

Introduction In [1-4] was studied the relation of ozone resistance to the volume and structure of the interphase layer and the amounts of crosslinks in the interlayer for covulcanizates of acrylonitrile-butadiene rubbers (NBRs) of various polarities with ethylene-propylene-diene (EPDM) elastomers that differed in the comonomer composition and stereoregularity of propylene units. It was shown that the rate of ozone-induced degradation of the diene matrix is determined by the compatibility of the components, phase structure, the interlayer volume and density, the amount of crosslinks in the interlayer, and the strength of the EPDM network. The most dense and voluminous interlayer with the largest amount of crosslinks provides the most effective protection against ozone degradation to the diene matrix. In [1-4], it was found that the density of the interfacial layer and the number of interfacial crosslinks depend on the relative amounts of ethylene and propylene units and diene groups, the degree of isotacticity of the propylene chain segments in EPDM, and the isomer composition of the butadiene units in NBR that primarily exist in the trans-1,4-configuration. The most dense and voluminous interlayer with the largest amount of crosslinks provides the most effective protection against ozone degradation to the diene matrix. The ozone resistance, interfacial layer structure, and composition of covulcanizates of acrylonitrile-butadiene rubbers containing different amounts of acrylonitrile units with ethylene-propylene terpolymers were studied using the stress relaxation and ESR and FMIR IR spectroscopy techniques. It was used ethylene-propylene-diene elastomers manufactured by Uniroyal, DSM and domestic EPDM which differ in the comonomer ratio and in the stereoregularity of propylene sequences [1-4]. In the case of peroxide crosslinking of EPDM, it is possible to estimate the density of the interfacial layer and the number of crosslinks in this layer from deviation of the equilibrium degree of swelling of covulcanizates from additive values in a nonpolar selective solvent, n-heptane (the Zappa method) [5, 6]. The deviation toward an increase is provided by a weak interfacial interaction between thermodynamically incompatible polymers, one of which contains polar units. These systems show only local mutual solubility of the segments of nonpolar chain fragments with a lower degree of crosslinking of the components than that in the phases [7-10]. The most effective ozone-protection is provided by the compatibility of NBR with EPDM having a large proportion of ethylene units at a high isotacticity of propylene sequences and a moderate amount of diene groups. Copolymers EPDMs with different compositions and different stereoregularities of propylene sequences were studied. It was shown that the structural characteristics of EPDM control the efficacy of modification during the addition of NBRs for improvement of such characteristics of the crosslinked blends as ozone resistance and physicomechanical parameters. In this study, the characteristics of NBR covulcanizates with different contents of polar acrylonitrile units (AN units) and EPDM whose macromolecules contain attached fragments of the accelerating agent have been investigated. It is of interest to estimate the effect of modification on the compatibility of polar copolymers with nonpolar elastomers. The relationship between the

characteristics of the blends by introducing the crosslinking system into NBR has been studied. Experimental A heterophase crosslinked blend of NBR and EPDM with a ratio of 70:30 (by weight), which represented a system of interpenetrating crosslinked networks, was studied. Commercial acrylonitrile-butadiene rubbers (trademarks BNKS-18, BNKS-28, and BNKS-40) were used. The AN-unit contents were 18, 28, and 40 wt %, respectively, and the values of the Mooney viscosity (at 100°C) were 40-50, 45-65, and 45-70 rel. units, respectively according to Russia technical specifications. They contained no more than 5 wt % calcium stearate and 0.35 wt % ionol. The weight loss during drying did not exceed 0.8%. The changes in the weight of the vulcanizate in an isooctane-toluene mixture were below 65, 34, and 25% for BNKS-18, BNKS-28, and BNKS-40, respectively. For all the NBRs, the solubility in methyl ethyl ketone was no less than 95%. The content of trans-1,4-, 1,2-, and cis-1,4-units of butadiene was estimated via IR spectroscopy (bands at 967, 911, and 730 cm⁻¹) [11] with the use of extinction coefficients from [12] (Table 1). Table 1 - Isomeric composition of butadiene units in different AN-butadiene copolymers

Copolymer	Content of units, %	trans-1,4-	1,2-	cis-1,4-
BNKS -18	82.0	76.4	93.0	8.2
BNKS -28	14.4	4.4	9.8	9.2
BNKS -40	2.6			

The domestic EPDMs had different compositions and stereoregularities of propylene units. The weight losses during drying were below 0.5%. The weight fractions of ash, vanadium, the alcohol-toluene extract, and the antioxidants Naphthame-2 or Agidol-2 were 0.2%, 0.008%, 4%, and within 0.15-0.30%, respectively. Elastokam 7505 contained no more than 0.1 wt % ash and 0.15% of the stabilizing agent, Agidol-2; the weight loss during drying was below 0.1%. Table 2 shows the data on the Mooney viscosity; the content of ethylene, propylene, and ethyldenenorbornene units (according to the manufacturer's data); and the degree of isotacticity of propylene sequences of EPDM chains, α , estimated via IR spectroscopy [13, 14]. The composition of sulfur-containing crosslinking systems for NBR and EPDM includes stearic acid, zinc oxide, mercaptobenzothiazole, tetramethyl-thiuram disulfide, and sulfur [15]. Each of the rubbers was mixed with its crosslinking system on rolls at 40-60°C for 15 min. Then, the blends of the rubbers were prepared under the same conditions. Vulcanization was performed at 155°C for 20 min at a pressure of 19.6 MPa. During rubber blending and vulcanization, the redistribution of vulcanizing agents took place [16]. For the peroxide vulcanization of EPDM, Peroximon F-40 on a carrier was used; its content was 5.5 weight parts [3, 4]. Table 2 - Characteristics of domestic EPDM

EPDM trademark	η	Mooney viscosity, rel. units	Ethylene: propylene α , %	Content of ethyldene-norbornene, %
EPDM-40	36-45	67	60	62
Elastokam 6305	83	70/30	74/26	60/40
EPDM-60(I)	60/40	60/40	60/40	29
EPDM-60(II)	9,5	13	13	9,5
Elastokam 7505	4	5,4	4	6,7
	5,1			

To improve the compatibility and crosslinking of the components, domestic EPDM was modified heating with the accelerating agent and sulfur for 30 min at 160°C (in the absence of crosslinking of EPDM). The crosslinking system was introduced via mixing with EPDM modified by the sulfur-containing accelerating agent via mixing with NBR with the same composition of the vulcanizing group as that in the

case of the unmodified EPDM. Fig. 1 - Decay curves of force F in drawn specimens of NBR covulcanizates containing (1) 15 and (2) 30 phr EPDM. See the text for details. The ozone resistance of the blends was studied via the method of stress relaxation at an ozone concentration of 8.5×10^{-5} mol/l, 30°C and at a tensile strain of 30-150% on an IKhF-2 relaxometer [3, 4]. Relaxation rate v_r in the ozone-containing medium in the steady-state region next to the region of the fast physical relaxation reflects the kinetics of accumulation of chain ruptures in the diene matrix (Fig. 1). The efficacy of retardation of degradation during the introduction of EPDM, v_{rrel} , corresponds to the intensity of the decrease in the rate in the presence of the ozone-resistant component relative to that in the presence of the NBR vulcanizate. The region of a low relaxation rate with quasiequilibrium stress σ^* reflects the strength of the EPDM network because it represents the superposition of stresses in the network and in the matrix connected through interfacial layers [3, 4]. The absence of the continuous structure of EPDM or its breakdown during tensile drawing is accompanied by a stress drop to zero due to propagation and merging of ozone microcracks. The physicochemical tests of the covulcanizates were performed according to GOST 261-79 on an Instron universal tensile machine at a strain rate of 500 mm/min. The error of breaking-strength measurements was $\pm 10\%$.

Results and discussion It was shown in [1-4] that the most developed interfacial layer is formed in the blend of NBR and EPDM with a high content of ethylene units neighboring stereoregular propylene chains that are integrated with individual AN units. The above EPDMs show the maximum efficacy in retardation of the ozone degradation of polydiene [3, 4]. In the case of low degree of isotacticity of propylene units, α , compatibilization is possible only with butadiene units of NBR. In this case, the density of the interfacial layer and the number of interfacial crosslinks depend on the ratio between the isomers of the butadiene units that primarily exist in the trans-1,4 configuration (Table 1). The higher the overall content of cis-1,4- and 1,2-isomers, the higher the volume of the interfacial layer and the higher the degree of crosslinking of the phases [1-4]. It was found in [17] that the isomers of butadiene units that exist in low concentrations and disturb the geometric similarity of chains reduce the dimensions of the ordered structures preventing interfacial interaction. With an increase in the content of polar AN units in NBR and a decrease in the volume of the interfacial layer, the protective effect of the saturated component decreases. Ethylene units are compatible with all butadiene isomers. The efficacy of retardation of degradation is minimum for the butadiene-nitrile EPDM rubber with a high content of propylene units and a low degree of isotacticity. In the case of the sulfur vulcanization of EPDM, the above tendencies are preserved. The effect of modification of domestic EPDM with different compositions and different stereoregularities of propylene sequences via heating with an accelerating agent on the characteristics of covulcanizates with BNKS-28 was studied in [15]. It was shown that the structural characteristics of EPDM control the efficacy of modification during the addition of NBRs for improvement of such characteristics of the crosslinked blends as ozone resistance

and physicomechanical parameters. In the case of the sulfur vulcanization of EPDM, the degree of crosslinking of the phases in the interfacial layer cannot be estimated from the deviation of equilibrium degree of swelling Q_r in n-heptane from the additive value, because of the high content of the extracted species in the crosslinked mixture [5, 6]. Therefore, in this study, the structure of the crosslinked blends, the intensity of interfacial interaction, and the degree of crosslinking of the phases for unmodified and modified EPDMs were estimated from the equilibrium swelling in n-heptane and toluene. The ratio between the number of crosslinks and physical junctions was calculated from the data on swelling in the above solvents: $1/Q_h : 1/Q_t = Q_t/Q_h$. In this case, the following speculations are taken into account. The equilibrium swelling of NBR in both solvents decreases in almost direct proportion to an increase in the content of acrylonitrile units (Fig. 2). The mixtures are crosslinked by the same curing system. The equilibrium degree of swelling decreases not only because of the increase in the number of crosslinks in NBR due to an increase in the concentration of the crosslinking agents in the butadiene part of copolymer but also because of changes in the affinity of a solvent for a polymer [18]. Similar dependences for the covulcanizates are nonlinear, and the degree of swelling is higher. Fig. 2 - Equilibrium swelling in (a) toluene and (b) n-heptane for the NBR covulcanizates with (1, 4) Elastokam 6305, (2, 5) EPDM-60(I), and (3, 6) EPDM-40 plotted against the content of AN-units: (1-3) unmodified samples, (4-6) samples modified by sulfur the containing accelerating agent, and (7) NBR vulcanizates. These results are explained by the low compatibility of the components, loosening of the phases, and formation of a transition layer with a density lower than that in the phases and a lower degree of crosslinking of the components. The equilibrium swelling of NBR in n-heptane is low in comparison to that in toluene (Figs. 2a, 2b, curves 7) and lower than Q_r of the EPDM vulcanizates in n-heptane. Hence, the degree of swelling of the covulcanizates in n-heptane primarily reflects the degree of crosslinking of the EPDM phase and the interfacial layer. At the same time, the swelling of elastomers in toluene corresponds to the overall degree of crosslinking. Hence, ratio Q_t/Q_h characterizes the fraction of crosslinks in the EPDM phase and between the phases with respect to the overall number of crosslinks. In the case of peroxide crosslinking of domestic EPDMs [1, 3, 4], there is a linear dependence of this ratio with an increase in the content of AN in NBR (Fig. 3). The slopes of the curves depend on the difference in the intensity of decay in the affinity of these solvents for NBR; hence, this value is not considered. Thus, in the case of the peroxide crosslinking of EPDM (Fig. 3), the fraction of interfacial crosslinking in the overall number of crosslinks slightly decreases with a decrease in the volume of the regions of segmental solubility when the content of the polar units in NBR is increased. When Peroximon F-40 on a carrier, which is incapable of diffusion displacements, is used [1, 3, 4], the degree of crosslinking of the EPDM phase is likely controlled by its concentration. A similar dependence is observed for DSM 712 [3] that contains 48 wt % propylene units and has a degree of isotacticity of 11%. For EPDM R 512 that

contains 32 wt % propylene units and has $\alpha = 20\%$ after peroxide vulcanization, ratio Q_t/Q_h is higher than that for EPDM with a low stereoregularity of the propylene units (Fig. 3). Therefore, for EPDM with a high content of ethylene units and a large value of α , the volume of the interfacial layer in the blends with all NBRs is higher [4, 5]. Fig. 3 - Q_t/Q_h plotted against the content of AN-units in BNR for covulcanizates of (1, 2) NBR with (1) domestic EPDM and EPDM 712 (DSM) and (2) R 512 after peroxide crosslinking. During the sulfur vulcanization of unmodified EPDM-60(I) and EPDM-40, the number of crosslinks in the interfacial layer with respect to the overall number of crosslinks (Q_t/Q_h) decreases with an increase in the content of the polar units in NBR (Fig. 4a). For EPDM-40 with a high degree of isotacticity of propylene microblocks (integration with individual AN units is possible [1, 2, 4]), this dependence is almost linear. For EPDM-60 (I) with a low degree of isotacticity, whose segments are compatible only with the butadiene units of NBR, this dependence is nonlinear. In the blends with BNKS-18 and BNKS-40, the fraction of crosslinks in the interfacial layers is lower than that with EPDM-40. For BNKS-28 with the maximum content of cis-1,4- and 1,2-units assisting compatibilization [1, 2, 4, 17], the volume of regions of segmental solubility for EPDM-60 (I) is increased. For Elastokam 6305 with a high content of diene, which is compatible only with the fragments of chains containing cis-1,4- and 1,2-units of butadiene [4, 11], there is an increase in the fraction of the crosslinks in the interfacial layer with an increase in the content of the above elastomers (Fig. 4b). Fig. 4 - (a) Ratio Q_t/Q_h plotted against the content of AN units for NBR covulcanizates with (1) unmodified EPDM-60(I), (2) unmodified EPDM-40, and (3) EPDM modified by the accelerating agent; (b) Q_t/Q_h plotted against the content of cis-1,4- and 1,2-units for NBR covulcanizates with (1) unmodified Elastokam 6305. Table 3 presents data on the efficacy of protecting NBR from the action of ozone with the use of various EPDMs: the intensity of ozone degradation rate v_{rel} and the strength of the EPDM network, σ^* . In addition, this table shows content m of the sol fraction in n-heptane for peroxide crosslinking or toluene. This table shows data for the blends with EPDM for peroxide and sulfur crosslinking and for modification with the sulfur-containing accelerating agent during introduction of the crosslinking system into NBR. Note that the ozone-resistant effect of the unmodified EPDM during sulfur crosslinking is higher than that during peroxide crosslinking. This reasoning largely for the above blends (Figs. 3, 4). The only exceptions are EPDM-60(I) with a low content of diene and agrees with higher values of Q_t/Q_h Elastokam 7505 with a high Mooney viscosity in the blends with BNKS-28 ($v_{rel} = 2,3$, $\sigma^* = 0$). Table 3 - Characteristics of EPDM vulcanizates and covulcanizates with NBR EPDM Mode of crosslinking v_{rel} σ_x , MPa m, % v_{rel} σ_x , MPa m, % BNKS -28 BNKS -18 BNKS -40 Butadiene-nitrile rubbers - 0 5,3 - 0 4,2 - 0 1,9 Elastokam 6305 Unmodified F-40 2,2 0,11 4,1 11,6 0,34 - 2,0 0 2,3 Unmodified Sulfur 4,5 0,16 21,0 20,5 0,35 22,3 2,1 0,19 18,7 Modified Sulfur 11,2 0,18 4,7 18,3 0,27 3,1 1,8 0,23 11,0 EPDM-60(I) Unmodified F-40 2,8 0,16 4,1 12,1 0,30 - 3,2 0,08 4,1 Unmodified Sulfur 3,7 0 27,0 49,1 0,28 30,9 2,0 0,15 1,0 Modified Sulfur

8,5 0,15 5,0 19,6 0,24 4,1 3,0 0 0 EPDM-40 Unmodified F-40 1,8 0,10 6,9 48,0 0,27 - 2,9 0,15 - Unmodified Sulfur 6,4 0,16 27,0 41,6 0,31 27,7 6,2 0,36 23,0 Modified (at 160°C) Sulfur 5,7 0,13 8,2 4,5 0 4,9 - - - Modified (at 170°C) Sulfur 2,6 0 1,0 - - - - - EPDM-60(II) Unmodified Unmodified Modified F-40 Sulfur Sulfur 1,8 5,7 4,8 0,13 0,18 0,12 3,9 26,3 3,6 - - - - - - - - - - - - - - - The unmodified EPDM-40 with a very high degree of isotacticity of propylene microblocks (29%) is the most efficient for retarding the ozone degradation of NBR (Table 3). Chain fragments of such EPDMs [1-4] are compatible not only with butadiene but also with individual polar units of NBR; as a result, the volume of the interfacial layer increases and the density of crosslinks locally decreases [1-4]. Consequently, in the mixture with BNKS-28 (the maximum volumes of regions of segmental solubility) [1-4, 17], network strength σ^* of EPDM-40, as in other EPDMs, is lower than that in the covulcanizates with NBR but with different contents of AN units. In contrast to EPDM-40, the copolymers with a low stereoregularity of propylene units (Elastokam 6305 and EPDM-60 (I)), which are compatible only with butadiene units, provide less effective protection of the diene elastomer from ozone degradation (Table 3). When the content of diene is high, the protection of BNKS-28 by EPDM-60 (II) is better than that of Elastokam 7505 with a lower content of ethylydenenorbornene and a high Mooney viscosity. In the latter case, during peroxide crosslinking, $v_{rrel} = 1.9$ and $\sigma^* = 0.10$; during sulfur crosslinking, $v_{rrel} = 2.3$ and $\sigma^* = 0$. With consideration for the high initial efficacy of EPDM-40, its modification by the sulfur-containing accelerating agent does not lead to improvement in the ozone resistance of the blend. When the heating temperature is increased from 160 to 170°C for the mixtures of BNKS-28 with the accelerating agent and sulfur, the ozone resistance decreases. In [15], this effect has been explained in terms of EPR spectroscopic data. It was shown that EPDM-40 with a high degree of isotacticity of propylene units contains ordered regions formed by propylene sequences and regions with a mixed composition that contain ethylene and propylene chain fragments. The heat treatment of EPDM-40 during its modification with the dissociation of propylene supramolecular structures (the maximum dissociation temperature is 170°C [19]) and their formation during cooling leads to the concentration of chemical reagents in relatively small (by volume) disordered regions. As was shown in [15], with an increase in the modification temperature, the molecular dynamics of the EPDM-40 phase in the covulcanizates slows down. This behavior attests the intra phase crosslinking of EPDM, which is confirmed by a marked decrease in the content of the sol fraction in the covulcanizates with an increase in the temperature of heating with the accelerating agent and sulfur (Table 3). As a result, the compatibilization of components is hindered, and the ozone protective effect of EPDM decreases. In contrast to the modification of EPDM-40, the modification of Elastokam 6305 and EPDM-60(I) in the mixtures with BNKS-28 with a high content of cis-1,4- and 1,2-units by the accelerating agent and sulfur [4, 15] leads to an increase in the ozone resistance of the blends with regard to v_{rrel} and σ^* (Table 3). In the mixtures with BNKS-18 and BNKS-40 with a

higher order of trans-1,4 isomers (with a lower content of cis-1,4 and 1,2- units), their efficacy does not increase, because of reduced compatibilization [17]. In the least compatible crosslinked mixtures with BNKS-40 with the minimum volume of regions of segmental solubility, the modification of Elastokam 6305 provides a moderate effect, while EPDM-60(I) with a low content of diene reduces compatibilization and crosslinking of the phases and σ^* decreases to zero (a strain of 30%). According to the EPR data, the molecular mobility in the vulcanizates of Elastokam 6305 and its covulcanizates with NBR before and after modification with the sulfur-containing accelerating agent is the same or higher than that in EPDM-40 [15]. The above EPDMs do not contain the ordered structures of the propylene units that break down at high temperatures. A complete dissociation of fluctuation structures formed by ethylene units occurs at 140°C, which is below the vulcanization temperature. The heat treatment of the elastomer (160°C) does not lead to any deterioration of its compatibilization with NBR. The modification of EPDM-60(II) with a high content of diene turns out to be inefficient for improvement of the ozone resistance of covulcanizates (Table 3). In addition, the modification of Elastokam 7505 with a high Mooney viscosity does not provide any increase in the ozone resistance of the blend based on BNKS-28 ($v_{rel} = 2.6$ and $\sigma^* = 0$). When the modified EPDMs are used, the content of the sol fraction in the covulcanizates markedly decreases owing to an increase in the degree of crosslinking of the EPDM phase. For EPDMs modified by the sulfur-containing accelerating agent, ratio Q_t/Q_h is almost the same (Fig. 4a). Differences in the intensity of the interaction of EPDM with the NBR phase of different polarities diminish because they are controlled by the number of the bonded radicals of the accelerating agent. These radicals interact with sulfur with the participation of the vulcanization promoter ZnO, α -methylene groups of the diene unit, and the ternary carbon atoms of the AN unit. As a result, the number of crosslinks along the entire interfacial boundary (not only in the regions of segmental solubility) and the overall number of crosslinks increase. Therefore, ratio Q_t/Q_h for the blends with the modified EPDMs does not reflect the degree of crosslinking of the components in the interfacial layer. This evidence shows that, when EPDM is modified with the sulfur-containing accelerating agent, the ozone resistance increases only for the BNKS-28-based covulcanizates using the elastomers with the preferential atactic configuration of propylene units and contents of diene groups of 4 and 5.4%. Therefore, it may be concluded that a negative effect occurs owing to the introduction of accelerating groups into EPDM with a high degree of isotacticity of propylene units that, as was shown earlier, are initially compatibilized not only with butadiene but also with AN units [1-4, 15] and that ensure better protection of the polybutadiene matrix from ozone attack. The modification of EPDM critically changes the physicomechanical characteristics of the covulcanizates. Figure 5 presents conditional tensile strength σ_{br} for (a) the blends with unmodified EPDM, (b) EPDM modified by the sulfur-containing accelerating agent. Figure 6 presents the relative elongation at break, ϵ_{br} , for the

same species. For the unmodified EPDMs, σ_{br} slightly increases with an increase in the overall content of cis-1,4- and 1,2-units of butadiene in NBR, and this increase is associated with the structure of the interfacial layer and the increase in its volume, density, and number of crosslinks [1, 2, 15]. This reasoning agrees with the speculations that, in polymer blends, the interfacial layer is the weakest structural element [7, 8]. Fig. 5 - σ_{br} of the NBR covulcanizates plotted against the content of (a) cis-1,4- and 1,2-units and (b, c) AN units: (a) (1) unmodified Elastokam 6305, (2) EPDM-60(I), and (3) EPDM-40; (b) sulfur modified accelerating agent For the modified EPDMs, σ_{br} increases with an increase in the content of AN units in NBR. This result validates the conclusion that the degree of crosslinking of the components along interfacial boundary increases during the addition of radicals of the accelerating agent. The maximum increase in the conditional tensile strength is observed after mixing with the modified EPDM with a low degree of isotacticity of propylene units and an increased content of diene (Elastokam 6305). Fig. 6 - (a) ϵ_{br} plotted against the content of AN units for NBR covulcanizates with (1, 4) Elastokam 6305, (2, 5) EPDM-60(I), and (3, 6) EPDM-40 for (1-3) unmodified samples and (4-6) samples modified by the sulfur-containing accelerating agent For the blends with unmodified EPDM, the relative elongation at break is practically independent of the content of AN-units. For EPDM modified by the sulfur-containing accelerating agent, ϵ_{br} increases with an increase in the content of AN. Therefore, the effect of the structure of EPDM (Table 1) on the features of the development of the interfacial layer in the crosslinked blends with NBR, which are observed during peroxide crosslinking, is preserved in the case of sulfur vulcanization and modification of EPDM. The best results are obtained for the modification of EPDM with a low stereoregularity of propylene units. When the degree of isotacticity of the propylene sequences is high (EPDM-40), the content of diene is high (EPDM-60(II)), and the Mooney viscosity is high (Elastokam 7505), the modification of the copolymer does not provide any increase in the ozone resistance. In many cases, modification results in improvement of the rubbery characteristics and causes an increase in the conditional tensile strength. Conclusion Not only the composition of EPDM but also the stereoregularity of propylene units affect the efficacy of the modification of EPDM during its sulfur vulcanization in the blends with NBR. The modification of EPDM to increase the ozone resistance of the crosslinked blends with NBR leads to the improvement of the characteristics of covulcanizates only when certain brands of EPDM are used.