

Thermomechanical Study of Butyl Rubber Mastication During Compounding

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ABSTRACT: A thermomechanical method was used to study the topological and molecular structure of model rubber compounds. This structure changes because of mastication during compounding. It was found that raw butyl rubber has a diblock structure. The molecular weight distribution of the chains between the junctions of the polymer network, the coefficient of polydispersity, a share of low-temperature and high-temperature blocks, and changes in their glass transition temperatures as a result of the mixing of butyl rubber depend on both the presence of sulfur and the kind of sulfur (polymeric or mineral). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2159–2167, 1998

Key words: butyl rubber; sulfur; mastication; thermomechanical method; block structure; molecular weight distribution; solid polymer

INTRODUCTION

Intermolecular interactions of ingredients and changes in their structure during rubber compounding are one key factor of rubber technology. During compounding and later extrusion, calendaring, or injection molding of rubber compounds, many chemical and physical processes activated by temperature, shearing, and stretching forces take place. As a result, the properties of rubber during processing have been changed. These processes for natural rubber have been studied for many years. Nevertheless, butyl rubber, as far as we know, was not deeply studied. The aim of our

research was to study the influence of mastication time and sulfur on the butyl rubber structure. Usually, the process of mixing is optimized by the use different traditional methods,¹ but they have limited possibilities in determining what is changing in the molecular and topological structure of rubber, especially filled with carbon black. A method of thermomechanical analysis (TMA) gives some new information about the structure of polymeric materials. This method is applicable for studying the molecular and topological structure of a network of crosslinked material, impossible to be dissolved without degradation of the chemical and physical bonds. Analyzing the molecular weight distribution^{2,3} and determining both the presence of the different blocks^{4,5} and the crystallinity degree⁶ are also possible.

By use of the TMA method, the well-known polymeric nature of polymeric sulfur was confirmed and it was found that mineral sulfur could behave like a polymer.⁶ Number-average and

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weight-average molecular weights, coefficients of polydispersity, and the molecular weight distribution (MWD) of both kinds of sulfur were calculated. The well-known fact that mineral sulfur predominantly has a crystalline structure (95%) and a polymeric–amorphous structure was confirmed. These conclusions suggest the possibility to use TMA to test some processes in rubber technology. In this study, TMA was used to evaluate changes of the molecular and topological structure of butyl rubber (IIR) during mixing with different kinds of sulfur. These processes could occur during the manufacturing of typical rubber compounds, for example, for tire tubes.

METHODOLOGY

The TMA method is based on measurements of sample deformation under a very low load in the thermal field being variable against time [the thermomechanical curve (TMC)] and, next, evaluation of the glass transition temperature and the temperature of the beginning of the molecular flow. The methodology of the measurements and calculations of the molecular weight distribution (MWD), the share of different blocks, and related characteristics are described in detail in refs. 4, 6, and 7.

EXPERIMENTAL

Material

For this study, a compound containing EXXON butyl rubber was used. It is a linear copolymer composed of a series of isobutylene molecules added to one another in a head-to-tail fashion with isoprene units distributed along the chain statistically randomly⁸ and linked predominantly in a *trans*-1,4-configuration with about 10% of a second structure, possibly 1,2-units.^{9,10} Unsaturation of this rubber is about 3 mol % and isoprene moieties occur as isolated units in the polymer chains.⁸

The recipes of the tested compounds were as follows: butyl rubber 100 phr and mineral* or

* Sulfur S95 from Siarkopol (Grzybow, Poland) containing 5% of mineral oil.

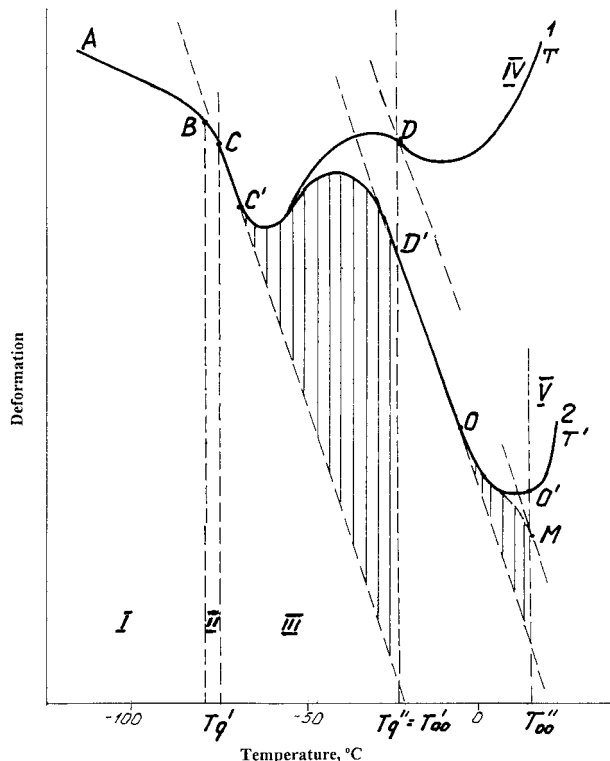


Figure 1 Combined TMC for (1) butyl rubber masticated 10 min and (2) masticated 7.5 min; (I) glassy state; (II) transitional zone between glassy and high elastic states; (III) high elastic state; (IV) flow of rubber masticated 10 min; (V) flow of rubber masticated 7.5 min.

polymeric[†] sulfur 5 phr. These compounds were prepared on a laboratory mixing mill with a friction ratio of 1 : 1.04. The mixing rolls before the start of compounding were heated to over 60°C. The compounding procedure was as follows: (1) preliminary mastication of rubber, 5 min; and (2) addition of sulfur and, next, homogenization of such a blend. To equalize the milling time for all samples, butyl rubber without sulfur was preliminary masticated 5 min and then homogenized.

Samples for TMA were taken 2.5, 5, 7.5, 10, 15, and 20 min after the start of the homogenization time. They were tested as described in our previous article.⁷

Testing of IIR

In Figure 1 is shown the TMC for butyl rubber after mixing on the open mill for 7.5 and 10 min.

[†] Sulfur Polsintex 33 from Siarkopol (Grzybow, Poland) containing 33% of naphthenic oil and characterized by 65% by weight of insoluble sulfur.

It is visible that after 7.5 min of mastication it has diblock structure. This structure after 10 min of mastication is transformed into the structure typical for thermoplastic elastomers. Mixing IIR on an open mill causes many processes, that is, degradation and recombination of both physical and chemical bonds in the chain of rubber, some branching, and orientation of its macromolecules. This is the reason for the structure changes of each block. We believe that parts of one macromolecule could be in different blocks as a chain passing through them. A similar structure was found earlier by the use of TMA in copolymers of butadiene with styrene,⁴ butadiene with nitril of acrylic acid,¹¹ ethylene with propylene, and butadiene with methyl styrene.⁵

Analyzed blocks have different thermomechanical and molecular characteristics. Butyl rubber masticated both 7.5 and 10 min could be in a glassy state characterized by the same straight line of thermal expansion AB (Fig. 1) and in a transitional one from a glassy to a high elastic state (fragment BC of curve). The next increase in temperature is characterized by the common straight line of a high elastic expansion (CC'), being the result of the expansion of the free volume. It means that a low-temperature block has the same properties for rubber masticated 7.5 and 10 min. By extrapolation of the CC' line up to crossing the vertical dashed line running through point D' (beginning of a plateau of high elasticity), it is possible to evaluate temperature T'_∞ . An increase in temperature over point C' gives different shapes of the TMC for the second block in the zone of high elastic thermomechanical deformation, that is, for rubber masticated 10 min ($C'D$) and masticated 7.5 min ($C'D'$). Later, an increase in temperature gives a molecular flow of rubber masticated 10 min (DT). Rubber masticated 7.5 min behaves differently than that masticated 10 min. Here, a high elastic thermal expansion (straight line $D'O$) is visible, which is extended by thermomechanical deformation of a high-temperature block (fragment OO'). Fragment $O'T'$ of the curve shows a molecular flow of this block.

For IIR masticated 7.5 min, the transitional zone of the TMC of the first, low-temperature physically crosslinked block is between temperatures T'_g and T'_∞ in Figure 1. Temperature T'_∞ characterizes the end of the transitional zone of the first block and, simultaneously, the beginning

of segmental motions of chain segments in the second, high-temperature block, that is, the glass transition temperature T''_g . The segment of the TMC between points C' and D' and the hatched zone gives information about the MWD in the chains between junctions of the first block. The same information for the second block gives the segment of a curve between points O' and O . The latter, after dividing the thermomechanical deformation from the molecular flow in this fragment of the curve, is transformed into the integral MWD curve (OM).⁶

We believe that the main reason for the block structure found in IIR is the presence of chain fragments, containing polyisoprene sequences between the polyisobutylene sequences of the chains. Probably, these fragments of chains, characterized by different cohesion energy¹² ($\delta_{IR} > \delta_{PIB}$), create conditions to form a physically crosslinked structure of a low-temperature block. Junctions of this network are aggregates of chains segments with the structure of 1,4-polyisoprene.

The second reason could be the presence, in its macromolecules, of fragments of chains, containing isoprene 1,2 units characterized by different cohesion energy ($\delta_{1,2} > \delta_{1,4}$). Here, junctions are aggregates of chain segments with 1,2 and 1,4 configurations.

Testing IIR Blended with Sulfur

On the TMC of the rubber blended with sulfur (Fig. 2), there are zones related to the chain's deformation in both blocks. A difference in the temperatures of the beginning of the segmental motions of the chains in the second IIR block (below 0°C) measured here and in the amorphous part of both kinds of sulfur (about 50°C) was noticed. From a combined curve, at temperature over 0°C, fragments of additive deformation caused by IIR macromolecules (in the zone of molecular flow) and that caused by sulfur (being in the zone of its high elastic and glassy states) are revealed. Especially, the presence of mineral sulfur gives visible changes in the shape of the TMC in the temperature zone between T_m^b and T_m^e , when a deformation jump ε_{cr} from the melting of any crystalline fraction is observed. The value of this deformation jump is directly proportional to the weight share of a crystalline fraction in the composition.⁶ Some influence of mineral sulfur on the shape of the TMC is visible also in a zone of high elastic expansion (a high elasticity plateau)

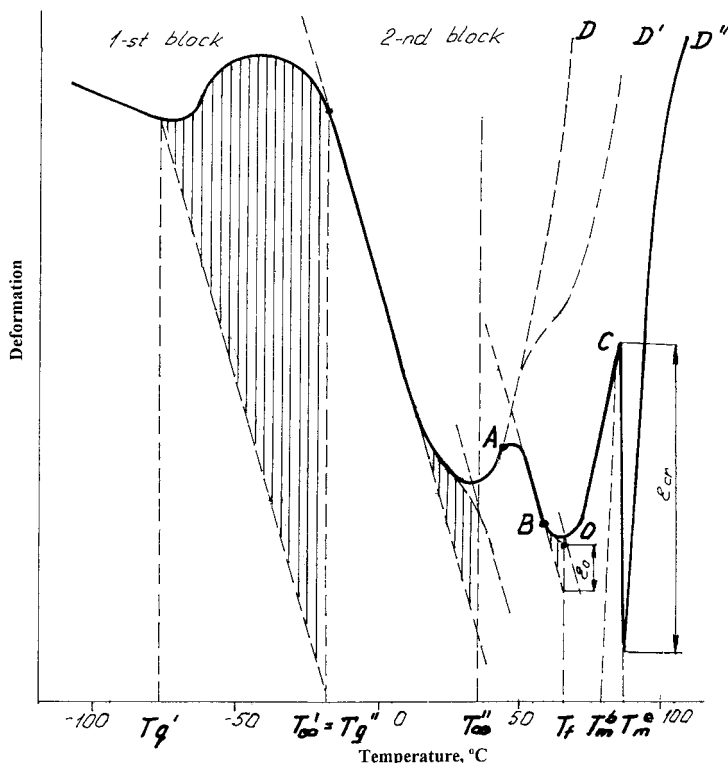


Figure 2 Typical thermomechanical curve for butyl rubber mixed with sulfur, with fragments related to polymeric (AD') and a mineral ($ABOCD''$) sulfur; T_m^b , temperature of the beginning of melting of the crystalline fraction; and T_m^e , ending of this process.

of the amorphous part of the sulfur (fragment ABO) and in a zone of molecular flow of the blend (fragment OC).

The thermomechanical curve of IIR blended with polymeric sulfur overlays the fragments in the zone of the first and second blocks of the rubber. Only in the zone of the predicted molecular flow of the rubber (AD) close to the temperature of the beginning of the expansion of an amorphous fraction of mineral sulfur (in a point A) on the combined curve in the zone AD' is the threshold of slowing of the growth of deformation observed. In the tested compound, a smaller influence of polymeric sulfur in comparison with mineral sulfur is observed. This evidences a higher density of intermolecular interaction between IIR and the crystallites of mineral sulfur. Due to this, it can be stated that a well-homogenized blend of IIR with mineral sulfur has the structure of a ternary block copolymer. So, the reproducibility of the TMC could be used as a measure of the homogenization degree of these ingredients. Here, the ϵ_0 value could be interpreted as a summarized high

elastic deformation of an amorphous fraction of mineral sulfur.

Influence of Mastication Time

Thermomechanical characteristics and parameters of the MWD in blocks of IIR and in its blends with sulfur are given in Table I and Figures 3–7. The value of the T_g of a low-temperature block for IIR is about -84°C [Fig. 3(a), curve 1]. The level of the noticed glass transition temperature of the first block is similar to that for polyisoprene and polyisobutylene. It is reduced to -70°C when the mastication time is prolonged. Nonmasticated rubber of about 94% by weight contains a low-temperature physically crosslinked block. Here, the fluctuation of the average molecular weight when mastication time is prolonged may be explained as a result of the mechanical and chemical degradation of rubber, especially high molecular fractions, some branching especially visible in the beginning of mastication process, chain transfer

Table I Some Molecular Weight Characteristics of Butyl Rubber and Its Blends with Sulfur

Mixing Time (min)	Low-Temperature Block			High-Temperature Block		
	\bar{M}_n	\bar{M}_w	K	\bar{M}_n	\bar{M}_w	K
Butyl rubber						
0.0	15,000	20,900	1.40	18,600	24,900	1.3
2.5	8730	12,200	1.40	60,100	805,000	13.4
5.0	9530	13,300	1.40	58,900	412,000	7.0
7.5	7100	9900	1.39	10,700	83,000	7.8
10.0	11,000	15,400	1.40	K_s	K_s	
15.0	12,700	17,800	1.41	K_s	K_s	
20.0	15,500	23,300	1.40	K_s	K_s	
Butyl rubber + polymeric sulfur						
2.5	21,500	29,600	1.39	33,200	175,000	5.3
5.0	23,800	33,100	1.39	21,000	210,900	10.0
7.5	17,300	23,800	1.38	26,500	149,600	5.7
10.0	19,800	26,800	1.36	33,500	143,600	4.3
15.0	15,000	20,400	1.36	28,500	113,100	4.0
20.0	9300	12,600	1.35	23,100	121,000	5.2
Butyl rubber + mineral sulfur						
2.5	22,600	31,800	1.41	19,400	74,900	3.9
5.0	20,000	27,100	1.30	15,800	42,300	2.7
7.5	23,600	32,000	1.37	17,000	51,000	3.0
10.0	29,500	46,500	1.38	K_s	K_s	
15.0	35,000	48,700	1.36	K_s	K_s	
20.0	16,200	22,300	1.36	K_s	K_s	

Each parameter is calculated as an average from three to five parallel experiments; \bar{M}_w , the weight-average molecular weight between the crosslinks of a polymer network; \bar{M}_n , the number-average molecular weight between the crosslinks of a polymer network; $K = \bar{M}_w/\bar{M}_n$, the polydispersity coefficient of chains between the crosslinks; K_s , Kuhn's segment.

with rapture, and redistribution of fragments of macromolecules between blocks.

The second block for raw IIR has a $T_g = -32^\circ\text{C}$. How to explain the reason for the existence of the second block? It is well known that IIR is a subject of very fast oriental crystallization despite that this polymer is characterized by a very low rate of isotropic crystallization.¹³⁻¹⁵ For PIB, the temperature of maximal crystallization is -35°C .^{14,15} Simultaneously, IIR is characterized by a very wide zone of a defrosting glassy state. Due to this, it could be considered that T_g'' is the temperature of the beginning of a high elastic deformation of the second block and that the zones $C'D$ and $C'D'$ (Fig. 1) are transitional zones resulting from a high elasticity of the first block.

The process of IIR mastication on the mixing mill is followed not only by redistribution of the monomeric content of the macromolecules and their fragments, passing through the blocks, but also by changing the share of the polymer in these blocks (Fig. 4, curve 1). For IIR rubber, this mech-

anism is different during the first 2.5 min and later. This is evidenced by the changing share of low-temperature and high-temperature blocks.

The mastication of IIR during 2.5–7.5 min already causes a noticeable degradation of the initial “networking” structure and, next, its transformation into the structure with shorter chains between junctions in the first block and higher \bar{M}_n and \bar{M}_w values of the fragments of the chains in the second block (Table I and Fig. 5, curve 1). In the first block, the value of the polydispersity coefficient K is independent of the mastication time and practically also on presence of the sulfur. For the second block, the picture is different. Here, in the case of IIR, the high values of the polydispersity coefficient being reduced from 13 to 8 as mastication time increases to 7.5 min evidences that mechanochemical processes take place. Further mastication of the rubber only slightly changes the length of “a network” of a low-temperature block but gives an increase of its share and later its stabilization (Fig. 4). Molecu-

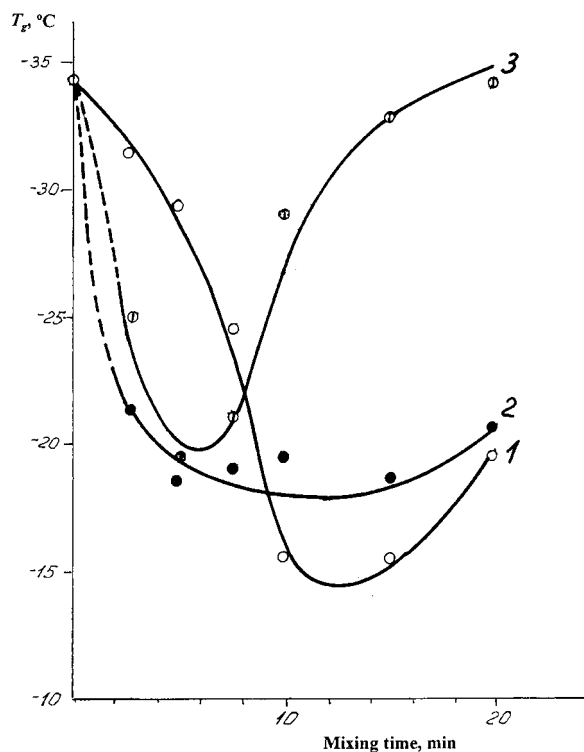
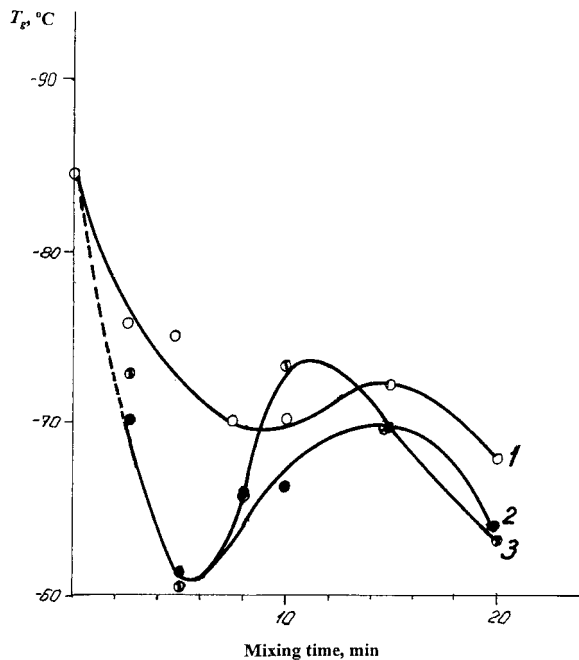


Figure 3 Dependence of glass transition temperature (T_g) on mixing time: (1) butyl rubber; (2) butyl rubber with polymeric sulfur; (3) butyl rubber with mineral sulfur; (a) a low-temperature block; (b) a high-temperature block; accuracy $\pm 2^\circ\text{C}$.

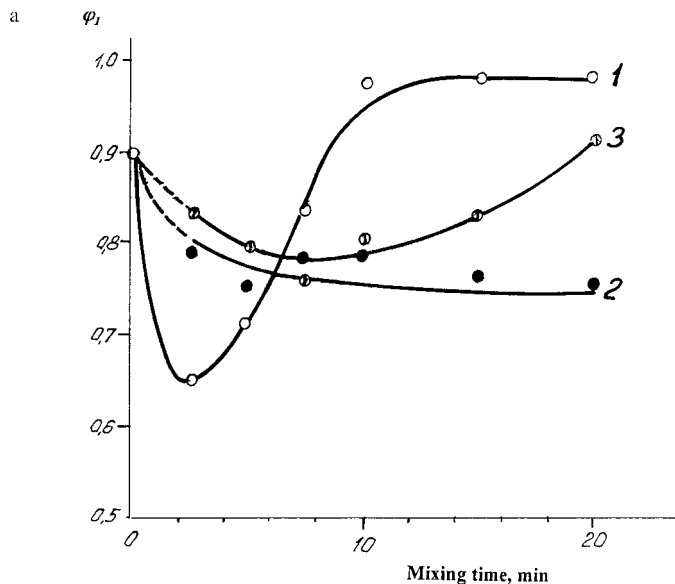


Figure 4 Changes of a share of a low-temperature block φ_l in the rubber compound versus mixing time: (1) butyl rubber; (2) butyl rubber with polymeric sulfur; (3) butyl rubber with mineral sulfur.

lar parameters of a high-temperature block are noticeably reduced and stabilized on the Kuhn segment,¹⁶ being of 250–300 units of molecular weight (Fig. 6).

Evaluated by TMA, \bar{M}_n and \bar{M}_w for both a low-temperature and a high-temperature block, of course, do not have the same values as evaluated by any method for testing a dissolved polymer, that is, by a gel permeating chromatography. It is because testing a structure of a dissolved polymer in the solution takes place under the condition of interactions between macromolecules and these macromolecules and a solvent. These interactions are different from that characteristic for polymers during processing in a molten state and during exploitation in a solid state when a solvent is absent.

Influence of Sulfur

The character of T_g and φ_l (where φ_l is the share of the low-temperature block) dependencies on the mixing time, shown in Figures 3 and 4, evidences that the presence of sulfur and the kind of sulfur influences the molecular redistribution when IIR is masticating. Sulfur changes the character of the processes taking place in the blend during IIR mastication. A different influence of the sulfur structure (polymeric or mineral) on the character

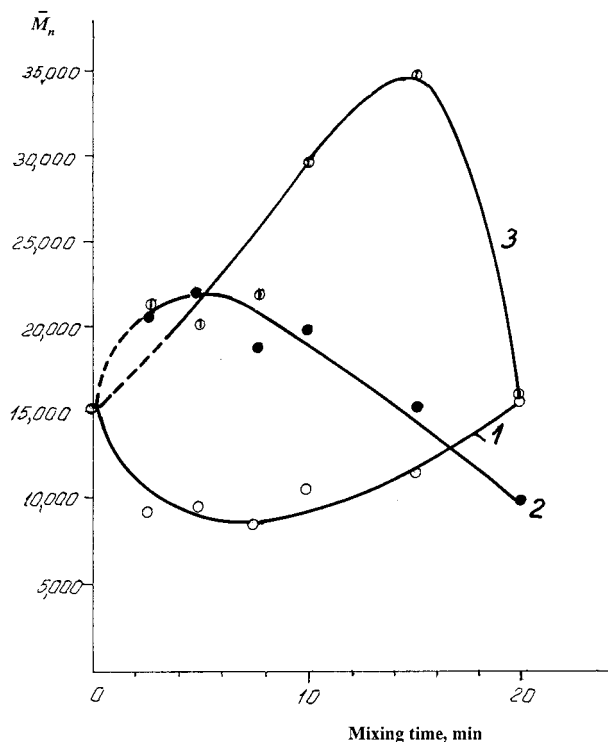


Figure 5 Dependence of molecular weight between junctions of branches in a low-temperature block on mixing time: (1) butyl rubber; (2) butyl rubber with polymeric sulfur; (3) butyl rubber with mineral sulfur.

of the intermolecular interactions of the macromolecules in both blocks was found. During the first 5 min of mixing [Fig. 3(a), curves 2 and 3], when the blend is still inhomogeneous, a comparable influence of both kinds of sulfur on a change in the glass transition temperature of a low-temperature block of rubber is observed. However, some difference in the T_g value is visible. Further mastication does not reveal a great influence both of sulfur structures and itself as a component of the blend on intermolecular interactions in a polymeric matrix of the low-temperature block. Here, the coefficient of polydispersity is stable. Its value depends only a little on the presence of sulfur and the kind of sulfur (Table I). In the high-temperature block [Fig. 3(b)], a different picture is observed if mastication of IIR and its blends with polymeric sulfur on an open mill is compared. The presence of mineral sulfur in the rubber in this period of mixing diminishes significantly the intermolecular interactions. It is expressed by a 15–20°C lowering of the glass transition temperature.

In contrast to the mastication of IIR in the presence of polymeric sulfur (Fig. 5), during the first 5

min of mixing, the “network” of a low-temperature block is loosened, indicating that the length between junctions grows. The depth of this loosening is similar to that in the presence of mineral sulfur. However, further mastication gives different changes in the structure of the rubber. If polymeric sulfur is present, reduction of \bar{M}_n is observed as mastication time increases. If mineral sulfur is present, first, up to 15 min of mastication, an increase of \bar{M}_n and, next, a decrease of \bar{M}_n is observed. In the second block, the influence of both kinds of sulfur on the mixing processes is also noticeable. Here, the presence of polymeric sulfur gives, first, some growth and, next, a small decrease of the molecular weight between junctions (Fig. 6, curve 2). Mineral sulfur stabilizes the molecular weight in the beginning of mastication, and, later, after 7.5 min until 10 min, reduces the \bar{M}_n value. Further mastication is not followed by changing molecular weight, exactly as for the absence of sulfur.

The influence of both kinds of sulfur on the distribution of the polymer (by weight) between blocks (Fig. 4) is the same. To 5–7.5 min of mix-

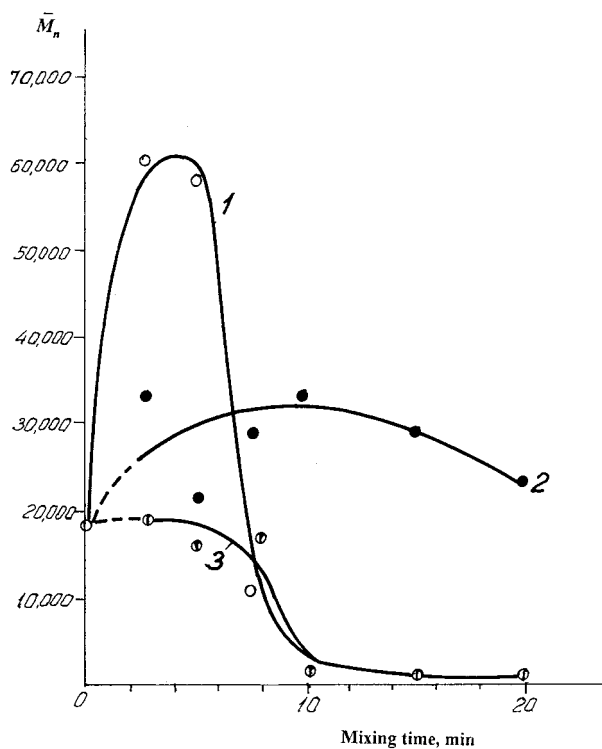


Figure 6 Dependence of molecular weight between junctions of branches in a high-temperature block on mixing time: (1) butyl rubber; (2) butyl rubber with polymeric sulfur; (3) butyl rubber with mineral sulfur.

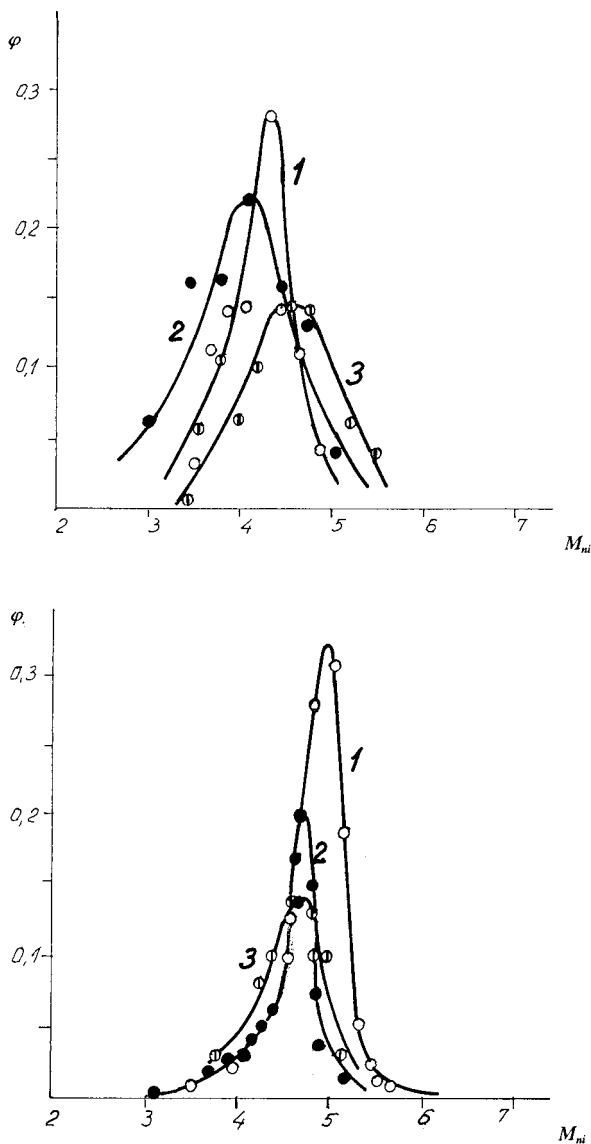


Figure 7 MWD in (a) a high-temperature and (b) a low-temperature block after 5 min of mixing: (1) butyl rubber; (2) butyl rubber mixed with polymeric sulfur; (3) butyl rubber mixed with mineral sulfur.

ing, a small reduction of φ_l is noticed. Further extension of the mastication time is followed by its stabilization, if the rubber is mixed with polymeric sulfur. Longer mixing of IIR with mineral sulfur gives some growth of a share of a low-temperature block.

The functions of the MWD for chains between junctions of a physically crosslinked structure in a low-temperature block and for aggregated fractions, acting as junctions of branching in a high-

temperature block, are shown in Figure 7. The unimodal character of these curves points to the same "mechanism" of arrangement in both blocks. The term "mechanism" is understood here as the initial reason for the arrangement on the molecular and/or supermolecular level of any structure or phenomenon, being analyzed in every particular case. In the frame of this definition, butyl rubber and its blends with mineral and polymeric sulfur are, to different degrees, polymodal structures. This is valid if these systems are considered as a composition of components with a unimodal-type structure.

CONCLUSIONS

1. Mastication of IIR changes the MWD of chains between junctions of the polymer network, the coefficient of polydispersity, the share of low-temperature and high-temperature blocks, and their glass transition temperatures.
2. These changes in the structure of IIR depend on both the presence of sulfur and the kind of sulfur (polymeric or mineral) during mixing. This suggests that the sequence of rubber compounding and the rubber recipe influence not only the dispersion and the distribution of ingredients (which is well known) but also the structure of the rubber matrix.

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