with respect to motor oil, gasoline, kerosene, etc. was studied, and resistance to gasoline of the resulting elastomer compositions was significantly improved.

It should be assumed that furan oligomers can play an important role in forming the structure of composite elastomer materials with the ability of donor-acceptor interaction, inhibition, thermo-, photochemical processes. The stabilizing effect of furan oligomers was studied in SKN-18 and SKN-40. The obtained results show that the duration of the induction phase of the oxidation reaction increases with the increase in the amount of furan oligomers in rubber. In this case, the rate of oxygen absorption almost does not change even after the end of the induction period. It should also be noted that at high concentrations of furan oligomers, an increase in the induction period is observed with an increase in the rate of oxygen absorption during the induction period. The critical concentration of furan oligomers corresponding to the turning points in the "Induction period - antioxidant concentration" curve was determined to be 0.014% (2.4.10-3 mol/kg) for SKN-18.

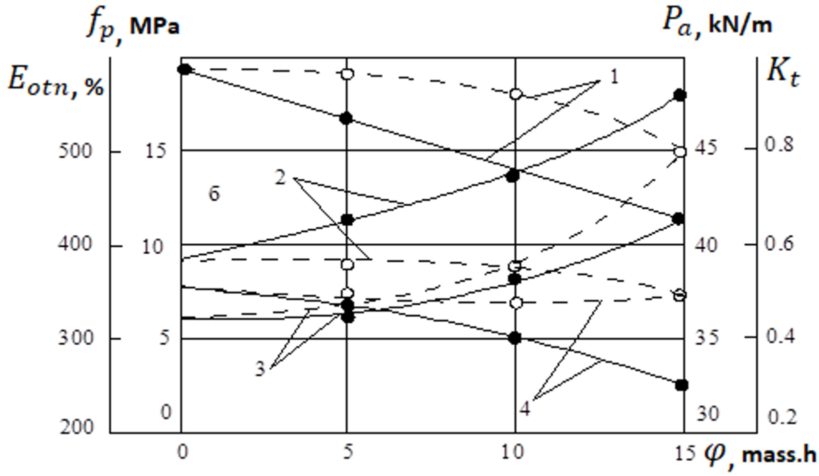

Fig. 2. Dependence of the technical properties of rubber based on SKN-40 rubber on the amount of modifiers: FO (-o-), DBF (-●-), tensile strength (f_p) -1, relative elongation (E_{otn}) -2, heat resistance (K_t) -3, tear resistance (P_a) -4

The critical concentration of furan oligomers in the oxidation of SKN-40 corresponds to 0.5%, which is much higher than that of dibutyl phthalate. The effective utilization constant of furan oligomers in SKN-18 rubber is 3.2.10-4s-1, and for SKN-40 it is 1.9.10-4s-1, which indicates its great effect on addition reactions to slow down the oxidation of elastomers.

The study of heat aging of composites stabilized with furan oligomers showed that with increasing aging time, a decrease in the relative elongation of the composites is observed, compared to samples stabilized with neazon D. Apparently, in the process, heat effect, additional structure occurs under the influence of furan compounds, resulting in an increase in the stiffness of the composites and a decrease in the relative elongation values.

The expediency of using furan oligomers as effective oxidizing additives for elastomeric compositions with special properties was determined, which made it possible to target the structural and physical-mechanical properties of the compositions without changing the existing production technology and equipment.

4 Conclusions

The analysis of the research results showed that the furan oligomer added to the composition caused the formation of additional structuring during the vulcanization process, and as a result, the density and hardness of the vulcanization network in the composite increased and the value of the relative length decreased. This allows for purposeful control of the structure and physical-mechanical properties of composites.

It was shown that the optimal amount of furan oligomers in the composition of rubber compounds is equal to 10 weight units per 100 weight units of rubber.

With the inclusion of the secondary product of acetylene production in elastomer compositions, it was found that the amount of carbon-rubber gel and the vulcanization network increased, and the level of vulcanizate shrinkage decreased, which was shown to be mainly due to the presence of oligomeric components on the surface of carbon particles.

It can be concluded that the inclusion of this raw material in the composition of elastomeric compositions based on butadiene nitrile rubber enhances the interaction at the "rubber-filler" boundary and creates additional bonds between the rubber macromolecules and functional groups of the oligomer, because of which the general technological and technical properties of the compositions are improved.

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