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Mechanochemical Modification of Natural Rubber

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Abstract. Thermomechanochemical changes of SVR 3L natural rubber after the treatment in the internal rubber mixer in the self-heating mode were studied. The effect of the molecular mass and content of the gel fraction of natural rubber is shown. Properties of rubber compounds and vulcanized rubber are presented. Taking into account modern requirements, a new alternative technology of obtaining halogenated elastomers based on the solid-phase (mechanochemical) halide modification is created. New halogen-containing natural rubber produced by this technology proves themselves in the conditions of rubber production. New fluorinated natural rubber produced by this technology proves themselves in the conditions of rubber production.

Keywords: rubber, rubber technology, mechanochemistry, composite materials, material modification

AIMS AND BACKGROUND

Now the world elastomeric market consists of natural rubber (NR) (55%) and synthetic rubbers (45%). According to the prediction of experts, the tendency to an increase in the share of NR is observed. It is supposed that its share will make 60% by 2020. To expansion the volume of natural rubber in manufacturing, halogen-containing NR is of interest since it is known that halogen in the macromolecular structure of rubber affects properties of rubber composites. Based on the historical data on halide modification (HM) of a high-molecular compound derived in 1859, natural rubber was modified and the addition to NR was dissolved in perchloromethane, through which chlorine gas was running through. Modified NR is a powder product with the fixed chlorine content not over 62–68 mass %, which has no properties of elastomer [1–4]. A halide modification of NR may be referred to as one of the first attempts to give new properties to polymers by chemical modification.

Nowadays, HM of polymers together with obtaining of halogen-containing polymers with the help of synthesis is one of the intensively developing directions in production of halogen-containing polymers. Due to halide modification of polymers, which have technologically smooth and large-capacity industrial production, elastomer materials and composites can be obtained with a wide complex of new specific properties: high adhesion, fire-, oil-, gasoline-, heat-resistance, ozone resistance, incombustibility, resistance to corrosion and microorganisms, high strength, gas permeability, etc. [5–8].

A new method was developed for the halide-containing elastomer production, which is an alternative to the existing method (polymer solution halogenation), namely, the method of mechanochemical halide modification that sufficiently simplifies and cheapens the process of halide-containing rubber production. The developed method is based on the effect of initiation of radical polymer cleavage [9, 10] and participation of produced radicals in the bimolecular reaction with radical scavengers [11–14]; it allows us to halogenate polymers without halogen gases in solution and in the solid phase.

RESULTS AND DISCUSSION

In this work as starting materials we take natural rubbers SVR 3L (Vietnam), NKHC (Cameroon), SMR GP (Malaysia), and fluorine-containing saturated paraffin, which have the length of the carbon chain C_{30} and contain ~60% of fluorine (wt).

TABLE 1. Structural parameters of NR

Type of rubber	η	$M_{\eta} \times 10^{-4}$	$C_g, \%$
SVR 3L, Vietnam	6.27	138	19.5
NKHC, Cameroon	5.9	127.5	13.3
SMR GP, Malaysia	6.4	144	2.5

Mechanochemical haloid modification of the synthetic analog of NR, SKI-3 isoprene [15] rubber, was earlier investigated; it was established that molecular mass (M_{η}) and content of the gel fraction ($C_g, \%$) have an essential impact on the depth of the reaction of the halogen addition to thermomechanical activated macromolecules of rubber.

The aim of this work is to study features of mechanochemical transformations of NR in the course of its processing in a two-rotor high-speed rubber mixer for the identification of the most optimum temperature and time intervals (ranges of modification) of mechanochemical haloid modification.

At the first stage, we determine values of M_{η} and the content of the gel fraction of samples of NR of main suppliers of this natural polymer to the world market.

Certain structural parameters of NR and the producer country are specified in Table 1.

From the tabulated data, it is visible that rubber of the Vietnamese production (SVR 3L) most fully meets the earlier designated requirements for M_{η} and the content of the gel fraction.

Further, the process of conversion of natural rubber of the SVR 3L brand (Vietnam) was studied and structural parameters of samples of the processed natural rubber and properties of elastomeric compositions on their basis are determined.

Mechanical processing of NR was carried out on a laboratory two-rotor rubber mixer of the RVSD-01-60 type (with friction 1:1.5). The duration of machining of SVR 3L rubber samples was 5, 10, 20, 30, 40, 50, and 60 min. Test samples of rubber were treated in the self-heating mode. The change in M_{η} , content of the gel fraction, and temperatures of rubbers are studied depending on the duration of mechanical influence.

Results of the research of thermomechanicochemical transformations of SVR 3L rubber are presented in Fig. 1.

From the provided data it is visible that at thermomechanical processing of NR mechanical degradation proceeds generally at an initial stage of processing (up to 10 min) in the field of rather low temperatures (from 20 to 110°C). In this time interval, the change of the molecular mass from 140 to 68×10^4 and of the content of the gel fraction from 20 to 5% is observed. At the processing times from 10 to 60 min, a slight change of M_{η} from 68 to 50×10^4 and of the gel fraction from 5 to 3% is observed. The temperature of rubber processed during 10–60 min changes from 110 to 130°C.

To study the influence of structural parameters of NR samples processed in various temperature and time intervals on properties of rubber compounds and rubbers on their basis, rubber mixes were made within the standard compounding for NR [16], and their vulcanizing properties and physicomechanical properties of vulcanized rubbers were defined.

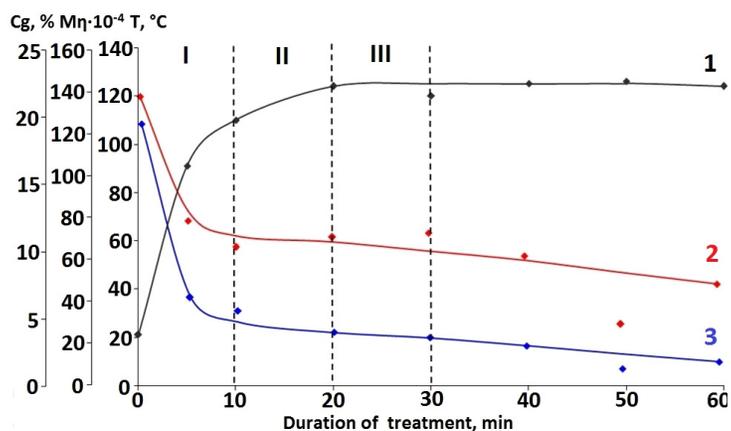


FIGURE 1. Temperature (1), average molecular mass (2), and content of the gel fraction (3) depending on the duration of mechanical processing of SVR 3L (Vietnam)

TABLE 2. Curing characteristics of rubber compounds based on fluorine-containing natural rubber

Basis of rubber compounds	Curing characteristics						
	M_{st} , dN×m	M_{min} , dN×m	M_{max} , dN×m	M_{opt} , dN×m	t_s , min	t_c , min	V_c , %/min
NR	9.2	7.9	35	32.3	2	6.7	21
FNR-2	7	5	33	29.7	1.5	4	40
FNR-4	7	5	33	29.7	1.5	4	40
FNR-6	7	5	30	27	1.7	4.5	36
FNR-8	7	5	33	29.7	1.5	4	40

The obtained data show that with increasing processing time the plasticity of rubber mixes increases due to a reduction in torque, which is connected with a decrease in the rubber molecular mass on account of destructive processes. Some fall of the maximum torque (M_{max}) with an increasing overtime of NR processing is noticeable that points to a reduction of strength properties of vulcanized rubber samples.

By considering physicochemical properties, at the increased overtime of rubber and decreased strength characteristics (conditional stress at 200 and 500% and conditional durability in tension), relative lengthening insignificantly decreases and relative residual lengthening increases after a gap. It should be noted that to 30 min of processing inclusive, the parameters specified above change insignificantly while at the overtime 40, 50, and 60 min their sharp change is observed.

Further we obtain samples of fluorine-containing NRs using the technology of the solid-phase mechanochemical haloid modification (FNR-2, FNR-4, FNR-6, and FNR-8). Ciphers in the notation point to the amount of the fluorine-containing modifying agent added to rubber in weight fraction (w.f.). Natural rubber was modified when the study of the mechanochemical conversion of NR was in optimal conditions on a lab rubber mixer in the self-heating mode (during 20 min). To determine the presence and content of fluorine in modified elastomeric samples, the method of mass-spectrometric analysis was used, thus comprising 1.16, 2.31, 3.21, and 4.44% for FNR-2, FNR-4, FNR-6, and FNR-8, respectively. To define the presence of fixed fluorine in a NR macromolecule, the IR-spectroscopy of extracted samples FNR was used. Extraction was carried out in a Soxhlet apparatus with dimethylformamide during 20 hours. The content of fixed fluorine is 1.6, 2.31, 3.21, and 4.44% (wt) for FNR-2, FNR-4, FNR-6, and FNR-8, respectively.

Then we studied curing characteristics of rubber mixes and physicochemical properties of rubbers prepared by using the standard formula for NR based on NR and FNR [16]. Results are presented in Table 2.

Curing characteristics shows that the mechanochemical modification of NR by fluorine-containing organic compounds refers to an almost two-fold increase in the vulcanization rate in comparison with the vulcanization rate (V_c) of rubber based on initial NR (21%/min for NR and 40%/min for all FNR). Other characteristics hardly change.

We also study physicochemical properties of rubbers based on fluorine-containing natural rubber. Results are presented in Table 3.

TABLE 3. Physicochemical properties of rubbers based on fluorine-containing natural rubber

Properties	Basis of rubbers				
	NR	FNR-2	FNR-4	FNR-6	FNR-8
Conventional strength at elongation, MPa at 200%	2.2	1.8	1.9	2.0	2.4
Conventional strength at elongation, MPa at destruction	21.9	24.3	24.8	26.1	23.6
Tensile strain, %	644	690	700	700	660
Elongation set after destruction, %	29	32	38	38	43
Tear resistance, kgs/cm	110.9	102.4	96.2	111.6	113.6
Shore hardness number	57	60	56	56	60
Rebound elasticity, %	38	29	30	32	28

The results of the investigations show that the addition of fluorine in the macromolecular structure leads to some increase of tensile strain (650% for NR and 700% for FNR) and conventional stress (21.9 MPa for NR, 34.3 MPa for FNR-2, 24.8 MPa for FNR-4, 26.1 MPa for FNR-6, and 23.6 MPa for FNR-8).

CONCLUSION

Thus, the conducted researches allow us to establish the nature of the structural parameter change in SVR 3L natural rubber (M_n and the content of the gel fraction) depending on the duration of mechanical processing of polymer, to study the influence of these parameters on properties of elastomeric compositions on the basis of rubbers subjected to a thermomechanical influence. Taking into account the nature of the proceeding mechanochemical processes observed at the processing of natural rubber and also properties of elastomeric compositions on the basis of these rubbers, the most acceptable temperature and time intervals of mechanochemical haloid modification are defined. It is supposed that processing of rubbers in the above-stated temperature and time intervals in the presence of the fluorine-containing modifier should reveal the influence of mechanical degradation and mechanoactivation processes on the depth of reaction of halogenation. Therefore, we learned a new fluorine-containing natural rubber obtained by the method of mechanical-chemical halide modification. Some structural characteristics of rubbers, vulcanized and physicomechanical properties of rubber mixes and rubbers based on them were studied. A perspective of production and application consists in specific properties of modified natural rubber (high mechanical characteristics of FNR). These properties are caused by the structure of both initial NR and fluorine-containing rubbers (FNR). Fluorine-containing NR also has a high rate of sulfuric vulcanization in comparison with initial NR.

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