

MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Specific Features of Separate and Joint Mastication of Natural and 1,4-*cis*-Butadiene Rubbers in the Presence of Dibenzoylaminodiphenyl Disulfide

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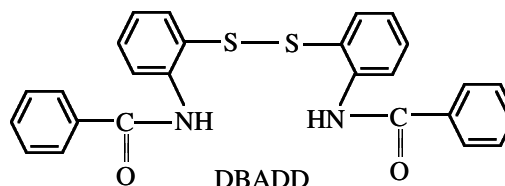
Abstract—Variation of the molecular structure characteristics and properties of natural and 1,4-*cis*-polybutadiene rubbers (gel content, molecular weight, degree of branching of macromolecules, viscosity) in the course of their separate and joint mastication in the presence of dibenzoylaminodiphenyl sulfide as mastication accelerator or without it was studied.

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Natural rubber (NR) and its blends with other rubbers (e.g., *cis*-butadiene rubber, SKD) are widely used in rubber industry, in particular, for production of treads and sidewalls of R-type tyres. Industrial processing of NR is more labor- and power-consuming than that of synthetic rubbers, because it requires preliminary mastication with the aim to decrease the molecular weight and viscosity to the level suitable for processing into rubber stocks and semifinished products on the existing equipment. With polymer blends, the viscosity of compounds can be significantly decreased owing not only to a decrease in the molecular weight of rubber macromolecules, but also to formation of a specific structure. The causes of such a decrease in the viscosity of blends consisting of different rubbers are described in detail [1]. The most pronounced decrease in the viscosity of NR–SKD blends, measured at shear rates less than 100 s^{-1} , is observed at their ratios in the range from 80/20 to 50/50 [2]. However, in view of the free-radical nature of mechanochemical reactions, we should take into account the possibility of recombination of free radicals [3], which can lead to an increase in the molecular weight and decrease in the mastication effect.

It is well known that the molecular weight of rubbers can be decreased by introducing special additives, so-called chemical mastication accelerators [3, 4]. In this connection, it is appropriate to study specific features of joint mastication of NR and SKD in the pres-

ence of a commercially used additive, dibenzoylaminodiphenyl disulfide (DBADD), and without it.



The commercial name of the accelerator is Pepton-22. It is a light yellow crystalline powder melting at $136\text{--}143^\circ\text{C}$ [5].

EXPERIMENTAL

Experiments were performed with RSS-1 NR (Indonesia), SKD [GOST (State Standard) 14924–73], and an NR–SKD blend (1 : 1). The mastication of NR, SKD, and their blends was performed on Lb 320 160/160 laboratory rollers with addition of DBADD (0.3 wt % relative to rubber) or without it. The clearance between the rollers was 2.3 mm at a friction of 1 : 1.14. The mastication was performed for 5, 10, and 15 min. DBADD mastication accelerator was added in all the cases on the second minute after the rubbers adhere to the roller at the initial rubber temperature of 35°C . In the course of mastication, the rubber temperature increased to $75\text{--}80^\circ\text{C}$.

To evaluate changes in the rubber structure, we determined viscometrically at 25°C the intrinsic vis-

Table 1. Influence of the rolling time and DBADD content on the properties and molecular characteristics of NR, SKD, and their 1 : 1 blend

Sample	τ , min	Weight fraction of gel, %	Mooney viscosity, Mooney units	$[\eta]$, dl g ⁻¹	K_H , (dl g ⁻¹) ⁻²
NR:					
without DBADD	0	18.23	95.0	4.78	1.00
	5	3.33	77.5	4.20	0.3
	10	3.06	69	3.43	0.34
	15	1.68	58	2.40	0.80
with DBADD	5	4.43	66	3.32	0.57
	10	3.45	54.5	2.33	0.96
	15	1.55	44	2.64	0.33
SKD:					
without DBADD	0	3.95	–	2.52	0.14
	5	2.83	45	2.46	0.18
	10	2.11	46	2.39	0.28
	15	3.11	45	2.36	0.33
with DBADD	5	2.74	48.9	2.06	0.67
	10	3.30	49.8	2.18	0.49
	15	3.19	48.8	2.20	0.39
NR + SKD					
without DBADD	5	5.56	72.3	3.27	0.59
	10	4.19	73.9	3.17	0.72
	15	4.19	58.2	2.36	0.74
with DBADD	5	4.18	72.2	2.95	0.80
	10	3.46	71.3	2.97	0.53
	15	5.12	70.6	3.20	0.63

cosity $[\eta]$ of the sol fraction soluble in toluene. From the slope of the linear concentration dependence of the reduced viscosity, we determined the branching coefficient from which we calculated the Huggins constant K_H characterizing the degree of macromolecule branching [6].

The content of the gel (insoluble fraction) was determined by two methods: from the weight of the residue on the filter and from the difference in the solution concentrations before and after filtration. From these data, we determined the constant of mechanical degradation K_σ and the degree of degradation φ [3]. The degradation constant was calculated by the equation

$$(\eta_t - \eta_\infty)/(\eta_0 - \eta_\infty) = \exp(-K_\sigma t), \quad (1)$$

where η_0 , η_t , and η_∞ are the intrinsic viscosities of the rubber before rolling, after the treatment for time t , and after the 60-min treatment (limiting degradation).

The degree of degradation was calculated as

$$\varphi = (\eta_0 - \eta_t)/(\eta_0 - \eta_\infty). \quad (2)$$

The viscosity of rubbers and their blends was deter-

mined on a Mooney shear disk viscometer and evaluated in Mooney units (1 Mooney unit = 0.0846 N m) [7].

Table 1 shows how the rolling time τ and DBADD content affect the properties and molecular characteristics of NR, SKD, and their blends, and Table 2 shows how these factors affect the constant of mechanical degradation and degree of degradation of these materials.

An increase in the time of NR mastication without chemical accelerator is accompanied by a monotonic decrease in the gel content, intrinsic viscosity, and Mooney viscosity. The degree of degradation grows monotonically, but there is no definite trend in variation of the degree of branching: In the case of NR, it first decreases upon mastication for 5 min and then gradually increases. This may be due to the development of nonlinear degradation [3]. On the whole, the changes observed are consistent with the well-known views [8] that the viscosity of polymers in the condensed state of macromolecules decreases with a decrease in the gel content and in the molecular weight and with an increase in the degree of branching.

Table 2. Influence of the rolling time and DBADD content on the constant of mechanochemical degradation K_{α} and degree of degradation φ of NR and SKD

Sample	τ , min	K_{σ} , min	φ	
NR: without DBADD	5	0.120	0.24	
	10		0.57	
	15		0.88	
	with DBADD	5	0.15	0.57
		10		0.90
		15		0.81
SKD: without DBADD	5	0.008	0.039	
	10		0.078	
	15		0.095	
	with DBADD	5	0.013	0.256
		10		0.191
		15		0.182

Addition of DBADD mastication accelerator noticeably increases the rate and degree of degradation of NR and SKD macromolecules. At the same time, more pronounced decrease in molecular weight (MW) at a mastication time of 5 and 10 min results in increased branching of macromolecules in the sol fraction and higher gel content in the masticated rubber. For example, after mastication of NR for 5 min, the branching of the macromolecules is characterized by the Huggins constant of $0.57 \text{ (dl g}^{-1}\text{)}^{-2}$ and gel content in the masticated rubber of 4.43%; after rolling for 10 min, these parameters become $0.96 \text{ (dl g}^{-1}\text{)}^{-2}$ and 3.45%, respectively. Longer rolling (15 min) results in a certain increase, rather than decrease, in the molecular weight; in the process, the degree of branching and gel content sharply decrease: from 0.96 to $0.33 \text{ (dl g}^{-1}\text{)}^{-2}$ and from 3.45 to 1.55%, respectively. The Mooney viscosity monotonically decreases. Larger branching of macromolecules observed in the initial period of mastication in the presence of mastication accelerator indicates that the major pathways of deactivation of polymeric radicals in the initial period of the process are their recombination and reaction with nondegraded macromolecules, rather than addition of the sulfide radical of DBADD. Longer mastication results in more uniform distribution of the mastication accelerator and hence in higher probability of the reaction of polymeric radicals with DBADD. The high melting point of DBADD also plays a certain role, impeding its dispersion at the mastication temperature of 75–80°C.

Thus, mastication of NR for 15 min without masti-

cation accelerator results in the formation of a rubber structure with decreased MW and increased branching of macromolecules. In the presence of DBADD, a decrease in the molecular weight is accompanied by a decrease in the polymer chain branching.

An increase in the time of SKD mastication without accelerator to 15 min results in monotonic but slight decrease in the molecular weight, with the Huggins constant increasing (from 0.14 to 0.33). The gel content in the initial period of the mastication decreases, but after the treatment for 15 min somewhat increases. The observed changes in the structure do not lead to noticeable changes in the Mooney viscosity. Addition of the mastication accelerator leads to a more noticeable decrease in the molecular weight of SKD rubber, with a considerable increase in the Huggins constant (to 0.67). An increase in the mastication time to 10 and 15 min results in a certain increase, rather than decrease, in the molecular weight. At the same time, the degree of branching of the macromolecules decreases to 0.39, and the gel content in the masticated rubber somewhat increases. The trends in the kinetics of degradation and branching of SKD and NR show certain analogy determined, as noted above, by decelerated dispersion of the mastication accelerator in the rubber matrix due to high melting point of its crystals.

Joint mastication of NR and SKD without mastication accelerator leads to a decrease in the intrinsic viscosity of the rubber blend, indicative of a decrease in the MW of the elastomeric components. The intrinsic viscosity of the rubber blend is close to the additive value. At the same time, macromolecules in the ash are characterized by increased degree of branching relative to the sum of the contributions of the components at the separate mastication. The masticated rubbers are characterized by the increased gel content, which imparts to them higher Mooney viscosity. Apparently, higher branching of macromolecules in the sol fractions is due to recombination of chain radicals of NR and SKD, and also to the presence of fragments of the three-dimensional structure of the initial gel, which is broken down during mastication. Somewhat lower degree of the gel degradation may be caused by the lower shear stress in the initial period of the mastication, due to a decrease in the initial viscosity of the combined system [1].

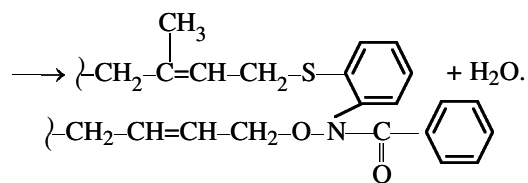
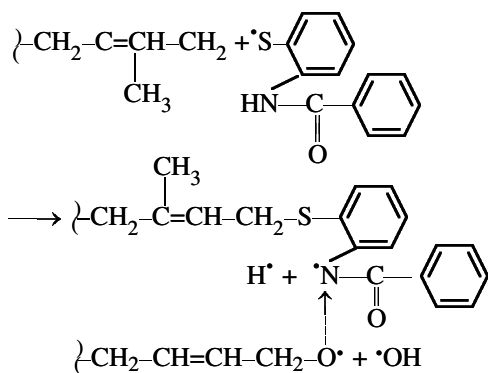
The effect of DBADD on the elastomer blend is similar to its effect in mastication of each rubber taken separately. More pronounced decrease in the MW in the initial period of the process (the intrinsic viscosity decreases from 3.27 in rolling without accelerator to

2.97 in the presence of DBADD) is accompanied by its increase with an increase in the mastication time. Initially high values of the Huggins constant decrease in the course of the mastication. At the same time, the gel content in the masticated rubber increases.

In joint mastication of NR and SKD both in the presence of DBADD and without it, the degree of branching of macromolecules and the gel content in the masticated rubber are higher than in mastication of the rubbers taken separately. This fact indicates that the role of the recombination of polymeric radicals and their reaction with macromolecules in rubber blends is more significant. It was interesting to additionally estimate the probability of the reaction of chain radicals belonging to different elastomers. To this end, the sol fraction of 1 : 1 NR + SKD blends masticated in the presence of DBADD and without it (rolling time 15 min) was dried and subjected to quantitative analysis by pyrolytic gas chromatography (Biokhrom-1 chromatograph):

Masticated rubber	NR/SKD rubber content in sol fraction, %
Without DBADD	50/50
With DBADD	55/45

These data show that, in the mastication without DBADD, the ratio of the rubbers in the sol fraction and hence in the gel is equal to their initial ratio. This fact suggests (though tentatively) formation of a chemical bond NR-SKD, which also follows from the stronger branching of the blended masticated rubber. In the joint mastication of NR and SKD with DBADD, a part of the macromolecules becomes incorporated in the gel structure. This fact also suggests that the joint mastication of NR and SKD is accompanied by chemical reaction of the chain radicals of different elastomers. The following scheme of formation of a chemical bond between polyisoprene and polybutadiene radicals in the presence of DBADD can be suggested:



The primary or peroxy radical of polyisoprene reacts with *o*-benzoylaminophenylthio radical to form macromolecules incorporating an amine-type antioxidant. Hydroperoxides of butadiene rubber, forming successively or simultaneously, readily decompose into products to form low-molecular-weight and chain radicals [3, 4]. These radical chemically bind the amine radical which is already bound chemically to a polyisoprene macromolecule. Repeated degradation of the linked chains can lead to an increase in their molecular weight, branching, and gel formation. The sequence of the reactions of polyisoprene or polybutadiene radicals with DBADD is apparently random. Thus, on the one hand, DBADD accelerates the mastication of *cis*-1,4-polyisoprene and *cis*-1,4-polybutadiene whose addition favors a decrease in MW; on the other hand, DBADD is an antioxidant and acts oppositely, promoting formation of interpolymers and enhancing the interactions at phase boundaries of different rubbers. It should also be noted that this accelerator is the most effective at treatment temperatures in the range 80–140°C [9]. This is apparently associated with its high melting point. In the course of mastication in closed rubber mixers and preparation of rubber stocks, rubbers are subject to simultaneous action of the mechanical and thermal energy. The temperature of extended rubber stocks in their preparation in closed rubber mixers increases to 160°C and more [5], which should lead to prevalence of processes leading to a decrease in the molecular weight.

In this study we examined the possibility of preparing rubber stocks with NR and performing the mastication directly in the step of stock preparation. Under industrial conditions, we prepared tread rubber stocks from nonmasticated NR in combination with SKD (85/15), with addition of 0.3 wt % DBADD in the first step of compounding. The properties of the experimental rubber stocks and vulcanized products were compared with those of the commercial product of the same composition in which NR was taken as P-3 masticated rubber prepared in a rubber mixer without mastication accelerator. The experimental and commercial rubber stocks were prepared under the same conditions. Their technological properties appeared to be the same. At the same time, vulcanized

Table 3. Physicomechanical parameters of vulcanized rubber stocks prepared by joint mastication of NR with SKD in the presence of DBADD

Parameter	Reference	Experimental value
Nominal tensile strength, MPa	171	187
Rebound elasticity, 20°C/100°C, %	38/50	41/56
Endurance at repeated 150% extension, thousands of cycles	35.1	53.7
Coefficient of resistance to thermal aging* at 100°C, 48 h, with respect to:		
nominal strength	0.73	0.84
relative elongation	0.58	0.69
tear resistance	0.70	0.97
De Matthias head buildup, T , °C:		
before aging	123	111
after aging at 100°C, 48 h	142	128
Mir-1 abrasability, $m^3 TJ^{-1}$:		
before aging	80	62.2
after aging at 100°C, 48 h	133.9	110.5
Schopper abrasability, mm^3	64	58

* The coefficient of resistance to thermal aging is defined as the ratio of the indicated parameter before aging to that after aging.

products from experimental rubber stocks exhibit higher values of certain parameters (Table 3), in particular, higher elasticity, higher endurance at repeated extension, and lower heat buildup, which is attributable to weaker branching of NR macromolecules, at a considerably higher content of NR compared to SKD. Experimental rubbers have also a higher coefficient of resistance to thermal aging and wear. In this case, DBADD behaves as an aging inhibitor. According to [10], stabilizers incorporated in the polymer chain decrease the abrasability of rubbers. Also possible is a positive effect of stronger bonding between the phases, due to formation of interpolymers of types NR-SKD and NR-DBADD-SKD.

CONCLUSIONS

(1) In separate mastication of natural and 1,4-*cis*-butadiene rubbers without using dibenzoylaminodiphenyl disulfide as mastication accelerator, the molecular weight monotonically decreases and the degree of branching of the macromolecules increases. In the presence of this mastication accelerator, the pattern is different.

(2) In joint mastication of natural and 1,4-*cis*-butadiene rubbers in the presence of dibenzoylaminodiphenyl disulfide and without it, the degree of branching of the macromolecules, gel content, and Mooney viscosity of the masticated rubbers are higher than the

sum of the contributions of the components, determined at their separate mastication.

(3) Joint mastication of natural and 1,4-*cis*-butadiene rubbers can be combined in one step with the preparation of extended rubber stocks in closed rubber mixers in the presence of dibenzoylaminodiphenyl disulfide. The resulting stocks exhibit the required processing characteristics, and the physicomechanical properties of the resulting vulcanizates are improved owing to weaker branching of natural rubber macromolecules, incorporation of an *o*-benzoylaminophenylthio fragment, behaving as amine-type antioxidant, in the macromolecules, and stronger bonding between the polymer phases owing to formation of interpolymers.

REFERENCES

1. Kuleznev, V.N., *Smesi polimerov* (Polymer Blends), Moscow: Khimiya, 1980.
2. Folt, V.I. and Smith, L.W., *Rheology of Blends, Rubber Chemistry and Technology*, 1973, vol. 46, pp. 1193–1209.
3. Baramboim, N.K., *Mekhanokhimiya vysokomolekulyarnykh soedinenii* (Mechanochemistry of Macromolecular Compounds), Moscow: Khimiya, 1978.
4. Simionescu, C. and Opreo, C., *Mecanochimia Comusilor Macromoleculari*, Bucharest: Academiei, 1967.
5. Koshelev, F.F., Kornev, A.E., and Bukanov, A.M., *Obshchaya tekhnologiya reziny* (General Technology

- of Rubber), Moscow: Khimiya, 1978, 4th ed.
6. Serenson, W.R. and Campbell, T.W., *Preparative Methods of Polymer Chemistry*, New York: Interscience, 1961.
 7. Zakharov, N.D., Zakharkin, O.A., Kostrykina, G.I., et al., *Laboratornyi praktikum po tekhnologii reziny: uchebnoe posobie dlya vuzov* (Laboratory Manual on Rubber Technology: Textbook for Higher Schools), Moscow: Khimiya, 1988, 2nd ed.
 8. Vinogradov, G.V. and Malkin, A.Ya., *Reologiya polimerov* (Rheology of Polymers), Moscow: Khimiya, 1977.
 9. Betts, G.E., Karmin, B.K., Eitingon, I.I., et al., *Kauchuk Rezina*, 1960, no. 5, pp. 24–27.
 10. Il'ina, E.A., Role of Chemical Factors in Wear Failure of Vulcanized Rubbers, *Cand. Sci. Dissertation*, Moscow, 1977.