

On a Structure of NR and BR Carbon Black Filled Rubber Compounds and Vulcanizates

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ABSTRACT: Rubber compounds containing natural rubber (NR) filled with carbon black were investigated with the help of the thermomechanical method according to the procedure described in a previous article (Jurkowska et al. *J Appl Polym Sci*, in press). It was stated that NR filled with carbon black has two amorphous blocks differing in the transition temperatures and one pseudo-crystalline structure. A ratio of these morphology structures changes during mixing with carbon black depending on the carbon black content and mixing time. A crystalline structure has two or three temperatures characterizing the beginning of melting and the beginning of flow. This evidences its complex architecture. Vulcanized rubber of NR mixed with butadiene rubber (BR) in a ratio of 70/30, filled with carbon black, has two-block amorphous structure without a pseudo-crystalline structure. A dynamics of forming molecular and topological structures of vulcanizates depends on carbon black content. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3305–3315, 1999

Key words: NR; BR; compounding; topological structure; molecular structure; TMA; rubber networks; free volume

INTRODUCTION

Previously, the thermomechanical method (TMA) was applied to study both topological and molecular structures of *cis*-1,4-butadiene rubber (BR) mixed with carbon black.¹ It was found that mixing on an open mill during 2.5 min completely suppressed BR recrystallization. The obtained compound has diblock amorphous structure in a temperature interval from $\approx -70^\circ\text{C}$ to $+110^\circ\text{C}$. In this interval also one rubber/carbon black

pseudo-crystalline structure exists having a melting temperature over $+100^\circ\text{C}$. A weight share of rubber in this structure dependent on mixing time varies between 0.54 and 0.88. Mechanochemical transformations during mixing give not only a quantitative redistribution of macromolecules or its segments between the different structures of a rubber compound, but also redistribution of isomeric content. Molecular weight characteristics of the chains between the junctions of an amorphous phase were calculated.^{1,2} Now similar studies are described for natural rubber (NR) and its blends with polybutadiene.

METHODOLOGY

The thermomechanical method of evaluation properties of macromolecules of solid thermoplas-

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tic or crosslinked polymers in a thermal field being variable against time is based on measurements of thermal expansion of polymer samples under a very low load and is described in details in previous articles.¹⁻³

EXPERIMENTAL

Material

The following was used for this study:

1. Compound of NR (SMR 5CV) filled with 50 phr of carbon black N330. It was prepared on a laboratory mixing mill with the friction ratio of 1 : 1.04. The mill rolls were heated to 60°C in the beginning of compounding. Here, the compounding procedure was as follows: a. preliminary mastication of rubber; b. addition of carbon black to form a compound and, next, c. homogenization of the compound.

Samples for the TMA were taken 2.5, 5, 7.5, 10, 15, and 20 min after the beginning of the homogenization process. Raw rubber taken for comparison was milled at the same conditions.

2. Compounds containing natural rubber (SMR 5CV) and *cis*-1,4-polybutadiene (BR) SKD type (from Russia) in a ratio of 70/30, and 0, 10, 20, 30, and 50 phr of carbon black grade N330. The compounding procedure was as follows: loading into the internal mixer (2L Banbury type) raw rubbers, additives except curatives, and next, carbon black and softener. The batch was dumped at 145°C. In the finishing stage of mixing, the curatives were added on the open mill (laboratory type with a friction ratio of 1 : 1.04) at a temperature not exceeding 80°C. This mixing time was 5 min. Samples for testing were cured during 30 min at a temperature of 150°C.

RESULTS AND DISCUSSION

Molecular and Topological Structures of NR Filled Rubber Compounds

To separate processes occurring in the tested rubber during mixing in the presence of carbon black and without it, all experiments were arranged in

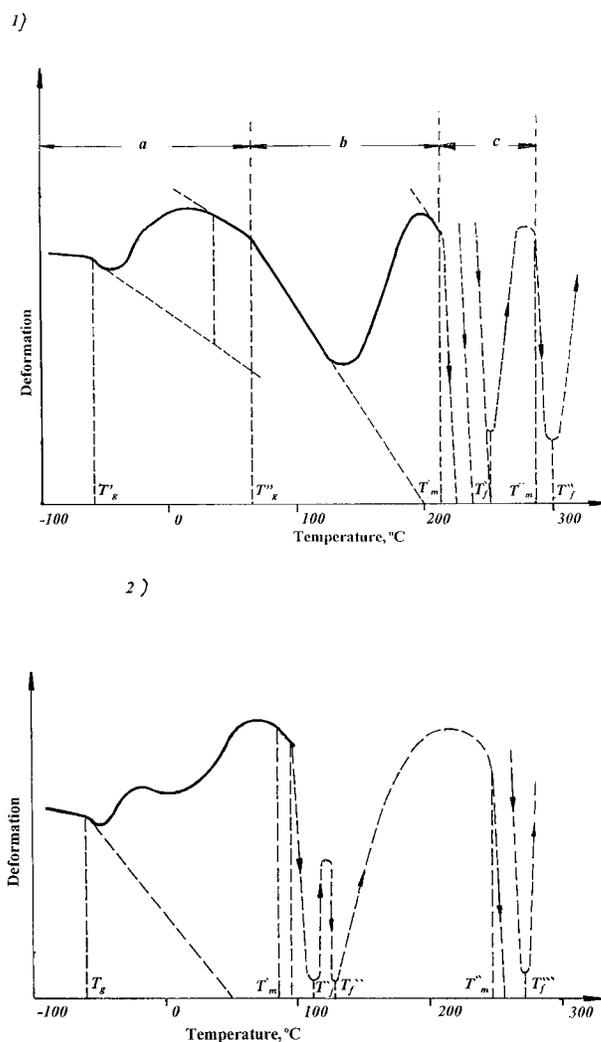


Figure 1 Typical thermomechanical curves for natural rubber/carbon black compound milled during 2.5 min (1) and 20 min (2); (a) a low-temperature amorphous block; (b) a high-temperature amorphous block; (c) a zone of melting of a pseudo-crystalline structure; T'_{g} , the glass transition temperature of a low-temperature amorphous block; $T'_{g''}$, the transition temperature of a high-temperature amorphous block; $T_{m'}$, temperature of the beginning of melting process of the first (') and the second (") crystalline structures; T_f , temperature of molecular flow.

two steps. Molecular and topological structures of NR filled with 50 phr of carbon black N330 and changes of this structure in consequence of different mixing time, τ , were evaluated. Thermomechanical curves for NR/carbon black compounds mixed on an open mill during 2.5 and 20 min are shown in Figure 1 curves (1) and (2), respectively. The topological structure analyzed here is similar to that for BR/carbon black compounds.¹ In both

cases exist a diblock amorphous structure and a pseudo-crystalline structure. The latter consists of fragments of macromolecules interacting with active sites of a carbon black surface. The acceptance of this structure as pseudo-crystalline is based on the results of analysis of an accumulation rate of polymer deformation in the melting zone of this fraction. The accumulation rate of deformation in a system is related to an analogical rate in a crystalline polymer. It is generally accepted that in a presence of carbon black, creating the really crystalline structure is impossible. Therefore, the structure created by rubber and carbon black is called pseudo-crystalline.

After 2.5 min of mixing [Fig. 1, curve (1)] in the pseudo-crystalline structure in the temperature interval between 206 and 304°C (the beginning of melting and the beginning of molecular flow) after degradation practically of all the junctions between carbon black and rubber molecules at least two kinds of pseudo-crystalline structures are present simultaneously. They differ in rubber/carbon black interaction energy, what gives a difference in temperatures of the beginning of melting (T'_m and T''_m) and in temperatures of the beginning of molecular flow (T'_f and T''_f). Probably, this is related to a presence of active sites with different interaction energies on a surface of carbon black.

Mixing time 5–15 min does not principally change a topological structure of the rubber compound. However, during this time essential lowering of T'_m for low-melting crystalline structure was observed. Such temperatures for the high-melting once do not change so much (300–272°C) to accept that this dependence is described by the function with extremum.

We believe that the reason for such a character of the dependence T'_m vs. mixing time is formation of a low-melting crystalline structure in time which is resulting from the competitive interaction between flexible fragments of rubber chains (crystalline fractions 1 and 2 at $\tau = 2.5$ min) and hard fragments from a high-temperature amorphous block. In this process, the last loosens the compact rubbery fraction on the surface of carbon black (tightly bound rubber), reducing what is probably its melting temperature. This process runs until the moment when full homogenization of both amorphous blocks into a single block and adsorption of all the remaining polar fragments of a high-temperature amorphous block on the surface of carbon black is reached. This process results in drastic compaction of a polymer layer

adsorbed on a surface of carbon black and in the growth of the temperature of the beginning of molecular flow.

Obtained here a structure of a rubber/carbon black compound has a pseudo-networked character, when the junctions are carbon black particles with fragments of polymer chains adsorbed on their surface. Such topological structure when passing rubber chains create the amorphous block is confirmed by Leblanc.^{4–6}

In Figure 2(a) and (b) are shown dependencies of the temperature interval $\Delta T = T_f - T_m$ of the existence of a pseudo-crystalline structure in the rubber compound and $\Sigma\varphi$ (a sum of fractions of a pseudo-crystalline structure) on mixing time. These relations for NR/carbon black compounds [curve (1)] have the extreme for mixing time equal to 10–12.5 min. It is related with (i) removal of internal stresses of the chains in the beginning of NR mastication, which is resulting in the growth of crystallization, and (ii) mechanical degradation of crystallites during further mixing. The same relations obtained earlier for a pseudo-crystalline structure of BR/carbon black compounds, shown as curve (2), had another character.¹ In BR, most likely, lack of considerable internal stresses of macromolecules and mastication process result in a decrease of crystallization degree observed from the start of processing.

Compounding of the multi-ingredient polymer compositions results from many processes like adsorption-desorption, diffusion of low-molecular ingredients, segmental diffusion in the boundary layer between polymeric phases, mechanochemical transformations, and many others. All of them have kinetical character. Because of this, manufacturing technology of polymer compounds accepts that homogenization of them could give a state in which every carbon black particle creates “junctions” in a pseudo-network of a low-temperature block. This state in analyzed rubber compound (Table I) is reached at the 10th min of milling. There, creation of maximal number of junctions, N , at minimal molecular weight, M , of their chains ($M \sim 1/N$) is obtained. When mixing time is extended, the shortest chains between the junctions, being the most strained, are degraded with the highest intensity. As a result, the growth of the average molecular weight of the chains between the junctions of the network is obtained. Because of this, the dependence $M = f(\tau)$ has extremal character. The same is concluded for the related values like $K = f'(\tau)$ and $N = f''(\tau)$.

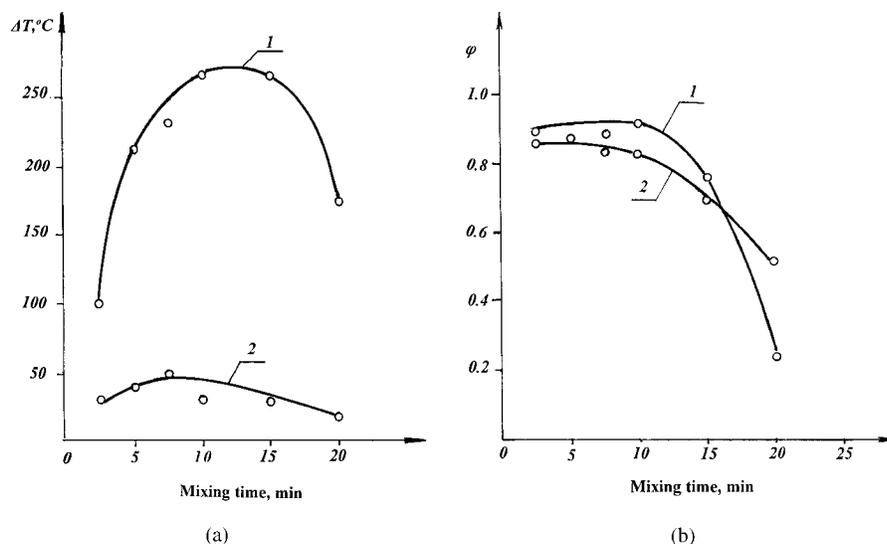


Figure 2 Dependence of an interval of existence of the pseudo-crystalline structure ΔT (a) and a share of pseudo-crystalline structure φ (b) on mixing time in carbon black filled rubbers: 1, NR; 2, BR; $\Delta T = T_f - T_m$, where T_f is the temperature of the starting of molecular flow and T_m is the temperature of the beginning of melting.

Dependencies of T_g vs. τ for a low-temperature block (Table I) have logical direction from -61°C to -65°C . However, taking into account that T_g magnitudes are determined here with the accuracy of $\pm 5\%$ or $\pm 3^\circ\text{C}$ it is impossible to state whether the T_g is changing or is preserved constant during milling.

The level of the T_g of a low-temperature block T'_g for NR/carbon black compound (Table I) is comparable with that for unfilled rubber. It results from the fact that in a low-temperature block, are present mainly the cluster junctions (carbon black free well-oriented fragments of the chains with strong intermolecular interactions) of rubber macromolecules not interacting with a

surface of active filler reducing its mobility. The T'_g for this compound has the value similar to that for BR/carbon black compounds ($-63 \div -67^\circ\text{C}$). However, macromolecules of BR and NR differ in flexibility and related ability to chains interaction. Because of this, it is concluded that T'_g magnitude is determined not only by properties of polymer macromolecules alone, but resulting from both their properties and some adsorption activity of filler particles to individual macromolecules or its fragments. Investigations done previously¹ and described in this article confirm this conclusion.

Character of intermolecular interactions and interactions of NR macromolecules with a surface

Table I Properties of a Low-Temperature Amorphous Block of NR/Carbon Black Compounds

Mixing Time (min)	T'_g ($^\circ\text{C}$)	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K'	φ'
2.5	-61	24,550	36,320	1.48	0.073
5	-62	19,020	27,980	1.47	0.026
7.5	-62	1330	1670	1.44	0.017
10	-64	540	680	1.26	0.010
15	-65	7270	9790	1.35	0.060
20	-65	94,820	154,020	1.63	0.240

T'_g , the glass transition temperature; $\bar{M}_{n(n)}$, the number-average molecular weight between the junctions of a polymer network; $\bar{M}_{n(w)}$, the weight-average molecular weight between the junctions of a polymer network; $K = \bar{M}_{n(n)}/\bar{M}_{n(w)}$, the polydispersity coefficient of the chains between the junctions; φ' , a weight fraction of a block.

Table II Properties of a High-Temperature Amorphous Block and a Pseudo-Crystalline Structure of NR/Carbon Black Compounds

Mixing Time (min)	A High-Temperature Amorphous Block					A Pseudo-Crystalline Structure		
	T_g'' (°C)	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K''	φ''	T_m^b , °C	T_f , °C	$\Sigma\varphi$
2.5	64	146,200	209,200	1.43	0.09	220; 275	250; 300	0.837
5	34	135,700	181,200	1.34	0.08	87; 263	107; 304	0.894
7.5	16	102,400	139,500	1.36	0.09	73; 240	102; 310	0.893
10	-24	25,600	35,900	1.40	0.06	54; 115	120; 327	0.930
15	-34	40,200	56,800	1.41	0.16	28; 208	38; 300	0.780
20	—	—	—	—	—	93; 120; 252	108; 127; 272	0.760

T_m^b , the temperature of the beginning of melting process of each fraction of a pseudo-crystalline structure; T_f , the temperature of the beginning of flow of each fraction of a pseudo-crystalline structure; $\Sigma\varphi$, a sum of fractions of a pseudo-crystalline structure; for other abbreviations see Table I.

of carbon black during milling of the rubber compound is practically unchanged, but some mass exchange is noticed between two amorphous blocks. During 20 min of milling, the low-temperature block was assimilated and one amorphous structure was created. In BR/carbon black compound this phenomenon is not observed.¹

In the beginning of milling for the high-temperature amorphous block the transition temperature T_g'' is by 120°C higher than that for the low-temperature amorphous block T_g' (Table II). However, mechanochemical processes in rubber accompanying the milling and permanent run of transformations of the chains fragments between blocks give changes in the molecular structure of the high-temperature amorphous block. This is evidenced by a gradual decrease in a gradient of the transition temperatures $\Delta T_g = T_g'' - T_g'$, shown in Figure 3 as curve (1), until complete disappearing of the low-temperature amorphous block after 20 min of milling. For comparison, curve (2) of Figure 3 displays T_g' vs. mixing time for BR/carbon black compound. The character of these two curves is not the same. This suggests different sensitivity of macromolecules of these polymers to mechanochemical action during mixing. This sensitivity is determined by monomer and isomer content and also results from their different reactivity with a surface of carbon black.

The weight ratio of components of a topological structure of a rubber compound determined by use of the TMA corresponds not only with a polymeric component of a system. Because of this, a low-temperature block content, φ' , does not correspond with a quantity of *cis*-1,4-isoprene being the isomer characterized by the lowest interaction

energy. It could be concluded from Table I where φ' values go through the minimum when T_g' is unchanging. Also, it is concluded that arrangement of a low-temperature block is not determined by properties of rubber macromolecules,

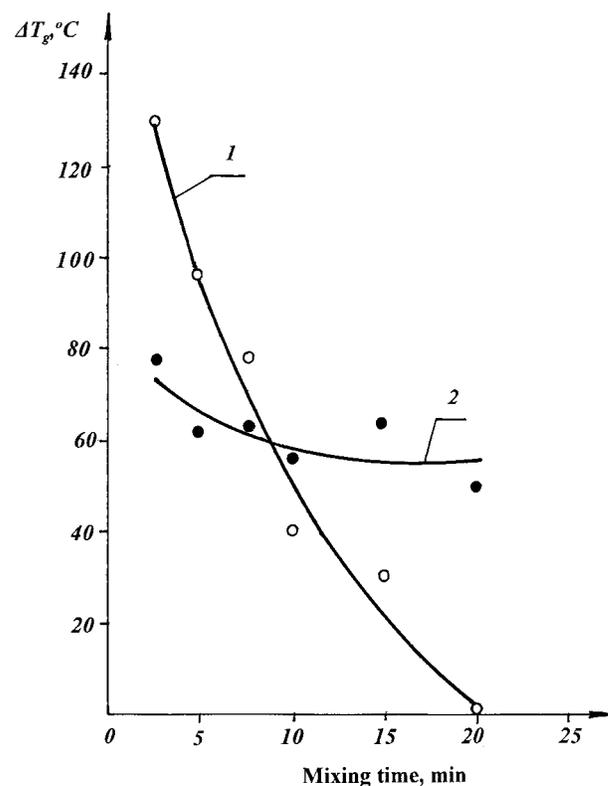


Figure 3 Dependence of a decrement (increment) of the glass transition temperature ΔT_g for natural rubber (1) and *cis*-1,4-butadiene SKD rubber (2) on mixing time.

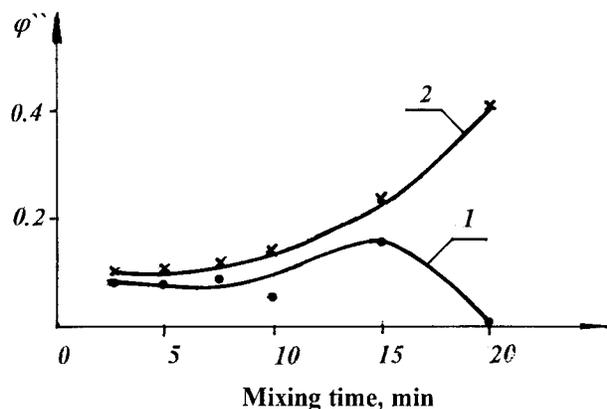


Figure 4 Changes in a weight share of a high-temperature amorphous block during milling for NR (1) and BR (2).

but by polymer chain interaction with some active sites on the surface of carbon black particles. Small value of ϕ' for the compounds both with NR and with BR (maximum 7%) milled up to 15 min (Table I and taken from the article¹) is determined, probably, by a low quantity of active sites on the surface of carbon black particles accessible for segments of polymer chains.

Quantities of both a high-temperature amorphous block and a pseudo-crystalline structure vary in a wide interval and depend on mixing time and a kind of rubber (Table II and Fig. 4). The presence of these blocks is most likely determined by the chemical structure of polymer chains and related to interaction energy of fragments of the chains with most of the active sites on the surface of carbon black particles. Because of this, main mechanochemical transformation under application of mechanical stress occurs inside these structures.

Comparing a dynamics of changes in a content of a high-temperature block, ϕ'' , during milling was found (Fig. 4) that different character of transformations of compared rubber compounds confirms conclusions, formulated above, on a role of a chemical structure of virgin rubber in creation of a topological structure of its filled compounds, especially architecture of a pseudo-crystalline structure.

A weight share of a polymer in a content of a pseudo-crystalline structure is between 76 and 93% and it is practically unchanged during the first 10 min of milling (Table II). Later it is reduced. The same phenomenon was found previously for BR/carbon black compound.¹ This sug-

gests that mixing time equal to 10 min is critical, and after that the irreversible processes of mechanical degradation of rubber start. Probably, these processes correspond with molecular parameters of amorphous blocks. The quantity of a crystalline structure is evaluated with accuracy of $\pm 3 \div 5\%$. Because of this, it is also possible to consider that content of a crystalline structure is preserved constant independently of the mixing time.

From Figure 5 it is concluded that after 10 min of milling, some reduction of compaction of pseudo-crosslinked structures in both amorphous blocks takes place. Here, also some lowering of concentration of the branching junctions in both a low-temperature and a high-temperature block in a glassy state and in a pseudo-crystalline structure is observed. The coefficient K of polydispersity of the chains between the junctions in the network also depends on mixing time. In a low-temperature block, the most uniform network is noticed for 10 min of milling. Here, $K = 1.26$ (Table I). In the second amorphous block, the polydispersity coefficient is almost independent of mixing time (Table II). However, despite these transformations resulting from extension of mixing time, the molecular weight distribution (MWD) between the junctions in the network of a low-temperature block, except the mixing time equal 20 min, is unimodal and symmetrical. In the last case it is bimodal because a dissimilation of two topological blocks is not complete (Fig. 6).

Contradictory to a low-temperature block, a pseudo-crosslinked structure of a high-temperature block is less uniform. Here, the MWD is transformed from practically two separated unimodal curves for mixing time 2.5 min [Fig. 7 curve (1)] to composed bimodal curve after 15 min of milling [curve (2)]. Nonuniformity of the network of this block and its changes during milling are predetermined by a presence of macromolecules of the diphillic structure (what is unlike that was for a low-temperature block) and the nonuniform distribution of active sites on the surface of carbon black particles.

Distinctive interactions of rubber with carbon black consist of the fact that most of its macromolecules interact with the filler surface forming pseudo-crystalline structures with a different architecture and related compactness. These structures have different temperatures of the beginning both the melting T_m and the molecular flow T_f of crystallites (Table II). Changes in formed structures and in both the T_m and the T_f values

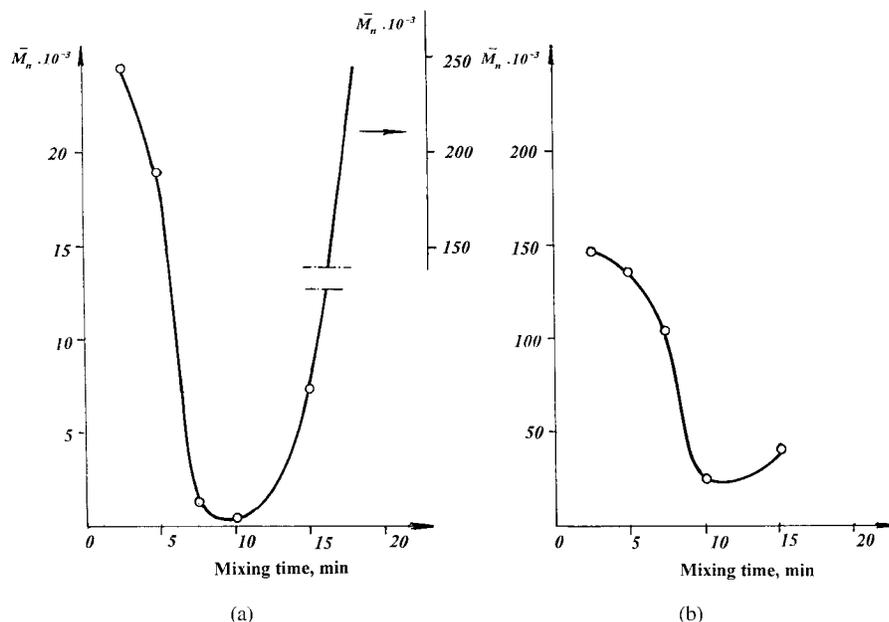


Figure 5 Dependence the number-average molecular weight between the junctions in the low-temperature block (a) and the high-temperature block (b) for NR compound filled with 50 phr of carbon black N330 on mixing time.

vs. mixing time characterize them as structures with unsteady equilibrium state.

Molecular and Topological Structures of NR/BR Filled Vulcanizates

Character of the thermomechanical curves of NR/BR unfilled vulcanizates (Fig. 8) is typical for

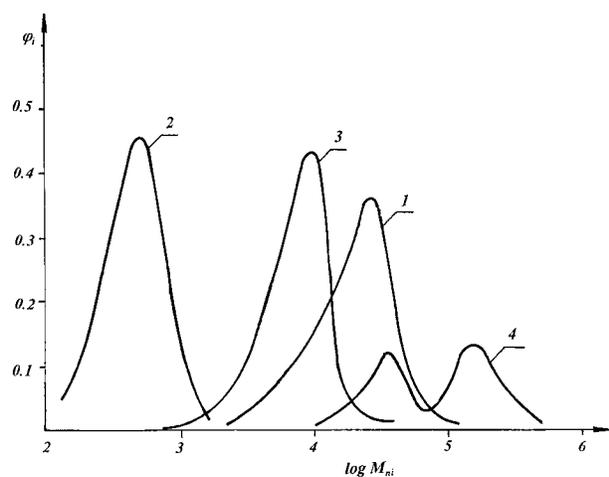


Figure 6 The molecular weight distribution between the junctions in the low-temperature block of NR rubber filled with 50 phr of carbon black N330 on mixing time: 1, 2.5 min; 2, 10 min; 3, 15 min; 4, 20 min.

rubbers with diblock structure of the chains without topological junctions. The network structure of vulcanizate has the covalent branching junctions and some quantity of the cluster origin junctions. The presence of the cluster junctions determines the relatively low initial temperature of degradation of the network ($T_d = 136^\circ\text{C}$) and character of the MWD of the chains between the junctions in vulcanizate (Fig. 9). This concerns especially the presence of a high molecular tail on the curve (1).

Introduction of different quantities of carbon black into a rubber principally changes its topological structure and makes the temperature's interval of their existence wider. The single block structure with one T_g (point *B* in Fig. 8) and one temperature of the beginning of thermal degradation of the network in point *T* for unfilled rubber is transformed for filled rubbers into the diblock structure with two T_g s (points *B* and *D*) and with two plateaus of a high elasticity being characterized by straight lines *CD* and *C'D'*. A tangent of the inclination angle of a straight line *CD* or a straight line *AB*, characterized by coefficients of linear thermal expansion in a high elastic state α_2 or in a glassy state α_1 , have values characterizing respectively networks with the covalent junctions or the cluster origin junctions. For the high-temperature block the ratio α_2/α_3 has anomaly

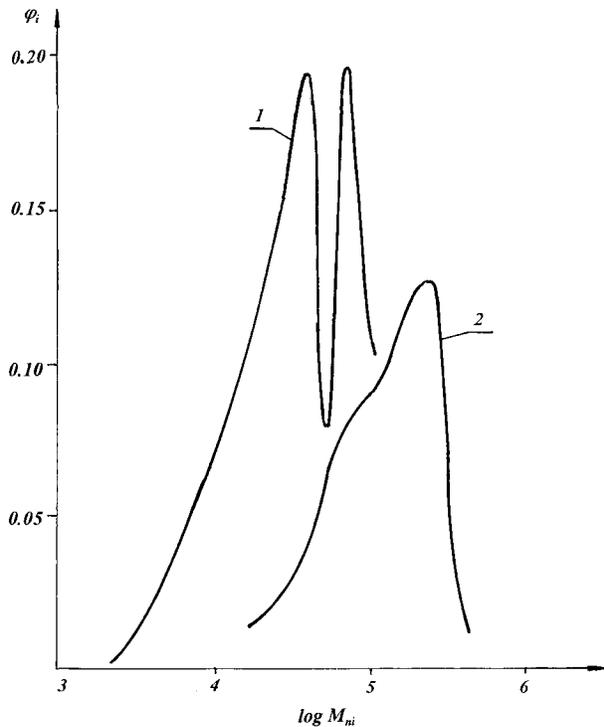


Figure 7 The molecular weight distribution between the junctions in the high-temperature block of NR rubber filled with 50 phr of carbon black N330 on mixing time: 1, 2.5 min; 2, 15 min.

value, typical for crosslinked structures with a predominance (about 90%) of the topological junctions resulted from interweaving high-molecular chains between the junctions.⁷

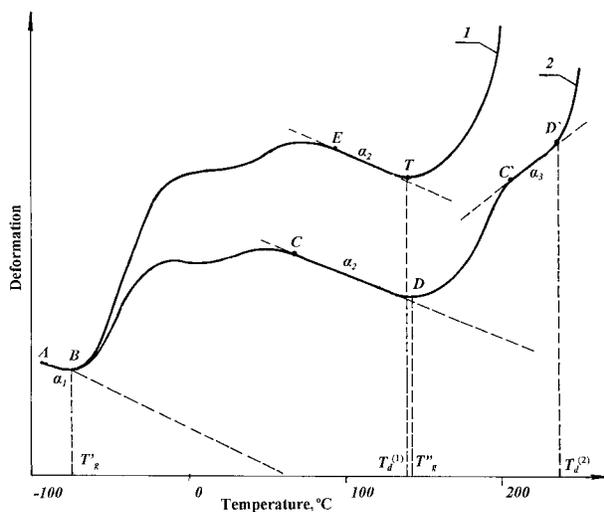


Figure 8 Typical thermomechanical curves for un-filled NR/BR compound (1) and NR/BR rubber compound filled with carbon black (2).

Introduction of 10 phr of carbon black into the rubber results in creation of a high-temperature block (Table III) engaging into a zone of its influence about 20 wt % of rubber. It is twice more than that for un-filled rubber and it is preserved constant despite a further increase in concentration of carbon black. This fact shows a priority of the chemical structure of a polymer chain in the architecture of this block. It especially concerns these isomers in virgin rubbers, which are responsible for arrangement of a high-temperature block (having $T_g \geq 100^\circ\text{C}$) in carbon black filled compounds.² In polybutadienes these are probably isomers with 1,2(vinyl) structure and for polyisoprenes, 1,2 and *trans*-1,4 structures. Also here the activity of carbon black is important, especially the distribution on its surface of active sites differing in energy of interaction with rubber. Based on this, analyzing results of the TMA investigations of rubber compounds containing different concentrations of carbon black and typical curing system is necessary to take into account an interaction energy and the influence on it from other ingredients of the rubber compound.

Comparing the T_g' values for a low-temperature block of NR and NR/BR filled with carbon black (Tables I and IV) it is visible that in NR rubbers, the interaction attribute T_g' is by 15–20°C lower than that for NR/BR rubbers. This difference is kept independently on the concentration of carbon black.

Unfilled cured rubber lacks a pseudo-crystalline structure, which is present in filled rubber

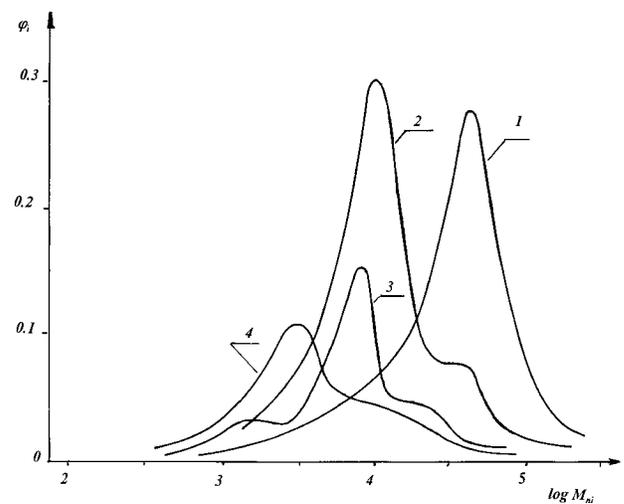


Figure 9 The molecular weight distribution between the junctions in the low-temperature block of NR/BR compound with carbon black content: 1, 0 phr; 2, 20 phr; 3, 30 phr; 4, 50 phr.

Table III Properties of a High-Temperature Amorphous Block of NR/BR Vulcanizates Differing in Carbon Black Content

Carbon Black (phr)	T_g'' (°C)	$\bar{M}_{n(n)}''$	$\bar{M}_{n(w)}''$	K''	φ''	$\alpha_3 \cdot 10^5$ (deg ⁻¹)	$\nu \cdot 10^4$ (mol/cm ³)	$\nu_c \cdot 10^4$ (mol/cm ³)
10	105	18,040	24,560	1.36	0.19	-50.0	0.053	0.003
20	117	7750	10,800	1.40	0.31	-45.5	0.123	0.009
30	132	8930	12,280	1.38	0.43	-40.0	0.106	0.011
50	136	4650	6460	1.39	0.37	-40.0	0.204	0.020

ν , summary concentrations of the chains between the covalent and topological junctions in the network; for other abbreviations see Table I.

compounds. However, in this cured rubber exists an analog of this block. This is a high-temperature amorphous block. These two facts, according to our opinion, show that some ingredients being present in rubber compound and crosslinking process prevent creation of the pseudo-crystalline structure.

In unfilled vulcanizate a spatial structure is arranged mainly due to both the chemical reactions of curing system and the cluster junctions, being destroyed at a temperature lower than that for covalent bonds. Introduction of carbon black into the rubber could destroy the energetic balance of intermolecular interaction existing there before milling. New junctions are created. Now conditions to create the cluster junctions having the same strength like that without active filler are disturbed. As the concentration of carbon black increases, the cluster junctions with the degradation temperature $\geq 105^\circ\text{C}$ are supplemented by stronger rubber/carbon black branching junctions having higher temperature (Table III). They enhance both the branching junctions' concentration in the high-temperature block (ν) and the T_g'' value in a complex system of the junctions in the rubber network. In this way the

concentration of carbon black grows, the number-average molecular weight of the chains between the junctions, $\bar{M}_{n(n)}$, is reduced. Simultaneously, the T_g'' is grown until reaching approximately the value 132–136°C at which degradation of the cluster branching junctions in a high-temperature block of unfilled vulcanizate starts.

The MWD in a low-temperature block (Fig. 9) shows a dynamics of accumulation of high-molecular weight fragments of chains between the junctions in rubbers, both unfilled and filled with different quantities of carbon black. Additional junctions are created because of interaction of rubber chains with active sites on the surface of carbon black without the curing system action.

The MWD in a high-temperature block is presented in Figure 10. These dependencies are similar to that for a low-temperature block discussed above. Both cases in the same way are changing also the number-average molecular weights of the chains between the junctions (Tables II and III). This confirms a role of carbon black as networking agent not only during mixing with other ingredients of rubber compounds but also during vulcanization.

Table IV Properties of a Low-Temperature Amorphous Block of NR/BR Vulcanizates Differing in Carbon Black Content

Carbon Black (phr)	T_g' (°C)	$\bar{M}'_{n(n)}$	$\bar{M}'_{n(w)}$	K'	φ'	$\alpha_1 \cdot 10^5$ (deg ⁻¹)	$\alpha_2 \cdot 10^5$ (deg ⁻¹)	V_f	$\nu_c \cdot 10^4$ (mol/cm ³)	$\beta T_g'$
0	-77	37,340	66,350	1.78	1.0	5.05	27.80	0.134	0.014	0.163
10	-78	16,950	33,130	1.96	0.81	3.91	24.39	0.120	0.029	0.143
20	-81	14,960	16,060	1.99	0.69	3.75	22.06	0.106	0.036	0.127
30	-78	7540	14,440	1.92	0.57	3.13	20.52	0.102	0.066	0.120
50	-83	5710	10,510	1.84	0.63	2.97	21.58	0.104	0.090	0.123

α , the coefficient of linear thermal expansion; V_f , free volume; ν_c , concentration of the chains between the covalent junctions of the rubber network; $\beta = 3\alpha$; for other abbreviations see Table I.

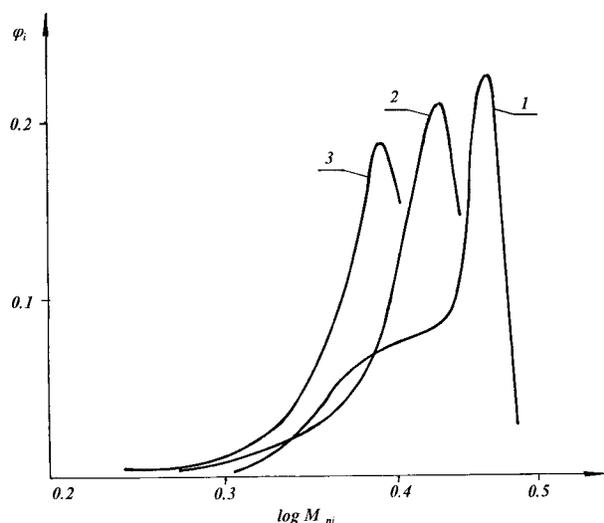


Figure 10 The molecular weight distribution between the junctions in the high-temperature block of NR/BR compound with carbon black content: 1, 10 phr; 2, 30 phr; 3, 50 phr.

By analogy to the theoretical investigations of rubber crosslink density⁸ it could be expected that changes in the compactness of rubber structure dependent on a quantity of carbon black incorporated in rubber compound should give a growth of both the glass transition temperature T_g and the free volume V_f . A directly proportional growth of the free volume as carbon black content grows (Table IV) is evident. However, such relation for the T_g is not observed. Here, the T_g practically is independent of carbon black content, and V_f becomes smaller and reaches a value ($V_f = 0.106$) characteristic for many polymeric materials with flexible chains including NR.^{8,9} Relations between α_1 and α_2 were investigated by many scientists. Simha and Boyer¹⁰ found experimentally that for polymers characterized by lack of visible molecular motions below T_g the following expressions are fulfilled:

$$V_f = (\beta_2 - \beta_1)T_g = 0.113 \quad (1)$$

and

$$\beta_2 T_g = 0.2 \quad (2)$$

where β is the volumetric thermal expansion coefficient in a glassy state (1) and in a high-elastic state (2), respectively.

Other investigators¹¹⁻¹³ noticed that for polyalkylmethacrylates the value of $(\beta_2 - \beta_1)T_g$ is

lowering as the length of side-chains grows. It was assumed^{10,14} as the result of intensive motions of these side groups below the T_g . If thermal expansion is measured at $T < 143$ K the following expression is valid:

$$(\beta_2 - \beta_1)T_g = 0.12 \quad (3)$$

Boyer mentioned that expressions (1) and (2) represent the free volume at the T_g according to two alternate definitions, which have been used in the literature, but equation (1) is more rigorous.⁸ The V_f values calculated from the eq. (1) varied usually between 0.1 and 0.13. In filled polymer compounds, it is higher than that for virgin polymers.^{15,16} In a case studied here the same relations is visible (Table IV). Also, the $\beta T_g'$ value depends on carbon black concentration. It grows as carbon black content lowers. To explain the reason for this phenomenon some role of remaining ingredients of rubber compounds (sulfur, accelerators, softeners, zinc oxide, and others) must be accepted. This should be a subject of further investigations.

CONCLUSIONS

NR filled with carbon black grade N330 has two amorphous blocks and one pseudo-crystalline structure. A ratio of these morphology structures changes during mixing with carbon black dependent on the carbon black content and mixing time. A crystalline structure has two or three temperatures characterizing the beginning of melting and the beginning of flow. This evidences its complex architecture.

Two amorphous blocks in a filled rubber compound when mixing change their molecular parameters in the same manner as that when carbon black is absent in the rubber compound. The T_g of the low-temperature block is independent on mixing time. All these facts evidence a full indifference of macromolecule fragments of this block on a presence of carbon black. For this filler, what was discussed above, the indifference is observed more clearly also in the low-temperature block of vulcanizate. Explanation for this phenomenon probably could be found in supernumerary action of other ingredients of rubber compounds to form a complex structure of cured rubber. This problem should be the aim of further investigations.

NR mixed with *cis*-1,4-polybutadiene (SKD type from Russia) in a ratio of 70/30, filled with carbon black grade N330 after curing has a diblock structure without a pseudo-crystalline structure. It shows that ingredients of the curing system and the curing process itself suppress crystallization of macromolecules in such a system.

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