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The Role of Defective Structures of Butadiene-Nitrile Elastomers in Interphase Interactions in Mixtures with Ethylene-Propylene-Diene Rubbers

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Abstract—The deviation of the equilibrium degree of swelling of nitrile-butadiene and ethylene-propylene-diene rubbers (NBR and EPDM, respectively) in the selective *n*-heptane solvent (the Zapp method) from the additive values, which characterizes the density and volume of the interphase layer, was determined. This quantity was correlated with the free volume fraction in the defects of the NBR structure formed by acrylonitrile units and stereoirregularities of the butadiene copolymer. The increase in the free volume fraction in the defects calculated from the individual contribution of each structural unit favors the formation of a more developed interphase layer, whose density and volume also depend on the content of flexible ethylene units in EPDM and the degree of isotacticity of the propylene sequences.

Keywords: nitrile-butadiene rubber, ternary ethylene-propylene copolymer, structure defects, chemical cross-linking, microstructure, free volume fraction, compatibility, ozone resistance

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INTRODUCTION

The nature of the sorption centers of low-molecular compounds in polymers (these include the topological inhomogeneities: nodes, folds, intertwining of macromolecules, chain ends, etc.) is of great interest for researchers. The structure of defective microregions in which the paramagnetic probes and solvents absorb in statistical and microblock-type copolymers of butadiene with acrylonitrile of different polarities was determined in [1, 2]. It was shown that the sorption centers are structure defects formed by acrylonitrile (AN) units and *cis*-1,4- and 1,2-butadiene units, which are stereoirregularities of the butadiene component, which is predominantly in the *trans*-1,4-configuration [1–3]. In the ordered structures formed by the *trans*-1,4-butadiene units, the absorption of low-molecular substances is hindered. It was shown that the sorption centers in rubbers and vulcanized rubbers based on them are identical, which indicates that the structure of defects does not change when a vulcanizing system and other low-molecular additives are introduced or when cross-linking is performed at high temperatures (150°C) under pressure.

Earlier [3], it was assumed that the interphase layer in mixtures of elastomers can also form with participation of defective structures of nitrile-butadiene rubbers (NBRs). A number of monographs and reviews

[4–12] were devoted to a study of compatibility of polymers and the regularities of interphase interaction in their mixtures; in particular, they considered the interphase interaction of polymers with different polarities, including mixtures of NBRs with ethylene-propylene copolymers. The possibility of improving the compatibility of these systems by introducing modified polyethylene (for example, chlorinated and chlorosulfonated) as compatibilizer or by modifying the components of the mixture with a mercapto group and oxazoline was shown in [8–12]. To investigate the properties of mixtures, the authors used an ultrasonic interferometer, atomic force microscopy, differential scanning calorimetry, IR Fourier spectroscopy, and dynamic mechanical analysis.

The present study deals with the role of defective NBR structures with different contents of AN units and free volume fractions in them calculated from the individual contribution of each structural unit in the formation of an interphase layer in mixtures with ethylene-propylene-diene rubbers (EPDM) of different comonomer compositions and degrees of isotacticity of propylene units. The density and volume of the interphase layer were determined from the deviation of the equilibrium degree of swelling Q_{eq} of covulcanizates in the selective *n*-heptane solvent from the additive values (Zapp method) [13]. The dependence of this

Table 1. Isomer composition of butadiene units in butadiene copolymers with AN of various grades

NBR grade	Content of units, %		
	<i>trans</i> -1,4	1,2	<i>cis</i> -1,4
NBRC-18	82.0	8.2	9.8
NBRC-28	76.4	14.4	9.2
NBRC-40	93.0	4.4	2.6

The absorption coefficient (L/(cm mol)) is 195.5 for the 910 cm^{-1} band (1,2-units); 77.7 for 967 cm^{-1} (1,4-*trans*-); and 32.2 for 730 cm^{-1} (1,4-*cis*-) [15].

quantity on the free volume fraction in the defects of the NBR structure was investigated. The correlation between these quantities is direct evidence for the participation of defective structures in the formation of the interphase layer and makes it possible to determine the structure of defects involved in the interphase interaction in a particular mixture depending on the composition of copolymers and isomerism of unit components.

EXPERIMENTAL

The objects of investigation were NBR covulcanizates with EPDM of different grades. The industrial NBR of NBRC-18AMN, NBRC-28AMN, and NBRC-40AMN grades was used with 18, 28, and 40% polar acrylonitrile units, respectively. The characteristics of these rubbers correspond to the specifications. The Mooney viscosity at 100°C is 40–50, 45–65, and 45–70 arb. units, respectively. The content of *trans*-1,4-, 1,2-, and *cis*-1,4-butadiene units was determined by IR spectroscopy from the absorption bands at 967, 911, and 730 cm^{-1} , respectively [14]. The isomer content was calculated using the extinction coefficients

from [15] (Table 1). The error of the isomer content of butadiene units is ~5%.

The EPDMs used included Royalen R512, R505, and R521 (Uniroyal, United States); DSM 778, 714, and 712 (Holland); EPDM-40 and EPDM-60(II) (Ufaorgsintez, Russia); and EPDM-60(I) and Elastokam 6305 (Nizhnekamskneftekhim, Russia). The content of ethylene and propylene units and diene component (ethylidenenorbornene (ENB) in Royalen and DSM and dicyclopentadiene in EPDMs of Russian production), the degree of isotacticity of the propylene units, and Mooney viscosity are shown in Table 2. The degree of isotacticity of the propylene units was determined by IR spectroscopy [16, 17]. In EPDMs of Russian production, the content of catalysts, emulsifiers, and stabilizers corresponds to the specification. The nitrile-butadiene rubbers were combined with EPDM in a ratio of 70 : 30 wt %.

The composition of the vulcanizing system for NBR (mass fractions) is as follows: stearic acid 2.0, sulfenamide C 1.5, zinc oxide 5.0, and sulfur 0.75. The EPDM elastomers were vulcanized with peroximone F-40 on a substrate in an amount of 5.5 mass fractions. Each rubber was mixed with its vulcanizing system on rollers at 40–60°C for 15 min. Then a mixture of rubbers was obtained under the same conditions. The mixtures were vulcanized at 170°C for 15 min. The mixing of rubbers and vulcanization occurred with partial redistribution of sulfur-containing vulcanizing agents and covulcanization of rubbers [18, 19].

The density and volume of the interphase layer and the number of cross-links in it were determined by the swelling method in a selective solvent *n*-heptane [13, 20]. The components of the systems under study differ in the polarity and structure of the nonpolar sections of the chains. The compatibility of the polymer components can be estimated from the solubility parameter $\delta = \text{CED}^{1/2}$, where CED is the cohesion energy

Table 2. Composition, degree of isotacticity of propylene units, and Mooney viscosity of the ethylenepropylenediene elastomers

EPDM grade	Ethylene/propylene, wt %	Degree of isotacticity, %	Diene content, wt %	Mooney viscosity, arb. units	
				100°C	125°C
R512	68/32	20	4	80	57
R505	57/43	24	8	82	55
R521	52/48	22	5	45	29
DSM 778	65/35	13	4.5	—	63
DSM 714	50/50	12	8	—	63
DSM 712	52/48	11	4.5	—	63
EPDM-40	70/30	29	4	36–45	—
EPDM60(I)	60/40	13	4	60	—
Elastokam 6305	74/26	9.5	5.4	67	—
EPDM-60(II)	60/40	13	6.7	62	—

density [21]. The composition and structure of NBR affect the solubility parameter; $\delta \times 10^{-3}$ ((cal/m³)^{1/2}) is 8.7 for the composition 82 : 18, 9.38 for 75 : 25, 9.64 for 70 : 30, and 10.30 for 61 : 39 for butadiene-acrylonitrile copolymers; 14.5 for polyacrylonitrile; 7.95 for ethylene-propylene copolymers; 8.44 for polybutadiene; and 7.4 for *n*-heptane. Thus, *n*-heptane is a selective solvent for the nonpolar components of the mixture.

The deviation of the equilibrium degree of swelling from the additive value $-\alpha$ was calculated by the equation [20]

$$-\alpha = [(Q_{\text{add}} - Q_{\text{eq}})/(Q_{\text{add}} - Q_2)] \times 100\%,$$

where Q_{add} is the additive value of swelling in a given solvent calculated from the equilibrium degree of swelling of vulcanizates for each rubber; and Q_2 is the swelling fraction of the second elastomer (NBR). The vulcanization of EPDM with peroximone F-40 on a substrate allows us to obtain vulcanizates with a minimum amount of leachable substances during the swelling in a solvent. The error of the equilibrium degree of swelling is ~5%.

We obtained the linear dependences of $-\alpha$ based on the 100% content of butadiene units, $-\alpha^{100\%}$, on the total amount of *cis*-1,4- and 1,2-butadiene isomers in NBR (Fig. 1a) or the number of all butadiene units (Fig. 1b). Exceptions are covulcanizates with R521 (Fig. 1a) and EPDM-40 (Fig. 1b) either with very high isotacticity of propylene units (EPDM-40) or with their significant content with increased stereoregularity (R521) (Table 2). For mixtures with R505 and Elastokam 6305 with a large amount of bulky diene or the lowest degree of isotacticity of the propylene units (Table 2), $-\alpha^{100\%}$ was also recalculated for the 100% content of *cis*-1,4- + 1,2-butadiene isomers $-\alpha^{cis+1,2}$. All the figures show the reliability of approximation R^2 . According to Fig. 1, the density of the interphase layer and its volume increase ($-\alpha$, $-\alpha^{100\%}$, or $-\alpha^{cis+1,2}$ decrease) with the increasing total content of *cis*-1,4- and 1,2-butadiene units (Fig. 1a) or the total number of butadiene units (Fig. 1b) in NBR [22–24]. The data were interpreted using the concept that in mixtures of copolymers with different polarities, the interphase layer forms by diffusion of segments of nonpolar polymers in the microregions of polar chains with nonpolar sections [4–13, 22–24].

The deviation of Q_{eq} from Q_{add} to larger values is due to the lower density of the interphase layers and the smaller number of cross-links in them than in the phases. This is explained by the weak interphase interaction of the thermodynamically incompatible polymer components [4–13], one of which contains polar units statistically distributed in NBRC-18 or in the form of microblocks in NBRC-40 [3, 25]. The decrease in the volume of the interphase layer causes a decrease in the number of interphase cross-links.

It follows from the given data that the structure of the interphase interaction zone and its volume in the

covulcanizates also depend on the comonomer composition of EPDM, the amount of diene, and the stereoregularity of the propylene units (Table 2). The covulcanizates with EPDM with a large number of ethylene units and predominantly isotactic propylene units R512 and EPDM-40 (Table 2, Fig. 1b) are characterized by the maximum density and volume of the interphase layer, which increase with the decreasing AN content in NBR (Fig. 1b). The better compatibility of NBR with these EPDMs is explained by the high flexibility of the ethylene sections of the chains and penetration of isotactic propylene sequences in the regions of the NBR matrix containing polar units. This is due to the increased rigidity of the latter because of the hindered conformational transitions. The potential barrier of transitions between the rotational isomers of the monomer units of isotactic polypropylene is 21 kJ/mol, while for polyethylene, the potential barrier is 2.5 kJ/mol for T–G transitions and 8.8–10 kJ/mol for G–G transitions [26]. As a result of the penetration of stereoregular propylene units in the NBR regions containing polar links, the volume of the interphase zone increases, but its density locally decreases [22].

The compatibility with EPDM whose propylene fragments of chains have a predominantly atactic configuration (DSM and Russian EPDM except for EPDM-40 and EPDM-60(II), Table 2) is much worse. The interphase layer is looser, and the region of the diffusion penetration of phases is limited by the presence of nonpolar links (Fig. 1) [22–24].

The compatibility with EPDM with high stereoregularity of propylene units and increased contents of diene units (R505) is determined by the hindrances caused by cumbersome diene. The EPDM R505 elastomer is compatible only with the butadiene sections of chains containing *cis*-1,4- and 1,2-links (Fig. 1a) [22–24]. However, the higher content of diene groups provides better cross-linking of EPDM with the matrix. As a result, the total number of cross-links between phases is higher than in mixtures with EPDM with close contents of ethylene units, but with smaller amounts of ENB (cf. EPDM DSM 714 and 712, Table 2 and Fig. 1a). For EPDM-60(II) with 6.7% ENB and low isotacticity of propylene units (13%, Table 2), $-\alpha^{100\%}$ increases significantly with the content of butadiene units, which indicates that the structure of the interphase interaction zone is loose (Fig. 1b).

Thus, it follows from the given data that the density and volume of the transition layer in the mixtures of NBR with EPDM depend on the polarity of NBR and the content of stereoirregularities of the butadiene units. The density and volume of the interphase layer increase ($-\alpha$ decreases) with the content of stereoirregularities of the butadiene units in the copolymer, which is indicative of the role of defective NBR structures in the interphase interaction. This is confirmed by the data given below on the correlation of $-\alpha$ with

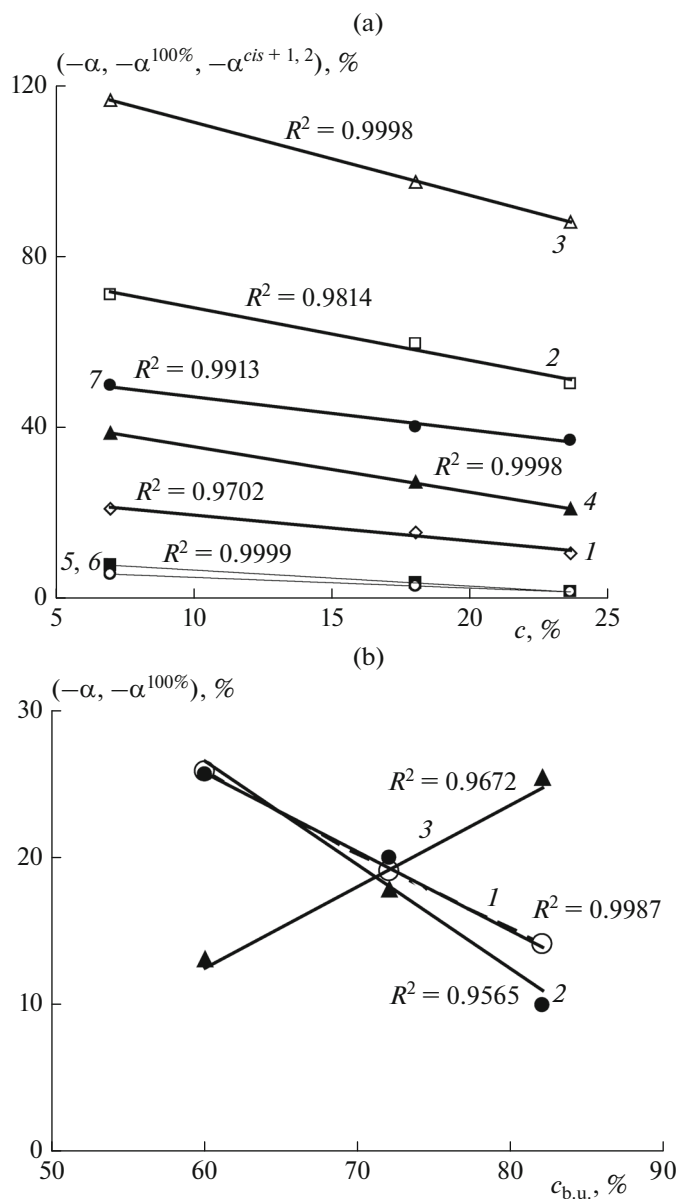


Fig. 1. (a) Dependence of the deviation of the equilibrium degree of swelling on the additive $-\alpha$ value for copulcanizates with (4) R521; $-\alpha^{100\%}$ for copulcanizates with EPDM DSM (1) 778, (2) 714, (3) 712, and (7) EPDM-60(I); and $-\alpha^{cis+1,2}$ for copulcanizates with (5) R505 and (6) Elastokam 6305 on the total content of *cis*-1,4- and 1,2-butadiene units c ; (b) dependence of $-\alpha$ for copulcanizates with (1) EPDM-40 and of $-\alpha^{100\%}$ for copulcanizates with (2) R512 and (3) EPDM-60(II) on the content of butadiene units $c_{b.u.}$.

the free volume fraction in the NBR structure defects formed by the acrylonitrile and *cis*-1,4- and 1,2-butadiene units.

It was shown [2] that the defective microregions of NBR that adsorb low-molecular compounds are formed by the AN and *cis*-1,4- and 1,2-butadiene units. It can be assumed from the data shown in Fig. 1 that in the elastomer mixtures, the interphase layer is formed by diffusion penetration of the most flexible sections of the chains of one component (EPDM) into

the defective regions of the more rigid polymer (NBR) of the indicated structure. To confirm this, we considered the dependence of the structure and volume of the interphase layer on the free volume fraction in the defective microregions of NBR which differ in the comonomer composition and isomerism of butadiene units.

The structure of the defective regions of NBR with different polarities is considered below, and the free volume fraction in them was calculated. The data on the ratio of AN units and butadiene conformers (Table 1)

and the NMR data on the structure of butadiene copolymers with acrylonitrile were preliminarily analyzed [27–31]. From Table 1 it follows that there is a correlation between the content of the polar AN units and the polybutadiene conformers. The total content of *cis*-1,4- and 1,2-structures is approximately equal to the number of AN units in NBRC-18 and NBRC-28; in NBRC-40, it is approximately six times smaller.

Thus, NBRC-40 has, on the average, one *cis*-1,4- or vinyl unit per five to seven AN units, this number being much larger than in NBRC-18 and NBRC-28. This agrees with the NMR data on the length of the sequences of alternating AN links (A) and *trans*-1,4-butadiene units (B) [27, 28]. In block copolymers with 40% AN units, the alternative AB blocks increase to seven to eight units (the amount of BBB decreases to zero) [28]. The alternation of the AN and *trans*-1,4-butadiene units is explained by the regularities in the combination of units during copolymerization [32, 33]. The rate constant of the reaction of the acrylonitrile polymer radical with the butadiene monomer is 50 times higher than that with the acrylonitrile monomer.

It follows from [29–31] that the alternating copolymers of butadiene with acrylonitrile of different compositions have AVC and ACC triads and also AV, AC, CC, and CV diads, where T is the *trans*-1,4-, V is 1,2-, and C is *cis*-1,4-butadiene unit, in addition to the ATA triads according to the aliphatic and olefinic regions of the spectrum. Based on these data, the free volume fraction in defective NBR structures was estimated from the content of AN units and the isomer composition of the butadiene units, as well as the individual contribution of each structural unit to the free volume.

For this purpose, the free volume fraction in polybutadienes (PBs) at room temperature was preliminarily evaluated from the thermal expansion coefficient α_L in the highly elastic state and the glass transition temperature T_g using the Simha–Boyer rule: $(\alpha_L - \alpha_g)T_g \approx 0.113$, where $\alpha_L - \alpha_g \approx 5 \times 10^{-4} \text{ cm}^3/\text{K}$, and $\alpha_L T_g \approx 0.16$ [34, 35]:

$$f_g = 0.025 + \alpha_L(294 - T_g).$$

According to the calculation, $f_g = 0.1447$ for *cis*-PB with $\alpha_L \approx 9.5 \times 10^{-4}$ and $T_g = 168 \text{ K}$; 0.04732 for *trans*-PB with $\alpha_L \approx 6.2 \times 10^{-4}$ and $T_g = 258 \text{ K}$; and 0.03975 for 1,2-PB with $\alpha_L \approx 5.9 \times 10^{-4}$ and $T_g = 269 \text{ K}$. Likewise, the free volume fraction was evaluated for butadiene-nitrile elastomers: $f_g = 0.0741$ for NBRC-18 with $\alpha_L \approx 7.11 \times 10^{-4}$ and $T_g = 225 \text{ K}$; 0.0601 for NBRC-28 with $\alpha_L \approx 6.9 \times 10^{-4}$ and $T_g = 241 \text{ K}$; and 0.0562 for NBRC-40 with $\alpha_L \approx 7.2 \times 10^{-4}$ and $T_g = 246 \text{ K}$.

The free volume fraction of AN units (A) was calculated from the contents of AN and butadiene isomer units in NBR (Table 1) and the free volume fraction in *cis*-1,4-, *trans*-1,4-, and 1,2-polybutadienes:

$$f_g^A c^A + 0.1447 c^{cis} + 0.04732 c^{trans} + 0.03975 c^{1,2} = f_g.$$

The free volume fraction of AN units (A) is $f_g^A = 0.099$ for NBRC-18, 0.0174 for NBRC-28, and 0.0167 for NBRC-40.

Then the free volume fraction in structural defects was calculated from the above NMR data on the sequence of units in defects, the composition of copolymers, and isomerism of butadiene units (Table 1): (ATAVC) $\times 0.082 = 0.0352$, (ATACC) $\times 0.008 = 0.0043$, and $\Sigma = 0.0395$ for NBRC-18; (ATAVC) $\times 0.092 = 0.0245$, (ATAVTATAV) $\times 0.026 = 0.007567$, and $\Sigma = 0.0321$ for NBRC-28; I. (ATATATATATA-TATATAVC) $\times 0.026 = 0.0185$, II. (ATATATATA-TATATAV) $\times 0.018 = 0.01024$, and $\Sigma = 0.0288$ for NBRC-40.

Figures 2 and 3 show the dependences of $-\alpha$ on the free volume fraction in defects of the NBR structure in covulcanizates with EPDM. The relationships between these quantities are linear (proportional). The reliability of approximation R^2 is 0.90 – 0.99 . The exceptions are EPDMs with very low or high contents of isotactic propylene sequences (curves 1 and 6, respectively, Fig. 2), which are compatible not only with butadiene, but also with AN units.

The deviation of the equilibrium degree of swelling Q_{eq} from the additive values ($-\alpha$) for all NBR and EPDM covulcanizates with low isotacticity of the propylene units (of both foreign (DSM) and Russian (Figs. 2 and 3) production) increases with the free volume in the defects of the NBR structure. Consequently, at low isotacticity of propylene units, the density of the interphase layer is small; the larger its volume, the greater the $-\alpha$ value.

The EPDM R512 elastomer with high isotacticity of the propylene units and EPDM-40 (Table 2) form a much denser interphase layer, and $-\alpha$ decreases as the free volume fraction in defective regions increases (Figs. 2 and 3). This occurs even at low contents of ethylene units in EPDM R521; only at high contents of ENB diene in EPDM R505, the layer is significantly loosened (Fig. 2).

All DSM EPDMs, EPDM-60(I) with low isotacticity of propylene units, and Royalen with high isotacticity but with high diene (R505) or low ethylene (R521) contents (Figs. 2 and 3) are compatible only with defects containing AVC structures in NBRC-18 and NBRC-28 and (AVC + AV) in NBRC-40 characterized by the maximum distance between the chains due to the increased number of AN units and their block arrangement (five to nine AT diads) [25, 36]. The EPDM elastomer with a high content of ethylene units and very low (Elastokam 6305) and high isotacticity of propylene sequences (R512 and EPDM-40) and also with a high diene content (EPDM-60(II)) are

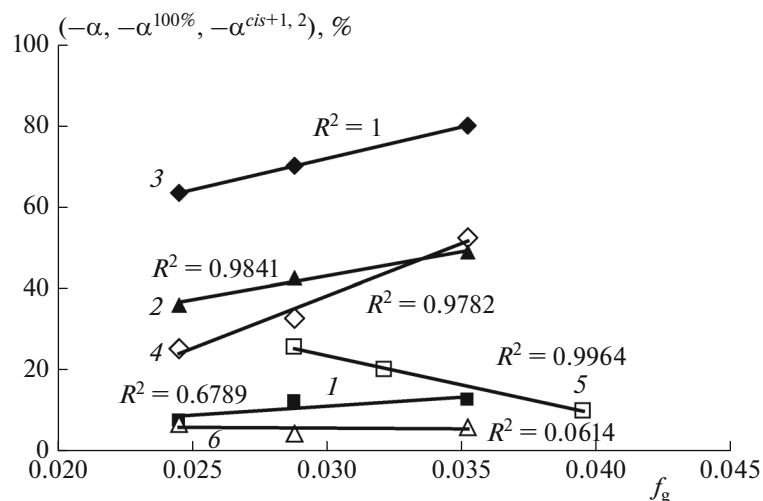


Fig. 2. Dependence of $-\alpha$ on the (1–4) free volume fraction in the structural defects AVC in NBRC-18 and NBRC-28 and (AVC + AV) in NBRC-40 and (5) the total value of f_g for covulcanizates with EPDM DSM: (1) 78, (2) 714, and (3) 712; (4–6) for Royalen R505 (4); similar dependences of $-\alpha^{100\%}$ for covulcanizates with (5) R512 and (6) of $-\alpha^{cis+1,2}$ for R521.

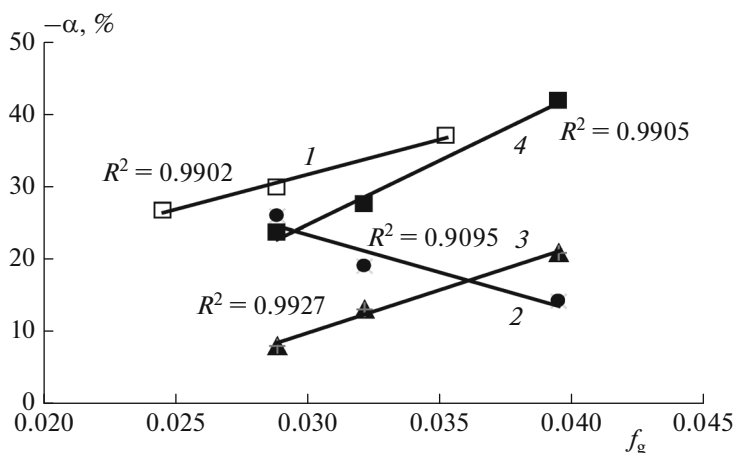


Fig. 3. Dependence of $-\alpha$ on the (1) free volume fraction in the structural defects AVC in NBRC-18 and NBRC-28 and (AVC + AV) in NBRC-40 for the covulcanizate with EPDM-60(I) and (2–4) the total value of f_g for covulcanizates with (2) EPDM-40, (3) EPDM-60(II), and (4) Elastokam 6305.

compatible with all structure defects: (AVC + AV) and (AVC + ACC) in NBRC-18.

It can be concluded that at high contents of ethylene units with high flexibility, a more developed interphase layer of larger volume forms regardless of the degree of isotacticity of the propylene units (which is very low in Elastokam 6305 or high in EPDM-40 and R512), but its density and the number of cross-links in it depend on the degree of isotacticity of the propylene units. At high stereoregularity of propylene units, the density of the interphase layer is much higher than at low stereoregularity. In this case, EPDM R512 with lower isotacticity compared to EPDM-40 is compatible only with butadiene units in

all defective NBR structures because the dependence is proportional when $-\alpha$ is recalculated for the 100% butadiene content. EPDM R521 with a low content of ethylene units is compatible only with the sites containing the *cis*-1,4- and 1,2-structures (recalculated for 100% butadiene content and 100% contents of *cis*-1,4- and 1,2-units) in the AVC and (AVC + AV) defects in NBRC-40. For the remaining EPDMs, $-\alpha$ was not recalculated (Figs. 2 and 3).

Earlier, the mechanism of the ozone-protective action of a saturated polymer in covulcanizates with NBR was studied and shown to be structural, i.e., depending on the compatibility of the components that determines the structure of phases and interphase

layer [22–24, 37, 38]. The rate of stress relaxation in an ozone-containing medium is minimum due to the destruction of diene rubber molecules during the formation of a continuous spatial framework of the saturated component and increases when the deformation comes the point of interfacial stratification. In mixtures with polyvinyl chloride, the interphase layer is stable due to the dipole–dipole interactions of chlorine and nitrogen atoms, hydrogen bonding, and chemical cross-linking during the reaction of the functional groups of polymers (formation of graft copolymers) [37–39]. In mixtures of elastomers in a highly elastic state at normal temperatures, the interphase contacts are stable due to the presence of chemical cross-links [22–24]. An important role is also played by the degree of cross-linking of the ozone-resistant phase. It was also found [22–24] that the rate of the ozone destruction of NBR covulcanizates with EPDM depends on the comonomer composition of EPDM and the degree of isotacticity of the propylene units, i.e., the kinetic flexibility of the chain sections of the copolymer that is present in a smaller amount (in this case, for the 70 : 30 mixture). It was shown [40] that the rate of ozone destruction of NBR in covulcanizates with EPDM also depends on the free volume fraction in the structural defects of the most rigid component of the mixture (NBR) and the kinetic flexibility of the sections of EPDM chains, which confirms the results of this study.

CONCLUSIONS

Thus, it was found that the defective NBR structures formed by acrylonitrile units and stereoirregularities of butadiene units are involved in the formation of the interphase layer in mixtures with EPDM. The correlation of the density and volume of the interphase layer in mixtures of NBR with EPDM with the free volume fraction in NBR structure defects was shown to be linear. As the free volume fraction increases, a more developed interphase layer forms in them. The density of the interphase layer and its volume increase with the content of the most flexible ethylene units in EPDM and the degree of isotacticity of the propylene sequences.

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