Butadiene-acrylonitrile rubbers are used for the manufacture of different mechanical rubber goods. One of the shortcomings of these rubbers is their relatively low ozone resistance. In connection with this, the aim of the present work was to study the influence of the structure of elastomers on their interaction with ozone in the stress state.

Information on the structure of butadiene–acrylonitrile rubbers, obtained by NMR spectroscopy [1, 2] and X-ray diffraction analysis (XDA) [3-5], makes it possible to explain features of the influence of the structure of rubbers on their properties. Variation in the conditions of crosslinking of their macromolecules results in vulcanisates of different structure, which has a certain influence on their physical properties [3, 6, 7] and physico mechanical properties [8, 9] and may show up in the process of chemical reactions and, in particular, during interaction with ozone in the stress state.

The investigation was conducted on vulcanisates based on industrial butadiene–acrylonitrile rubbers SKN-18, SKN-26, and SKN-40. The isomeric composition of the butadiene part of the copolymers, determined by IR spectroscopy with the use of extinction coefficient values given in Kozlova et al. [10], is presented in Table 1. The molecular weight of the rubbers was $\sim 3 \times 10^5$. The sulphur vulcanisation of copolymers was carried out in a press under a pressure of $\sim 20$ MPa at 145 and 170°C, using the process accelerators N-cyclohexyl-2-benzothiazyl sulphenamide (CBS) and mercaptobenzothiazole (MBT). The degree of crosslinking of the vulcanisates was determined by equilibrium swelling in chloroform.

The ozone resistance of vulcanisates of the copolymers was investigated using the stress relaxation method in an ozone-containing medium at an ozone concentration of $8.6 \times 10^{-6}$ mol/L at 30°C under different tensile strains on an IKHF relaxometer [11] and was characterised by the magnitude of the stress relaxation rate $V_r$, as determined on a stationary section of the curve of drop in the force in the specimen. This section follows the section of a high relaxation rate governed by the segmental mobility of the chains [11] and reflects the kinetics of accumulation of ruptures of macromolecules in the vulcanisate under the action of ozone [12]. An analysis was made of SKN vulcanisates with an identical degree of crosslinking in order to eliminate the possibility of its influence on the ozonisation process. For this, the sulphur concentration and vulcanisation accelerator in the formulation were varied, as elastomers based on

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Content of butadiene units (wt%)</th>
<th>$T_{fl}$</th>
<th>$T_{tfl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,4-trans</td>
<td>1,2-units</td>
<td>1,4-cis</td>
</tr>
<tr>
<td>SKN-18</td>
<td>68.3</td>
<td>8.2</td>
<td>5.5</td>
</tr>
<tr>
<td>SKN-26</td>
<td>64.3</td>
<td>8.2</td>
<td>4.4</td>
</tr>
<tr>
<td>SKN-40</td>
<td>47.3</td>
<td>3.0</td>
<td>9.7</td>
</tr>
</tbody>
</table>
SKN butadiene–acrylonitrile rubber, obtained by using the same formulation, differ considerably in the chemical crosslink network density [13].

The ozone resistance of the vulcanisates was assessed, starting with a relative elongation of 30%. This strain of the vulcanisates is near critical [14]. Under this strain, the maximum degradation rate of the macromolecules is observed as a result of the interaction of butadiene double bonds of the rubber in cis-1,4- and trans-1,4-units with ozone [11]. The ozonisation of the double bonds of 1,2-butadiene units does not lead to decomposition of the main chain of the SKN macromolecules [12], and consequently has no influence on the process of stress relaxation in the vulcanisates in an ozone medium.

The dependence of Vr on the degree of elongation for vulcanisates based on SKN, obtained at 145°C in the presence of CBS, is presented in Figure 1. As is the case with other elastomers, with increase in the degree of elongation under above-critical strains, the ozone resistance of all the vulcanisates increases (Vr decreases). This is a consequence of an increase in the degree of orientation of chain fragments of the vulcanisates under elongation, which depends on the comonomer composition of the copolymers, as established earlier using XDA [13]. The possibility of this effect was suggested earlier by Zuev and Degteva [14].

The ozone resistance of vulcanisates based on SKN rubber with different contents of acrylonitrile units differs, in spite of the identical chemical crosslink network density, and it is especially small (Vr is great) in the case of vulcanisates of SKN-18 (Figure 1). This difference is a consequence of the difference in the content of butadiene double bonds (Table 1) and the degree of orientation of chain fragments of the vulcanisates under elongation [13]. At relative elongations of the vulcanisates of over 100%, Vr hardly depends on the degree of strain. Evidently, under such elongations, the packing density of the chain fragments of the vulcanisates increases on account of their orientation to such an extent that it creates practically identical steric hindrances for reaction with ozone having a high molar volume with the double bonds of the copolymers.

The degree of change in the rate of drop in stress in the 30-70% range of relative elongations increases with increase in the overall content of cis-1,4- and trans-1,4-butadiene units $w_1$, i.e. in the number of double bonds, especially on changing from vulcanisates of SKN-26 to vulcanisates of SKN-18 (Figure 2).

In the case of using MBT, the nature of the dependence of the rate of drop in stress on the degree of elongation of the vulcanisates is the same as in the case of using CBS. Comparison of the data in Figures 2a and b indicates that the application of MBT as the accelerator of the crosslinking of the macromolecules at the same vulcanisation temperature (145°C) led to a considerable increase in ozone resistance of vulcanisates of SKN-18 and SKN-26, but had practically no effect on the ozone resistance of vulcanisates based on SKN-40 with the same chemical crosslink network density. Thus, with a
relative elongation of 30%, $V_r$ for vulcanisates of SKN-18 and SKN-26 was reduced by ~33%. At the same time, there was an increase in the stress relaxation rate in the 30-70% range of relative elongations in the case of vulcanisates of SKN-18, but it fell for vulcanisates of SKN-26 and SKN-40 by comparison with the corresponding vulcanisates obtained in the presence of CBS.

The dependences of certain physicochemical properties on the acrylonitrile content for vulcanisates of SKN with the same chemical crosslink network density and obtained using MBT and CBS also match. The possible causes of this are the difference in the type of chemical crosslinks and the changes in the ordered structural organisation of the elastomers in the process of crosslinking of the macromolecules.

In order to explain the role of the type of sulphur vulcanisation accelerator in the formation of ozone resistance of vulcanisates of butadiene–acrylonitrile rubbers, an investigation was made of the influence of the content of stearic acid. It is known [15] that stearic acid takes no part in the process of crosslinking of macromolecules of rubbers. It is introduced only in order to facilitate the process of mixing of the ingredients of the rubber mix [16].

Halving of its content led to a sharp increase in the ozone resistance of vulcanisates based on all the rubbers investigated, even in the presence of CBS (with retention of an unchanged chemical crosslink network density (see Figure 1)). Thus, the rate of drop in stress under a relative elongation of 30% decreased for vulcanisates of SKN-18 and SKN-26 by ~60 and ~40% respectively, while for vulcanisates of SKN-40 it decreased by ~70%. At the same time there was an increase in the stress relaxation rate in the case of vulcanisates of SKN-18, but it was maintained for vulcanisates of SKN-26. The dependence of $V_r$ on the degree of elongation for vulcanisates of SKN-40 acquired a linear nature in this case.

The negative effect of stearic acid on the ozone resistance of elastomers in the stress state, which was found for the first time, cannot be explained by change in the nature of chemical crosslinks with increase in its content [15]. Evidently, stearic acid acts as a structural plasticiser. It lowers the viscosity of the polymer melts [16] and ensures in this case an increase in the degree of ordering of elastomers based on SKN owing to an increase in the volume content of ordered formations made up of microblocks of trans-1,4-butadiene units. With such a change in the structure of the elastomers, the orientation capacity of the chain fragments during elongation is reduced, and consequently there is a deterioration in their ozone resistance in the stress state. This is due to the fact that the ordered formations of sequences of alternating units are stronger than microblocks of trans-1,4-butadiene units, and they do not break down under strains of less than 60%, ensuring increased ozone resistance of the elastomers [13].

The choice of two different accelerators for the sulphur vulcanisation of SKN rubbers is dictated by the considerable difference in the nature of the kinetic curves of crosslinking of their macromolecules in the presence of MBT and CBS.

It can be assumed that the observed difference in ozone resistance of such vulcanisates is due to the difference in the kinetics of their vulcanisation. Thus, according to rheometric data, in the case of CBS there is an induction period of vulcanisation lasting 22, 10, and 8 min during the vulcanisation of SKN-18, SKN-26, and SKN-40 respectively. During the induction period preceding the formation of a chemical crosslink network there is an increase in the volume fraction of ordered formations of sequences of alternating units that do not break down during vulcanisation, especially in SKN-40 [3, 4]. This in turn leads to an uneven distribution of chemical crosslinks in the volume of the elastomers, the more so the greater the volume content of such formations. In the process of subsequent cooling of the obtained vulcanisates to room temperature, chemical crosslinks create steric hindrances to the recovery of the ordered formations of microblocks of trans-1,4-butadiene units that broke down during heating in the press. In the less ordered structure of elastomers, the degree of orientation of chain fragments during elongation decreases [13], which leads to a reduction in their ozone resistance in the stress state.

In order to obtain additional confirmation of the influence of the structural organisation of elastomers on their ozone resistance in the stress state, recorded by replacing MBT with CBS, the vulcanisation temperature of SKN was raised to 170°C.

Increase in the crosslinking temperature of macromolecules in the presence of MBT led to a small increase in ozone resistance of vulcanisates of SKN-18 and SKN-40 ($V_r$ decreased by ~20 and ~30% respectively) and to a reduction in ozone resistance in the case of vulcanisates of SKN-26 ($V_r$ increased by ~40%) with a relative elongation of 30% and with retention of an unchanged chemical crosslink network density (Figure 2b). In this case, the drop in stress in an ozone medium in all the elastomers slowed down, especially in the case of vulcanisates of SKN-18. The noted changes in ozone resistance of the elastomers led to inversion of the dependence of the rate of drop in stress in vulcanisates on the overall content of cis-1,4- and trans-1,4-butadiene units (Figure 2b). In other words, increase in the crosslinking temperature of macromolecules from 145 to 170°C led to an increase in the orientation capacity of chain fragments during elongation in the case of vulcanisates of SKN-18 and SKN-40 with the same chemical crosslink network density, evidently as a consequence of an increase in this case in the volume content of ordered formations of sequences of alternating units.
In the case of using CBS as an accelerator of the crosslinking of SKN macromolecules, increase in the vulcanisation temperature to 170°C led, on the other hand, to deterioration in the ozone resistance of the elastomers, in spite of retention of an unchanged chemical crosslink network density (Figure 2a). The rate of drop in stress under a 30% relative elongation increased in the case of vulcanisates of SKN-18 and SKN-26 by ~18 and ~35% respectively, while for vulcanisates of SKN-40 it remained practically unchanged. At the same time, the process of stress relaxation in an ozone medium slowed down in the case of vulcanisates of SKN-18 and especially for vulcanisates of SKN-26, but hardly changed for vulcanisates of SKN-40. In connection with the noted features of stress relaxation in vulcanisates in an ozone medium, the dependence of the rate of drop in stress on the content of cis-1,4- and trans-1,4-butadiene units under strains of over 50% underwent a change (Figure 2a).

Thus, in the case of using CBS, with increase in the crosslinking temperature of the macromolecules, owing to the existence of an induction period, albeit a shorter induction period than at 145°C, the process of formation of additional ordered formations of alternating units proceeds more fully than in the case of using MBT. Accordingly, with subsequent cooling of the elastomers to room temperature, fewer ordered formations of microblocks of trans-1,4-butadiene units are recovered than in the case of MBT. The degree of ordering of such elastomers is lower than that of vulcanisates obtained in the presence of MBT, which is shown, in particular, by a reduction in their ozone resistance in the stress state and in the stress under <300% elongations, in spite of the retention of the chemical crosslink network density.

With increase in the vulcanisation temperature of SKN rubber to 170°C in the presence of both vulcanisation accelerators there was also a change in the nature of the dependences of the physicomechanical properties on the content of acrylonitrile units with the same chemical crosslink network density. The change in the physicomechanical properties and ozone resistance of vulcanisates of SKN in the stress state with increase in the temperature of crosslinking of the macromolecules, found for the first time, cannot be attributed to any change in the type of chemical crosslinks and is a reflection of the rearrangement of the ordered structure of the rubbers during vulcanisation.

With variation in the conditions of crosslinking of the SKN macromolecules, it is the ordered structure of vulcanisates based on SKN-26 that changes most significantly. This is indicated particularly clearly by the greatest change in their ozone resistance and physicomechanical properties with increase in the vulcanisation temperature in the case of using MBT (Figure 2).

Thus, change in the crosslinking conditions of macromolecules (temperature, type of accelerator, content of stearic acid), which have a considerable influence on the physicomechanical properties of the vulcanisates, also leads to a change in ozone resistance, which not only confirms the existence of a certain structural organisation in the elastomers but also its rearrangement in the process of crosslinking of the macromolecules.

REFERENCES

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