

Effect of Coal Tar on the Properties of Butadiene–Nitrile Rubbers

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Abstract—The analysis of coal tar as a by-product of a merchant-coke plant (Karaganda) was carried out for the use of this tar as a plasticizer of rubber compounds. The replacement of bitumen by this tar as a rubber constituent in a weight ratio of 1:10 showed that the kinetics of vulcanization was noticeably accelerated and rubber characteristics such as conditional tensile strength, hardness, freeze-proof factor, and relative residual deformation were improved. It was found that the derivatives of phenol as the constituents of this tar exerted a considerable effect on the acceleration of the vulcanization process. In connection with this, the dephenolization of the product was performed, and it was used in a rubber formulation in the same ratio; as a result, the best characteristics of frost resistance, resistance to a hostile environment (an isoctane–toluene mixture), and ultimate elongation were obtained.

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INTRODUCTION

Butadiene–nitrile rubber (BNR) is widely used for the manufacture of different oil- and gasoline-resistant rubber products (liners, sleeves, rings, cups, gaskets, plates, gasoline cans, etc.) because of high resistance to the action of oils and other aggressive agents.

The physical properties of BNRs essentially depend on the acrylonitrile content. The BNRs are readily soluble in ketones, aromatic and chlorinated hydrocarbons, and esters and very sparingly soluble in aliphatic hydrocarbons and alcohols. With increasing the bound acrylonitrile content of the polymer, intermolecular interactions between polymer chains and density considerably increase, the glass transition temperature increases, dielectric properties and solubility in aromatic solvents decrease, and swelling resistance in aliphatic hydrocarbons increases. However, the introduction of different technological additives, in particular, softeners and plasticizers, has an essential effect on the physicomechanical characteristics of the finished rubber products [1].

Previously, development works for the use of bitumen and tar as the plasticizers of rubber compounds have been performed. A technical result of this development was patented [2]; it consisted in an improvement in the physicomechanical properties of rubber by the modification of bitumen with oil–polymer resins [3]. A problem of the application of low-temperature

carbonization coal tar as a softener for butadiene–nitrile rubbers was formulated. However, the carcinogenic properties of coal tar are well known; in this con-

Table 1. Comparative characteristic of the component compositions (%) of the initial and dephenolized tars

Individual composition	Low-temperature carbonization coal tar	Dephenolized coal tar
Phenol	4.18	2.22
Methylcyclohexane	6.84	–
Toluene	29.29	–
Heptane	7.53	–
2-Methylphenol	3.22	1.73
4-Methylphenol	8.97	–
2-Ethylphenol	0.95	–
3,4-Dimethylphenol	4.42	2.31
3,5-Dimethylphenol	6.81	–
Naphthalene	16.00	1.47
2-Ethyl-4-methylphenol	3.46	1.13
2-Methylnaphthalene	1.55	4.7
Tridecane	1.19	3.95
Tetradecane	0.95	3.51
Pentadecane	0.95	2.80

Table 2. Comparative characteristic of the physicochemical indices of high-temperature coal tar and low-temperature carbonization coal tar

Index	High-temperature coal tar	Low-temperature carbonization coal tar from TOO Sary-Arka Spetskoks	Determination method
Density at 20°C, kg/m ³	1190	1042	GOST 3900 GOST 11126
Volume fraction of water, %	4	traces	GOST 2477-65 GOST 2770 GOST 2177-99
Fractional composition, weight fraction (on an anhydrous tar basis), %, (°C):			
to 180	~1	3.0	
180-230	13	7.2	
230-270	10	15.1	
270-300	10	17.1	
End bp 300	18	6.2	
Total distillate, %	~52	48.6	
End boiling point, °C:			
in vapor	320	315	
in liquid	400	390	
Weight fraction of substances insoluble in toluene (α fraction), %	6-10	3.8	GOST 7847
Weight fraction of substances insoluble in quinoline (α_1 fraction), %	4-6	Not detected	TU 14-7-100-89
Ash content, %	No higher than 0.3	0.12	TU 14-7-100-89
Phenol content, %	1-2	>20	GOST 2177-99
Naphthalene content, %	7-12	traces	GOST 2177-99

text, it is necessary to examine the physicochemical properties of rubbers obtained with the use of both crude tar and tar purified by the removal of phenol as the main carcinogen.

The aim of this study was to search for an optimum rubber formulation based on butadiene-nitrile rubbers of two brands (BNKS-18 AMN and BNKS-28 AMN) with the application of low-temperature carbonization coal tar as a softener. A large quantity of valuable products can be obtained from different coal tar fractions by their deep conversion [4]; however, it was reasonable to use this product in the composition of a rubber compound without fractionating. The introduction of this tar into a rubber compound can improve the kinetics of vulcanization and the physicochemical properties of the final product.

EXPERIMENTAL

Low-temperature carbonization coal tar. The composition of the test low-temperature carbonization coal tar was analyzed by gas chromatography-mass spectrometry on an HP 5890-5972 MSD instrument from Agilent (the United States). The substances were identified using the NIST98 mass-spectrometric database. The concentrations of substances were determined semiquantitatively with reference to fluoranthene. High-performance liquid chromatography

(HPLC) on an HP 50 instrument with a diode array detector allowed us to detect the presence of polyaromatic hydrocarbons and phenols in the tar (Table 1).

The physicochemical properties of tar were analyzed for the following main characteristics: density, fractional composition, end boiling temperature, weight fraction of water, volume fraction of ash, weight fraction of substances insoluble in toluene (α fraction), weight fraction of substances insoluble in quinoline (α_1 fraction), and concentrations of phenols and naphthalene, which are important for predicting the technological properties of a rubber compound and the final product (Table 2).

The softening temperature was determined by a ball and ring softening procedure [5]. For determining the weight fraction of water, a petroleum product sample was heated with a solvent insoluble in water in accordance with the Dean and Stark method [6].

The weight fraction of ash was found by the combustion of a test petroleum product and the heat treatment of the solid residue to constant weight [7]. The weight fraction of volatile substances was determined by sample drying [8]. The dephenolization of the low-temperature carbonization coal tar was performed according to TU [Technical Specifications] 6-10-1261-80.

Analysis of the resulting rubber. The tensile strength, failure elongation, and tension stress were determined

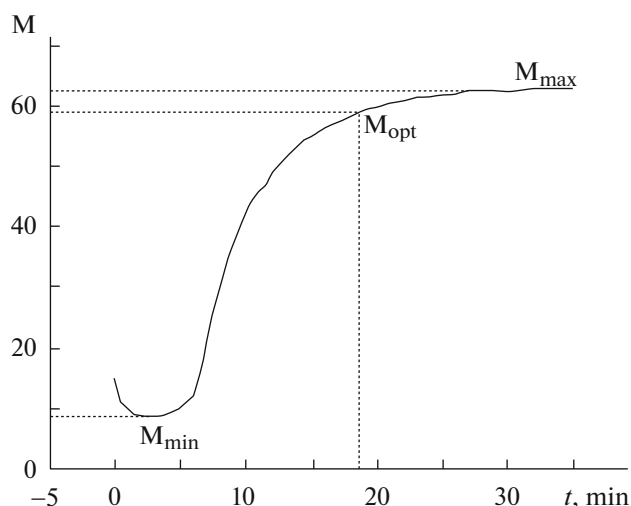


Fig. 1. Kinetic curve of the modulus in tension (M) as a function of time (t) for formulation no. 1.

with the use of dumb-bell and ring specimens in accordance with a procedure for the determination of tensile elastic and strength properties. The tests were conducted at room temperature and elevated temperatures (to 100°C) [9].

The hardness of rubber was determined according to a published method [10] by measuring the resistance of rubber at $(23 \pm 2)^{\circ}\text{C}$ on sinking an indenter into it.

The kinetics of vulcanization was measured on a Monsanto rheometer at temperatures of 151, 120, and 100°C in accordance with GOST [State Standard] 10722–76 [11]. The freeze-proof factor was determined according to a method of determining the ability of a sample compressed at a temperature of -24°C to restore its height at a low temperature after unloading [12]. The residual deformation was determined by the repeated compression of a sample under specified conditions to the establishment of a conditional temperature equilibrium, when the rate of heating was no higher than 0.5 K/min and the measurement of the temperature and residual deformation of the sample after a rest during a specified time [13].

The testing of rubber for resistance to hostile environments was performed using methods for studying samples in an unstressed state under the action of media at specified temperatures and exposures with the subsequent determination of their resistance to the above action from changes in the weight, volume, or sizes [14].

RESULTS AND DISCUSSION

A mixture of individual organic substances, each exerting a specific effect, in concentrations of 2–5% on a rubber weight basis is commonly used as a softener. As is well known from the literature, softeners should correspond to the following requirements: they should be compatible with rubber, i.e., miscible with

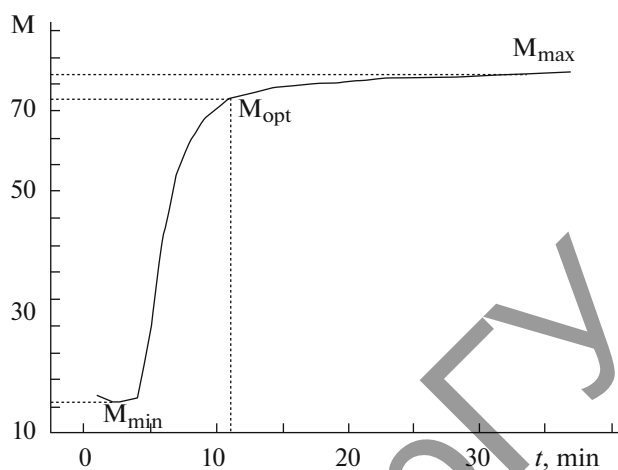


Fig. 2. Kinetic curve of the modulus in tension (M) as a function of time (t) for formulation no. 2.

it, and strongly retained in the rubber compound and vulcanized rubber over a wide temperature range; they should exhibit chemical and thermal resistance during vulcanization; they should have a low saturated vapor pressure and a high volatility at the temperatures of the treatment and vulcanization of mixtures; their flash point should be as high as possible; they should be non-toxic, odorless, and also readily available and inexpensive. The application of bitumen in an amount of 10 wt % as a softener of rubber compounds is well known.

In this work, we were the first to use low-temperature carbonization coal tar as a softener in a ratio identical to that with bitumen. In the course of studying rubbers, we obtained kinetic curves, with the aid of which we constructed graphs for the vulcanization of the following three test rubber formulations: a formulation with the use of typical bitumen, a formulation

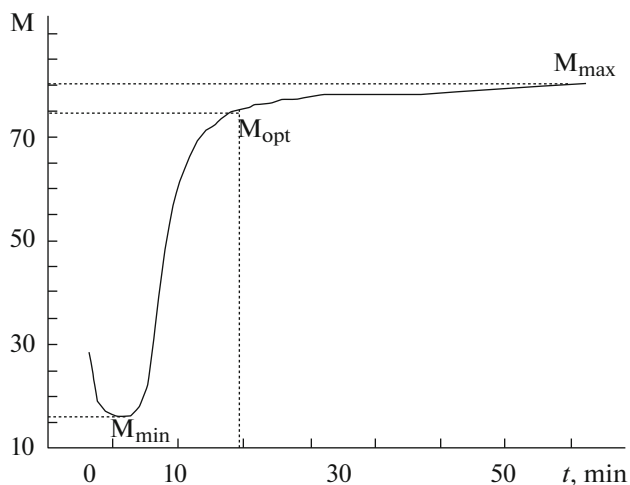


Fig. 3. Kinetic curve of the modulus in tension (M) as a function of time (t) for formulation no. 3.

Table 3. Physicomechanical characteristics of an MBS 51-6712 rubber compound

Characteristic	Regulated test method	Rate according to GOST	Formulation		
			No. 1 (bitumen)	No. 2 (coal tar)	No. 3 (dephenolized tar)
Conditional tensile strength, MPa	GOST 270-75	≥7.0	8.0	8.2	9.0
Failure elongation, %	GOST 270-75	≥200	340	270	390
Shore A hardness	GOST 263-75	55–70	64	69	65
Exposure to an isooctane–toluene mixture, %	GOST 9.030-74	No higher than 20	19.0	23.0	16.1
Freeze-proof factor	GOST 13808-79	No lower than 0.2	0.75	0.83	0.89
Relative residual strain	GOST 9.029-79	No higher than 50	20.5	22.0	20.6

with crude low-temperature carbonization coal tar, and a formulation with the use of the dephenolized low-temperature carbonization coal tar.

Because butadiene–nitrile rubbers are special-purpose rubbers, they can be vulcanized at a high temperature (100–200°C) without the use of a curing agent. In this case, we carried out vulcanization at a temperature of 151°C with the use of commercial ground sulfur and thiazole as vulcanization accelerators. In the course of the study of the resulting rubber product, we plotted the kinetic curves of the modulus in tension (M) as a function of time (t) (Fig. 1).

The majority of products is vulcanized at 140–170°C. With the use of high temperatures, the curing time of products can be shortened; therefore, the productivity of equipment can be increased.

Based on the graphic data, we calculated an optimum of vulcanization to be 57.58:

$$M_{\text{opt}} = 0.9[M_{\text{max}} - M_{\text{min}}] + M_{\text{min}}, \quad (1)$$

$$M_{\text{opt}} = 0.9[63 - 8.8] + 8.8 = 57.58. \quad (2)$$

This optimum of vulcanization is a good result, which makes it possible to forecast sufficiently productive conditions for processing in a given rubber formulation. Note that the vulcanization plateau (Fig. 1) remained stable for a long time; this fact indicates that the possibility of overcuring is reduced.

For optimizing the properties of rubber and improving the physicomechanical parameters based on this rubber, we introduced low-temperature carbonization coal tar instead of bitumen in the same ratio (10, by weight) into the rubber formulation and constructed a graph (Fig. 2) for the kinetics of vulcanization as a result of the study.

In accordance with Eq. (1), the optimum of vulcanization was

$$M_{\text{opt}} = 0.9[80 - 16] + 16 = 73.6. \quad (3)$$

According to the graph (Fig. 2), a time of 11 min corresponds to a point of 73.6. This fact indicates that the rubber compound manifests insignificant instability on treatment; however, this can give a negative result

upon extrusion, calendaring, and further working of rubber products. In this case, phenol could play the role of an accelerator.

For this purpose, we carried out the dephenolization of tar in order to subsequently use it as a softener. Note that the extraction of phenols with the solutions, for example, of alkalis is an ambiguous process. A significant quantity of neutral oils, which cannot be sufficiently fully separated, is extracted together with the phenols.

In this case, the alkaline solution of phenols is extremely unstable. Within a short time interval, polycondensation reactions occur to significantly change the composition of separated fractions; therefore, we carried out the distillation of low-temperature carbonization coal tar in an alcohol solution. As a result, we acquired the following data on the kinetics of the vulcanization process (Fig. 3):

According to Eq. (1), we found the optimum of vulcanization

$$M_{\text{opt}} = 0.9[80 - 16] + 16 = 73.6, \quad (4)$$

where, according to the graph, a point of 73.6 corresponds to a time of 18 min.

This optimum of vulcanization is a more improved result than the optimums of vulcanization for formulation nos. 1 and 2 in terms of both economical and technological process conditions and the chemical stability of a mixture under the given conditions. According to the graph, the vulcanization plateau remained stable for a longer period than that in formulation nos. 1 and 2, which suggests that the possibility of overcuring is reduced to a minimum. For the determination of physicomechanical characteristics, the rubber obtained was tested for the following indices: conditional tensile strength, failure elongation, hardness, change in the sample weight after the action of an isooctane–toluene mixture (7 : 3) at 23°C, freeze-proof factor based on elastic restitution upon compression at –24°C, and relative residual compressive strain by (20 ± 5)% in air at 70°C for 24 h. Table 3 summarizes the experimental data of the rubber tests. The comparative analysis of the physicomechanical

properties of rubbers shows that the replacement of bitumen (as a softener) by low-temperature carbonization coal tar exerts a positive effect on the properties of rubber: the conditional tensile strength, hardness, and freeze-proof factor have higher values than those in the presence of bitumen. However, in this case, an increase in the hardness is not a positive point because the properties of rubber products can deteriorate in service.

A change in the sample weight after the action of an iso-octane–toluene mixture (7 : 3) (liquid B) on a rubber compound with crude low-temperature carbonization coal tar as a constituent was lower than that with bitumen. This can be explained by the fact that the tar contains a large amount of the phenol derivatives of hydrocarbons, which are washed out from the mixture in a hostile environment.

The formulation with processed low-temperature carbonization tar had the best frost resistance characteristics. The plasticizers that only facilitate the processing of rubbers by decreasing the flow point of rubber compounds but do not improve the frost resistance of vulcanized rubber are referred to as softeners; usually, these are paraffin-naphthenic and aromatic petroleum oils, paraffins, rosin, the reaction products of vegetable oils with sulfur (factices), mineral rubbers, and coumarone–indene resins. Hence, it follows that this tar can be related to plasticizers.

CONCLUSIONS

(1) The introduction of plasticizers into rubbers decreases the risk of scorching and reduces hardness, hysteresis losses, and heat generation upon repeated rubber deformations. A comparative analysis shows that the hardness of a rubber compound is somewhat reduced. Plasticizers, which cause the swelling of rubber, separate its molecules and decrease intermolecular interactions; because of this, the mutual slip of the structural elements of uncured rubber is facilitated, and its plasticity increases; simultaneously, the tensile strength of rubber, tension stresses, and hardness decrease and relative elongation increases.

(2) The test low-temperature carbonization coal tar is a petroleum product, and it contains surfactants, which form monomolecular adsorption layers on the surface of filler particles. These adsorption layers facilitate the dispersion and uniform distribution of fillers in the mixture with the formation of a strong bond between the filler and the rubber and the activation of

the filler with an increase in the physico-mechanical characteristics of the rubber.

(3) The dephenolized low-temperature carbonization coal tar exerts a higher positive effect on the physico-mechanical parameters of butadiene–nitrile rubbers because phenol acts as a vulcanization accelerator.

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