Introduction The problem of increasing the stability of unsaturated rubbers [in particular, of the butadiene-acrylonitrile rubbers (NBR)] with respect to ozone by blending them with saturated polymers was extensively studied [1-5]. Only a small proportion of the saturated polymers are capable of providing the ozone protection [PVC, perchloro vinyl polymer, ethylene-propylene diene terpolymer (EPDE), ethylene-propylene rubber (EPR)] [1-7]. There is no commonly accepted opinion concerning the mechanism of the ozone-protective action. In particular, Zateev [6] showed that effective protection is provided only if the polymer forms a continuous phase and is highly homogenized. Khanin [7] explained the protective properties by the formation of a surface layer in elastomer enriched with the saturated polymer. It was established [1-5] that necessary conditions for the obtaining of materials with high ozone resistance include a sufficiently high degree of homogeneity and the formation of a continuous framework of the ozone-resistant component (achieved at a 30% PVC content in the blend). In the works [4, 5] was studied the relation of ozone resistance to the volume and structure of the interfacial layer and the amounts of crosslinks in the interlayer for covulcanizates of acrylonitrile-butadiene rubbers 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 ozone resistance 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. As the content of nitrile groups in NBR grows, the polarity of the rubber and, hence, its compatibility with polar PVC, tend to increase [1-3, 8-16]. However, this is accompanied by the loss of elasticity, a drop in the cold stability, and a decrease in the electrical properties of vulcanizates [1]. In this connection, there are many works devoted to attempts made to improve the miscibility of PVC with rubbers having medium contents of nitrile groups. Experiments using various blending techniques (low- and high-temperature mechanical blending, latex coagulation, coprecipitation from solution) [10-16] showed that the final blends may acquire, depending on the blending method used, the properties of both a homo- and heterogeneous system. The mechanical blending typically leads to nonequilibrium systems, whereby the two phases formed by each of the components are separated by a transition layer formed as a result of mutual diffusion. This layer is manifested in thermograms [10, 11], NMR spectra [12, 13], and the temperature dependence of the mechanical loss tangent [14]. The purpose of this work was to establish a relationship between morphology of the interphase contact region and the ozone resistance of vulcanized blends and to refine the above mechanism of the ozone-protective thermoplast action in the systems of components with various degrees of compatibility and homogeneity. Likewise we have performed this work in order to establish the most important structural and technological parameters affecting stability of the PVC-NBR system with respect to ozone. For this purpose, we have varied polarity of the NBR matrix by changing the content of nitrile groups and PVC (obtained by emulsion or suspension polymerization) and employed the technology of low- temperature blending followed by high-temperature treatment of the blend to facilitate the mutual diffusion of components at the phase boundaries and high-temperature mechanical blending. Experimental The experiments were performed using vulcanized blends of NBR (commercial SKN-18, SKN-26, and SKN-40 grades containing 18, 26, and 40% of acrylonitrile units) and PVC (obtained by emulsion or suspension polymerization-PVC-E and PVC-S, respectively) with the 70 : 30 ratio of components. The rubbers with 26-28% content of acrylonitrile groups were represented by Paracril BJ (Uniroyal Co., USA) containing 28% of acrylonitrile units (series I), SKN-26 (series II), and SKN-26M (series Ш). Paracril BJ is characterized by the Mooney viscosity 50 ± 7 at 118°C. The samples of SKN-26 and SKN-26M had Mn=(1-3) x 10s, the Mooney viscosities above 70 and 55, and the Defo hardnesses about 20 and 10 N, respectively. PVC-E was represented by a commercial PVKh-E- 6250-Zh grade with Mn= (7.0-7.5) x 104. The PVC-S samples were as follows: PVC VISTA 5305 grade (USA)-a GAS 980-Z-86-2 homopolymer with an intrinsic viscosity of 0.72 (series I) and PVC S-7058M grade with Mn= 6.4 x 104, Mw = 2 x 105, and a specific viscosity in dichloroethane of 1.31 (series II and III). SKN-26 and SKN-40 were blended with PVC-E at 40°C as described in [17], followed by treatment in a thermostat at 120, 140, or 160°C (series A). Analogous procedures were used to obtain the blends of NBR with PVC-S (series B). The high-temperature blending of NBR samples containing 26-28% of acrylonitrile (AN) with PVC-S was performed by 8-min treatment at 170°C in a mixer operated at 60 rpm (series C). The treatment was performed in the presence of thermostabilizing agents: an epoxidated soybean oil Paraflex G-62 (3 wt fractions) for Paracril BJ (series I) or an ED-20 epoxide resin (2 wt fractions) for SKN-26 (series II) and SKN-26M (series П1). For the comparison, one sample was prepared by blending SKN-26 with PVC in the same mixer operated at a reduced speed of 30 rpm. The blending with vulcanizing system was performed according to a conventional roller technology for 20 min at 40°C, and the vulcanization was effected for 20 min at 165°C. The vulcanizing systems in series A and B, C were as follows (wt fractions): thiuram, 1.2 (A) and 1.4 (B, C); sulfenamide C, 1.2 (A) and 1.4 (B, C); stearic acid, 0.6 (A) and 0.7 (B, C); zinc oxide, 3.0 (A) and 3.5 (B, C); calcium stearate, 2.0 (A) and 0 (B, C). The structure and ozone resistance of vulcanized blend samples were studied by measuring the rate of stress relaxation in air (vph, physical relaxation) and in an ozone-air mixture (v) with the ozone concentration 10-5 mol/1. The relaxation measurements were performed on an IKhF-2 relaxometer [17, 18]. The temperature dependence of the relaxation rate was studied in the range from 303 to 363 K on 30%-strained samples. This deformation level is close to a critical value, for which a maximum rate of the ozoneinduced degradation of rubbers is observed [19, 20]. The stress relaxation rate as function of the sample deformation level was studied at 303 K. The samples had the form of 0.2-0.4-mm-thick plates. The experimental error of measurement of the relaxation rate was ±10%. The relaxation rates were averaged over the results of five independent determinations. The dynamics of molecules in the blend compositions was studied by the EPR spin-probe technique, using 2,2,6,6-tetramethyl-l-piperidinyloxy (TEMPO, radical 1) and TEMPO-4-benzoate (radical 2) as the spin probes. Radical 1 was introduced into vulcanized samples from the vapor phase, by exposure for 1-2 days at room temperature, followed by equilibration for 1-2 weeks. Radical 2 was introduced into the samples from an acetone solution, followed by the solvent removal in vacuum at 100°C. The radical concentration in the samples was 10-4 mol/1. The X-band EPR spectra were measured using an EPR-V spectrometer. The rotational mobility of nitroxyl radicals was characterized by the corresponding correlation time. Results and discussion The oxidation process is initiated at the surface. Since the rate of ozone diffusion in polymers is extremely small [19], this oxidizing agent can penetrate deep into a sample only via cavities, pores, voids, and cracks. Mechanism inhibiting the ozone-induced degradation of unsaturated rubbers must be operative in their blends with PVC can be related to a phase structure of the blend and certain morphological features in the region of contact between the blend components. In the previous works [4, 5, 17], we have demonstrated a relationship between the ozone-protective effect of a thermoplastic component and the structure of an interphase transition layer [17, 21, 22]. The protective effect of PVC was explained by termination of the growth and coalescence of the ozone-induced microcracks in the interphase transition layer. The protective effect decreases with increasing temperature and deformation of a blend because of activation of the segmental mobility in NBR and PVC [17] as a result of the microphase separation occurring in the transition layers-the weakest structural elements of the strained material. Thus, a high energy of interphase adhesion in blends of compatible components is a factor that imparts strength to the transition layer and renders a vulcanized blend resistant with respect to the ozone-induced cracking. The compatibility of NBR and PVC depends on the content of polar AN units in the rubber. Rubbers containing 26 and 40% of AN units (SKN-26 and SKN-40) are compatible with PVC. A lower content of AN units (SKN-18) results in a limited miscibility of components, and these blends exhibit very low ozone resistance [1-3]. The ozone-protective thermoplast effect depends on the degree of blend homogeneity [1-3, 17]. The homogeneity of NBR-PVC blends depends on the method of thermoplast preparation and drops sharply on the passage from PVC-E to PVC-S. This is explained by differences in the size, structure, and density of PVC particles and the amount and composition of impurities [23, 24]. A homogeneous blend of NBR with PVC-S can be obtained by high-temperature blending in a mixer [25]. The compatibility and phase structure of NBR-PVC blends were studied by various methods [10-16]. It particular, it was found [12, 14] that the temperature dependence of the mechanical loss tangent of the blends of NBR (with different polarities) and PVC exhibit peaks related to the mechanical vitrification of rubber and plastic components. An additional (intermediate) maximum reflecting the ψ-process of activation of the segmental mobility of macromolecules in the transition layer was reported in [16, 26]. The temperature of the ψ-transition in a blend exhibits a shift depending on the degree of component compatibility [17] and on the temperature of heat-treatment of the SKN-26 and SKN-40 rubbers blended with PVC-E in series A (Fig. 1). The temperature effect was less pronounced for the most compatible blend of SKN-40 (Fig. lb) and a system of limited compatibility based on SKN-18 (Fig. 1c). For the blends of SKN-26 (Fig. la), the maximum activation energies and temperatures of the ψ-transition (and, hence, a maximum density of the interphase transition layer) were observed in the samples treated at 120°C. This regime of blending is optimum for the given system. Treatment at a higher temperature (especially at 160°C) is accompanied by HC1 evolution from PVC and the thermal vulcanization of NBR. This results in increasing hardness of the blend and decreasing homogeneity of the component distribution upon introduction of the vulcanizing system, which eventually leads to lower a degree of the sample homogeneity. The absence of other transitions is indicative of a sufficiently high homogeneity (single-phase character) of the blends. An increase in the compatibility (miscibility) of NBR and PVC with increasing polarity of the rubber is manifested by the increasing homogeneity of the mixture provided otherwise equal conditions (i.e., the same thermostat temperature). The higher the compatibility, the lower is the PVC content at which the phase inversion takes place (due to a higher dispersity of PVC particles), with the corresponding change in the transition layer structure. This change accounts for the different physicomechanical and relaxation properties of high-compatibility (NBR-26 or NBR-40 based) and limited-compatibility (NBR-18) PVC- NBR systems. As is seen from Fig. 1, the plots of the stress relaxation rate versus temperature show evidence of a relaxation transition (at 30-40°C for SKN-26-PVC and 25-30°C for SKN -18-PVC and SKN-40-PVC), which is absent in the pure rubber. Therefore, the appearance of this transition is related to the presence of a second component (PVC) in the blend. An increase in the physical stress relaxation rate with the temperature can be explained by a change in the relaxation mechanism caused by the activation of the segmental mobility chains entering into a looser transition layer. Similar phenomena (ψ -transition), related to the structure of microphases and transition layers, were observed in the NBR-PVC systems by various methods (mechanical loss tangent, DTA, wideband NMR, and acoustic measurements). Using the temperature dependence of the physical stress relaxation rate above the transition point, we have determined the activation energies for the segmental mobility of in the transition layer. This energy had close values for the NBR-26-PVC and NBR-40-PVC systems containing 20-30% PVC-E (20 and 18-19 kJ/mol, respectively) and was somewhat lower for NBR-18-PVC-E (13 kJ/mol). Thus, the ψ -transition in NBR-18-PVC vulcanizates is observed at a lower temperature and has a lower activation energy as compared to those in the systems based on NBR-26 and NBR-40. This is consistent with the above assumption concerning facilitated increase of the segmental mobility in loose transition layers in comparison to the compatible systems. (103/T),K Fig. 1 - Temperature dependence of the rate of physical stress relaxation at 30°C in 70 : 30 (a)

SKN-26-PVC, (b) SKN-40-PVC and SKN-18 with PVC-E blends obtained by low-temperature blending followed by the heat-treatment in a thermostat at T = 120 (1), 140 (2), or 160°C (3) (series A, ε = 30%) We should like to emphasize the coincidence of the temperature interval of the ψ -transition with the published data [10-16]. The NBR-18-PVC system of limited-compatibility shows an additional transition in the region of 60°C, which is not observed in the systems with NBR-26 and NBR-40. This difference can be explained by a higher homogeneity of the latter blends. The transition in the region of 60°C - is λ-relaxations related to formation of fluctuation structures involving trans-butadiene units [27, 28]. The experimental data obtained show evidence that the method of stress relaxation rate determination is sensitive to phase transitions and structural changes in the transition layer. Figure 2 shows the plots of the strain at break (εb) and the conventional stress at a 300% strain (σ300) determined at room temperature versus the PVC-E content in its blends with NBR-18, NBR-26, and NBR-40 obtained upon the treatment at 120°C. As is seen, the strain at break decreases with increasing content of the rigid-chain polymer in all rubber compositions. After the formation of a more or less (depending on the polarity of rubber) developed spatial network of the PVC-E particles. The εb value attains a plateau. As the compatibility of rubber and thermoplast increases, the εb plateau is reached at a lower PVC-E content: 30% for NBR-18 and NBR-26 against 20% for NBR-40. In all the composition ranges, the strain at break is much higher for vulcanizates based on the rubbers of higher polarity (NBR-26, NBR-40) than for the system based on NBR-18. This is evidence of a stronger contact between the blend components in the former two systems as compared to the latter one. σ300, kgf/cm2 [PVC], % Fig. 2 - The plots of (a) conventional stress σ300 and (b) strain at break εb vs. PVC-E content in vulcanized blends based on (1) NBR-18, (2) NBR-26, and (3) NBR-40 (T=293 K; air) A difference between the structures of vulcanizates is well manifested in the plots of O300 versus composition. In the NBR-18 based composition, the a300 value monotonically increases with the PVC-E content, while the plots of the NBR-26-PVC-E and NBR-40-PVC-E systems have an S-like shape. In the region of a 30% polymer content, the modulus increases 6-7 times as compared to the values typical of the pure rubber and reaches a level characteristic of the PVC-E component. In the NBR-18 based system, the isolated coarse PVC-E particles play the role of a reinforcing filler. Compatible blends based on NBR-26 and NBR-40 exhibit phase inversion at a PVC-E content of 20-30% [26,29,30]. This implies the formation of a strong spatial framework of polymer molecules, which imparts high strength and hardness to the vulcanizates. Below this threshold concentration, the PVC particles are isolated from one another and produce no reinforcing effect. The size of the thermoplast particles is apparently comparable to the radius of curvature (below 10 pm) at the crack vertex, at which the reinforcing effect vanishes [26]. We may suggest that PVC is partly dispersed on a molecular level, while the main part enters into molecular agglomerates not possessing the properties of a microphase. These systems are characterized by the especially large role of the transition layer between phases. The pattern of variation of the mechanical properties of blends with the composition shows correlation with the behavior of the ozone resistance of vulcanizates (Fig. 3) tested at a strain of 30% and a temperature of 60°C (for the NBR-PVC-E blends heat-treated at 120°C). These conditions of testing were selected because the 30% tensile strain is close to the critical level featuring the maximum rate of the ozone-induced rubber degradation. A comparison of the pattern of variation of the σ300 stress (Fig. 2) to the curve of the stress relaxation rate versus composition (Fig. 3), which also has an S-like shape, shows that the formation of a continuous spatial framework of PVC molecules in the compatible systems leads to a jumplike increase in the ozone resistance by two orders of magnitude: the rate of stress relaxation due to the ozone-induced cracking decreases to a level corresponding to the physical stress relaxation rate. The limited-compatibility system NBR-18-PVC-E exhibits, irrespective of the composition, a higher stress relaxation rate in the ozone-containing atmosphere (that is, a lower ozone resistance) as compared to that of the pure NBR-18 rubber. Apparently, the isolated coarse PVC particles may serve as stress concentrators in the extended elastomer matrix weakly bound to these particles via the transition layer. This circumstance favors the accelerated reaction between ozone and the double bonds of rubber [20]. Fig. 3 - The plots of stress relaxation rate in ozone vs. PVC-E content in vulcanized blends based on (/) NBR-18, (2) NBR-26, and (3) NBR-40 (T = 333 K; ε= 30%) Thus, our results obtained by the method of stress relaxation confirm the previous data that PVC provides protection of the compatible rubbers from the ozone-induced cracking only when its concentration in a rubber-PVC blend is not less than 30% [1-3, 6, 7]. Another condition for the protective effect of PVC consists in homogeneity of the system. The replacement of PVC-E by PVC-S results in sharply increasing heterogeneity of the blend structure and decreasing ozone resistance of the vulcanized samples upon the treatment at 120°C (series B). Figure 4 shows the plots of stress relaxation rate in the ozone-containing atmosphere versus deformation at 30°C. A sharp drop of the ozone resistance is evidence of a reduced interphase adhesion and easy phase separation. It should be noted that vulcanized samples prepared from the Paracril BJ robber exhibit a higher ozone resistance as compared to that of the domestic vulcanizates. Indeed, the former material is characterized by a low relaxation rate in the ozone-containing medium up to a deformation level of 40%, whereas the latter samples cannot withstand even smallest tensile deformations. Fig. 4 - The plots of stress relaxation rate at 30°C in an ozone-containing atmosphere vs. strain for vulcanized 70 : 30 blends of various NBRs (series I-III) with PVC obtained by low-temperature blending followed by the heat-treatment in a thermostat at 120°C (series B) Vulcanizates possessing very high ozone resistance were obtained by the high-temperature blending of NBR containing 26-28% of AN units with PVC-S (series C). The temperature dependence of the stress relaxation rate in these samples measured in an ozone-containing atmosphere (Fig. 5) exhibit a degenerate ψ-transition except the blend with

SKN-26 M (cf. with a curve for SKN-26 blended with PVC-E at low temperature and treated at 120°C in series A). Degeneracy of the ψ-transition can be considered as evidence of a higher degree of homogeneity provided by the high-temperature blending. Apparently, PVC in the samples of series C is dispersed either on a molecular level or in the form of very small molecular associates. The transition layer has a small total volume and its properties are not significantly manifested in macroscopic characteristics such as the stress relaxation rate. The high ozone resistance of these blend systems is confirmed by data on the effect of deformation on the rates of the physical relaxation and the relaxation process in ozone (Fig. 6). As seen, the stress relaxation in both media proceeds apparently by the same mechanism. ln v {min-1] 3.0 3.4 (103/Г), к-1 Fig. 5 - Temperature dependence of the rate of stress relaxation in an ozone-containing medium for 70: 30 blends of various NBRs (series I-III) with PVC obtained by high-temperature blending for 8 min at 170°C (Series C, e = 30%; see the text for explanations) The mechanism of the ozone-protective effect of PVC in a highly homogeneous system is probably somewhat different from that described above. For a nearly molecular mixing, the homogeneity of a thermoplast distribution in an elastomer matrix markedly increases. The matrix has proved to be rather uniformly filled with stretches of PVC macromolecules, which hinder the opening of submicrocracks and inhibits the ozone penetration deep into the sample. A difference in the structure of vulcanizates in series B and C is also manifested by their mechanical properties. Insufficiently homogenized samples of series B, having poorly-developed loose transition layer, are characterized by low ultimate strength (not exceeding 7.7 MPa), whereas the strength of homogeneous samples in series C is 2.5-7 times higher (reaching 17-24 MPa). The most ozone-resistant samples in series B (Fig. 4) exhibit a maximum strength of 7.7, 2.6, and 3.6 MPa in series I-Ш, respectively. In heterogeneous blends, both characteristics are apparently related to the properties (strength) of the transition layer. Fig. 6 - The plots of (1) the physical relaxation rate and (2) the stress relaxation rate in an ozone-containing atmosphere at 30°C versus strain for vulcanized 70: 30 blends of various NBRs (series I-III) with PVC-C obtained by high-temperature blending at 170°C (series C) The replacement of SKN-26 by SKN-18 (incompatible with PVC) in series C leads to a dramatic decrease in the ozone resistance of vulcanizates (the samples are broken within 3-5 min). Therefore, even forced high-temperature blending of thermodynamically incompatible components cannot ensure the obtaining of ozone-resistant blends. This is related to morphological features of the interphase contact regions. The interphase contact regions may have the structure of two types [30]. We may suggest that a high ozone resistance is inherent in the elastomer-polymer pairs featuring a structure with two-component transition layer and the segmental solubility of components in this region. The data of Fourier-transform IR spectroscopy reported in [9] showed that chlorine atoms of PVC and nitrogen atoms of NBR participate in a dipole-dipole interaction and, in addition, hydrogen bonds are formed between the two polymers. These contacts account for the compatibility of polymers in this system. Morphology of the transition layer may apparently sharply vary with decreasing content of AN units in the rubber component. Heating of the rubber results in thermal vulcanization [31, 32]. The plasticization of NBR with PVC at 170-175°C leads to the chemical interaction between the active groups of rubber and thermoplast, which results in the formation of grafted copolymers [33-35]. Fig. 7 - Temperature dependence of the rotation correlation time of nitroxyl radicals 1 and 2 in vulcanized 70:30 NBR- PVC blends: (a) SKN-26 with (1) radical 1 and PVC-E (open symbols) or PVC-S (60 rpm, black symbols), (2) radical 1 and PVC-S (30 rpm), (3) radical 2 and PVC-E, (4, 5) radical 2 and PVC-S (30 and 60 rpm, respectively); (b) SKN-18 with (1) radical 1 and PVC-E (open symbols) or PVC-S (60 rpm, black symbols), (2) radical 2 and PVC-E, (3) radical 2 and PVC-S (60 rpm) The above notions concerning the structure of NBR-PVC blends of various homogeneity are also confirmed by the results of our investigation of the rotational mobility of nitroxyl radicals 1 and 2 as function of the temperature (Fig. 7). As seen, the rotation correlation times τc of both radicals are smaller in the blends with SKN-18 than with SKN-26, which is explained by the matrix being more rigid in the latter case. The plots of τc versus temperature obtained for the TEMPO radical (Fig. 7) exhibit breaks corresponding to the relaxation transitions in the interphase layer (30- 35°C) and in NBR (50-60°C) [27, 28] and large elements of the spatial network of PVC (~80°C). Therefore, the TEMPO radical adsorbs in a sufficiently large amount within the most mobile regions of these structural elements. The positions of these breaks allow us to judge on the blend structure and the size of homogeneous regions in the polar component framework. The blends of SKN-18 obtained by any method are highly heterogeneous, whereby PVC occurs in the form of both small and coarse inclusions, possessing the properties of macrophase, as indicated by the transition in the glass transition region of bulk PVC at 80°C. Note that the same transition is observed in a heterogeneous blend of SKN-26 with PVC obtained upon the high-temperature blending at a reduced mixer speed (30 rpm, see table, sample 7). In this blends is observe the transition in the region of 60°C - is λ-relaxations related to formation of fluctuation structures involving trans-butadiene units [27, 28]. This is evidence of a high polydispersity and the presence of coarse particles of the thermoplast. The resulting vulcanizates exhibit very low ozone resistance. In contrast, the highly homogeneous ozone-resistant blends exhibit no breaks in this temperature region, which can be interpreted as indication of a sufficiently high degree of PVC dispersion in these systems