UDC 678.028.6; 678.046.1

DOI: 10.15372/CSD20170402

Use of the Ketonization Method to Obtain Functionalised Regenerates of Comminuted Rubber

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(Received November 11, 2016; revised July 10, 2017)

Abstract

The paper studied the effect of conditions of oxidative treatment of comminuted rubber with nitrogen (I) oxide (the so-called ketonization) obtained by mechanical grinding of truck and passenger tires on the main characteristics of the resulting regenerate samples. As established, treatment of comminuted rubber with the initial amount of nitrogen (I) oxide of 2 mol for 1 h or 1 mol for 6 h at the process temperature of 230 °C ensured obtaining the regenerate with the optimum ratio of oligo- and macromolecules containing statistically distributed C=O groups. The reactive oligomeric component formed in the technical synthesis process provides the regenerate with the level of rheological properties required for the use in the content of elastomeric compositions. The presence of functional groups in the oligomer and polymer components of pilot regenerate samples leads to a decrease in the induction period of vulcanisation, which is driven by the acceleration of the formation process of a benzthiazolyl radical arising during decomposition of a vulcanisation accelerator and by the involvement of free sulphur that enters into regenerate composition into the vulcanisation process. The found character of the influence of pilot regenerates on structurisation processes of carbon-chain polymers allows carrying out the optimisation of the content of compositions in which it is planned to use the regenerate, and also adjusting technological modes for vulcanisation of rubber mixtures. As demonstrated in the carried out comparative study of strength-elastic properties of the pilot and industrial regenerate samples, vulcanisates based on trial regenerate samples had high conditional tensile strengths at 200 % elongation. The resulting effect of an increase in strength is reached due to a more homogeneous distribution of the applied load and realisation of orientational phenomena in a low-modulus elastomeric matrix.

Key words: rubber, nitrogen (I) oxide, regeneration, regenerate

INTRODUCTION

The proportion of using products of polymer materials has been growing consistently with the development of modern industry areas, and fields of application are constantly being extended. Due to a long period of decomposition of polymer products and waste, and also the lack of efficient technologies for their disposal, the annual growth of hard-to-degrade wastes (in particular, waste tires and other rubber technical goods (RTG) reaches tens of millions of tons [1, 2]. The reuse of these wastes to obtain solid products with a high extra cost is of considerable interest since properties of polymer base do not significantly change [3]. In this regard, the search for rational and efficient reuse methods of elastomer-containing wastes that assume their complex recycling with obtaining a wide range of raw materials and semi-finished products is relevant in solving environmental issues related to the production and consumption of polymer products.

Currently, there are many techniques for the regeneration of rubbers that have found applications in industry or are under development and implementation [4–6]. They are based on the use of mechanical, thermomechanical or other impacts on elastomer-containing compositional material that lead to the destruction of intra- and intermolecular chemical bonds. The resulting plastic product *i.e.* regenerate is able to combine with the polymer base of rubber mixtures and to covulcanize with it during structuring [2–9].

A new method for regeneration of rubbers with various contents that consisted in the treatment of comminuted rubber or large fragments of rubber products with nitrogen (I) oxide in organic solvents at 200–230 °C temperatures and 3-5 MPa pressures (so-called carboxylation or ketonization method) has been developed in the Boreskov Institute of Catalysis, SB RAS (Novosibirsk) [10, 11]. A part of double bonds of the carbon-chain base of vulcanisate is selectively oxidized during this treatment, and statistically distributed carbonyl groups are formed in polymer chains. A process of ketonization is accompanied by partial destruction of a macromolecular matrix on C=C bonds reacting with N_2O, with the result that vulcanisate turns into plastic products. The resulting regenerate can be processed using technological equipment, and when introducing into the composition of elastomer compositions, it ensures the improvement of their technological and performance characteristics [12].

The goal of the present work is the study of treatment conditions of comminuted rubber with nitrogen (I) oxide on properties of the resulting regenerate samples and compositions therefrom.

EXPERIMENTAL

Comminuted rubber obtained during mechanical grinding of auto and medium truck tires with the following fractional composition: 4 mm and over – 2 % of particles from the total mass; 1.25–4.0 mm – 51 %; 1.25–0.5 mm – 35 %; <0.5 mm – 12 %. The treatment process of comminuted rubber with N_2O (a ketonization process) was carried out in a high-pressure Parr-reactor with 2000 cm^3 capacity equipped with a manometer and a stirrer. The reactor was loaded with 160 g of comminuted rubber and 100 mL of benzene (solvent), closed, purged with helium to remove air, and 1–3 mole of N_2O were introduced. Afterwards, the reactor was heated with 6 °C/min rate until the reaction temperature of 230 °C, the process was carried out for 1–10 h. Reaction pressure reached 5 MPa.

On completion of the reaction, the reactor was cooled to a temperature of 23 °C. Pilot samples of tire regenerate obtained by the ketonization method (the symbol is RTR) were isolated from a solution by benzene distillation at 50 °C using rotary vacuum evaporator.

Major varied parameters at the technical synthesis of the regenerate using ketonization are reaction time and the ratio of the initial amounts of N_2O and comminuted rubber on the constancy of other conditions.

Industrial regenerates produced by Chekhovo regenerate plant JSC (symbol is RSHT-CHRZ) and Tamplier-Center JSC (symbol RShT-TTs) were used in the work as comparison objects in assessing the quality of trial samples of regenerate.

The destruction degree of the elastomeric base of comminuted rubber was assessed by the content of compounds extracted by organic solvents (acetone, chloroform). The maintenance of free and bound sulphur in regenerate samples under study was defined by the technique recommended in [13].

To assess the regenerate quality a composition containing regenerate (110 mass parts), sulphur (1.5 mass parts), zinc oxide (2.5 mass parts), and 2-mercaptobenzothiazole (0.9 mass parts) were used. Compositions based on regenerate samples under study were prepared using SM 320 160/160 L roller mixer. The composition of regenerate compositions, the temperature-time mode of their production followed by vulcanisation, and also the technique for determining the quantitative content of extractable substances corresponded to TU 38.108053–89 “Tire thermomechanical regenerate”. Plasticities of regenerate compositions were defined by GOST ISO 7323-96 using Wallace plastometer at 70 °C.

Calculations of rheological and vulcanisation kinetic characteristics of regenerate compositions were defined by GOST 12535–84 based on the results obtained when piloting rubber mixtures on RCS-5 irrotational vibration rheometer (deformation angle is 3°, the amplitude is 100 min^{-1}) at 143 °C.

Elastic-strength characteristics of vulcanisates were defined in accordance with GOST 270–75. Measuring hardness of samples was carried out by GOST 263–75.

RESULTS AND DISCUSSION

Two competing processes proceed in the synthesis of the regenerate. They are functionalisation of macromolecules due to the formation of statistically distributed carbonyl groups in their composition and partial destruction of macromolecules [14].

Acetone extract of the regenerate comprises low-molecular-weight components of elastomeric compositions that can be used upon their manufacturing, and also oligomeric compounds formed during the destruction of the carbon-chain basis of a vulcanisate.

Based on the data of Table 1a, the contents of acetone extract in the obtained regenerate samples, and consequently, and oligomeric destruction products increase with a rise in a synthesis time of the regenerate from 1 to 10 h under identical conditions. The minimum content of substances extracted with acetone in experimental regenerate samples is observed after treatment of comminuted rubber for 1 and 3 h (see Fig. 1, *a*, curve 1). A further increase in synthesis time contributes to even the more intense formation of an oligomeric phase.

However, with regard to functional significance, a more precious component of the regenerate is the high-molecular component that is able to further structuring during repeated vulcanisation. Its content in the regenerate depends on the content of chloroform extract. With increasing synthesis time, the content of chloroform extract (and hence, high-molecular fraction) in experimental regenerate samples subjected to preliminary extraction with acetone passes through a maximum which is observed at 3–6 h (see Fig. 1*a*, curve 3). A further increase in the time of regenerate synthesis contributes to intensifying destruction process and decreasing the amount of extractable high molecular weight compounds, which is accompanied by an increase in the number of oligomeric compounds released by acetone (see Fig. 1 *a*, curve 1). This is evidenced by almost unchanged contents of chloroform extract in pilot samples of the regenerate synthesized for 6–10 h (see Fig. 1 *a*, curve 2).

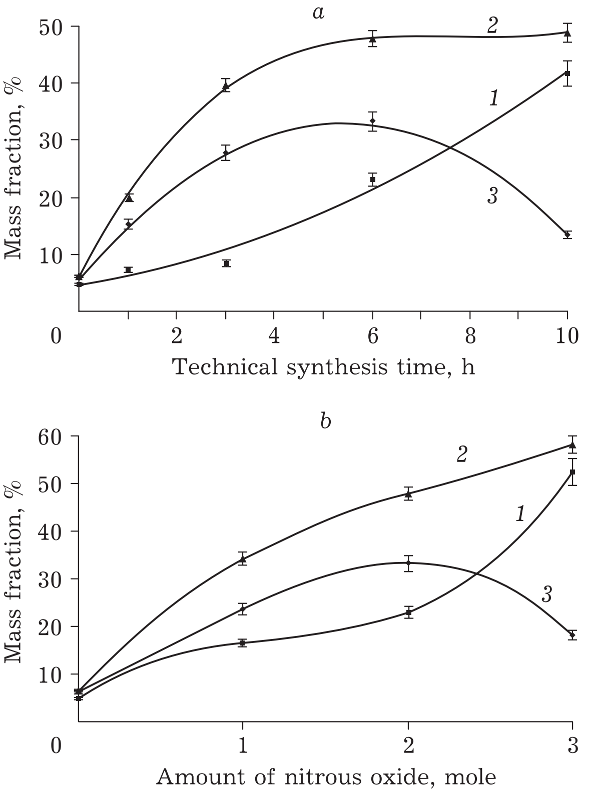

Fig. 1. Content of substances extractable with acetone (*1*) chloroform (*2*) and chloroform after acetone (*3*) depending on the time of synthesis of the regenerate by the ketonization method (temperature is 230 °C, 2 moles of N_2O) (*a*) and the amount of used nitrogen (I) oxide (temperature is 230 °C, synthesis time is 6 h) (*b*).

With increasing nitrogen (I) oxide content in the reaction mixture used for regenerate synthesis at the constancy of other conditions (160 g of comminuted rubber, synthesis time is 6 h, temperature is 230 °C), as a whole, a similar picture is observed: the destruction process of carbon-chain basis of a vulcanisate is intensified, with the result that both oligomeric and high-molecular fractions are formed. Herewith, extreme dependence of the amount of chloroform soluble compounds, and consequently, the proportion of high molecular weight unstructured fraction on the amount of N_2O in the reaction mixture is observed (see 1 *b*, curve *3*). Obviously, this is related to the fact that the high molecular weight fraction, on the one hand, is accumulated resulting from the vulcanisate destruction but simultaneously consumed during the reaction with N_2O due to its own destruction with oligomer formation. Accordingly, the proportion of the oligomeric fraction soluble in acetone constantly grows with increasing the amount of N_2O (see Fig. 1 *b*, curve *1*).

The findings demonstrate that the optimum ratio of non-structured oligomeric and high molecular weight fractions in the regenerate is reached only under certain conditions of its synthesis. Considering this, for further more detailed studies, two samples of the pilot regenerate were selected: a sample with the symbol RSHK-1, obtained by processing of comminuted rubber by nitrogen (I) oxide (2 mol) at 230 °C for 1 h, and a sample with the symbol RTR-2, obtained under similar conditions but using 1 mol of N_2O at reaction time of 6 h. Selection of precisely these regenerate samples is driven by the presence in their composition of significant amounts of the oligomeric phase that ensures an opportunity to process compositions, and also high molecular-weight components that are able to take part in the vulcanisation process. All oligomers and polymers extracted from pilot samples of the regenerate are functional compounds, which is con-

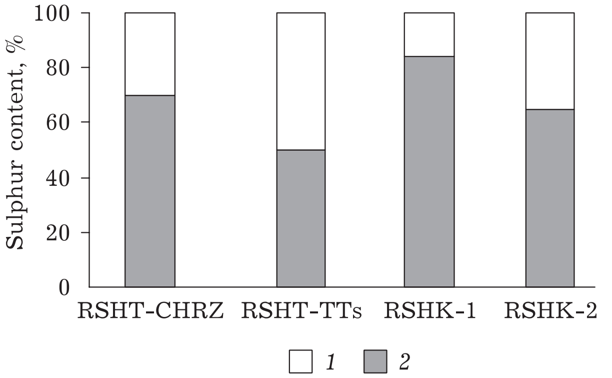

Fig. 2. Relative content of free (*1*) and bound (*2*) sulphur in regenerate samples under study.

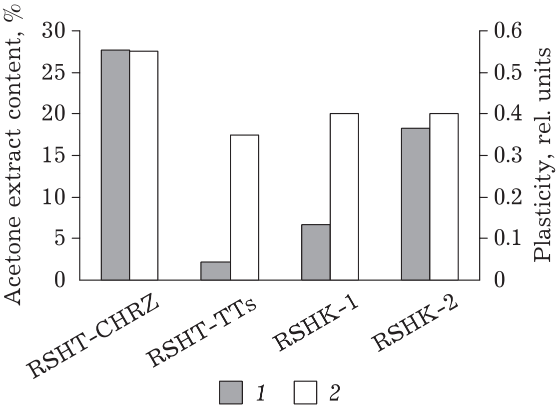

Fig. 3. Content of low-molecular-weight compounds (*1*) in regenerate samples under study and their plasticity (*2*).

firmed by the presence in their IR spectra of absorption bands in a region of 1710–1740 cm^{-1} that correspond to the stretching vibrations of C=O groups in carbonyl (ketone and aldehyde) groups.

Analysis of pilot samples of the regenerate and industrial RSHT-CHRZ and RShT-TTs regenerates for sulphur content demonstrated that it is present not only as intramolecular sulphide bonds (bound sulphur) but also in a free state (Fig. 2). This indicates that the regeneration process of rubbers by the ketonization method similarly to industrial methods does not lead to complete devulcanisation of the composite, *i.e.* the total destruction of intermolecular sulphide bonds.

The regenerate quality is defined by the level of rheological and elastic-strength properties that depend on the degree of destruction of the initial vulcanisate and the content of auxiliary components.

Considering that technological process of regenerate production in each enterprise has individual peculiarities, the ability of industrial samples of the regenerate to plastic deformation is mainly defined by the type and content of a plasticizing agent introduced into their composition [15]. The highest plasticity of RSHT-CHRZ regenerate, compared to other studied samples (Fig. 3) is ensured by the introduction of hydrocarbon oils into its composition. The use of bituminous plastifiers in the composition of regenerate RShT-TTs decreases plasticity by 36 %, compared to RSHT-CHRZ, which complicates the reprocessability of this regenerate using technological equipment, coupled with a low content of acetone-soluble compounds (2.2 %). The presence of the oligomeric component in pilot samples of RSHK-1 and RSHK-2 regenerates in the amount of 6.5 and 18 %, respectively, ensures the required plasticity of these products of tire processing, and consequently, their good reprocessability using technological equipment.

Functionalisation of oligomeric and polymeric components in pilot samples of RSHK-1 and RSHK-2 regenerates defines peculiarities of vulcanisation characteristics of regenerate compositions based therefrom (Table 1). A relative decrease in the induction period is observed in the vulcanisation of these compositions, which is probably due to the acceleration of the formation process of a benzothiazolyl radical arising during decomposition of a vulcanisation accelerator and involvement of free sulphur that is a part of regenerate into the vulcanisation process.

As demonstrated, vulcanisates based on samples of pilot RSHK-1 and RSHK-2 regenerates on the background of a slight decrease in a conditional stress at 200 % elongation have high conditional tensile strengths compared to vulcanisates based on industrial RSHT-CHRZ and RShT-TTs regenerates (see Table 1). One may assume that this effect is related to the lower defectiveness of the structure of the resulting vulcanisation grid. The homogeneous distribution of the applied load accompanied by orientational phenomena in an elastomeric matrix ensures dissociation of stress, and consequently, high strengths of compositions in critical (destructive) deformations. At the same time, vulcanisates based on pilot samples of RSHK-1 and RSHK-2 regenerates have almost identical hardness levels, compared to vulcanisates of industrial regenerates (see Table 1).

CONCLUSIONS

1. It was found that treatment of comminuted rubber with nitrogen (I) oxide with the initial amount of N_2O of 2 mol at 230 °C for 1 h or 1 mol for 6 h ensured obtaining the regenerate with the

TABLE 1

Vulcanisation kinetic and physicomechanical characteristics of regenerate compositions

Indicators	Regenerate type			
	RSHT-CHRZ	RShT-TTs	RSHK-1	RSHK-2
Minimum torsion moment, N · m	0.21	0.04	0.07	0.07
Maximum torsion moment, N · m	1.21	1.52	1.95	1.56
Structuring degree ΔM, N · m	1.00	1.48	1.88	1.49
Initial time of vulcanisation, min	2.0	1.3	1.1	1.2
Optimum time of vulcanisation, min	5.7	3.8	4.3	3.8
Vulcanisation rate, min^{-1}	27.3	41.5	30.8	38.9
Conditional stress at 200 % elongation, MPa	4.77	4.78	4.65	4.70
Conditional tensile strength, MPa	7.33	6.60	8.0	7.5
Elongation at break, %	227	245	285	310
Shore hardness *A*, cu	62	62	64	58

optimum ratio of destructured oligo- and macromolecules comprising statistically distributed C=O groups.

2. It was determined that samples of pilot regenerates provided a reclaimed product with levels of rheological and vulcanisation properties required for the use in the composition of elastomeric compositions due to the presence of oligo- and macromolecules, and also free sulphur.

3. The carried out complex of comparative studies for elastic-strength properties of vulcanisates based on pilot and industrial regenerate samples demonstrated the advantages of tire processing products obtained by the ketonization method over traditionally used, which allows recommending it for use in the manufacture of compositions for various purposes.

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