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STUDY OF THE EFFECT OF THE VULCANISING GROUP INGREDIENTS MECHANOCHEMICAL PROCESSING ON THE PROPERTIES OF THE FILLED RUBBER COMPOUND AND NATURAL RUBBER VULCANIZATE

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The purpose of the article is to study the effect of mechanochemical processing (MCP) of vulcanising group components on the properties of rubber compound and natural rubber vulcanizate containing technocarbon N 330 with a small addition of high-dispersed silica filler. The processing of both individual components: zinc oxide as accelerator and all components of sulphuric curing group increases the speed and degree of rubber structuring during the main period of vulcanization, reduces the tendency of rubber to reversion at the postvulcanization stage. This increases both the conditional stress and tensile strength of rubber.

Introduction

Recently, solid-phase processes initiated by mechanical action have been associated with the prospect of using 'dry' process operations, which are more both ecologically and economical friendly. Mechanochemical activation is a process, causing structural failure, amorphisation and increased chemical reactivity of the material subjected to intense grinding [1-3]. The mechanochemical processing of ingredients proceed in various kinds of mills, disintegrators, etc. [4-7]. The mechanochemical preprocessing of rubber compound ingredients is an effective way to increase their vulcanisation activity and improve the rubber properties [8-11]. Mechanoactivation is based on the intermittence process with a local effect on the substance. The machining process does not generate a stress field in the entire volume of the solid, but only at its contact with another particles. Earlier [12] we studied the effect of mechanochemical processing of vulcanizing group (VG) components, as well as duration of processed ingredients storage of rubber screps and rubbers of model composition based on synthetic 1,4-*cis*-isoprene rubber SIR-3. The mechanochemical processing of vulcanizing group components increases the speed and degree of rubber structuring during the main vulcanization period, and decreases the reversibility of rubbers at the postvulcanization stage.

Study

It was interesting to assess the influence of the vulcanization process accelerated by the incorporation of VG components subjected to MCP in an electromagnetic apparatus on commercial rubber compounds.

For this reason, we choose a rubber compound based on SVR-3L natural rubber containing N330 active carbon black with a small addition of a highly dispersed silica filler (code NKS-1) as a reference one. In terms of the main components, it was similar for wire cord tyre breaker mixtures. The vulcanising group included polysulphur as vulcanising agent, sulphonamide type accelerator and activators - zinc white, technical stearin. In terms of mass ratio of sulphur and accelerator VG should be classified as conventional curing systems [13, p. 186]. We carry out the mechanochemical activation of VG components in apparatus. It is a chamber (reactor) surrounded by an electromagnetic coil producing a pulsating magnetic field, to which an alternating current of 220–380 V with a frequency of 50 Hz is applied. There are working magnetic elements made of magnetically hard material inside the reactor. When the inductor is plugged in, the working elements are subjected to a magnetic field and set in an intense, chaotic motion with energy transfer to the VG components for 2 minutes [12]. The processing included zinc white (NKS-2), vulcanisation accelerator (NKS-3) and all the ingredients in the vulcanisation group (sulphur, accelerator, zinc white, stearin) of NKS-4 at the same time. We prepared the rubber mixtures on lab mills. The temperature regime and total mixing time were the same for all mixtures.

We identify the viscoelastic properties of rubber compounds by the apparatus RPA 2000 [14]. The vulcanization characteristics of compounds in isothermal mode at temperatures 143, 155 and 170 °C - by the apparatus MDR-2000 (GOST R 54547-2011).

By Table 1, the introduction of MCP-treated VG components into the rubber compound increases its complex dynamic shear modulus G^* at low (0.98%) and high (1000%) strain amplitudes by increasing both its parts: both accumulation modulus G' and loss modulus G''. The pattern of module change is symbiotic to the change in minimum torque M_L correlating to the minimum viscosity of the mixtures during the induction curing period. By Figure 1, *a*, the M_L values for the processed mixtures components are higher at all test temperatures. This effect is slightly more evident during the processing of accelerator.

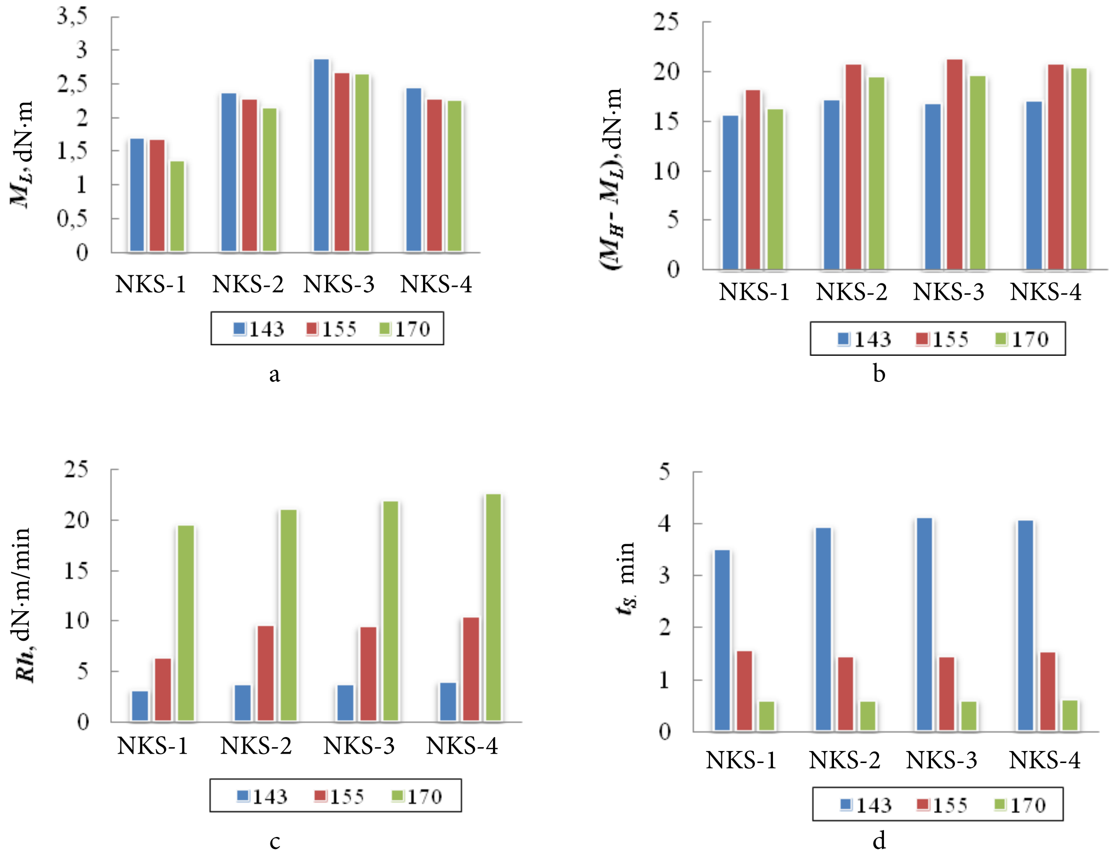
Probably, the change of viscosity of the mixtures is the formation of an additional amount of local cross-linkings, which are stable at the test temperature. This hypothesis is supported by the reduction of the mechanical loss angle tangent (tgδ) in the mixture, particularly at strain amplitude of 1000% (tgδ_{1000}%) (see Table 1) by RPA 2000 and the reduction in tgδ when the minimum torque is reached (tgδ@M_L) by MDR 2000(Table 2).

Increasing of shear modulus and viscosity are accompanied by increases the cohesive strength of unvulcanised mixtures. As known [15, p. 266–267], this parameter is extremely important for tyre core mixtures. The high cohesion strength provides the cord thread rarefaction and pore formation in non-vulcanised samples, which are subjected to significant deformations.

Table 1. Changes of the viscoelastic properties* of NR - based filled rubber compounds under the influence of mechanochemical processing of VG components

Parameters	Mixture code			
	NKS-1 (reference)	NKS-2	NKS-3	NKS-4
$G'_{0,98\%}$, kPa	206	289	342	294
$G''_{0,98\%}$, kPa	137	190	215	181
$G^{*}_{0,98\%}$, kPa	247	346	404	345
$G'_{1000\%}$, kPa	2.72	3.52	4.16	3.84
$G''_{1000\%}$, kPa	9.99	12.7	14.4	12.8
$G^{*}_{1000\%}$, kPa	10.35	13.18	14.99	13.36
tg$\delta_{1000\%}$, kPa	3.67	3.61	3.46	3.33

*Test mode on the RPA 2000: temperature 100 °C; frequency 0.1 Hz; strain amplitude range 0.56-1000%.



a

b

c

d

Fig. 1. Influence of MCP vulcanising group components on the rheometric and vulcanisation characteristics of NR-based filled rubber compounds

The results of the rheometer curves obtained by testing the mixtures on an MDR 2000 vibroreometer show that the MCP both the one component and the whole curing group increases the activity of VG. Is expresses in the increase of the maximum rate R_h of chemical crosslinking for the main period and the degree of crosslinking in the technological optimum of curing, which can be indirectly estimated [15, p. 269; 16] by the difference between the maximum and minimum values of torque (M_H - M_L) (Fig. 1, *b* and *c*). The duration of the induction period of curing of t_{S1} mixtures with MCP-treated components increases slightly compared to the reference at lower test temperatures (143 °C) and tends to decrease at higher test temperatures.

By Table 2, vulcanizates produced with the addition of MCP-treated VG components have a lower tendency to reversion, which was determined according to GOST 12535-84 using a time scale in minutes (t_r) from the beginning of the rheometric curve to the time corresponding to a reduction of M_H by the value $\frac{x}{100}\cdot\Delta M$, where $\Delta M = (M_H - M_L)$ and $x = 10\%$.

Table 2. Influence of MCP of curing group components on mechanical losses in rubber mixtures and the reversion of NR-based rubbers

Parameters	Mixture code			
	NKS-1	NKS-2	NKS-3	NKS-4
tgδ@M_L at temperature:				
143 °C	0.735	0.693	0.633	0.673
155 °C	0.766	0.759	0.720	0.755
170 °C	0.804	0.782	0.743	0.772
Reversing time at 170 °C t_r, min	18.3	20.8	20.8	20.2

By Table 3, MCP of the VG components leads to a significant increase in conditional stresses f_{100} and f_{300}, conditional tensile strength f_p and a slight decrease of elongation at failure ε_p for the same curing time. This indicates a higher degree of cross-linking of the experimental rubbers compared to the reference.

Table 3. Changes of the deformation and strength properties of NR-based rubbers at uniaxial tension under the influence of mechanochemical processing of VG components

Parameters	Mixture code		
	NKS-2	NKS-3	NKS-4
Δf_{100}	1.07	1.08	1.10
Δf_{300}	1.13	1.34	1.25
Δf_p	1.04	1.15	1.09
$\Delta \varepsilon_p$	0.98	0.96	0.97

Curing mode in an electric press 155 °C, 15 min.

we calculated Δ as the ratio of the index value of the tested rubber to the index value obtained in the reference test.

To assess the possible mechanism of MCP, we modelled the kinetics of curing of the compositions using the kinetic scheme of curing and the calculation method proposed in [17, 18]. As a result, the changes of kinetic parameters, presented in Fig. 1 and Table 2, observed in the experiments on vulcanization kinetics are caused by an increase of rate constants of formation of sulfidizing complex (actual agent of vulcanization, AAV) and its interaction with the rubber. Probably, during the processing of the components of the curing group there is a mechanochemical initiation of radical decomposition reactions of the accelerator and sulphur, leading to the formation of compounds which are part of the AAV.

Results and Conclusions

Thus, mechanochemical preprocessing of sulphuric curing group components allows to increase activity, improves deformation-strength properties of rubber mixtures and NR-based rubbers. It helps to increase their resistance of to reversion during vulcanization. By the cumulative effect of changing the properties of rubber mixtures and rubbers, a mechanochemical processing of the individual vulcanisation accelerator or the entire vulcanisation group is most appropriate. If the properties of mixtures and rubbers are maintained at the referenced level, the use of MCP components provides additional possibilities to reduce the content of structuring agents, especially accelerator, for the rubber mixture.

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