

Influence of Mixing Procedures and Curing Time on Molecular and Topological Structures of NR/BR Vulcanizate

B. JURKOWSKA,¹ Y. A. OLKHOV,² B. JURKOWSKI,³ O. M. OLKHOVA²

¹ Research and Developing Center for Tire Industry Stomil, Poznan, Poland

² Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, Russia

³ Plastic and Rubber Processing Division, Poznan University of Technology, Piotrowo 3, 61-138 Poznan, Poland

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ABSTRACT: A rubber compound containing butadiene rubber (BR), natural rubber (NR), and carbon black was investigated by thermomechanical analysis (TMA). A difference in dynamics of the formation of molecular and topological structures of a vulcanizate were found to be dependent on the mixing technology and curing time. Separation of the topological structure of cured rubber into two blocks with differing transition temperatures was visible after 20 min of vulcanization, when a share of a low-temperature block is minimal and $\bar{M}_{n(n)}$ reaches a stable value of about 2400. A low-temperature block had a predominant concentration of covalent branching junctions, independent of the mixing procedures, whereas the high-temperature block had covalent and topological junctions in concentrations that were dependent on the mixing method. For curing times longer than 20 min, the characteristic changes in values of $\bar{M}_{n(n)}$ are dependent on the procedure of rubber compound mixing. After additional homogenization of compounds and vulcanization, the rubbers are characterized by a diblock structure with the same qualitative structure of the branching junctions as for nonhomogenized ones. In some cases, the homogenization increases the relative concentration of the covalent junctions in the high-temperature block. When a preblend of BR and carbon black was prepared first, and then mixed with NR, this technology makes rubber compounds less sensitive to additional homogenization during further processing. A mechanism of creation and transformation of rubber-carbon black junctions during compounding and vulcanization of rubber compounds with two raw rubbers that differed in adsorption ability was proposed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 660–669, 2000

Key words: adsorption mechanism; compounding; curing; molecular structure; thermomechanical analysis; topological structure;

INTRODUCTION

Rubber technology is a term that covers problems related to compounding, shaping, and vulcanization processes. Various views on the methodology

of rubber technology have been elaborated in a number of studies.^{1–7} In addition, many physical and chemical processes during rubber processing are described in detail elsewhere. To date, however, some phenomena have not been fully explained, which has had a negative impact on optimizing and advancing this technology. Because of this, more laboratory- and industrial-scale experiments will be needed to optimize present technology toward improved future applications. The main indicator of effectiveness of rubber rec-

Correspondence to: B. Jurkowski (jurkowski@sol.put.poznan.pl).

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ipe modification or change in compounding technology is always a set of processing and exploitation properties, because it is impossible to predict all the consequences of every change in technology on both the structure and related properties of rubber.

Some aspects of butyl and butadiene rubber mastication,^{8,9} rubber mixing with sulfur⁸ or carbon black,⁹ and curing^{10,11} were investigated using thermomechanical analysis (TMA).^{10,12,13} For both uncured and cured rubbers, some changes were found in molecular and topological structures during processing, the presence of blocks, and a crystalline fraction of polymers. For a particular recipe, these changes are related to conditions of compounding and vulcanization processes. Also, changes in a microhomogeneity of blends of incompatible polymers were detected.¹³ From this, it was concluded that TMA could be useful to investigate the influence of technological factors on rubber morphology. This study presents the next part of our investigation concerning the influence of the mixing procedure and curing time on a structure of NR/BR vulcanizate.

EXPERIMENTAL

Methodology

The TMA method is based on evaluation of the thermal expansion and molecular flow of a solid polymer at a temperature variable against time, described in detail in previous studies.^{10–13} It could be applied for evaluation of the free volume V_f . For this purpose, the following equation¹⁴ is used:

$$V_f = (\beta_2 - \beta_1)T_g = 3(\alpha_2 - \alpha_1)T_g \quad (1)$$

where T_g is the glass transition temperature; β is the volumetric thermal expansion coefficient, which for isotropic material is the equivalent of three linear thermal expansion coefficients (α), mentioned in our previous studies for a polymer in a glassy state (1) and in a high elastic state (2), respectively. Deformation, temperature, and the free volume are evaluated with an accuracy of $\pm 5\%$, $\pm 2^\circ\text{C}$, and $\pm 5\%$, respectively.

It is known that in a polymer network, at least three kinds of branching junctions may coexist: chemical (covalent); physical (localized associated polar groups); and topological, created by entangled adjacent high-molecular weight fragments of rubber chains. In networks that do not contain

topological junctions, the total concentration of network junctions (ν) equals the concentration of the covalent and physical junctions and may be evaluated from thermomechanical measurements.¹⁰ With values of $\bar{M}_{n(n)}$, the calculation of the ν value from the well-known eq. (2) is possible:

$$\nu = \rho/\bar{M}_{n(n)} \quad (2)$$

where ρ is polymer density. Identification of the complex nature of the network's junctions is done by comparing the coefficients of thermal expansion in the glassy and high-elastic states.

The ratio of topological junctions ν_t to covalent junctions ν_c in the all-branching junctions in the rubber network may be calculated from eq. (3), which is a simplified version of that shown in a patent¹⁵:

$$\nu_t/\nu_c = 0.36 - 0.045 \cdot \alpha_{2m} \cdot 10^5 \quad (3)$$

where α_{2m} is the coefficient of linear thermal expansion in a high-elastic state for the model single-block network. Accepting that this equation is also valid for natural rubber networks, we substitute α_{2m} with α_2 . Analyzing data obtained from this equation one should consider that for $\alpha_2 = 8 \times 10^{-5}$ the value of $\nu_t/\nu_c = 0$. It means that under this condition, $\nu_t = 0$. Considering that α_2 for covalent networks could change, dependent on the chemical structure of the polymer chains and be related to their polarity, the main factor informing about the presence of topological junctions is a value of the ratio α_2/α_1 . The validity of the following expressions is generally accepted^{14,16,17}:

$$(\alpha_2 - \alpha_1)T_g = 0.12 \quad (4)$$

and

$$\alpha_2 T_g = 0.2 \quad (5)$$

Combining these equations, we obtain

$$\alpha_2/\alpha_1 = 2.5 \quad (6)$$

According to Ferry, when $\alpha_2/\alpha_1 > 6$, polymers are in amorphous state.¹⁸ It has been experimentally determined that, in covalent networks, α_2 could change depending on the chemical structure and polarity of the chains. For a value of $6 > \alpha_2/\alpha_1 \geq 2.5$, it is accepted that the network has the covalent nature junctions. For $\alpha_2/\alpha_1 < 2.5$, the

network has the complex (covalent, physical, and topological) nature of the branching junctions.¹⁵

Accepting that only covalent and topological branching junctions are present in rubber networks, a share of the topological junctions φ_t could be found from the relation:

$$\varphi_t = 1 - \varphi_c \quad (7)$$

where $\varphi_c = \nu_c/\nu$ is a share of the covalent junctions.

Material and Testing Conditions

For this study, the compound containing a blend of 70 phr of natural rubber (SMR 5CV, Malaysia) with 30 phr of *cis*-1,4-polybutadiene SKD II type (Voronez Sint. Rubber Factory, Russia) and 50 phr of carbon black grade N330 (Carbex 330 from Glivice Carbochem Factory, Poland) was used. The other ingredients of compound (in phr) were: a softener (aromatic oil; Plastyfikator P3, Silesian Refinery, Poland), 7.3; ZnO (Bedzin Metalurgic Plant, Poland), 5; stearic acid (Kedzierzyn Nitrogen Plant, Poland), 2.6; polyethylene wax (Chemical Plant Blachownia, Poland), 2.0; Santoflex 13 (Dusantox 6PPD, Duslo-Sala, Slovakia), 2.0; Polnox R (equivalent of Flectol H; Chemical Plant Organika, Zarow, Poland), 2.6; mineral sulfur (Siarkopol, Tarnobrzeg, Poland), 2.1; CBS (Vulkasil CBS, Chemical Plant Organika), 1.2; and Santogard PVI (Duslin P, Duslo-Sala), 0.2. A two- or three-stage mixing procedure was employed using an internal mixer (2 L Banbury type, Meccanice Moderne, Italy) for the first or the first and the second mixing stage. Compounding was done as follows in three ways: Compound (1)—traditional procedure: loading up both raw rubbers plus additives, carbon black, and softener, except curatives. Compound (2)—the master batch of SMR and carbon black was manufactured first; next, it was mixed with SKD and other ingredients of the compound, except curatives. Compound (3)—the master batch of SKD and carbon black was manufactured first; next, it was mixed with SMR and other ingredients of the compound, except curatives.

The batches were dumped at 145°C. The curatives were added on the open mill (laboratory type with a friction ratio of 1 : 1.4; VEB Erste Maschinenfabrik, Karl Marx Stadt, Germany) at a temperature not exceeding 80°C. Next, a part of each compound was additionally homogenized. Samples of the rubber compound were cured 20, 30, 40, and 50 min at a temperature of 150°C.

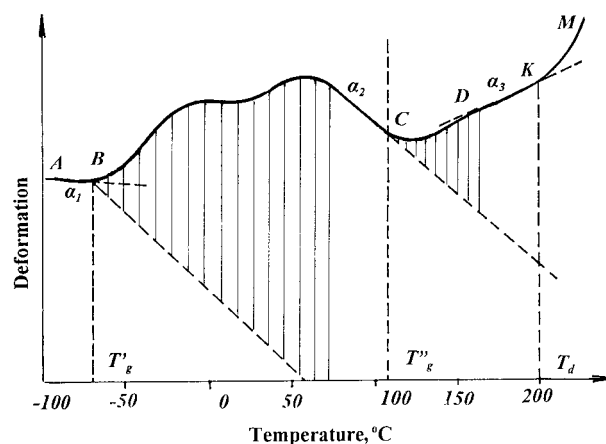


Figure 1 Typical thermomechanical curve for the tested rubber compounds. T_g^I , the glass transition temperature of a low-temperature amorphous block; T_g^II , the transition temperature of the high-temperature amorphous block; T_d , the temperature of degradation; α_1 , the thermal expansion coefficient of the low-temperature block in a glassy state; α_2 , the thermal expansion coefficient of the low-temperature block in a high-elastic state; α_3 , the effective thermal expansion coefficient of the high-temperature block in a high-elastic state.

A disc static mixer¹³ was used to try to change the distribution of carbon black in the polymer matrix. It was assembled as an intermediate element between the barrel and the head of the extruder equipped with a conveying screw. The following procedures of homogenization were used: a single or double passing of the rubber compounds through the static mixer [compounds (1) and (2), respectively], or a single passage through the static mixer and, next, through the open mill [compound (3)].

A 1.2-mm-thick sample was put into a thermostatic chamber of the TMA testing device. It was frozen without pressing under a scanning rate of 2–10°C/min to a temperature of –120°C and, next, was stored for 10–15 min to stabilize temperature. To obtain a thermomechanical curve (TMC), the sonde with a load of 0.2 g was moved down to contact the surface of a sample and, further, the sample was defrosted with a rate of 5°C/min. The deformation of the sample was measured during heating.

RESULTS AND DISCUSSION

Description of a Typical Thermomechanical Curve

The TMC for the tested cured rubbers (Fig. 1) has a shape typical for a diblock networked structure.

Table I Properties of a Low-Temperature Block of the Rubbers Prepared in Different Ways

Curing Time (min)	T_g^a (°C)	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K'	$\alpha_1 \times 10^5$ (deg ⁻¹)	$\alpha_2 \times 10^5$ (deg ⁻¹)	V_f	ϕ'	$\nu = \nu_c \times 10^4$ (mol/cm ³)
Rubber Compound (1)									
20	-75	2,400	4,340	1.80	2.08	16.9	0.09	0.42	2.19
30	-74	2,710	4,720	1.75	3.50	17.5	0.09	0.52	2.01
40	-73	2,840	5,200	1.80	2.67	17.3	0.09	0.55	1.82
50	-72	2,910	5,200	1.78	3.28	14.1	0.07	0.54	1.82
Rubber Compound (2)									
20	-69	2,440	4,220	1.75	3.00	16.7	0.084	0.38	2.25
30	-75	2,140	3,820	1.78	3.10	15.9	0.076	0.44	2.49
40	-68	2,140	3,720	1.74	3.51	15.6	0.074	0.57	2.55
50	-69	2,200	6,950	1.70	2.25	15.6	0.082	0.61	1.30
Rubber Compound (3)									
20	-69	2,350	4,020	1.71	2.95	11.5	0.058	0.29	2.36
30	-73	5,960	10,380	1.74	3.23	17.9	0.047	0.34	0.92
40	-69	3,740	6,580	1.76	3.51	15.9	0.056	0.49	1.44
50	-71	3,150	5,600	1.78	3.35	14.1	0.061	0.54	1.70

^a T_g is the glass transition temperature; $\bar{M}_{n(n)}$ is the number-average molecular weight of the chains between the junctions of a polymer network; $\bar{M}_{n(w)}$ is the weight-average molecular weight of the chains between the junctions of a polymer network; $K = \bar{M}_{n(n)}/\bar{M}_{n(w)}$ is the polydispersity coefficient of the chains between the junctions; α is the coefficient of linear thermal expansion; V_f is the free volume; ϕ is a weight share of the block. ν is summary concentration of the chains between the covalent and topological junctions in the network, calculated accepting $\rho = 0.95$; ν_c is concentration of the chains between the covalent junctions of the rubber network.

Depending on the mixing procedures, a low-temperature block in these rubbers is visible between the transition temperatures $T_g = -69 \div -75^\circ\text{C}$ (point B) and $T_g = 108 \div 137^\circ\text{C}$ (point C). It virtually consists of only covalent junctions (Table I). A high-temperature block is visible at temperatures over T_g . Here, a high elastic state of rubber

is determined by its rubber-carbon black fraction with intermolecular interactions both between macromolecules and between macromolecules and a surface of carbon black. These interactions are stronger than those in a low-temperature block. The analyzed high-temperature block consists mainly of topological junctions (Table II).

Table II Properties of a High-Temperature Block of the Rubbers Prepared in Different Ways

Curing Time (min)	T_g'' (°C)	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K''	$\alpha_3 \times 10^5$ (deg ⁻¹)	$\nu \times 10^4$ (mol/cm ³)	$\nu_c \times 10^4$ (mol/cm ³)	ν_c/ν
Rubber Compound (1)								
20	108	7,090	9,910	1.40	-125.0	1.34	0.03	0.02
30	117	6,310	8,670	1.37	-64.5	1.51	0.30	0.20
40	137	4,280	5,890	1.38	-52.6	2.22	0.89	0.40
50	134	4,690	6,450	1.38	-38.6	2.03	1.02	0.50
Rubber Compound (2)								
20	119	9,230	12,860	1.39	-100.0	0.74	0.03	0.04
30	120	5,630	7,900	1.40	-90.9	1.20	0.07	0.06
40	134	2,470	3,380	1.37	-83.3	2.81	0.28	0.10
50	134	4,480	6,070	1.36	-83.3	1.57	0.16	0.10
Rubber Compound (3)								
20	116	7,170	10,040	1.40	-76.9	0.95	0.11	0.12
30	115	16,600	23,120	1.39	-136.4	0.41	0.01	0.02
40	134	6,900	9,530	1.38	-100.0	1.00	0.01	0.01
50	133	3,980	5,480	1.39	-52.6	1.73	0.69	0.40

For abbreviations see Table I.

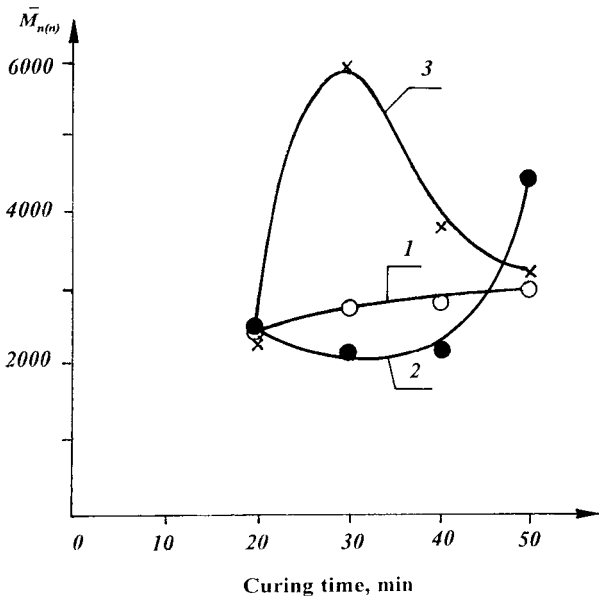


Figure 2 The number-average molecular weights of the chains between the junctions in a low-temperature block of rubbers made of compounds (1), (2), and (3) versus curing time.

The rubber with such a structure was also previously investigated.¹⁰ Then the concentration of topological junctions in the network was dependent, among other things, on a kind of curing system. A low concentration of covalent junctions was interpreted as resulting from a lower reactivity of double bonds in the rubber chains adsorbed on a surface of carbon black particles. In the present investigation, carbon black grade N330 was used as a filler with different surface activity than that for carbon black grade N220 in previous experiments.¹⁰ This influences the covalent network structure of a high-temperature block.

Influence of Mixing Method on the Molecular and Topological Structures of Cured Rubbers

The free volume V_f is a criterion of mobility and compactness of macromolecules. Changes in V_f and T_g , which are dependent on a technology of introducing carbon black (Table I), confirm some influence of carbon black's distribution between the polymer phases (as reported in the literature) on a structure of the amorphous low-temperature block.

Separation of a topological structure of cured rubber into low- and high-temperature blocks is visible for each of the tested rubbers after 20 min of vulcanization, when a share of a low-temperature block is minimal and $\bar{M}_{n(n)}$ reaches a stable

value of about 2400 (Tables I and II). Further, as curing time increases, an average molecular weight changes in a different way, dependent on the mixing procedure (Fig. 2). A weight share ϕ' of the low-temperature block in rubbers at each of the investigated mixing methods grows as curing time extends and reaches a value of $0.55 \div 0.6$ (Table I). The glass transition temperature of the low-temperature block T_g' and the free volumes are practically independent of curing time. For T_g' , the same conclusion was made earlier for other rubber networks,¹⁹ but Bukhina noticed that V_f reduces as curing time extends; however, in the investigations by Bukhina and colleagues, rubber was accepted as a single block material.

Structures of a low- and high-temperature block of the rubbers (1) and (2) demonstrate different changes (Figs. 2 and 3), that is, the curves (1) reflect changes in molecular parameters of the network versus curing time for the standard compounding procedure. In this instance, there is no optimal curing time τ_c , at which molecular structures formed in both blocks reflect the equilibrium state of adsorption layers of each of two raw rubbers introduced into the compound. Rather, this state is determined by adsorption activity of each raw rubber. The lack of clearly visible $\tau_{c(opt)}$ for compound (1) shows a process almost at equilibrium of NR and BR's competitive adsorption on active sites on the surface of carbon black during all tested curing times.

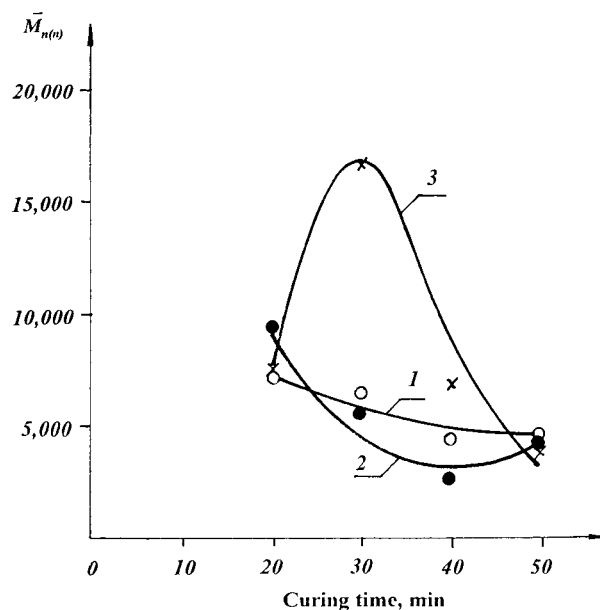


Figure 3 The number-average molecular weights of the chains between the junctions in a high-temperature block of rubbers made of compounds (1), (2), and (3) versus curing time.

Another experimental scenario is for mixing procedures (2) and (3), when carbon black was introduced into only one polymer and, next, this master batch was mixed with another polymer and additives. For these procedures, the equilibrium of adsorption is reached at approximately the same curing time of 30–40 min. For mixing procedure (2), when a NR/carbon black master batch is first made and then mixed with BR, the creation of a more networked structure of both blocks was noticed for optimal curing time. The crosslinking density of filled rubbers is determined, among other methods, by carbon black concentration.²⁰ Because of this, it is possible to assume that sulfur adsorbed on the surface of carbon black is more efficient in a crosslinking process than a nonadsorbed one. If this is true, an increase in the curing efficiency of procedure (2), compared with procedure (1) at $\tau_c \leq \tau_{c(\text{opt})}$, results from higher actual activity of sulfur to crosslink NR than BR. For $\tau_c > \tau_{c(\text{opt})}$, it could be explained by the following mechanism: chains of BR, due to its higher adsorption ability, force out the NR chain segments adsorbed on the surface of carbon black. As a result, a decrease is observed in the total crosslinking degree related to concentration of all types of junctions, including not only sulfur bonds but also clusters and products of both adsorption and chemisorption.

Another scenario is in the case when a surface of carbon black at the initial mixing of the BR/carbon black master batch and NR is predominantly occupied by BR chains, which is what takes place in compound (3). Now, competitive replacement of BR chains by NR during time up to $\tau_{c(\text{opt})}$ results in a lowering of the accumulation rate of the branching junctions in both blocks of rubber. For $\tau_c = \tau_{c(\text{opt})}$, it lowers to nil. Further replacement of the BR adsorption layer by NR results in a growth in the degree of crosslinking. To explain this fact, it is necessary to accept that the activity of NR adsorbed on a surface of carbon black to a sulfur-based curing system is higher and then the curve takes a shape as shown in Figure 3. This is related with differing stabilities of rubber–carbon black junctions participating in creation of the rubber network. Because of this, the dependence of $\bar{M}_{n(n)} = f(\tau)$ for the three mixing technologies tested is determined by the following:

1. Different curing effectiveness of sulfur against NR and BR, and an influence of carbon black properties on this process.
2. Different adsorption ability of tested raw

rubbers against a surface of carbon black and related different networking ability of the created structures.

3. Competition of sulfur and rubbers in adsorption on a surface of carbon black.

In a low-temperature block, an equilibrium structure of the rubber compound was reached at the termination of the mixing process, and also indirectly evidenced by independence of the T_g' on curing time. Formation of a high-temperature block is not ended during this period; both T_g'' (Table II) and a share of this block $\phi'' = 1 - \phi'$ are changing as curing time extends to 40 min.

It is generally accepted that networking of unfilled rubbers has only a slight influence on the glass transition process.^{16,19} For filled rubbers, this dependence is more distinct because active filler helps to redistribute the branching junctions between the blocks. Here, T_g' is related to the growth of physical contact of fragments of polymer chains with a surface of carbon black, which improves interfacial adhesion. This adhesion, due to interaction with an active surface of carbon black, increases when contact time (curing time in this study) extends. Based on this knowledge, it is concluded that other kinetic processes with participation of rubber compounds' ingredients and fragments of rubber chains, which are a frame of a high-temperature block, limit the formation of the structure during vulcanization. This is evidenced by (1) the growth of T_g as crosslink density increases and (2) a strong interface's interactions between the polymer chains and a surface of carbon black (the most probable case here) or interaction between the most polar fragments of adjacent chains (probably 1,2 vinyl isomers of a butadiene). A small concentration of the covalent branching junctions ν_c is observed in this block at the start of vulcanization. Its share increases as curing time increases, which for compound (1), for instance, reaches even as much as 40 to 50% (Table II). Such a tendency is evident from many other investigations. It could be supposed that the process of network structure formation in a high-temperature block of the tested rubbers even at 50 min of curing time is not fully ended. Considering this assumption, it is concluded that mixing procedures, which are compared here, essentially influence changes in the effective coefficient of the linear thermal expansion α_3 . Generally, it results from the change in the free volume and relaxation of the topological junctions. For a pure covalent network in the zone of a high-elasticity plateau, changes are not ob-

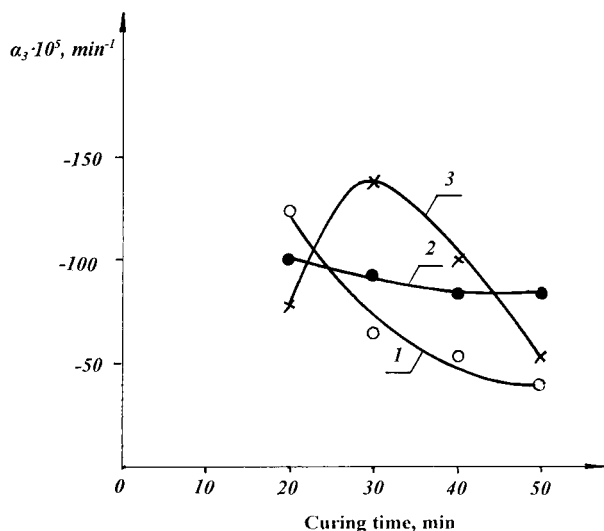


Figure 4 Effective linear thermal expansion coefficient α_3 of a high-temperature amorphous block of rubbers made of compounds (1), (2), and (3) versus curing time.

served in concentrations of the junctions. Here, the α_3 value results from the increase in the free volume as temperature grows (sample expanding).

Two processes are simultaneously present in the polymer network that contains both the chemical and topological branching junctions in a high-elasticity plateau zone at an arbitrarily chosen temperature. The first of these processes results from changes in the free volume, as was described earlier. In the second process, it is the relaxation of the topological junctions, in which the depth of penetration of the polymer sample by a sonde grows as temperature grows due to lowering of the Young modulus. The effect of these two processes is a decrease in the α_3 value, which results from a predominating role of the relaxation process on the topological junctions.

It was also noticed that the shape of curves in Figures 3 and 4 is similar. This suggests a direct correlation between the molecular structure of the polymer network of rubber and the character of changes in the free volume. This relation is dependent on the rubber mixing procedure. Therefore, the value of α_3 helps to study factors influencing a structure of the rubber network. Here, it results from the different distribution of carbon black between NR and BR phases and the different homogeneity of the rubber compound. A comparison of shapes of the curves characterizing the dependence of α_3 versus curing time (Fig. 4) gives indirect sup-

port for this conclusion. These shapes inform about a rate of accumulation of the branching covalent junctions in a structure of a high-temperature block. The concentration of the covalent branching junction increases in both blocks during vulcanization and probably the topological junctions would be less visible. Due to this, for mixing procedures (1) and (2) (Fig. 4), a decrease in the α_3 value is noticed as curing time extends. For procedure (3), a maximum was found for a curing time of 30 min. Differences among mixing procedures result in another mechanism of interaction between the rubber and other ingredients of the compound. There is no stabilization of α_3 versus curing time. From this, as well as from the preceding discussion concerning changes in concentration of the covalent branching junctions, it is concluded that the process of formation of the rubber network structure is not ended during vulcanization under described conditions.

The molecular weight distributions (MWDs) of the chains between the junctions in a low-temperature block of tested rubbers are bimodal, independent of curing time and mixing procedures. In Figure 5, as an example, is shown the MWD of the chains in the networks of both blocks in the rubber (2). These data are obtained for the second procedure of a mixing and curing time of 40 min, considering that processes occurring in a low-temperature block are limiting.

Free-radical interaction between the polymer chains and the carbon black particles during mixing, featured prominently in the development of bound rubber,²⁰⁻²³ is correlated with reinforcement of rubber.^{24,25} Active sites not uniformly distributed on the surface of carbon black^{26,27} (~ 3 on every particle)^{28,29} and associated with the stable free radicals observed in the bound rubber, participate in creation of a part of the junctions in the rubber network. These sites are magnetically heterogeneous.²⁷ From these, it is concluded that the main reasons for the bimodal shape of the MWD could be: the presence of active sites with different reactivity on a surface of carbon black; polyfunctionality of these sites; partial dispersion of ingredients; and also some scatters of sizes and development of active filler particles. More precisely, this conclusion corresponds to the fragments of macromolecules preserving their initial elasticity in the presence of carbon black.

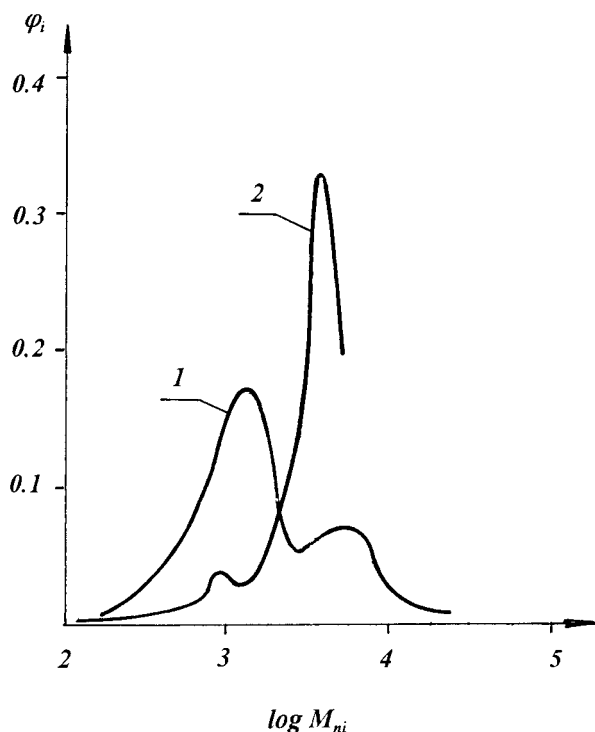


Figure 5 The MWD of the chains between the junctions in the low-temperature block (1) and in the high-temperature block (2) in rubber made of compound (2); curing time 40 min.

Influence of Additional Homogenization of the Rubber Compound on a Structure of Cured Rubbers

Additional homogenization of the rubber compound was performed according to the procedures

described earlier. After additional homogenization and vulcanization, all tested rubbers hold diblock amorphous structure (Tables III and IV). Low-temperature blocks also have here a network that is virtually without topological junctions. For a high-temperature block, a share of the covalent junctions is strongly dependent on the method of additional homogenization. Its initial value for a curing time of 40 min was in a wide range between 0.01–0.40 (Table II), depending on the mixing procedure before homogenization.

Additional homogenization of rubber compounds by using the static mixer or the static mixer and the mixing mill stretch elements of the polymer phase. This increases the contact surface between dispersed ingredients and a polymer matrix. On the other hand, it gives the higher probability of interactions between active sites on carbon black particles and both polymer chains and molecules of ingredients of the curing system. Due to this, accepting that such homogenization should promote creation of the physical junctions in the rubber network is possible.

Simultaneously, homogenization increases the accessibility to adsorption of many ingredients on a surface of carbon black particles. Later, during the vulcanization process, running at a temperature higher than that, when mixing, a gradual desorption of a part of these adsorbed ingredients occurs. It is probable that this desorption rate depends on the activity of particular sites on a surface of carbon black. Because of this, the concentration of the curing system participating in

Table III Properties of a Low-Temperature Block in the Rubbers Made from Additionally Homogenized Compounds^a

Method of Homogenization ^b	T'_g (°C)	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K'	$\alpha_1 \times 10^5$ (deg ⁻¹)	$\alpha_2 \times 10^5$ (deg ⁻¹)	V_f	ϕ'	$\nu = \nu_c \times 10^4$ (mol/cm ³)
Rubber Compound (1)									
1	-72	3,990	7,160	1.80	2.78	16.1	0.08	0.45	1.33
2	-69	7,180	12,080	1.66	5.26	17.4	0.07	0.39	0.79
Rubber Compound (2)									
1	-75	4,410	7,950	1.81	6.43	17.4	0.07	0.34	1.19
2	-71	4,960	8,660	1.75	4.05	15.3	0.07	0.39	1.10
3	-70	7,580	13,080	1.73	3.45	16.5	0.08	0.35	0.73
Rubber Compound (3)									
1	-69	2,300	3,990	1.74	3.61	11.2	0.05	0.38	2.38
2	-63	4,140	7,030	1.70	3.08	15.4	0.08	0.43	1.35
3	-78	3,040	5,430	1.79	3.77	12.2	0.05	0.41	1.75

^a Curing time 40 min.

^b (1) is single passing through the static mixer, (2) is double passing through the static mixer, (3) is single passing through the static mixer and, next, through the mixing mill. For other abbreviations see Table I.

Table IV Properties of a High-Temperature Block of the Rubbers Made From Additionally Homogenized Compounds, Curing Time 40 Min

Method of Homogenization	T_g'' (°C)	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K''	$\alpha_3 \times 10^5$ (deg ⁻¹)	$\nu \times 10^4$ (mol/cm ³)	$\nu_c \times 10^4$ (mol/cm ³)	ν_c/ν	ϕ''
Rubber Compound (1)									
1	117	9,190	12,780	1.39	-52.6	1.03	0.420	0.41	0.55
2	117	22,650	31,690	1.40	-125.0	0.42	0.014	0.03	0.61
Rubber Compound (2)									
1	141	19,720	27,280	1.38	-125.0	0.48	0.014	0.03	0.66
2	120	15,690	21,160	1.35	-166.0	0.61	0.014	0.02	0.61
3	127	30,410	42,000	1.38	-66.7	0.31	0.067	0.22	0.65
Rubber Compound (3)									
1	126	7,940	11,020	1.39	-66.7	1.20	0.240	0.20	0.62
2	123	10,640	14,830	1.39	-62.5	0.89	0.195	0.22	0.57
3	128	9,160	12,760	1.39	-55.6	1.03	0.406	0.39	0.59

For abbreviations see previous tables.

the crosslinking should, in fact, depend on the method of homogenization.

Comparing data from Tables II and IV, it is clear that additional homogenization changes the molecular characteristics of a high-temperature block of the tested rubber. These changes depend both on the mixing procedures used for preparing this compound and, later, on the homogenization method. A detailed explanation of these procedures and methods is needed to carry out further investigations. Nevertheless, some particular observations could be done.

Properties of a low-temperature block of the rubber made from compound (1), which are additionally homogenized, are characterized by almost the same value of the polydispersity coefficient K as that for nonhomogenized (Tables I and III). However, it was observed that values of $\bar{M}_{n(n)}$ and $\bar{M}_{n(w)}$ grow after passing the compound through the static mixer, especially after double passing. A share of a low-temperature block had a decreasing tendency, and its spatial structure was a little more compact (V_f drops from 0.09 to 0.08). Also, for a high-temperature block, molecular parameters of a structure such as $\bar{M}_{n(n)}$, $\bar{M}_{n(w)}$, and K changed in a similar way (Tables II and IV). For rubbers (1) and (3), the concentration of the covalent branching junctions was reduced noticeably after double passing through the static mixer (Table IV). It evidences that a contribution of the chemical and physical crosslinking in a process of rubber networking of this block was lowered essentially. Simultaneously, a share of the covalent junctions ν_c/ν is reduced for compound (1) and is preserved constant for compounds (2) and (3).

Additional homogenization results in a wider spectrum of curing system activity during formation of a network in a low-temperature block of rubber (1) made by using a traditional procedure. This is clear in the preservation of two extremes (bimodal distribution) on the MWD curve for chains between the junctions. Comparison of the MWD for rubbers without and after additional homogenization of compounds is shown in Figure 6. Here, when fractions of molecular weights of these samples are similar, only a narrow zone was found.

Rubber made of the homogenized compound (2) was characterized by a little more compact spatial structure of a low-temperature block (Tables I and III). Simultaneously, a share of this block was reduced. The value of $\bar{M}_{n(n)}$ became more than twice as large as for nonhomogenized compounds. The same phenomenon was found for changes in molecular parameters of a high-temperature block. This suggests that diluting of the SMR/carbon black master batch with SKD raw rubber makes a tested rubber compound sensitive to further homogenization.

For compound (3), all the tested methods of additional homogenization only slightly influenced the molecular structures of the cured rubber network in both blocks. It is probable that the reason for this outcome depends on the mixing method, where a preblend of BR and carbon black was prepared first, after which it was mixed with NR. This technology makes the tested rubber compounds less sensitive to additional homogenization during further processing.

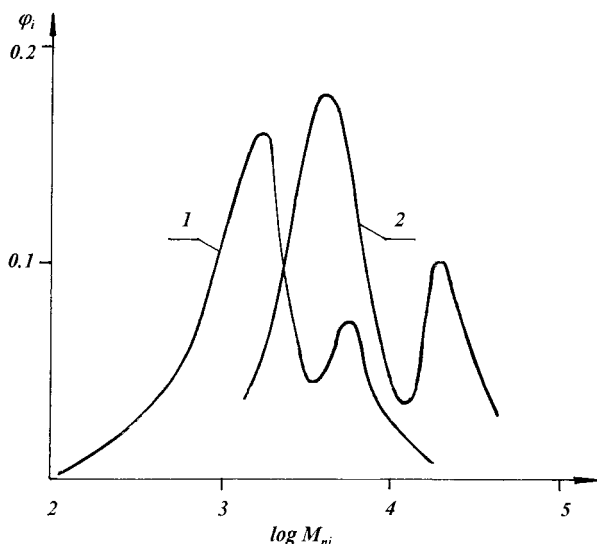


Figure 6 The MWD of the chains between the junctions in the low-temperature block of rubber (1); curing time 40 min; made by using standard procedures (1) and by using additional homogenization (2).

CONCLUSIONS

In this and previous investigations, it was found that topological and molecular structures of the rubber network change during successive stages of processing when mixing usually occurs. This transformation process depends on many technological factors such as order of loading of ingredients and the mixing method. Because of this, along with measurements of the average crosslink density (what is generally accepted), the topological and molecular structures of the rubber network should simultaneously be controlled to find the optimal architecture for every particular case. However, to achieve this outcome, further study of a correlation between the rubber properties and the network structure is necessary. It will help to limit the necessary compounding and curing experiments.

In tested NR/BR vulcanizates, a low-temperature block virtually has only covalent branching junctions. A high-temperature block simultaneously has covalent and topological junctions in shares that are dependent on the mixing method, including additional homogenization and the order of loading of ingredients.

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