The effect of boron nitride on the properties of rubber compounds

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Abstract. The work is devoted to research of vulcanization characteristics of mixtures and revealing of features of change of technological, dynamic and physical-mechanical properties of elastomers on the basis of isoprene rubber filled with carbon black N330 and boron nitride (BN). It has been established that with a gradual increase in the concentration of the inert filler BN a decrease in the curing rate by 33% and the density of the polymer cross-linking by 26% is observed, as well as an increase in the curing start time by almost 300% and the optimal curing time by 200%. At the same time, there is a 26% decrease in the "Payne effect", a 50% increase in the relative elongation at rupture and a 30% decrease in the tensile strength.

1. Introduction

At present, general purpose rubbers are widely used, including isoprene rubber (SKI-3), which is analogous to natural rubber. This polymer is highly technologically advanced, has less impurities and is better processed. At the same time, it has greater adhesion and lower cohesive strength relative to natural rubber [1].

In order to improve special properties, modification of polymer composites is widely used. For this purpose, the content of fillers in the formulation of elastomers, which can be organic and inorganic, active (reinforcing) and inert, most often vary [2, 3].

The popular active filler of isoprene rubber, which is widely used in the tire industry, is N330 grade carbon black, which has a high degree of dispersion and average structure. These characteristics give the finished material a good resistance to abrasion and high tensile strength [4,5].

In addition, the carbon black is subject to various modifications, for example, to increase the proportion of oxygen it is oxidized by gas, gas-liquid and liquid methods. The purpose of such transformations is usually to improve any properties in order to replace the previously produced grades of carbon black [6].

Carbon nanotubes can also act as a filler. They give rubber electrical conductivity, improve the elastic-strength properties [7].

At the same time, hexagonal boron nitride is a promising filler with low hardness, high dispersion and high thermal conductivity (among dielectrics). He gained special popularity in the synthesis of abrasive material, the production of high-temperature ceramics and high-temperature lightweight ("soft") coatings used in aviation technology [8,9]. In elastomers, the use of this filler is very limited, mainly only in silicones, and in other brands of rubbers have not been investigated.

In this connection, the aim of the work was to study the vulcanization characteristics of mixtures and to reveal the peculiarities of changes in the dynamic and physical-mechanical properties of elastomers on the basis of isoprene rubber filled with carbon black N330 and boron nitride (BN).

2. Materials and research methods

The object of the study was rubber based on isoprene rubber SKI-3 with sulfur vulcanizing group. Mixtures were prepared on laboratory rolls in accordance with GOST R 54548-2011. The samples were cured at a temperature of 135 ° C.

Compositions of the studied compounds are presented in Table 1.

Table 1. Compositions of the studied compounds

The name of the ingredient	Content, mass per 100 wt. rubber rubber							
Rubber SKI-3	100.0							
Stearic acid	2.0							
Zinc white, ZnO	5.0							
Sulfur ground	2.25							
TBBS	0.7							
Filler:	Serial mixture	1	2	3	4	5	6	7
Carbon black N330	35	30	25	20	15	10	5	-
Boron nitride	-	5	10	15	20	25	30	35
Total:	144.95							

The properties of the experimental samples were compared with the properties of standard rubber filled with N330 carbon black.

The study of the kinetics of vulcanization of rubber compounds was carried out in accordance with the method described in ASTM D 5289-12. D-RPA 3000 at a temperature of 135 ° C / 120 minutes, while the following indicators were determined: optimum cure time, cure rate, cure start time, and torque difference.

Vulcanization of the rubber mixture was carried out on a hydraulic press brand Joos in accordance with the method, according to ASTM D 3182-16. The minimum pressure during vulcanization is 3.5 MPa, the vulcanization temperature is 135 ° C, the dwell time in accordance with T90 for each sample is individual.

The dynamic properties of rubber were determined in accordance with the method of ASTM D 6204-07. The test specimens were subjected to shear deformation using a dynamic rotor-free vibroreometer D-RPA 3000 in MDR mode. The amplitude fluctuations were carried out at a frequency of 1 Hz and in the amplitude range from 1% to 300% at 60 ° C. As a result, the following indicators were determined: dynamic shear modulus, loss modulus, as well as the tangent of the angle of mechanical losses.

Elastic strength properties of rubber, such as modulus of elasticity, tensile strength and relative elongation at rupture, were measured on a Zwick/ Roell rupture machine in accordance with GOST 270-75. Samples were cut out of vulcanized plates, working area 25.0±1.0 mm, thickness of samples 2.0±0.2 mm. The sample was installed in the clamps of the breaking machine and stretched at a rate of 500 mm/min.

Results of research and discussion

The established vulcanization characteristics of studied rubber compounds are presented in table 2.

Table 2. Vulcanization characteristics of rubber compounds

Indicator	Values of rubber blends							
	Serial	Experienced						
		1	2	3	4	5	6	7
ML (N·m)	0.34	0.32	0.31	0.23	0.24	0.17	0.15	0.17
MH (N·m)	14.44	14.36	13.83	13.15	1.01	11.53	10.92	10.50
ΔM (N·m)	14.10	14.04	13.52	12.92	11.77	11.36	10.77	10.33
ts (min)	13.48	14.17	12.37	13.58	18.20	16.59	20.00	39.31
$\tau50$ (min)	20.23	20.45	19.07	20.24	24.30	23.51	27.26	47.15
$\tau90$ (min)	35.36	36.16	35.41	37.25	39.12	41.42	50.08	72.37
RV (min-1)	4.57	4.55	4.34	4.22	4.78	4.03	3.32	3.02
ML (N·m)	0.34	0.32	0.31	0.23	0.24	0.17	0.15	0.17

ML – is the minimum torque; MH – maximum torque; ΔM – is the torque difference; ts – is the start time of vulcanization; τ50 – time to reach 50% of the degree of vulcanization; τ90 – is the optimal time for vulcanization; RV – an indicator of the effectiveness of treatment

As can be seen, with the introduction of boron nitride into the rubber mixture in concentrations from 5% to 35%, the torque differences are reduced from 14.04 N•m to 10.33 N•m, which is due to a decrease in the density of crosslinking of the polymer. This is especially noticeable in samples with homogeneous filler No. 7, where the difference in torques in the sample filled with boron nitride is 26% lower than the values of the standard sample with technical carbon N330.

It was established that the start time of vulcanization with an increase in the concentration of boron nitride from 5% to 35% increases from 14.17 minutes, to 39.31 minutes, that is, almost 300%. At the same time, the optimum vulcanization time with an increase in the concentration of boron nitride from 5% to 35% gradually increases from 36.16 minutes. up to 72.37 minutes, that is 200%. These results show the possibility of replacing the active filler, carbon black N330 with inert boron nitride.

The induction period (time of onset of vulcanization) determines the resistance of the rubber compound to premature vulcanization during the various stages of processing that precede vulcanization. From the point of view of the economic component of the technological process, this is not very good. At the same time, such a slow cross-linking of rubber is very useful in the case of manufacturing multilayer products, since with an increase in the induction period, the co-vulcanization of individual layers of the rubber mixture is enhanced and therefore, the quality of the resulting product increases.

The chemical and physical interaction between the polymer base and the filler plays an important role in improving the dynamic properties of the resulting rubber [10, 11]. To assess the dynamic properties of rubber, the following parameters were chosen: G 'is the dynamic shear modulus; The Payne effect is the magnitude of the fall of the dynamic modulus with an increase in the amplitude of the shear strain; G " is the module of mechanical losses, characterizing plastic properties; tgδ is the tangent of the angle of mechanical losses [12]. The obtained dynamic properties of the investigated rubber are presented in table 3.

Table 3. Dynamic properties of rubber

Sample	Serial	Values indicators experienced rubber						
		1	2	3	4	5	6	7
Amplitude (%)		G' (kPa)						
1%	1014.2	1078.1	1001.9	892.1	690.3	681.6	753.7	760.0
10%	810.3	815.3	814.7	726.1	608.2	577.3	644.5	680.6
50%	553.8	542.1	548.5	503.1	477.8	409.8	470.3	519.0
100%	418.9	414.9	407.1	385.1	362.9	305.6	349.6	390.2
300%	284.9	290.9	280.9	265.8	203.4	202.1	219.5	220.8
Payne effect	729.3	787.2	721.0	626.3	486.9	479.5	534.2	539.2
Amplitude (%)		G" (kPa)						
1%	88.9	74.2	50.0	42.9	57.5	32.4	29.4	16.8
10%	63.6	64.5	42.9	36.1	43.7	26.0	23.6	17.9
50%	76.7	66.6	50.3	44.0	48.9	44.4	44.8	40.7
100%	95.9	69.9	51.7	47.0	68.7	48.1	53.2	56.3
300%	153.3	142.9	130.3	107.2	84.4	83.0	87.2	81.7
Amplitude (%)		tgδ						
1%	0,087	0,069	0,050	0,048	0,084	0,048	0,039	0,022
10%	0,078	0,079	0,053	0,050	0,072	0,045	0,037	0,026
50%	0,139	0,123	0,092	0,088	0,102	0,108	0,095	0,079
100%	0,229	0,168	0,127	0,122	0,190	0,158	0,152	0,145
300%	0,538	0,491	0,466	0,405	0,415	0,411	0,398	0,371

The dependences of the dynamic shear modulus G 'on the strain amplitude are shown in Figure 1.
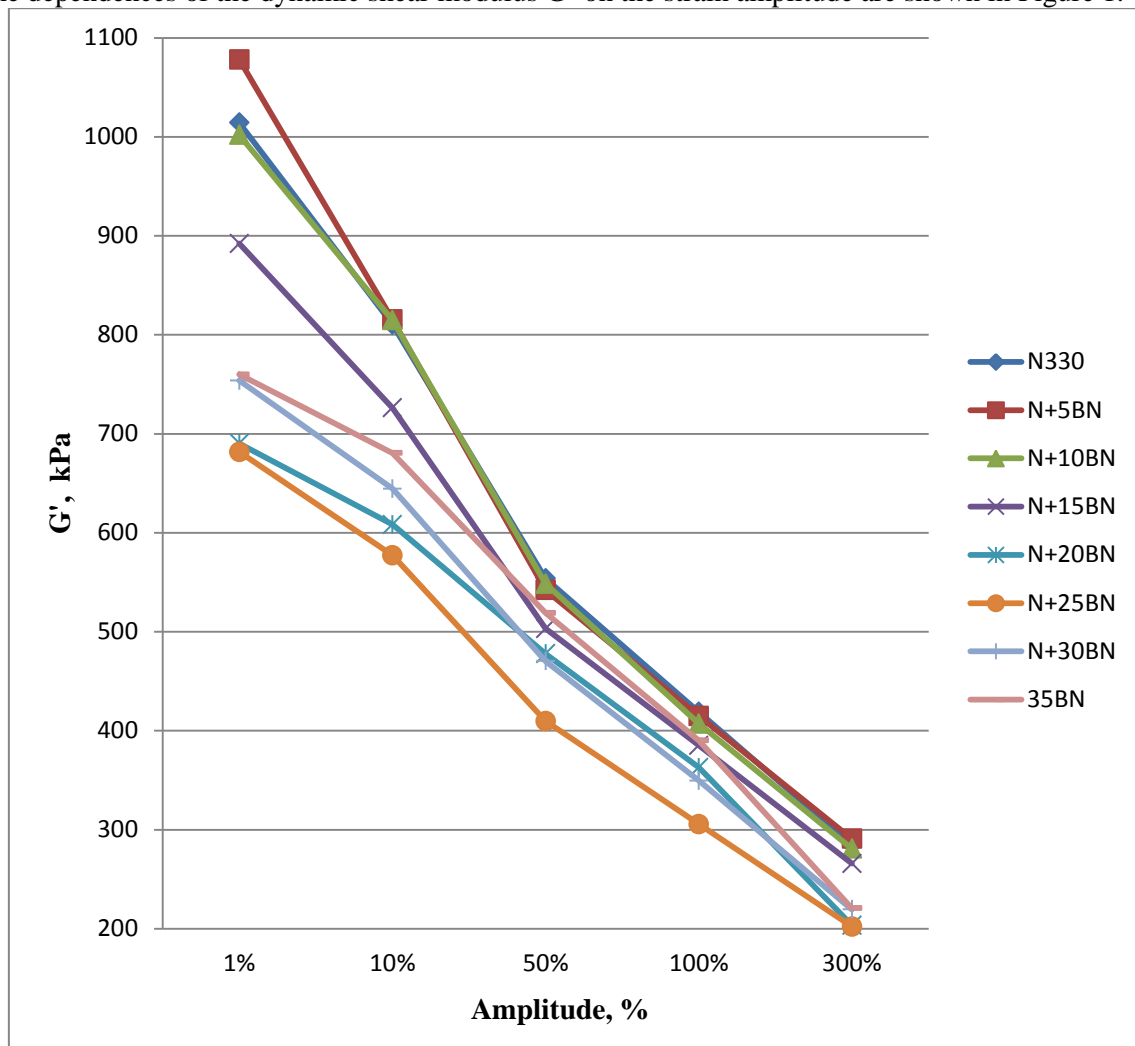

Figure 1. Dependences of the dynamic shear modulus G 'on the strain amplitude.

It is established that the minimum values of the dynamic shear modulus take place at an amplitude of 300% for the concentration of boron nitride of 20% and 25% (samples No. 4 and 5) of 203.4 kPa and 202.1 kPa. This means that in this case the maximum dispersion of the filler in the polymeric matrix is achieved. While for standard rubber filled with N330 grade technical carbon, this figure is 284,9 kPa, which is more than the minimum values of modified rubber by 30%.

It is also established that the value of the Payne effect changes symbiotically with the degree of dispersion of fillers in rubber. Such indicators testify to the better dispersion of fillers in rubber [13-15]. At further increase of boron nitride filler concentration in rubber up to 35% (sample No.7), the shear module increases up to 220.8 kPa, which indicates less interaction of polymeric matrix bonds with the filler and increase of the frequency of transverse bonds of the spatial grid of filler-filler.

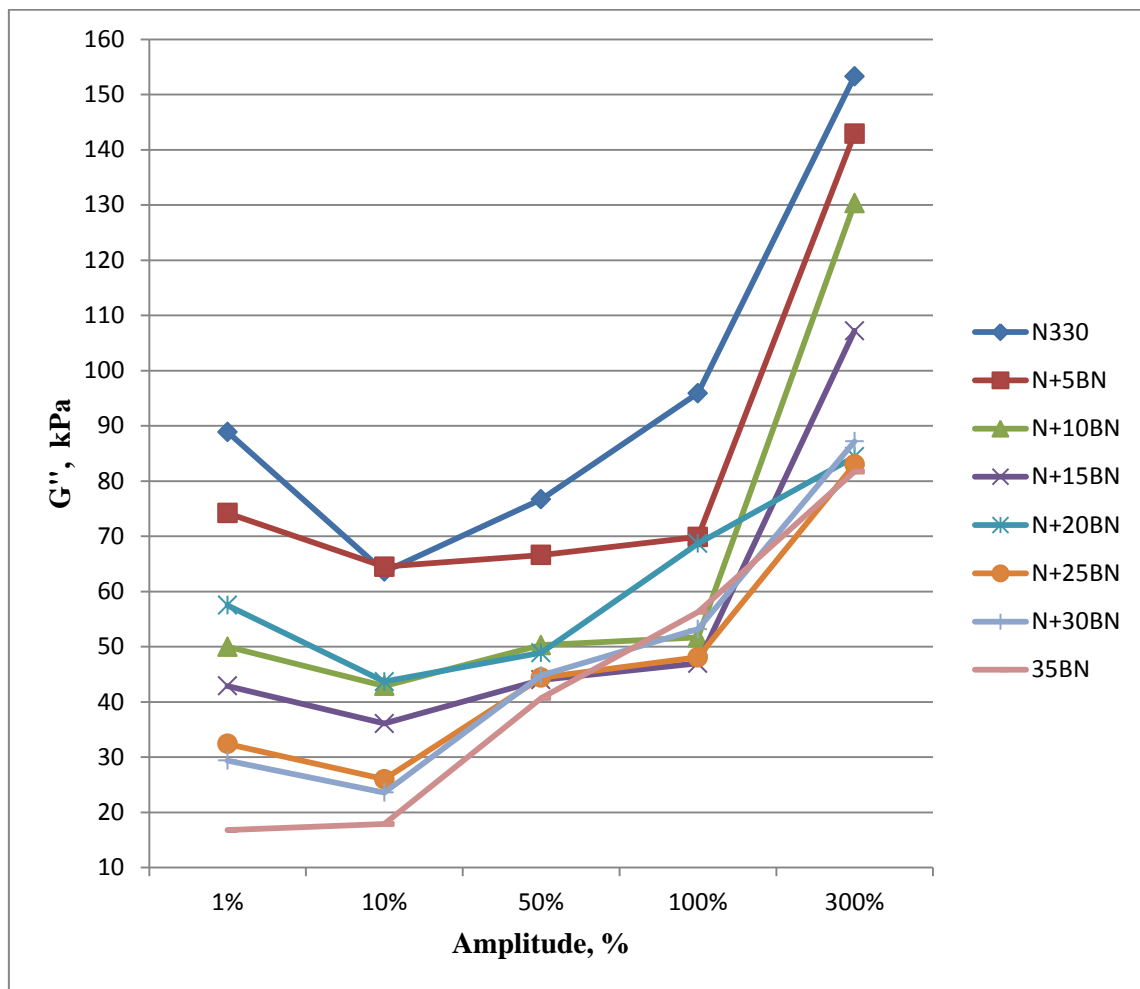The dependences of the modulus of mechanical loss in shear G '' on the strain amplitude are shown in Figure 2.

Figure 2. Dependences of the modulus of mechanical losses in shear G'' on the strain amplitude

Small amplitudes weakly destroy the structure of the elastomer, as can be seen from the G'' indices. With an amplitude of 1%, the modulus of mechanical loss with an increase in the concentration of boron nitride from 5% to 35% decreases from 74.2 kPa to 16.8 kPa. At large amplitudes, the structure is destroyed much more. In general, the module of mechanical losses in a sample filled with 35% boron nitride with an amplitude of 300% is almost 50% less than the values of standard rubber filled with N330 grade technical carbon. Thus, the values of the modulus of mechanical losses are proportional to the hysteresis losses and heat generation in rubber.

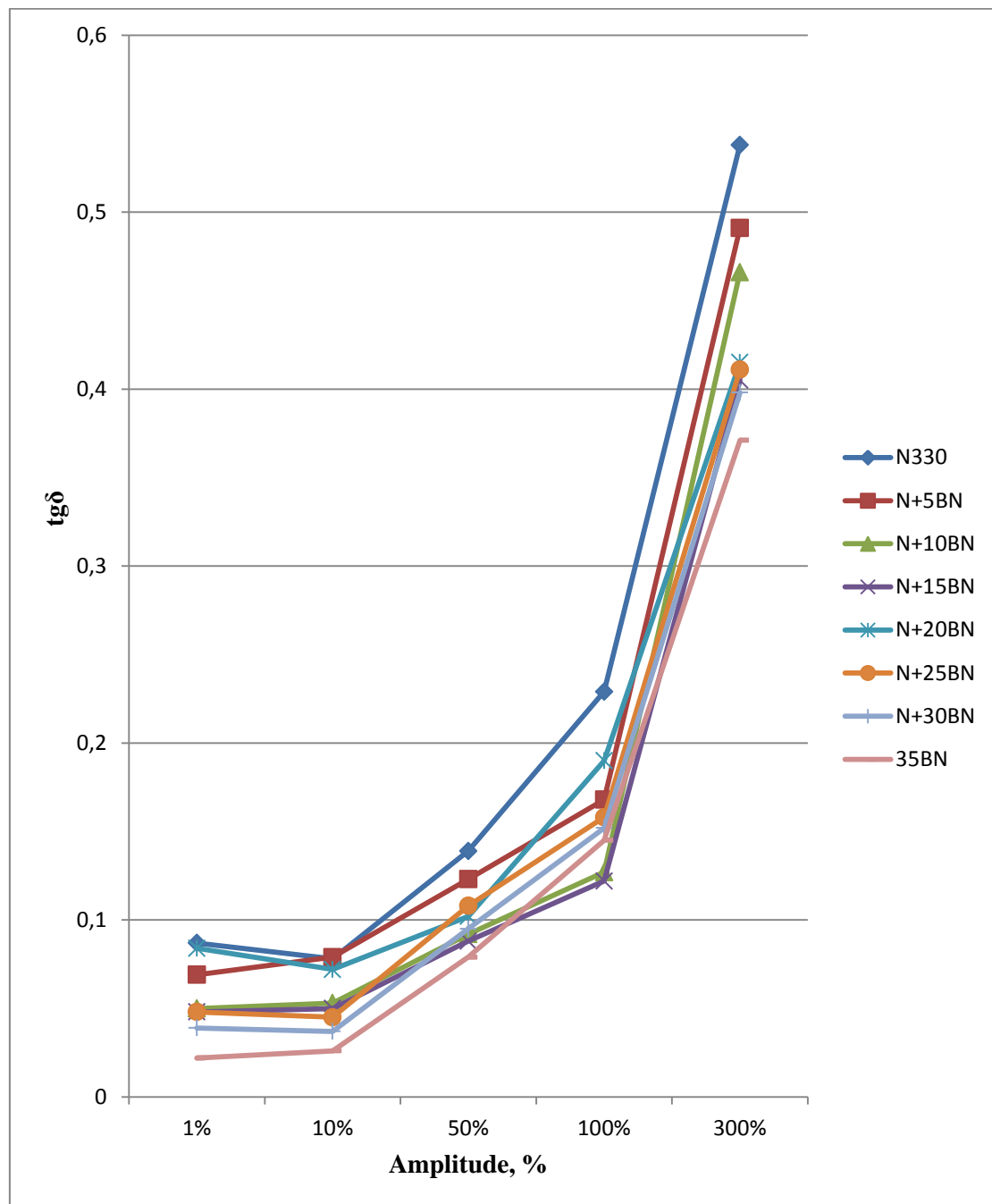Dependences of the tangent angle of mechanical losses tgδ on the amplitude of deformation are shown in Figure 3.

Figure 3. Dependence of the tangent of the angle of mechanical loss tgδ on the amplitude of deformation

It is established that the values of the tangent of the angle of mechanical losses in samples with boron nitride are smaller compared with the values of standard rubber filled with N330 grade technical carbon. At the same time, with an increase in amplitude, this difference decreases. Thus, with an amplitude of 1%, the tangent of the angle of mechanical losses in a sample filled with 35% boron nitride is less than the values of the standard sample filled with N330 grade technical carbon by 75%, and with an amplitude of 300% by 30%. This indicates an improvement in the elastic-hysteresis properties of rubbers filled with boron nitride, while sample No. 7 with the concentration of boron nitride of 35% is the most elastic.

Table 4 presents the rubber physical and mechanical properties.

Table 4. Physical and mechanical properties of rubber

Sample	Serial	Values indicators experienced rubber						
		1	2	3	4	5	6	7
f_{x300} (MPa)	3.39	3.62	3.30	3.01	2.28	2.22	1.96	2.09
E_t (MPa)	1.22	4.54	1.07	0.91	0.56	0.54	0.38	0.36
f_p (MPa)	18.4	21.4	18.5	17.7	12.8	12.7	13.9	12.7
ε_B (%)	1090.7	1215.2	1194.1	1243.9	1280.7	1337.9	1559.7	1562.8

f_{x300}. - conditional stress at 300% elongation; E_t - modulus of elasticity; f_p - tensile strength; ε_B - relative elongation at break

The modulus of elasticity(E_t) characterizes the density of the spatial curing mesh [16]. From the obtained results it follows that the filling of rubber 5% boron nitride gives the most optimal parameters The results showed that the tensile strength (f_p) relative to the values of standard rubber filled with N330 grade technical carbon decreased by 31%. and the relative elongation at break increased by 43% with an increase in the concentration of boron nitride to 35%.

The established gradual increase in the elongation at break shows that boron nitride increases the elasticity of the resulting rubbers. Compared to standard rubber. the elasticity of a sample filled with 35% boron nitride is 43% higher. At the same time. a decrease in tensile strength characterizes the rigidity of the obtained rubbers. From the obtained results it follows that the filling of 5% boron nitride forms a softer rubber.

In this way. by increasing the concentration of boron nitride from 5% to 35%. you can vary the special properties of rubber. from "soft" to elastic.

Conclusions

It was found that with a gradual increase in the concentration of inactive boron nitride filler from 5% to 35%. a decrease in the vulcanization rate by 33% and a polymer crosslink density by 26% was observed. the start time of vulcanization increased by almost 300%. and the optimum vulcanization time relative to standard rubber increased by 200 %

With an increase in boron nitride concentration. the Payne effect. which determines dynamic properties. decreases by 26% relative to standard rubber. which indicates an improvement in the dispersion of the filler. At the same time. a decrease in the tangent of the angle of mechanical losses is observed. meaning that the addition of boron nitride to the recipe of a standard rubber mixture based on isoprene rubber imparts greater elasticity to rubber.

In addition. with an increase in boron nitride concentration. an increase in the relative elongation at break of 50%. a decrease in tensile strength by 30% relative to the standard specimen filled with N330 grade technical carbon are observed.

Thus. varying the boron nitride filler makes it possible to obtain a complex of rubbers with different properties.

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