

Application of Thermomechanical Mass Spectroscopy for Analysis of Molecular and Topological Structure of Rubber

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ABSTRACT: A novel method was applied to study the topological and molecular structures of multicomponent rubber. This method is based on the thermomechanical analysis of a solid polymer. A diblock amorphous structure was found for the studied rubber network. These blocks differ a great deal in their glass transition temperature. The methodology of how to calculate the crosslink density in each block, the molecular weight distribution of the chains between the junctions of the network, and the shares of low-temperature (soft) and high-temperature (hard) blocks in a structure of the rubber network were also shown. Based on these data it is possible to calculate the number-average and weight-average molecular weight and the polydispersity coefficients of the chains between the junctions of the network. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 490–501, 1999

Key words: topological structure; molecular structure; rubber, thermomechanical analysis; molecular weight distribution; junction

INTRODUCTION

It is well known that properties of rubbers strongly depend on the molecular and topological structures of their network. Usually such measurements of the structure for linear polymers are made in solution, but for cured rubbers such a method is inapplicable. The problem was how to evaluate the molecular and topological structures of the crosslinked material, which is impossible to dissolve without degradation of the chemical and physical bonds. For this purpose a method of ther-

mechanical analysis of solid polymers was used.

METHODOLOGY

The method is based on the evaluation of two properties of macromolecules in a thermal field being variable against time. The first property is that segmental relaxation starts at the glass transition temperature T_g , and it ends when the molecular flow starts at a temperature T_f . The higher the molecular weight of a polymer homolog, the higher is the starting temperature of the molecular flow. This rule can be analytically described by the empirical Kargin–Slonimskii equation,¹ similar to the classical Williams–Landel–Ferry equation,² as follows:

$$\log M_i = \log M_0 + \frac{A\Delta T}{B + \Delta T} \quad (1)$$

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where M_i and M_0 are the molecular weights of a polymer homolog and a Kuhn's segment (minimal magnitude of the molecular weight of a polymer when it loses typical properties of a high molecular substance), respectively; $\Delta T = T_f - T_g$; $A = 11$, and $B = 100$ - coefficients.

The second property is that when the segmental relaxation ends they give to the system, which is under special loading, a jump of deformation $\Delta\varepsilon$, which is directly proportional to the weight fraction of the molecules involved. Based on this, the intermediate zone of the thermomechanical curve (TMC) of an arbitrary polymer can be shown as a fencing of deformation jumps. If it is true, the arbitrary TMC evaluated under special conditions is apparent equilibrium and could be used for analysis of the molecular weight distribution (MWD) of linear polymers and chains between the junctions of crosslinked polymers. However, the procedure of evaluation of the crosslink density and the MWD for a crosslinked polymer is different from those for linear³ polymers.

Concentration of Chains between Junctions

Two classical experimental methods to evaluate the concentration of the chains between the junctions (crosslink density), ν_e , are known. The first was elaborated by Flory-Rehner⁴ and the second by Cluff et al.⁵ Equilibrium swelling in solvent in both of them is used as a basis. The type of solvent is especially selected for each polymer and it is characterized by the polymer-solvent interaction parameter κ . For an arbitrarily chosen pair of polymer-solvents, some indefinite always exists in a measured value of the crosslink density. This is because the κ parameter depends not only on a kind of polymer, but also on the ν_e value. From this it is concluded that more information will give a method based on compensation of the swelling pressure appearing inside the swollen network. It allows the evaluation of the parameter κ and concentration of the chains between the junctions of the network in a single experiment.⁶⁻⁸ During swelling to equilibrium the polymer is subjected to the action of internal forces. As a result, some out of control fractions of the stretched chains between the junctions could be broken irreversibly, always reducing the value of ν_e differently. This phenomenon could appear in all methods based on the swelling in the solvent.

From this Mooney and Rivlin concluded that it is more proper to measure ν_e without preswelling

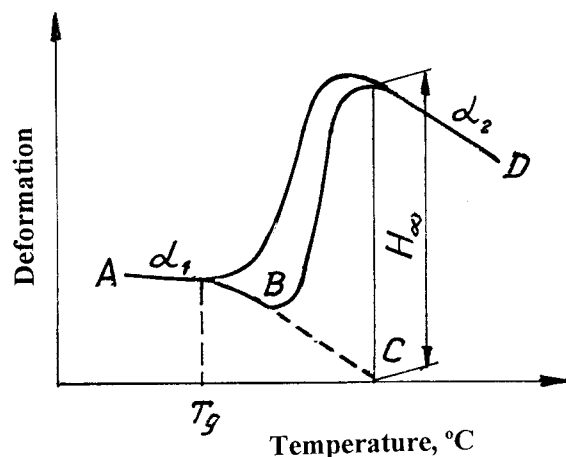


Figure 1 Typical thermomechanical curve for crosslinked polymers; ABC , dilatometric curve; ABD , thermomechanical curve; α , linear thermal expansion coefficients for (1) glassy and (2) high elastic states.

of a polymer.⁹ The thermomechanical method also belongs to such methods, the basis of which was elaborated by Olkhov and colleagues.¹⁰⁻¹⁴ The latter, as in Cluff et al.'s method,⁵ is based on the evaluation of the high elastic equilibrium modulus, E_∞ , and the ν_e calculation using the equation from the theory of high elasticity:

$$\nu_e = \frac{E_\infty}{3RT} \quad (2)$$

where ν_e is the concentration of the chains between the junctions (crosslink density), E_∞ is the high elastic equilibrium modulus, R is the universal gas constant, and T is the temperature.

Unlike to Cluff et al.'s method,⁵ discussed here in the thermomechanical method, the modulus of a crosslinked polymer is evaluated in a thermal field being linearly scanned from a temperature below the glass transition up to 20–50°C over the beginning of a plateau of high elasticity. Here a linear thermal expansion of the polymer by composing thermomechanical and thermal expansion curves is taken into account. To improve the accuracy of the modulus measurement, the TMC is drawn as a function of a deformation of the sample, measured as a penetration depth of the testing sonde. A load P during measurements is constant. The deformation H_∞ at the temperature T_∞ was found as a distance between the thermomechanical and dilatometrical straight lines (Fig. 1).

From the theory of high elasticity it is known that crosslink density is connected to E_∞ by eq. (2)

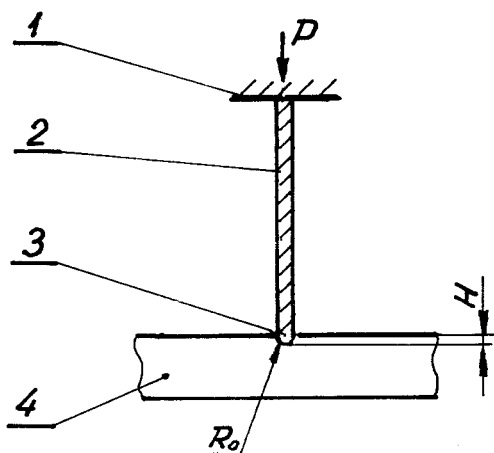


Figure 2 Deformation measurements scheme of a sample of cured rubber: (1) load P ; (2) a quartz sonde; (3) a hemispherical tip of the sonde; (4) a sample of rubber; H , deformation.

only when the measuring temperature of this modulus complies with a plateau of high elasticity. This means that it is equal to a temperature of full degradation of the physical junctions between macromolecules in the network. In the Cluff et al.'s method⁵ a degradation of the network of the physical junctions is obtained by equilibrium swelling of a polymer in solvent. Because of this it does not need to find a plateau of high elasticity. In the method used here the location of a plateau of high elasticity is found by measuring the deformation of a sample under a constant load versus temperature. However, such a TMC cannot be used directly to evaluate E_∞ , because the measured deformation is a result of a high elasticity deformation under the applied load and the thermal expansion due to changes in the free volume of the sample. To make the evaluation of E_∞ and a location of a plateau of high elasticity more accurate, measuring of a sample's thermal expansion versus temperature without applying a load or by applying a load as small as possible to reduce such compression is necessary. The accuracy of E_∞ measurements could essentially be improved if the load is applied on a minimal surface. The best is a sonde with a hemispherical tip (Fig. 2). Material of this sonde should be characterized by an essentially higher Young's modulus and an essentially lower coefficient of thermal expansion than those for material of the tested sample.

The beginning of a high elasticity state is accepted as over the glass transition temperature. However, the location of this temperature on the TMC (Fig. 3) in the transitional zone between the

end of a straight line of a glassy state (point B'') and the beginning of a straight line of the plateau of the high elastic state (point B) depends on the methodology used. Some accept this location in point B' . Here, as in our previous article,³ it is accepted that T_g is in point B .

Under these conditions the Hertz equation to evaluate E_∞ from the results of H_∞ measurements was used¹⁵:

$$E_\infty = \frac{3(1 - \mu^2)P}{4R_0^{1/2}H_\infty^{3/2}} \quad (3)$$

where μ is the Poisson coefficient, P is the load, and R_0 is the radius of the hemispherical sonde.

Evaluation of the concentration of the chains between the junctions is done by eq. (4) that is obtained by the substitution of eq. (3) into (2).

$$\nu_e = \frac{(1 - \mu^2)P}{4R_0^{1/2}H_\infty^{3/2}RT_\infty} \quad (4)$$

where T_∞ is the temperature of the beginning of a high elasticity plateau.

Because the Poisson coefficient for most crosslinked polymers is close to 0.5, eq. (4) without a large error could be transformed into (5) as follows:

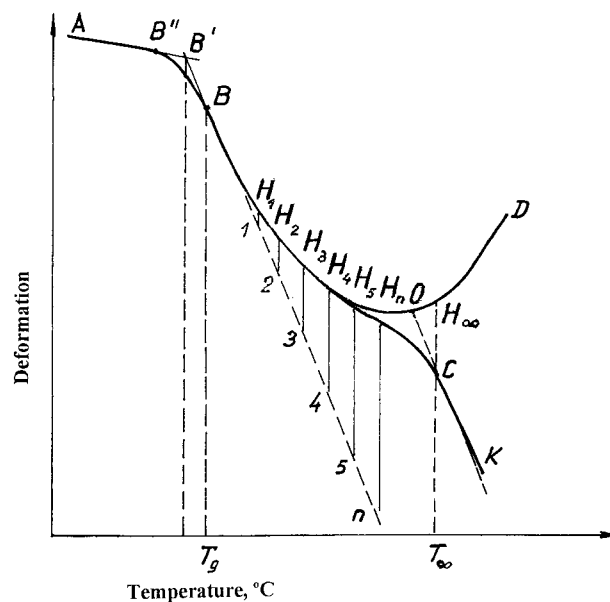


Figure 3 Exemplary thermomechanical curve of the linear ($ABOD$) and crosslinked (curve $ABCK$) polymers; AB , glassy state; OD , fixed flow of linear polymer; CK , high elastic state of a crosslinked polymer.

Table I Thermomechanical and Structural Parameters for One of Polybutadiene Diols Evaluated at Different Scanning Rates of Temperature and Under Constant Loading

Scanning Rate of Temp. (°C/min)	T_g (°C)	T_∞ (°C)	$H_\infty \cdot 10^3$ (cm)	$\Delta T = T_\infty - T_g$ (°C)	$\nu_e \cdot 10^4$ (mol/cm ³)
0.63	-101	27	30.0	128	0.43
1.25	-94	38	40.8	132	0.39
2.50	-90	40	39.9	130	0.40
5.00	-83	46	38.0	129	0.40
10.00	-78	55	34.2	133	0.44
20.00	-73	59	38.7	132	0.43
40.00	-68	62	36.4	130	0.41

$$\nu_e = \frac{0.19P}{R_0^{1/2} H_\infty^{3/2} R T_\infty} \quad (5)$$

To control the adequacy of this equation, many tens of crosslinked polymers with different crosslink densities and different polarities of the chains between the junctions were tested with the method used here and simultaneously by using Cluff et al.'s method.⁵ Comparable results were always obtained.

Table I contains exemplary data of the testing of polybutadiene diols. Independent of the scanning rate of temperature, H_∞ , ΔT , and ν_e values are practically constant. Based on this it is concluded that deformation processes in a transitional zone, at least under the condition of a scanning rate between 0.6 and 40°C/min, have a pseudoequilibrium nature.

It was found also (Table II) that if the loading of the sonde exceeds 2 g, the measured ΔT and evaluated crosslink densities are practically constant. Because of this, at a temperature arbitrarily chosen from the range of a plateau of high

elasticity, the polymer deformation H_∞ is directly proportional to the $P^{2/3}$ value and determines the polymers' average crosslink density. From this it is concluded that a plateau of high elasticity corresponds with equilibrium state at arbitrary conditions of polymer deformation (different load and scanning rates of temperature); it means also a full reversible deformation in this part of the TMC, when is absent residual deformation after removing a load applied before to the sample for $T \geq T_\infty$ (dilatometric conditions). Here, the TMC is relatively quickly transformed into the dilatometric curve.

MWD

There are some methods of indirect evaluation of the MWD between the junctions in crosslinked polymers.^{8,16-23} However, up to now none of the experimental ways has been widespread in practical applications. In this article usage of the thermomechanical method is discussed for evaluation of the weight-average, $\bar{M}_{n(w)}$, and the number-

Table II Thermomechanical and Structural Parameters for One of Polybutadiene Diols Evaluated at Different Loadings onto Sample

Loading P (g)	T_g (°C)	T_∞ (°C)	$\Delta T = T_\infty - T_g$ (°C)	$H_\infty \cdot 10^3$ (cm)	$\nu_e \cdot 10^4$ (mol/cm ³)	$\varepsilon = H_\infty/R_0$
0.2	-85	-62	23	0.0	—	—
0.5	-83	11	94	2.7	0.63	1.4
1.0	-81	15	96	5.3	0.48	2.7
2.0	-81	50	131	9.9	0.39	5.0
5.0	-83	44	127	16.8	0.37	8.4
10.0	-85	47	132	24.8	0.40	12.4
15.0	-85	44	129	31.8	0.42	15.9
20.0	-83	46	129	38.0	0.40	19.0
25.0	-85	47	132	46.2	0.39	23.1

average, $\bar{M}_{n(n)}$, molecular weight between the junctions of a polymer network. This method was proved theoretically and confirmed experimentally on model networks.^{12,13} The idea of this method was based on a presumption that chains between the junctions of every functionality behave during the thermomechanical relaxation in a transitional zone of the TMC adequate to linear macromolecules.

Known theories of a high elasticity of crosslinked polymers are based on the indifference of the branching junctions concentration to the equilibrium modulus.²⁴ To ensure it, a large investigation was done of dilatometric and thermomechanical behavior of model networks of linear and branched polymers with different crosslink densities. It was found that the location of the branching junctions has no influence on the T_g and a rate of segmental relaxation (constant value of a linear thermal expansion coefficient in a zone of high elasticity).

From our experiments not described in this article we concluded that the pseudoequilibrium character of the TMCs for crosslinked polymers is the same as found earlier for linear polymers. Here the rule is valid that an interval of temperatures is constant in a transitional zone for all spectrums of molecular weights of the chains of "polymer homologies" between the junctions in crosslinked polymers.

In Figure 3 the TMC (the line *ABOD*) for a linear polymer with a coefficient of polydispersity of about 2 is shown. If this polymer will be crosslinked by functional end groups, it is possible to select the load necessary to apply on a sample during thermomechanical measurements to ensure that these curves should be coincident with the interval between T_g and T_∞ . The difference in topology of these polymers is visible at higher temperatures. For a crosslinked polymer the TMC starting from the glassy state (point *A*) will pass through a transitional zone until a plateau of high elasticity (the straight line *CK*). For a linear polymer at higher temperatures a fixed flow (the curve *OD*) is observed. Of course, when deformations in the transitional zone of linear and crosslinked polymers are equal, the load will be essentially different. Because of this, using a calibrative equation of linear polymers³ to calculate the MWD in the crosslinked polymer is possible.

The essence of the method used is as follows: the TMC is accepted as a combined deformation curve, which in the zone of a plateau of high elasticity gives information about the average

molecular weight between the junctions, which could be also found by the Cluff et al.⁵ or the Flory–Rehner⁴ methods. It is also accepted that the successive terminating of the segmental relaxation by polymer homologies between the junctions in a thermal field are variable against time. According to this rule, in the transitional zone the measured deformation H_i is a sum of the deformations of all polymer homologies between the junctions. These polymer homologies terminate the segmental relaxation here and their deformation corresponds with the equilibrium modulus E_i and the average molecular weight \bar{M}_{ci} . Based on this, a system of equations could be formulated of a local averaging in n points. The molecular weights of all polymer homologies between the junctions are found by using the following equations:

$$\bar{M}_{c(n)} = \frac{1}{\sum_{i=1}^n \varphi_i / M_{ci}} \quad (6)$$

$$\bar{M}_{c(w)} = \sum_{i=1}^n \varphi_i M_{ci} \quad (7)$$

and

$$\varphi_i = \frac{H_{i+1} - H_i}{H_\infty} \quad (8)$$

The detailed procedure of such investigations using an UIP-70M apparatus made by the Russian Academy of Sciences,²⁵ is as follows: the cylindrical or cubic 2–5 mm high sample of the crosslinked polymer is put into the measuring cell of the thermostatic chamber and kept under a load of 0.1–0.2 g, which is minimal for this apparatus. Next, a dilatometric curve is recorded under a cooling down condition at a scanning rate between 0.6 and 20°C/min starting from room temperature until 20–30°C below the glass transition temperature. Here, the result of the thermal expansion, both the thermomechanical and molecular flow deformations of the sample, are understood as deformation. The direction of the thermal expansion is opposite to the two others. The straight line segments of the TMC in high elastic and glassy states is recorded in full. The sample seasoning at a minimal obtained temperature lasts 10–15 min. Next, a load dependent on the stiffness of the tested material is put on the horizontal plate of the quartz sonde. Further, the

sample is heated under the same scanning rate until 20–30°C over the end of a plateau of high elasticity. To compensate for the thermal expansion of the sample, the straight line of a plateau of high elasticity is extended through the point *B* in Figure 3. This line, as a rule, is parallel to the plateau of high elasticity (fragment *CK* of the curve). Then all the transitional interval (as shown in Fig. 3) is split into *n* intervals obeying $\Delta T = 5\text{--}7^\circ\text{C}$. In each of the *n* points, a value of deformation H_i until H_∞ is measured. For each measuring point, a decrement of deformation ΔH_i is calculated. Dividing them by H_∞ , the weight fractions φ_i are obtained. The system of equations of a balance for each point could be described as follows:

$$\bar{M}_{c(n)} = \bar{M}_{c(n-1)} + M_{c(n)}\varphi_n \quad (9a)$$

where

$$\varphi_n = \frac{H_n - H_{n-1}}{H_n}$$

$$\bar{M}_{c(n-1)} = \bar{M}_{c(n-2)} + M_{c(n-1)}\varphi_{n-1} \quad (9b)$$

where

$$\varphi_{n-1} = \frac{H_{n-1} - H_{n-2}}{H_{n-1}}$$

$$\bar{M}_{c(i)} = M_{c(i)}\varphi_i \quad (9c)$$

where

$$\varphi_i = \frac{H_i}{H_n}$$

In the above equations there is only one unknown value, which is the molecular weight of an individual fraction. According to the Williams–Landel–Ferry rule,² the molecular weights of the chains of the polymer homolog between the junctions is determined by the $(T_i - T_g) - (T_{i-1} - T_g)$ value. As the transitional zone is split into more fragments, the average molecular weights are closer and closer to that for a particular polymer homolog between the junctions.

For each point in the temperature interval $T_g \div T_g$ of the TMC, the values of $M_{c(i)}$ and φ_i found are used to draw curves of the molecular weight

distribution in coordinates $\varphi_i - \log M_{c(i)}$. Later, the above data were processed by using known equations for averaging, giving values of $\bar{M}_{n(n)}$, $\bar{M}_{n(w)}$, and $K = \bar{M}_{n(w)}/\bar{M}_{n(n)}$.

Share of Blocks

A share of each block could be calculated based on a presumption that a total deformation ε_∞ in the zone of a plateau of high elasticity is a sum of its constituents (Fig. 4). Because of this, shares of a low-temperature block φ' and a high-temperature block φ'' are

$$\varphi' = \frac{\varepsilon_\infty}{\varepsilon' + \varepsilon''} \quad (10)$$

$$\varphi'' = 1 - \varphi' \quad (11)$$

EXPERIMENTAL

Materials and Testing Conditions

For this study a compound containing 70 phr of natural rubber, 30 phr of *cis*-1,4-polybutadiene type SKD (from Russia), and 50 phr of carbon black grade N220 (ISAF with DBPA = 117 cm³/100 g) was used. The other ingredients of compound (phr) were as follows: aromatic oil, 7.5; ZnO, 5.0; stearic acid, 2.6; Santoflex 13, 2.0; Flectol H, 2.6; sulfur, 2.1; and CBS, 1.2. This compound was cured at 150°C for 20, 25, 30, 40, or 60 min. Next, a 1.2 mm thick sample was put into the thermostatic chamber of the testing device. The sample 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 the 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 at a rate of 5°C/min. The deformation of the sample was measured during heating.

RESULTS AND DISCUSSION

Figure 4 shows the TMC for rubber cured for 20 min. This curve is typical for all tested samples of rubber. The structure of cured rubber contains two blocks, which have different thermo-mechanical and molecular weight characteristics (Table III). Because of this, considering one

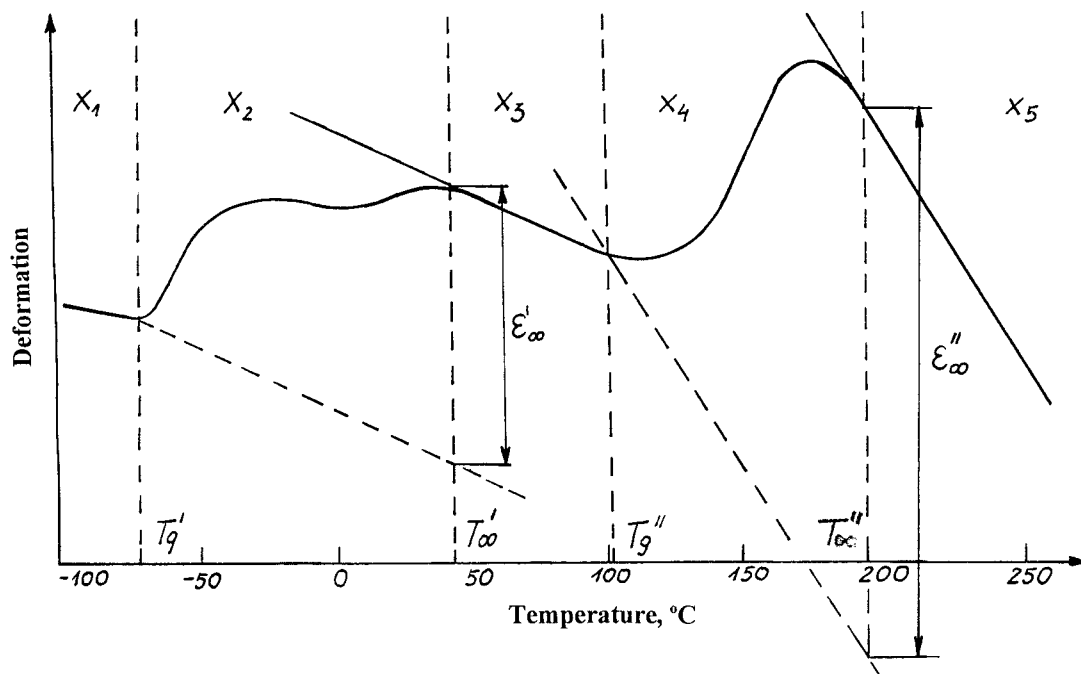


Figure 4 Thermomechanical curve for rubber cured for 20 min: X_1 , a glassy state of a low-temperature block; X_2 , a high elastic state of a low-temperature block; X_3 , a glassy state of a high-temperature block and a plateau of high elasticity of the low-temperature block; X_4 , a high-elastic state of a high-temperature block; X_5 , zone of a plateau of high elasticity of the high-temperature block; ϵ'_{∞} , deformation at a plateau of high elasticity of a low-temperature block; ϵ''_{∞} , deformation at a plateau of high elasticity of a high-temperature block; T'_g , the glass transition temperature of a low-temperature block; T''_g , the glass transition temperature of a high-temperature block.

Table III Molecular Weight and Thermomechanical Characteristics of Tested Rubber

Curing Time (min)	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K	T_g (°C)	φ	$\nu_e \cdot 10^4$ (mol/cm ³)
Low-Temperature Block						
20	5200	8880	1.71	-76	0.30	1.07
25	2380	4320	1.81	-93	0.25	2.20
30	1500	2700	1.80	-94	0.25	3.52
40	1590	3000	1.89	-96	0.20	3.16
60	1685	2080	1.83	-95	0.15	3.08
High-Temperature Block						
20	26,600	39,310	1.48	104	0.70	0.32
25	79,340	115,505	1.41	113	0.75	0.11
30	83,300	122,580	1.47	113	0.75	0.10
40	82,370	115,880	1.41	121	0.80	0.11
60	31,000	45,210	1.46	117	0.85	0.28

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

of them as a low-temperature block, characterized by a glassy state from -80°C and lower, is possible. The tested rubber also had a high-temperature block, which has a glass transition temperature of about $+100^{\circ}\text{C}$. The high-elastic state of the low-temperature block appears between -80 and $+50^{\circ}\text{C}$ and for the high-temperature block between $+100$ and $+200^{\circ}\text{C}$. A plateau of high elasticity for the first block begins at 50°C and lasts to 100°C . In this range it overlaps with the glassy state of the second block. This plateau of the second block starts at a temperature of about $+200^{\circ}\text{C}$ and lasts to a temperature of $+320^{\circ}\text{C}$. A further increase in temperature is followed by the thermal destruction of the polymers. This observation is not contradictory with the Mullins studies; many years ago they found a hard block in rubber compounds.

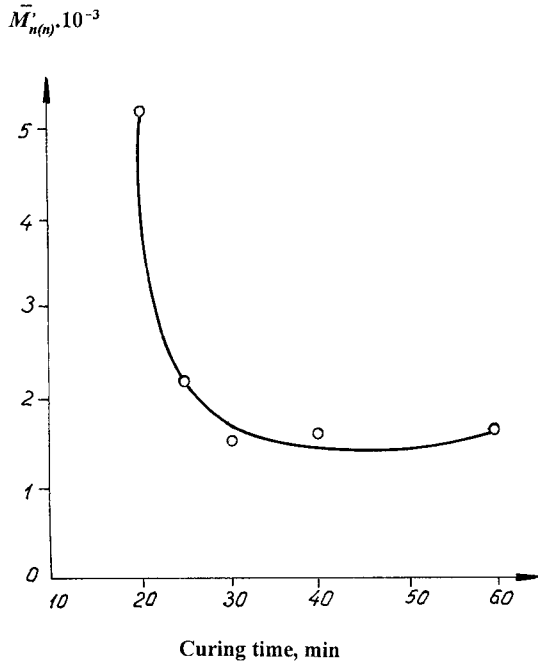
Information on the MWD of the chains between the junctions in both blocks and thermal characteristics of tested rubbers are shown in Table III. The measured properties of rubbers depend on curing time and they essentially differ for low- and high-temperature blocks. A rank of their T_g values shows a principal difference in the mobility of the chains between the junctions being included in these blocks. It is possible to interpret the structure of the chains in a low-temperature block as the chains of polybutadiene and polyisoprene. For the high-temperature block the structure is disputable. A high glass transition temperature of this block evidences strong intermolecular interactions of the chains. The most probable structure of the chains here, according to our opinion, is the structure of the chains adsorbed on the surface of carbon black. The structure of this block is formed in time and probably depends on transformation processes of the chemical structure of the chains. This is evidenced by changes in the T_g value, not only in the low-temperature block, but also in the high-temperature block. Table III shows that up to 25 min of curing, the spatial structure of rubber is not formed in full. Here the separation of polar groups is not ended. The glass transition temperatures of a low-temperature block are the highest and of a high-temperature block are the lowest in comparison to those for longer curing times. After a curing time of 40 min the maximum of separations of the polar groups ($\Delta T = T'_g - T''_g \approx 212 \div 217^{\circ}\text{C}$) is reached and the topological structure of the rubber is stabilized.

Molecular weight characteristics of the chains between the junctions in these blocks and the polydispersity coefficients are different. The difference in K values evidences the different regularity of networks in both blocks.

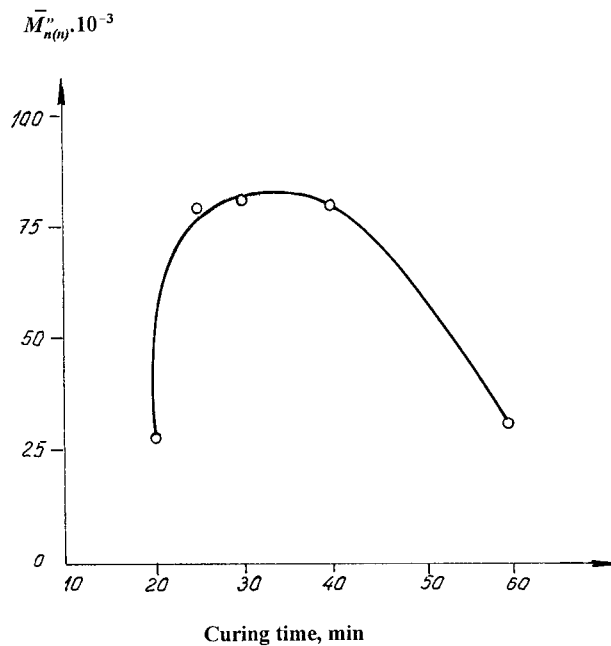
Figure 5 shows that dependencies of the average molecular weight on curing time in both blocks have an extreme character. However, the curves are inverse one against another. The reason for the opposite character of the dependencies for low- and high-temperature blocks could be the presence of *cis*-1,4-isomers in raw rubber simultaneously with *trans*-1,4-isomers. This is the reason for the existence of two rubber phases due to the different density of the cohesion energy in such isomers. The different reactivity of the active sites of these chains during vulcanization²⁶⁻²⁸ and the different character of the interactions of the curing agents' components and/or carbon black could be the reason for the extreme character of the curves.

The character of changes in the K parameters' values, characterizing the network structure regularity in both blocks, is evidence that carbon black, being active filler, plays an important role in the arrangement of a spatial structure in the high-temperature block.

In Figures 6 and 7 are shown the MWDs between the junctions in low-temperature and high-temperature blocks, respectively, that are changing because of the extension of the curing process. The dynamics of transformation of the shape of the MWD for the chains between the junctions of the network in a low-temperature block characterizes the vulcanization processes having a complex mechanism of chemical reactions with participation of at least two kinds of active sites with different reactivities (i.e., two rubbers). This conclusion is confirmed by the bimodal shape of the MWD during the first 25 min of vulcanization. Next, starting at 30 min, this shape is transformed into a unimodal shape. Here it could be accepted that the most reactive sites form a high molecular network (framework) of this block in the beginning of vulcanization. Simultaneously it runs a slower process, which forms another part of the branching junctions. From the moment of reaching the optimal vulcanization time (30 min), the concentration of the junctions in the bulk of the rubber is equalized. At this time the MWD becomes unimodal. This optimal vulcanization time is close to that found earlier by T_g measurements (Fig. 8).



(a)



(b)

Figure 5 Dependence of the number-average molecular weight in blocks on curing time: (a) a low-temperature block; (b) a high-temperature block.

It could be accepted that the reasons for the occurrence of active sites with different activities during the formation of a low-temperature block are not only double bonds from different isomers

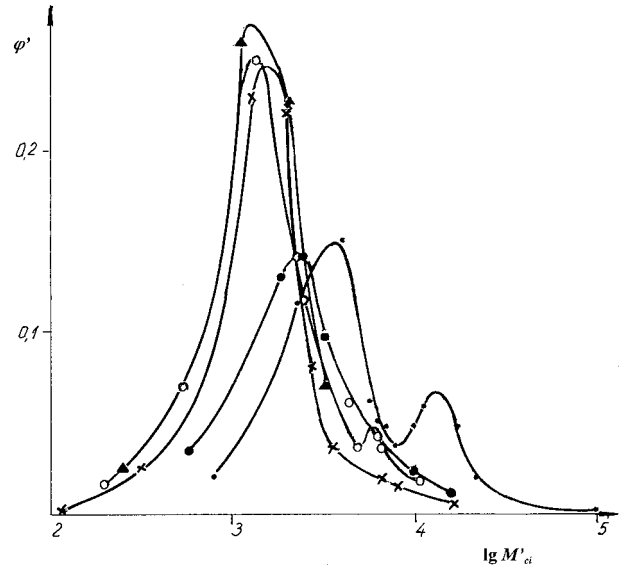


Figure 6 Curves of the molecular weight distribution in the low-temperature block on curing time: (●) 20 min, (●) 25 min, (○) 30 min, (×) 40 min, (▲) 60 min.

in the macromolecules of the rubbers used, but are also a different structure of complexes on the surface of the carbon black particles.

Fragments of macromolecules creating the framework of a high-temperature block of tested rubber during vulcanization, as is visible from the MWD collected in Figure 7, are distributed in the same manner for all curing times. However, note that between 25 and 40 min of vulcanization time, the location of these curves on a coordinate axe is practically unchanged.

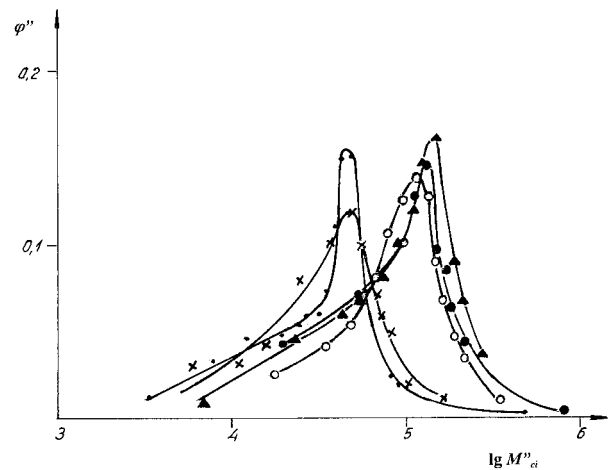
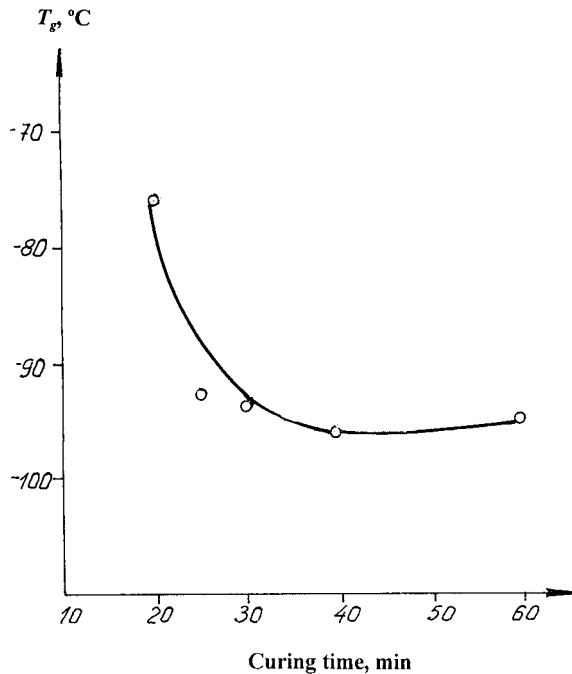
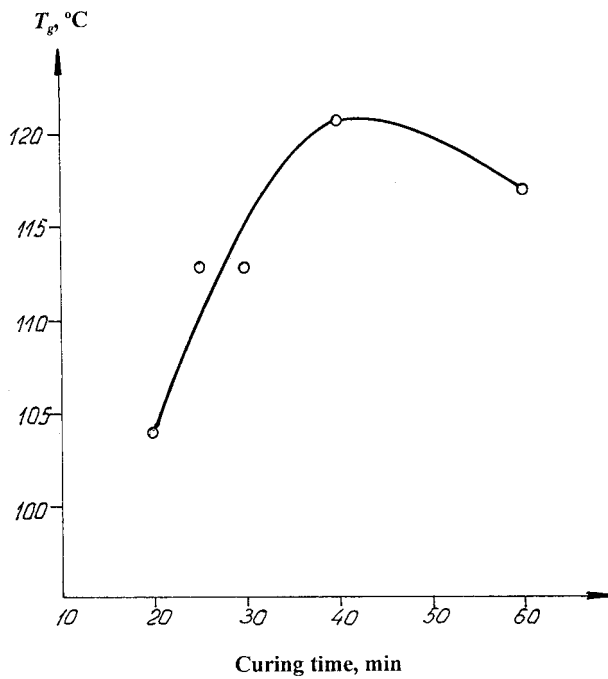


Figure 7 Curves of the molecular weight distribution in the high-temperature block on curing time: (●) 20 min, (●) 25 min, (▲) 30 min, (○) 40 min, (×) 60 min.



(a)



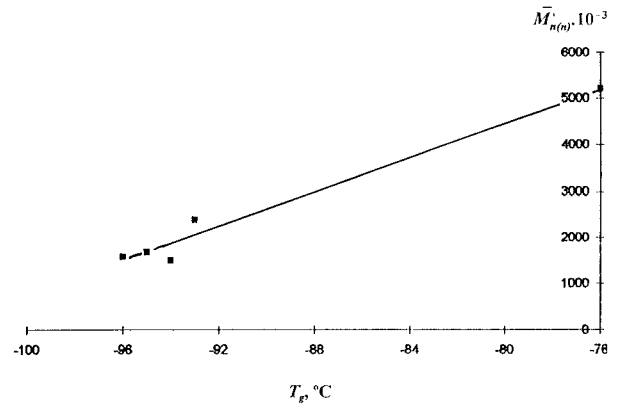
(b)

Figure 8 Dependence of the glass transition temperature T_g on curing time: (a) a low-temperature block; (b) a high-temperature block.

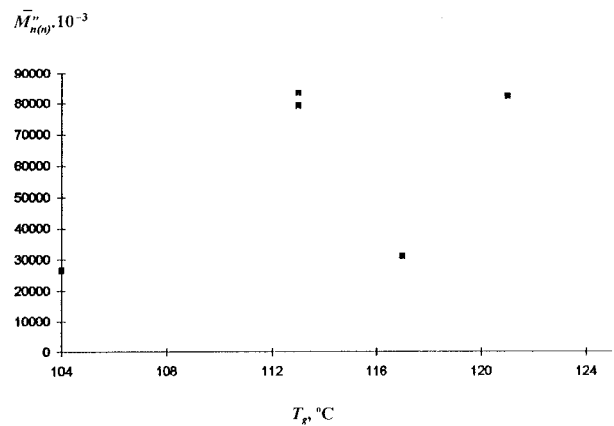
Only the crosslink density (Table III) is changing. From this parameter point of view the optimum is reached in 25 min.

Preliminary Evaluation of Possibility of Using Thermomechanical Spectroscopy for Rubber Testing

A question appears on how reliable the results are that are obtained by the TMA method. To partly answer this question, Figures 5 and 8 were compared. A correlation chart between the glass transition temperature and the average molecular weight between the junctions in each block was made. Figure 9(a) confirms that the average molecular weight between the junctions in a low-temperature block of rubber influences the T_g in the same manner as for the average molecular weight of low-molecular weight linear polymers.²⁹ The coefficient of correlation $r = 0.987$ and the Snedecor-Fisher test $F = 114.39$ show that the correlation analyzed above is essential. However, such a correlation for a high-temperature block [Fig. 9(b)] is disputable, because the coefficient of



(a)



(b)

Figure 9 Correlation chart $T_g - \bar{M}_{n(n)}$: (a) a low-temperature block; (b) a high-temperature block.

Table IV Comparison of Concentrations of Chains between Junctions of Tested Rubber Calculated by Using TMA Method and Swelling

Curing Time (min)	Low-Temperature Block		High-Temperature Block		For Rubber Accepted as Single Block Material	
	φ'	$\nu'_e \cdot 10^4$ (mol/cm ³)	φ''	$\nu''_e \cdot 10^4$ (mol/cm ³)	TMA Method Resultant Value $\nu_e \cdot 10^4$ (mol/cm ³)	Swelling Method $\nu_e \cdot 10^4$ (mol/cm ³)
20	0.30	1.07	0.70	0.32	0.54	1.02
25	0.25	2.20	0.75	0.11	0.63	2.09
30	0.25	3.52	0.75	0.10	0.95	3.52
40	0.20	3.16	0.80	0.11	0.72	3.50
60	0.15	3.08	0.85	0.28	0.70	2.89

correlation $r = 0.49$ and $F = 0.96$ are both very low. To understand this phenomenon one should consider that in this case the molecular weight between the junctions is much higher (Table III) than that in a low-temperature block. As a result, rubber behaves like a high-molecular weight linear polymer when T_g is usually not related to molecular weight.³⁰

It is also possible to compare the average crosslink densities of the tested rubber calculated by using the TMA method and by the well-known swelling method²⁹ (Table IV). This swelling method accepts that

$$\nu_e = \frac{0.0035}{Q_\infty^2} \quad (12)$$

where Q_∞ is a volumetric equilibrium of rubber swelling.

Based on data from Table IV, we calculated the coefficients of correlation between the crosslink density obtained with the swelling method and from the TMA, accepting the additive influence of each block. Here r is 0.829 when the value of the Snedecor–Fisher F test is equal to 6.59. This is evidence for the essential correlation between these values, despite a high difference in the crosslinking densities. Simultaneously, much better agreement is seen for the crosslink density obtained by the swelling method of a bulk rubber (rubber accepted as a single phase) and that in a low-temperature block of such rubber measured by the TMA method. Here the correlation coefficient is equal to 0.983 and the Snedecor–Fisher F test is equal to 84.76. This is understandable because the tested rubber has a structure similar to interpenetrating networks and, as the result, the equilibrium swelling factor of the bulk rubber is

limited by the network with the higher crosslink density. The rubber analyzed here is a low-temperature block.

The analysis shown above demonstrates that the TMA method could be used for evaluation of the crosslink density in rubber. However, further studies should be done to clarify factors influencing the difference in the crosslink density evaluated by these two methods.

CONCLUSIONS

In tested rubbers containing natural and butadiene rubber and N220 carbon black as filler the diblock structure of low-temperature (soft) and high-temperature (hard) blocks was found. Coefficient of polydispersity of the chains between the junctions in both blocks was found to be different, which is evidence of the different regularity of their structure and it is practically unchanged as curing time is extended from 20 to 60 min. The crosslink density in both blocks is different. It is much higher in a low-temperature block. The distribution of the molecular weight between the junctions in these blocks is also different. These results show that thermomechanical mass spectroscopy could be used for the structure investigation of crosslinked rubbers. If further model studies that also use a set of other methods acknowledges our preliminary conclusions, this thermomechanical analysis could possibly be used for a direct, quantitative finding of the presence of hard blocks, particularly in multicomponent rubber compounds.

Decreasing of the T_g as curing time increases was not anticipated. This phenomenon should be studied in detail on model blends.

REFERENCES

1. Kargin, V. A.; Slonimski, G. L. DAN SSSR 1948, 62, 239.
2. Williams, M. L.; Landel, R. F.; Ferry, J. D. J Am Chem Soc 1955, 77, 3701.
3. Olkhov, Y. A.; Jurkowski, B. J Appl Polym Sci 1997, 65, 499.
4. Flory, P. I.; Rehner, I. J Chem Phys 1943, 11, 521.
5. Cluff, E. F.; Glading, E. K.; Pariser, R. J. J Polym Sci 1960, 45, 341.
6. Seeley, R. D.; Rand, P. R. J Appl Polym Sci 1965, 9, 3903.
7. Olkhov, Y. A.; Baturin, S. M.; Entelis, S. G. Vysokomol Sojed 1977, A19, 1307.
8. Gehman, S. D. Rubber Chem Technol 1967, 40, 532.
9. Mooney, M.; Rivlin, R. In Reologia Polimerov; Vinogradov, G. V.; Malkin, A. Y., Eds.; Khimia: Moscow, 1977 [in Russian].
10. Olkhov, Y. A.; Irzhak, V. I.; Baturin, S. M. Rus Patent 1,763,952, October 27, 1989.
11. Baturin, S. M.; Olkhov, Y. A. Tech Machine Building 1995, 4(6), 20 [in Russian].
12. Olkhov, Y. A.; Baturin, S. M.; Irzhak, V. I. Polym Sci USSR 1996, A38(5), 1.
13. Irzhak, T. F.; Variukhin, S. E.; Olkhov, Y. A.; Baturin, S. M.; Irzhak, V. I. Vysokomol Sojed 1997, A39(4), 1.
14. Olkhov, Y. A.; Estrin, Y. I. Sov Patent 1,540,463, 1989.
15. Barton, J. M. Anal Proc 1981, 8, 411.
16. Yevreinov, V. V.; Tkach, Y. G.; Entelis, S. G. Vysokomol Sojed 1973, 15, 4.
17. Zabrodin, V. B.; Zykov, V. I.; Chuy, G. N. Vysokomol Sojed 1974, 16, 3 [Abstract].
18. Curro, J. G. J Polym Sci Polym Phys Ed 1976, 14(D), 177.
19. Eitel, M. Am Chem Soc Polym Prepr 1971, 12(2), 592.
20. Zabrodin, V. B.; Zykov, V. I.; Chuy, G. N. Vysokomol Sojed 1973, B5, 678.
21. Magen, P. A. Eur Polym J 1986, 22, 967.
22. Volkova, N. N.; Sandakov, G. I.; Sosikov, A. I.; Olkhov, Y. A.; Smirnov, L. P.; Sumanen, K. T. Vysokomol Sojed 1992, A34(3), 77.
23. Bills, K. W.; Solsedo, J. R.; Solsedo, F. S. J Appl Phys 1961, 32, 2364.
24. Priss, L. S. In Proceedings of the Second Conference on Mathematical Methods in the Investigation of Polymers: Pushchino: Moscow, 1981.
25. Teitelbaum, B. Y. Thermomechanical Analysis of Polymers; Nauka Publishers: Moscow, 1979; p 56 [in Russian].
26. Smith, F. B. Rubber Chem Technol 1961, 34, 571.
27. Treolar, L. R. Physics of Rubber Elasticity; Clarendon Press: Oxford, UK, 1978.
28. Chough, S. H.; Chang, D. H. J Appl Polym Sci 1996, 61, 449.
29. Marei, A. I. In Physical Properties of Elastomers; Khimia: Leningrad, 1975; p 31 [in Russian].
30. Olkhov, Y. A.; Kalmikov, Y. B.; Baturin, S. M. Vysokomol Sojed 1984, A26, 1681.