

Structure of Natural Rubber/Emulsion Butadiene Rubber (NR/EBR) Vulcanizates

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ABSTRACT: Diblock amorphous topological structure of a filled vulcanizate network made of natural rubber (NR) and Emulsion Butadiene Rubber (EBR) was found. These blocks differ in the transition temperatures about 200°C. Dual transitions of such rubbers have been assigned as a motion of the mixed soft block [low glass transition temperature (T_g)] in the glassy state and the motion in elements of a network around physical and chemical crosslinking sites in a rigid block (high T_g), respectively. Compaction of the topological structure of a high-temperature block during curing (manifested by the growth of T_g) was noticed. The molecular weight distribution of the chains between the junctions of the network and shares of these amorphous blocks in the structure of the rubber network vs curing time were calculated using the methodology shown. Introduction of Perkalink 900 at constant quantity of sulfur changes a structure of the junctions in the tested rubber network from mixed (10–15% of chemical bonds, and remaining are cluster type and topological junctions) into practically all chemical bonds. Optimal curing time evaluated by the thermomechanical analysis, at which molecular structures formed in both blocks reflect the equilibrium state of adsorption layers of two rubbers introduced into the compound, is close to that evaluated by the vulcametric tests. The location of the molecular weight distribution curve in both blocks one against another depends on rubber formulation. Also, a fact that crosslinks are gathered, as was predicted by Vilgis and Heinrich calculations, was confirmed experimentally. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 732–742, 2000

Key words: thermomechanical analysis; topological structure; molecular structure; MWD; junctions' structure

INTRODUCTION

Properties of rubbers strongly depend on the molecular and topological structures of its spatial network changing during curing of a rubber com-

pound. Usually vulcametric^{1–4} measurements and sometimes differential scanning calorimetry³ or nuclear magnetic resonance⁵ are applied to evaluate the structure of vulcanizate. Such measurements give only partial information, namely about changes in the crosslink density of the network and activation energy of some processes occurring when rubber compounds are heated.^{1,2,4} To better understand why the curing system and a way of curing influences properties of rubber, it is necessary to know what changes in the molec-

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ular and topological structures of the network. Usually the structure of linear polymers is investigated in solution, but for cured rubbers this method is inapplicable. To evaluate a structure of the crosslinked material, impossible to be dissolved without degradation of its junctions, a method of the thermomechanical analysis could be used.⁶⁻¹⁴ Some changes in such a structure resulting from rubber technology were discussed previously.^{11,13,14}

Problems of reversion are very important for sulfur-based vulcanizates. To prevent this, anti-reversion agents are added into the rubber compound. One of them is Perkalink 900. There are some works on the influence of this modifier introduction on service properties.¹⁵⁻¹⁸ However, what changes in a structure of such rubbers has not been fully clear to now. Because of this, the aim of this work is to show some changes in the molecular and topological structures of NR/EBR rubber during vulcanization and related to a presence of Perkalink 900. These data could be complementary information to well-known and usually measured changes in the average molecular weight between the junctions, a structure of these sulfidic junctions, and the crosslink density. This kind of study is one of the next steps to elaborate more reproducible technology of rubber goods having controlled physical and mechanical properties.

METHODOLOGY

The chosen method is based on measurements of sample deformation under a very low load and at temperature, which varies against time [thermo-mechanical curve (TMC)] and, next, evaluation of the glass transition temperature, T_g , and temperature at the beginning of molecular flow, T_f . This methodology of measurements and calculations of the molecular weight distribution (MWD), a crystallinity degree, and shares of topological blocks with different molecular mobility (if exists) are described elsewhere.^{10,11}

EXPERIMENTAL

Materials

Three compounds containing 70 phr of NR (SMR 5CV, Malaysia) and 30 phr of emulsion polybutadiene (EBR) KER 8512 (produced in Kombinat

Table I Additives Introduced into the Tested Rubber Compounds during the Second Stage of Mixing

Ingredients	Rubber Compound		
	(1)	(2)	(3)
Sulfur S95	2.2	2.2	3.0
CBS	0.6	0.6	0.6
Perkalink 900	—	1.0	1.0

Chemiczny Dwory, Poland; characterized by $T_g = -68^\circ\text{C}$) and 50 phr of carbon black grade N220 were used. They differ in the curing system (Table I). Compounds were prepared in a two-stage manner. In the first stage, rubbers were mixed with carbon black, oil, and remaining ingredients [except CBS, sulfur, and Perkalink 900—1,3-bis(citraconimido-methyl) benzene made by Akzo Nobel with melting point 87°C^{15}] for 6 min in an internal mixer of capacity 3l and dump at a temperature of 140°C . The master batch was kept 24 h. Next, it was divided into three parts and mixing was completed on a two-roll mill at 95°C by adding the curatives and Perkalink 900.

RESULTS AND DISCUSSION

The curing behavior of compounds was determined by using Monsanto Curemeter type 100 at 140, 150, and 160°C . Introduction of Perkalink 900 has no essential influence on the maximal value of the vulcanometric torque (Fig. 1) taken here as a measure of crosslink density, which is almost equal for compounds (1) and (2). However, Perkalink 900 reduces a reversion rate essentially, as was for compounds made of NR and NR/BR.^{15,16,18} It has now been found that addition of a higher dosage of sulfur, when content of Perkalink 900 was preserved the same, gives higher value of the vulcanometric torque for rubber (3) than those for (1) and (2). However, also here the reversion rate is similar to that for a rubber compound with a lower dosage of sulfur. These conclusions are low dependent on curing temperature.

Two glass transitions and the bimodal MWD of the chains between the junctions of the vulcanizate containing a blend of *cis*-1,4-butadiene (BR) and *cis*-1,4-isoprene (NR) rubbers cured with sulfur and CBS as accelerator, was shown previous-

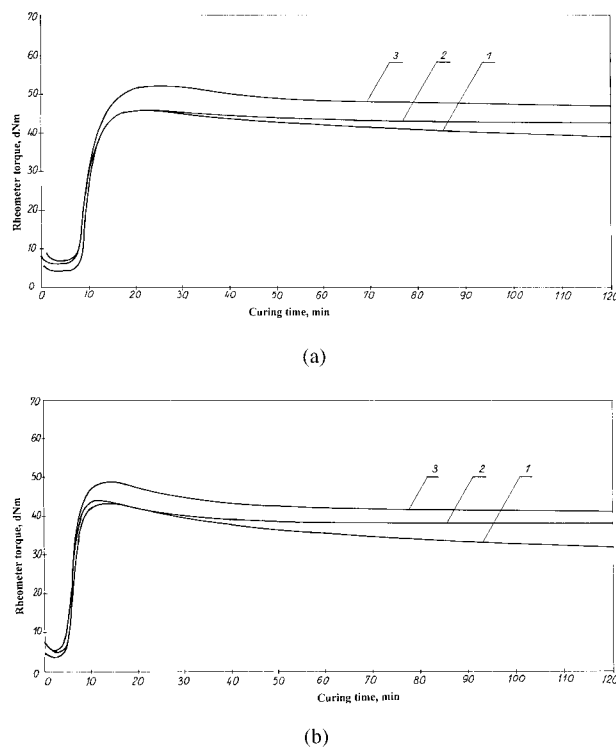


Figure 1 Vulcanometric curves for rubber compounds cured at 150°C (a) and 160°C (b); numbers of curves correspond with a recipe content according to Table I.

ly.¹¹ In the current work, when BR was replaced by EBR, the cured rubber in the indicated temperature interval also has two relaxation transitions (Fig. 2). This evidences a presence in a macromolecular structure of two amorphous phases with different molecular mobility (called blocks) with the temperatures of the beginning of segmental relaxation transition (T_g) about -80°C (a low T_g block called a low-temperature topological block) and about $+120^\circ\text{C}$ (a high T_g block called a high-temperature topological block), adequately. For BR a difference in these temperatures is also about 200°C .¹¹ The presence of these blocks is probably determined by the different interaction energy of fragments of the chains with most of the active sites on the surface of carbon black particles. This conclusion is supported by nuclear magnetic resonance investigations of other rubbers¹⁹ when it has been reported that more than two T_2 relaxation times are observed in carbon black-filled rubbers, reflecting the existence of rigid regions adjacent to the crosslinks or filler particle and soft regions distant from such rigid ones. The amount and distribution of the T_2 times are affected by the filler incorporation in

the rubber compounds.¹⁹ Also electron spin resonance investigations²⁰ show above the T_g the slow motion component of polyisoprene, which refers to the gel phase of higher matrix density with restricted segmental motions, while the motionally narrowed component is ascribed to spin probes in a matrix of lower local density or larger free volume fluctuation.

Figure 2 shows the TMC for rubber compounds cured until t_{90} according to the vulcanometric measurements. Similar temperatures for the beginning of segmental relaxation were found in every rubber that was compared.

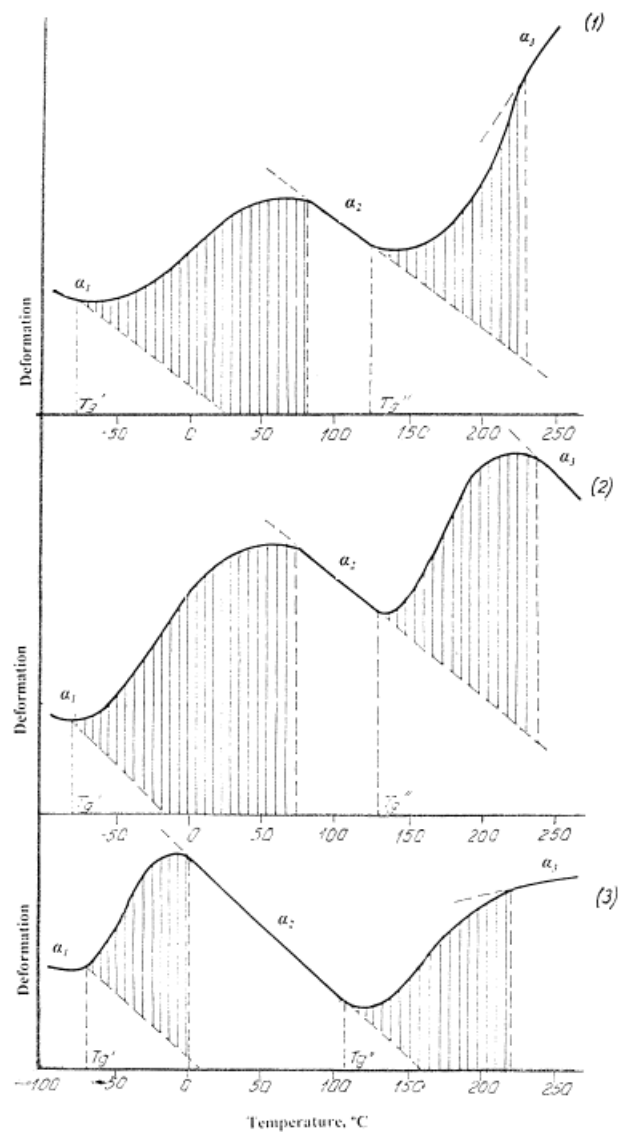


Figure 2 Thermomechanical curves for tested rubbers (1), (2), and (3), T_g' , the glass transition temperature for a low-temperature topological block; T_g'' , the transition temperature for a high-temperature topological block.

A structure of the chains between the junctions in the low-temperature block could be interpreted as having a mixed polyisoprene/polybutadiene nature because these polymers have similar glass transition temperatures.

The topological structure of the high-temperature block is disputable. Here could be present fragments of chains of both rubbers having groups of atoms with higher cohesion energy than that in *cis*-1,4 and in *trans*-1,4 configurations of polybutadiene. For instance, 1,2 (vinyl) structure is characterized by higher energy of intermolecular interactions. In NR, it could be *trans*-1,4 configuration. It is quite probable because EBR used here has about 40% of 1,2 (vinyl) structure. Additionally, a structure of the high-temperature block could be arranged also with participation of modifiers, e.g., active filler—carbon black, curing agent, and Perkalkink 900. The last could change the rubber chain chemical structure resulting in creation of complexes of its molecules with rubber chains.

It is known that in the carbon black filled compounds, even in the uncured state, the system is more rigid than that in unfilled formulations,²⁷ which introduces some anisotropy into the segmental motion due to the chemical adsorption of the carbon black aggregates.^{22,23} Two levels of rubber binding on the filler surface could be specified. More loosely bound material exhibits a vigorous, liquid-like motion but that is nonetheless constrained as compared with the neat polymer, and there is material that behaves much like an unfilled elastomer.^{24,25} For some cases, the removal of the chains (folds, cilia, and tie molecules) perhaps adsorbed rather than chemically attached to the particles of carbon black takes place. Strongly anchored chains may participate in multiple adsorptive links to the filler particle for which a significant part of the chain is within the tightly bound shell. This component will achieve the liquid-like character in the high-temperature regime, when the integrity of the composite structure eventually breaks down. The beginning of significant mobility in the more loosely bound phase clearly induces more vigorous motion than would otherwise be the case in the tightly bound layer, thus revealing cooperation in the chain dynamics between the phases in filled rubber. The influence of thickness of the bound layer on the severity of extraction and on temperature arises from adhesion energies of the polymer to filler. The mechanism by which the bound rubber molecules are progressively removed with increasing

temperature has Arrhenius character. The order of magnitude of the entropy value ΔS implies that extraction removes those polymer segments that would experience the greatest increase in ΔS by achieving the liquid-like character.²⁶ This all suggests that a low-temperature block could be related to the loosely bound rubber and a high-temperature block to the tightly bound rubber.

Comparing results for the blend of BR with NR¹¹ and data of this work one could find a principal difference in a structure of the high-temperature block. The criterion of this difference could be a location of a high elasticity plateau on the TMC. Previously it was shown that a tangent of the inclination angle α_2 of the straight line of a high elasticity plateau (the coefficient of the linear thermal expansion) characterizes the structure of the branching junctions in the polymer network and a quantitative ratio of different kinds of them.²⁷ It is valid mainly for two kinds of the junctions: first, for three and four functional chemical bonds being thermal stable; second, for the topological junctions created by the interleaved chains. The latter relax at a temperature in the zone of a plateau of high elasticity, what reduces anomaly the α_3 value, which is the larger, the higher is concentration of the topological junctions.

Table II shows the coefficients of the linear thermal expansion of cured rubbers: in a glassy state α_1 , and in a high-elastic state α_2 for a low-temperature block, and α_3 for a high-temperature block. It is visible that only in the beginning of the curing process (up to 20 min) tested rubbers differ essentially in the coefficients of the linear thermal expansion in a glassy state of the low-temperature block. For longer curing time, this coefficient is almost stable. Comparison of these data with the shapes of the vulcanometric curves (Fig. 1) for the same interval of curing time shows that creation of the low-temperature block is not the determining process of a general structure of tested rubbers. The coefficient of the linear thermal expansion of the low-temperature block of rubber in a high-elastic state changes in a different way dependent on the curing system. The reason for these changes is still unclear.

Figure 3 shows a dependence of α_3/α_2 parameter on curing time, τ_c . Its value characterizes quantitatively the ratio of the chemical and topological branching junctions. For analyzed rubbers, the probability to create the topological junctions depends not only on the nature of the curing system, but on curing time as well. Extremal

Table II Thermal Properties of Rubbers Cured at 150°C

Curing Time (min)	The Low-Temperature Block		The High-Temperature Block [$\alpha_3 \cdot 10^5$ (deg ⁻¹)]
	$\alpha_1 \cdot 10^5$ (deg ⁻¹)	$\alpha_2 \cdot 10^5$ (deg ⁻¹)	
Rubber compound (1)			
10	6.64	27.7	-47.9
14	5.88	23.8	-47.6
20	4.44	25.5	-59.9
30	3.70	27.0	-62.5
40	4.20	27.8	-63.5
60	4.00	26.3	-47.6
120	4.39	26.2	-19.6
Rubber compound (2)			
10	9.50	38.9	-14.2
14	5.80	37.3	-5.8
20	3.60	28.3	-5.9
30	3.15	28.6	22.7
40	3.03	26.4	24.4
60	3.16	25.8	0
120	3.23	23.25	-6.2
Rubber compound (3)			
10	7.40	29.1	-6.2
14	6.64	31.9	-19.7
20	4.48	27.3	-14.5
30	5.60	32.7	-17.0
40	5.82	30.9	-15.0
60	6.20	32.3	-20.5
120	4.44	22.7	-2.9

α_1 , the coefficient of linear thermal expansion of rubber in a glassy state, the low-temperature block; α_2 , the coefficient of linear thermal expansion of rubber in a high elastic state, the low-temperature block; α_3 , the coefficient of linear thermal expansion of rubber in a high elastic state, the high-temperature block.

character of a function of α_3/α_2 vs τ_c is observed for all three rubbers. Here, the optimal curing time, at which molecular structures formed in both blocks reflect the equilibrium state of adsorption layers of two rubbers introduced into the compound, was equal to 20–40 min for rubbers (1) and (2). Introduction of Perkalink 900 into the curing system principally changes character of a discussed dependence. Equal shape of it (with extreme) is preserved, but it is inverse to that for the standard rubber (1).

For this rubber, interval of the optimal curing time widens from 10 min to 60 min. However, even until 10 min and more than 60 min, the changes in this parameter are in the field of accepted error of evaluation. It could be said that introduction of Perkalink 900 into the rubber compound in the quantity like for rubber (3) sta-

bilizes the crosslinking process in all intervals of time. The main factor influencing the ratio of the chemical and topological junctions is the curing system. For instance, in rubber (1), after reaching the optimal curing time, only 10–15% of the branching junctions are chemical bonds. In rubber (2), which has the same curing system, but contains additionally 1 phr of a Perkalink 900, after the same curing time, practically all the branching junctions have chemical nature.

Based on these results, some ideas about a mechanism of Perkalink 900 action in creating a topological structure of rubber could be formulated. The mechanism of curing process discussed by Datta and co-workers^{15,16,18} took into account changes in concentration of sulfidic and C—C bonds. They did not discuss changes in cluster and topological junctions of the rubber network and multi-block structure of rubber. Our investigation shows that the topological structure of rubber obtained in the presence of Perkalink 900 essentially depends on the presence of this modifier. We hope that it is adsorbed on a surface of

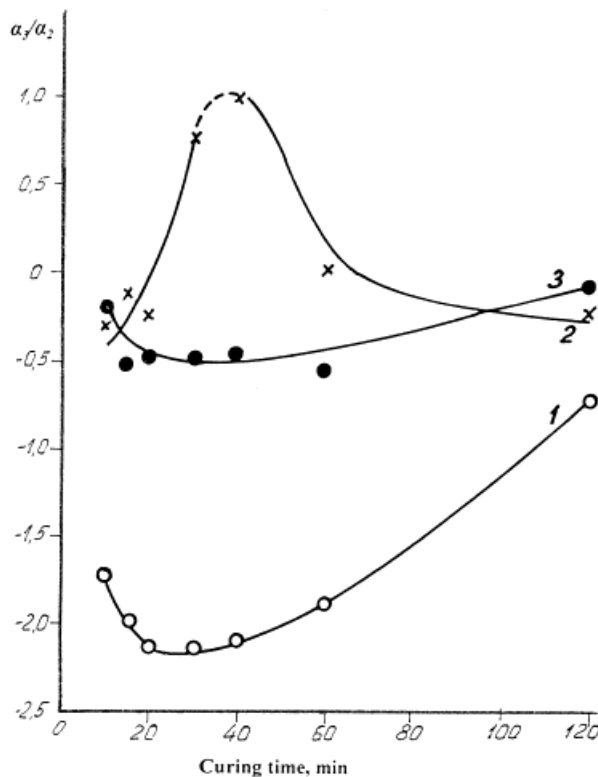


Figure 3 Dependence of the criterion of a quantity share of the chemical and topological junctions in the network α_3/α_2 in the high-temperature topological block on curing time for rubbers (1), (2), and (3).

carbon black and, next, activate sulfur also adsorbed there. It results in an increase in sulfur activity, which increases concentration of the chemical junctions in the network. This process, simultaneously, suppresses creation of the topological junctions. It is unexpected and not understandable in full because these reactions run only at optimal curing time (30–40 min). In other cases (Fig. 3), similar structure separates again into the chemical and topological junctions as in the control rubber. This fact is difficult to explain without the usage of the idea about selective action in this process, only a single raw rubber from the blend of two raw rubbers. Analogous explanation is the presence of optimum curing times of other rubbers, as we proposed earlier.²⁸ Also here we expect that all depends on the nature of rubber adsorbed on the carbon black surface at optimal curing time.

In rubber (3), which has a higher amount of sulfur in comparison to rubber (2), the chemical and topological junctions are present in similar concentration in all intervals of curing time. Introduction into the compound of additional quantity of sulfur changes a weight ratio of Perkalink 900 and sulfur. In this rubber [Fig. 2(c)], as in the control, in a high-temperature block are the chemical and topological junctions, but in an equal portion. These results confirm our supposition about joint action of Perkalink 900 and sulfur in formation of a rubber network what agrees with the mechanism proposed by Datta and co-workers^{15,16,18} Because of this, it changes a character of the dependence α_3/α_2 vs curing time shown in Figure 3 (curve 3). On this dependence practically disappears both extremal magnitude of this parameter, and related a ratio of the topological and chemical junctions in the network of a high-temperature block. For long-lasting curing process, this suggests stabilization in time of the rubber network structure in the presence of Perkalink 900 which also was proposed^{15,16,18} but based on different investigations. However, to be sure that its full stabilization is obtained, it is necessary to perform additional investigations about optimization of rubber compounds' components.

Calculation of parameters of the MWD of the chains between the junctions of the network, based on the TMC,²⁹ for both blocks are given in Table III. Dependencies $\bar{M}_{n(n)}$ on curing time shown in Figure 4(a) for the low-temperature block of all three rubbers have the same character like that found previously for NR/BR vulcani-

zates.¹¹ The difference is only that now $\bar{M}_{n(n)}$ values are many times higher. Such dependence for the high-temperature block now is principally different. Earlier this dependence had extremal character. Now, a monotonic reduction in $\bar{M}_{n(n)}$ is found as curing time extends [Fig. 4(b)].

Crosslinking of the high-temperature block, as shown in Figure 4(b), could not be optimized in time. Here, the role of curing agents in the formation of the rubber spatial structure is evident. It is visible, as was mentioned previously, in creation of a polymer network with a different ratio of the chemical and topological junctions. This, on the other hand, assumes a different reactivity of active sites on the polymer chains of this block during networking. Additionally, this reactivity is essentially lower than that in the chains of the low-temperature block. Nevertheless, despite these differences in reactivity, in the high-temperature block for rubbers (2) and (3), a stabilization of a ratio of the topological to chemical junctions of the network during long lasting curing is noticed (Fig. 3). For this block, the optimal curing time is the same as that for the low-temperature block.

As shown in Figure 5 for a low-temperature block, the curing system essentially influences a dependence of the polydispersity coefficient K of the chains between the junctions on curing time. However, for the high-temperature block, this characteristic of uniformity of the network practically is independent on curing time and the curing system, and its magnitude is about 1.41.

For random distribution of branching junctions along the rubber chains, an increase in the crosslink density is accompanied by more pronounced lowering concentration of the fractions with the highest MW as curing time extends. This changes the shape of the MWD curve. For each of the three series of experiments discussed here, the shape of the MWD of the chains between the junctions does not depend on curing time, which experimentally supports conclusions from theoretical investigations³⁰ that crosslinks are gathered (distributed not randomly). Because of this, Figure 6 shows the MWD for both blocks for optimal curing time only. For the tested rubbers, they are unimodal. This suggests that the curing mechanism is relatively simply. It means that all individual multistep chemical reactions could be represented by the complex crosslinking process and successive complex degradation process, and in the reaction system are present active sites having both similar chemical activity and concen-

Table III Molecular Weight and Thermomechanical Characteristics of Tested Rubber Cured at 150°C^a

Curing Time (min)	The Low-Temperature Block					The High-Temperature Block			
	T_g (°C)	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K	φ	T_g (°C)	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K
Rubber compound (1)									
10	-78	18.78	29.77	1.63	0.56	70	19.60	27.30	1.39
14	-74	9.95	16.00	1.61	0.51	114	17.00	24.20	1.42
20	-74	12.90	21.80	1.69	0.52	128	20.20	30.00	1.48
30	-79	7.05	12.90	1.84	0.54	123	12.65	17.93	1.42
40	-82	10.00	18.54	1.83	0.55	129	13.51	18.98	1.40
60	-86	11.30	21.53	1.90	0.62	135	10.10	13.82	1.36
120	-83	19.28	23.03	1.73	0.78	141	4.50	6.10	1.36
Rubber compound(2)									
10	-77	11.59	20.60	1.77	0.58	99	15.08	20.50	1.42
14	-71	11.80	19.10	1.69	0.60	124	14.60	20.70	1.42
20	-75	6.80	11.90	1.75	0.58	107	8.60	11.95	1.39
30	-73	9.52	17.20	1.81	0.62	130	8.52	11.78	1.39
40	-76	6.77	11.60	1.72	0.59	136	7.01	9.75	1.39
60	-70	11.84	20.66	1.75	0.74	134	4.44	6.21	1.39
120	-76	21.77	34.17	1.57	0.79	147	2.23	3.00	1.35
Rubber compound(3)									
10	-73	12.05	21.20	1.75	0.56	102	15.50	22.20	1.43
14	-75	12.20	18.90	1.58	0.57	108	20.50	24.70	1.41
20	-75	7.60	11.00	1.44	0.55	127	12.40	18.00	1.42
30	-77	6.40	9.17	1.42	0.61	114	6.40	8.80	1.38
40	-73	9.70	13.50	1.39	0.61	112	8.30	12.70	1.41
60	-71	33.56	50.00	1.49	0.72	135	8.40	11.50	1.37
120	-69	221.4	316.7	1.43	0.91	155	3.40	4.56	1.34

^a T_g , the glass transition temperature; $\bar{M}_{n(w)}$, the weight-average molecular weight between the junctions of a polymer network; $\bar{M}_{n(n)}$, the number-average molecular weight between the junctions of a polymer network; $K = \bar{M}_{n(w)}/\bar{M}_{n(n)}$, the polydispersity coefficient of the chains between the junctions, φ , the weight shares of the block.

tration. This is valid for the curing process in a low-temperature block. There, the influence of the curing system is manifested in a small variation of the averaged value of the molecular weight and the coefficient of polydispersity K .

It is also observed that a distance between maxima of MWDs of high-temperature and low-temperature blocks of rubbers is reduced for cases when Perkalink 900 is introduced. We hope that at optimal Perkalink 900 concentration (related to stabilization of a ratio of the chemical and topological junctions in the network) could be reached a full coincidence the MWD in both blocks (expressed for instance by similar magnitudes of $\bar{M}_{n(n)}$, $\bar{M}_{n(w)}$, and K) when a distance between maxima equals to nil and topological junctions will be replaced by a chemical one.

It is important to analyze changes in temperature of the beginning of defrosting of the segmental mobility in the rubbers. The T_g parameter

characterizes a level of the intermolecular interactions in the polymer and is determined not only by the chemical structure of the chains, but by the topology structure of all the material. Because of this, when the data of analyses collected in Table III are compared with those from the previous experiments¹¹ some questions are reasonable. First, why does the T_g value of a high-temperature block of cured rubber depend on the rubber compound's content, which differs little in amount of sulfur and Perkalink 900? Second, why do the T_g values of the low-temperature and high-temperature topological blocks differ by about 200°C?

Figure 7 shows a dependence of the T_g value on curing time in both blocks of tested rubbers and data from the previous report when a different type of polybutadiene was investigated.¹¹ A stabilization of the T_g value for a low-temperature block in time is visible and its dependence on the

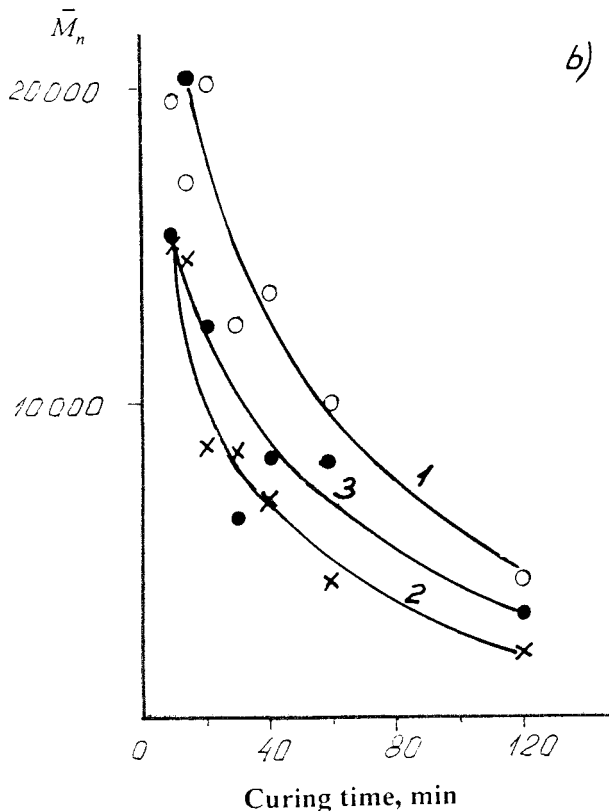
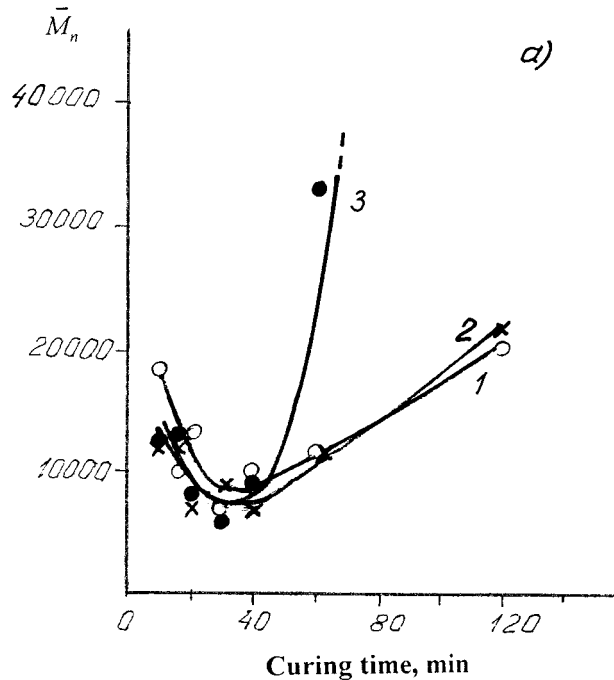


Figure 4 Dependence of the number-average molecular weight of the chains between the junctions in low-temperature (a) and high-temperature (b) topological blocks on curing time for rubbers (1), (2), and (3).

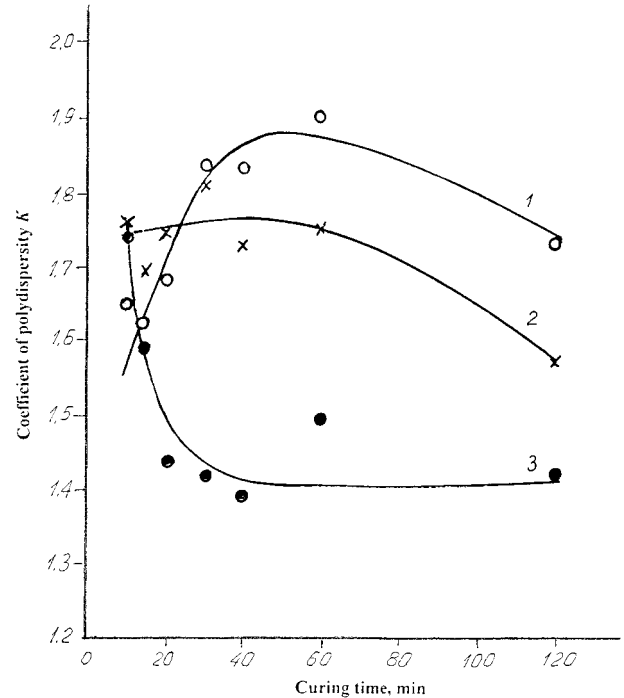


Figure 5 Influence of curing time on the polydispersity coefficient of the network of a low-temperature topological block for rubbers (1), (2), and (3).

curing systems, more exactly, on the presence of Perkalink 900. For a high-temperature block the rate of T_g increase, for curing time 20 min and longer, is similar for all tested rubbers. Time to reach this stabilization in the low-temperature block of rubber (1) is longer than optimal curing time. It is noticeable that the T_g value is 15–20°C higher than those for NR and EBR. We hope that introduction of Perkalink 900 accelerates the transformation process of adsorption groups on the surface of carbon black and stabilizes mobility of the chains between the junctions on the level corresponding with higher T_g (approximately 10°C higher than that in control rubber). This is related, according to our opinion, with the fact that a part of Perkalink 900 joints to the polymer chain through conjugated dienes/trienes formed by reversion^{16,18} and reduces its mobility to the level of mobility of the NR chains.

An increase in sulfur concentration gave some reduction in the mobility of the chains in the low-temperature block due to the same reasons that were discussed earlier when rubber (2) containing Perkalink 900 was described.

Introduction of Perkalink 900 has no essential influence on T_g' (with accuracy of T_g evaluation $\pm 5^\circ\text{C}$). The main reason for this phenomenon in

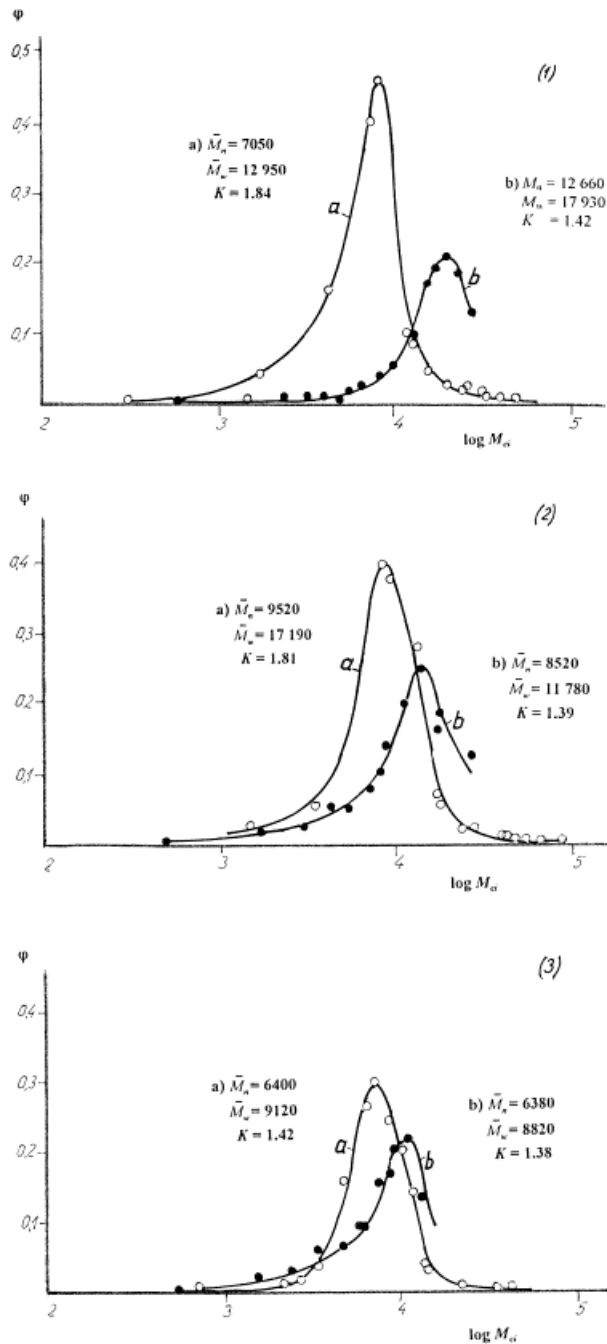


Figure 6 The molecular weight distributions of the chains between the junctions in low-temperature (a) and high-temperature (b) topological blocks on curing time for rubbers (1), (2), and (3).

listed rubbers could be uncontrolled contaminations with homologues of a different chemical composition resulting from the modification process during the second stage of mixing and curing (the first stage of mixing of these rubbers is identical). These fragments of the chains are characterized

by different cohesion energy, which could initiate, under some conditions, the creation of a topological block structure of rubber. A pseudo-crosslinked structure in the low-temperature block also could be present. If it is valid, this should change a mobility of fragments of the chains in the rubber structure and, as a result, the T_g of a low-temperature block. From this results a wide interval (up to 200 °C) between T'_g and T''_g .

Dependence of tensile strength of the tested rubbers with a different ratio of Perkalink 900 and sulfur vs curing time (Fig. 8) shows that this characteristic depends on concentration of both of these ingredients. Namely, for curing time longer than the optimal one, rubbers containing 1 phr of Perkalink 900 and 2.2 phr of sulfur (curve 2) have higher tensile strength than that for control rubber (curve 1). This agrees with results¹⁷ for other rubbers. Introduction of 1 phr of Perkalink 900 and 3.0 phr of sulfur (curve 3) gives the highest tensile strength within all the intervals of curing time. Similar character of such dependencies show that tensile strength of rubbers depends not only on concentration of Perkalink 900 and sulfur, but also on the kind of raw rubber, which is in higher concentration in the adsorption layer on the surface of carbon black after a given curing time. These results confirm the formulated above idea that Perkalink 900 influences the molecular and topological structures of rubber, and resulting properties. Thus, it is crucial to establish the optimal ratio of components of the curing system for every raw rubber, which differ in ability to be adsorbed on the surface of carbon black.

It should be mentioned that evaluating some quantitative relations between a content of a

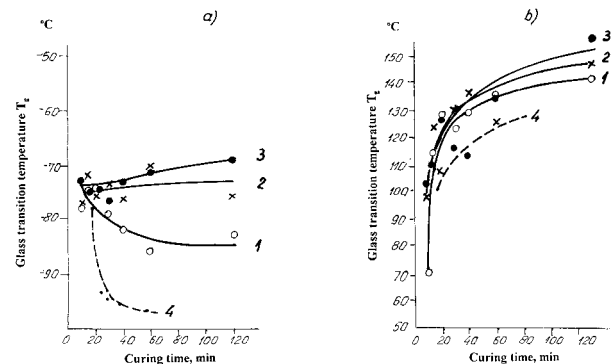


Figure 7 Dependence of the T_g s on curing time in low-temperature (a) and high-temperature (b) topological blocks for rubbers (1), (2) and (3), and (4) taken from the article.¹¹

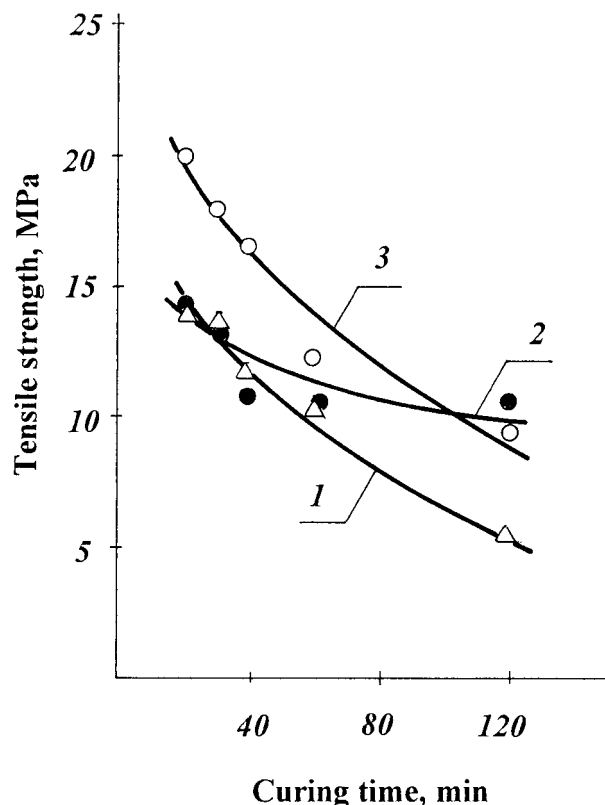


Figure 8 Tensile strength of rubbers vs curing time at 150°C; numbers of curves correspond with a recipe content according to Table I.

high-temperature block in rubber and its service properties is an important target of further investigations. If rubber is used at temperatures below T''_g , the high-temperature block is in a glassy state and distributed within a matrix of a low-temperature block. Because of this, it functions as active filler. For higher temperature of service (more than T''_g), this block is in a high-elastic state. Because of this, its reinforcing ability disappears which results in lowering the rubber's mechanical properties. From this it is concluded that in every case if mechanical properties are considered, it is advantageous if cured rubbers have a higher share of the high-temperature block with the highest magnitude of T''_g . It suggests a necessity to optimize rubber formulation, also taking into account these two parameters.

CONCLUSIONS

Diblock amorphous topological structure of a studied NR/EBR network was found. They differ

in the transition temperatures about 200°C as was also the case for NR/BR rubber. It was found that molecular structure of these blocks is sensitive to rubber formulation. Because of this, a necessity to optimize rubber formulation also taking into account a share of the high-temperature block and the magnitude of T''_g is suggested. Optimal curing time evaluated by the thermomechanical analysis of a rubber structure is close to that evaluated by vulcammetric tests. Both of them are on the level of that determined from T_g measurements, but different from that determined from mechanical properties.

The transformation of a high-temperature block during curing is observed. In tested cases [Fig. 7(b)] there exists a compaction of the topological structure of this block, which is manifested by the growth of T_g if curing time is extended. The reason for this may be slow running physical chemical processes with participation of both the components of the curing system and active filler. This block should influence the service properties of rubber. Because of this, in further experiments, studying the relations between a quantity of the high-temperature block and properties of such rubbers is reasonable. Also, the reasons for creation of different structures of both blocks in rubbers should be studied.

It was found that Perkalink 900 influences a ratio of the topological and chemical junctions in a structure of a rubber network. So, optimization of these junction concentrations could help to control properties of cured rubber. The fact that sulfur crosslinks are gathered, as was predicted by Vilgis and Heinrich³⁰ calculations, was confirmed experimentally.

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