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# Effect of Ozonation on the Kinetics and Composition of the Products of Thermal Dissolution of Rubber Crumbs in Tetralin

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## Abstract

Ozonation of rubber crumbs, accompanied by the accumulation of oxygen in the inactive form, causes changes in the group composition of the products of thermal dissolution: the fraction of tarry matter increases, while the yield of gases decreases substantially. The amount of ozone-modified organic matter of rubber is estimated on the basis of the results of non-isothermal dissolution; the effective activation energy of the process is calculated.

## INTRODUCTION

Utilization of worn-out automobile tyres is an actual ecological problem. Its main direction is considered to be preparation of reclaim which is used in the production of conveyer belts, working clothes, rubber boots, *etc.* [1, 2]. Pyrolysis processes were the basis to develop the technologies of processing general mechanical rubber goods; products are the components of stove oil and petrol. Dissolution in heavy technical solvents was used to obtain modifying agents for road concrete mix [3], waterproofing and corrosion-proof mastics [4]. Thermal dissolution of worked-out automobile tyres in supercritical solvents (toluene, alcohols or pentane) were studied [5]. It should be noted that the advantages of thermal dissolution process are a much higher yield of liquid products due to decreased gas formation, and the possibility to carry out the process under more mild temperature conditions than those of pyrolysis.

Rubber consists of a polymer basis and chemical additives including vulcanising agents (sulphur, organic peroxides, phenol formaldehyde resin), accelerators and activators of vulcanisation (zinc oxide, dithiocarbamates, thiuramsulphides), fillers (technical carbon, chalk, bentonite, magnesium and zinc oxides and silicates), plasticizers (black oil, tar, paraffin and fatty acids) and antiaging agents (aromatic phenols and amines) [6]. Taking into account the large number of components, it may be assumed that the introduction of functional oxygen-containing groups into an organic compound by means of ozonation would promote changes in the properties of products formed during thermal dissolution. This approach to modification of the organic substance of rubber has a number of advantages in comparison with other methods: there is no need for high temperature, pressure, catalysts; no wastes to be utilized are formed.

The goal of the present work was to investigate the effect of rubber crumb ozonation on the kinetics and the group composition of the products of thermal dissolution in tetralin.

## EXPERIMENTAL

The subject of investigation was rubber crumbs of worn-out automobile tyres with particle size less than 0.2 mm (humidity 0.8 %,

TABLE 1

Characteristics of rubber samples

| Sample | Ozonation time, h | Composition, % daf | | | | Oxygen content, % daf | | O/C | H/C |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | S | O | active | inactive | | |
| Initial | | 90.0 | 7.5 | 1.5 | 1.0 | 1.0 | – | <0.01 | 1.00 |
| Ozone-treated | 1 | 90.0 | 7.3 | 1.4 | 1.3 | 1.1 | 0.2 | 0.1 | 0.97 |
| | 2 | 88.9 | 7.2 | 1.2 | 2.7 | 0.7 | 2.0 | 0.2 | 0.97 |
| | 3 | 88.2 | 7.3 | 1.0 | 3.5 | 0.7 | 2.6 | 0.3 | 0.99 |

ash value 4.4 %, yield of volatiles 62.4 %). The elemental composition of samples is shown in Table 1.

Ozonation was carried out in the suspended particle layer in the flow of ozone-oxygen mixture (with ozone concentration 1.5–2.0 %) at room temperature. The formed ozonides were destroyed by heating at 140 °C for 1 h.

The active oxygen content was determined as the sum of oxygen in phenol, carbonyl and carboxylic groups; the amount of oxygen in the inactive form was determined as their difference. The amount of carbonyl groups was determined on the basis of the reaction with hydroxylamine hydrochloride, carboxylic groups were determined using the acetate procedure, the sum of carboxylic and hydroxyl groups was determined by means of ion exchange with sodium hydroxide.

Thermal analysis was carried out with a Netzsch STA 409 thermoanalyzer, with sample mass 50 mg, with a platinum-iridium crucible; heating was carried out to 1000 °C at a rate of 10 °C/min in helium. Mass loss and the rate of mass loss were recorded during analysis. The following parameters were used to characterize thermal decomposition: $T_{\max}$ – temperature of the maximal decomposition rate, $V_{\max}$ – decomposition rate in the inflection point. Mass loss $\Delta m$ was calculated within the intervals of the most intensive decomposition of rubber accepting the initial temperature to be 200 and final 600 °C.

Thermal dissolution of rubber was carried out in micro-autoclaves using the non-isothermic procedure [7]. Experimental conditions: solvent – technical-grade tetralin (87.2 %); the ratio of the organic mass of rubber (OMR) to the solvent was 1 : 2, heating rate 2.5 °C/min. Parameters under analysis: the degree of OMR conversion and group composition [8] (pyrobitumen, resin, oil). The yield of gases was determined on the basis of mass loss of the micro-autoclave after the removal of the gaseous reaction products and additional blowing of the reaction mixture with an inert gas (argon). The deviation between two or three parallel determinations of the degree of conversion, yields of resin and oil did not exceed 3 %.

Preliminary kinetic analysis of thermal dissolution process included the transformation of the experimental integral dependence of conversion degree $\alpha$ on temperature $T$ into the differential form: process rate $(d\alpha/dT) - T$ and calculation of the effective activation energy of the process $E_{\text{ef}}$ from the Arrhenius law $\ln[(d\alpha/dT)/(\alpha_\infty - \alpha) - 1/T$ where $\alpha_\infty$ is potentially achievable degree of conversion of the organic mass of rubber, $(\alpha_\infty - \alpha)$ is the kinetic function of pseudo-first order. The linear correlation coefficient for all the samples was not les than 0.99. The accuracy of determination of $E_{\text{ef}}$ values was ±5 kJ/mol.

## RESULTS AND DISCUSSION

The appearance of the curve of oxygen accumulation in the organic mass of rubber crumbs under ozonation (Fig. 1) corresponds to the autocatalytic radical chain oxidation mechanism [9, 10]. The maximal accumulation rate is observed at 2 h. Depending on process duration, the amount of oxygen in the active form decreases in the modified samples (see Table 1) with an increase in the amount of oxygen-containing groups that are not identified by the methods of chemical analysis involved in the investigation.

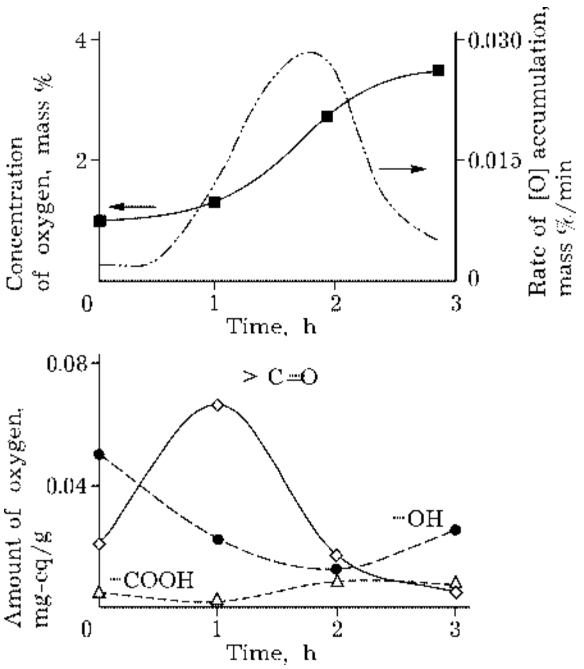

Fig. 1. Dependence of oxygen content of the organic matter of rubber and the rate of its accumulation on time of ozonation.

The dynamics of the accumulation of functional oxygen-containing groups is shown in Fig. 1. At the initial stage of ozone treatment, the amount of phenol groups decreases; then their amount increases. The amount of carboxylic groups changes only slightly during the entire process. The curve of accumulation of carbonyl groups in OMR exhibits the extremal dependence; it has a maximum for ozonation during 1 h. It was stressed in [1] that the ozonide formed as a result of ozone addition to the C=C bond of the polymer undergoes rapid decomposition with the formation of two fragments: a carbonyl compound and a bipolar ion. Then the carbonyl groups accumulated during the experiment can enter the reaction with the bipolar ion thus forming polymeric ozonides. This is likely to result in the extremal changes in the amount of carboxyl groups and an increase in the amount of oxygen in the inactive form.

According to the data of thermogravimetric analysis, total rubber mass loss under heating to 1000 °C is 66.3 % and has two maxima: at 395 and at 458 °C. After ozonation, independently of process duration, a decrease in the temperature of the first maximum and an insignificant increase in the temperature of the second one occur (Table 2). In this situation, the rate of rubber decomposition increases for both temperature points. An increase in mass loss occurs in each temperature range; the maximal mass loss is observed for rubber oxidized for 2 h. Taking into account the data obtained and the results of chemical analysis of functional groups (see Fig. 1), we carried out thermal dissolution of the rubber sample treated with ozone for 2 h.

The results of thermal dissolution of the initial rubber sample and that treated with ozone are shown in Fig. 2. The degree of conversion of the sample treated with ozone is higher than that of the initial sample within the whole temperature range. The largest increase in OMR conversion degree is observed within temperature range 350–450 °C. The temperature of the maximum of the rate of thermal dissolution of the initial rubber is 280 °C.

The appearance of the curve of thermal dissolution of ozone-treated rubber (see Fig. 2) provides evidence of the presence of two stages of the process with the maxima at 280 and 310 °C. The rupture of bridging bonds –C–O–C– formed in OMR during ozonation as a result of polymerization of the bipolar peroxide ions is likely to occur within temperature range 300–350 °C [11]. An increase in the amount of

TABLE 2

Results of thermogravimetric analysis of rubber samples

| Sample | Time of ozonation, h | $T_{1\,\max}$, °C | $T_{2\,\max}$, °C | $V_{1\,\max}$, %/min | $V_{2\,\max}$, %/min | $\Delta m$ (%) at temperature, °C | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | 200–300 | 300–450 | 200–600 |
| Initial | | 395 | 458 | 2.8 | 4.9 | 2.9 | 41.0 | 57.3 |
| Ozone-treated | 1 | 388 | 461 | 3.1 | 5.0 | 3.6 | 41.5 | 58.7 |
| | 2 | 385 | 461 | 3.2 | 5.2 | 4.0 | 43.5 | 60.6 |
| | 3 | 386 | 461 | 3.2 | 5.2 | 3.6 | 42.8 | 60.0 |

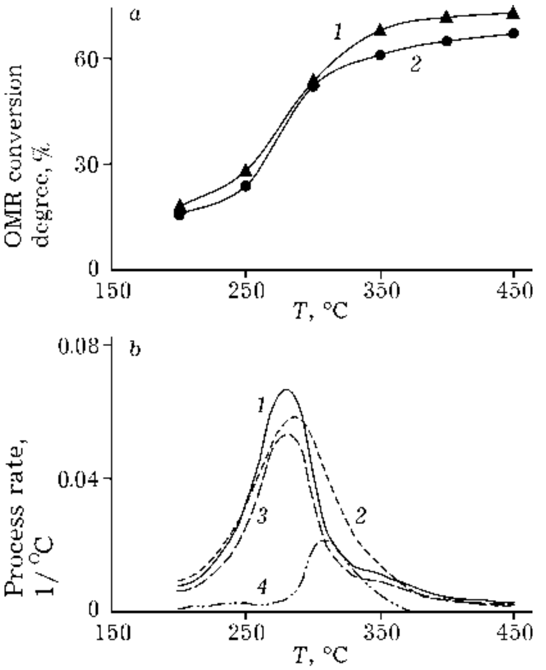

Fig. 2. Dependence of the degree of conversion of the organic matter of rubber and the rate of its thermal dissolution on temperature: *1, 2* – initial and ozone-treated samples, respectively; *3, 4* – the fractions of the initial and ozone-modified OMR, respectively.

oxygen in the inactive form (see Table 1) confirms the occurrence of these reactions.

The rate of thermal dissolution process in the case of the linear increase in the temperature of reaction mixture can be described by the differential equation of the first order [12]:

$$\frac{d\alpha}{dT} = \frac{k}{q}(\alpha_\infty - \alpha) \qquad (1)$$

where $T$ is temperature, K; $k = k_0 \exp(-E_{ef}/RT)$ is the effective rate constant of the process; $\alpha$, $\alpha_\infty$ are conversion degree and potentially achievable conversion degree, respectively, mass % of the initial OMR; $E_{ef}$ is effective activation energy, kJ/mol; $q$ is heating rate, °C/min.

Taking into account the independence of the stages of thermal dissolution of the initial (unaffected) and ozone-modified OMR, we can write down the kinetic equation for thermal dissolution of ozone-treated rubber as follows:

$$\frac{d\alpha^{oz}}{dT} = \frac{d\alpha^{init}}{dT} + \frac{d\alpha^{*}}{dT} = \frac{k}{q}(\alpha_\infty^{init} - \alpha^{init}) + \frac{k^{*}}{q}(\alpha_\infty^{*} - \alpha^{*}) \qquad (2)$$

where $\alpha^{oz}$ is experimentally determined total degree of conversion of ozone-treated rubber; $\alpha^{init}, \alpha_\infty^{init}$ are conversion degree and potentially achievable conversion degree of the initial OMR under the given conditions, which is determined by the amount of elastomer in rubber, respectively; $\alpha^{*}$, $\alpha_\infty^{*}$ are conversion degree and potentially achievable conversion degree of ozone-modified OMR, respectively; $k^*$ is effective rate constant of thermal dissolution of ozone-modified OMR.

The following boundary conditions were accepted for the quantitative estimation of the degree of conversion of ozone-treated rubber:

1) The experimentally determined conversion degree of ozone-treated rubber includes the degree of conversion of unaffected and ozone-modified OMR:

$$\alpha^{init} + \alpha^{*} = \alpha^{oz} \text{ and } \alpha_\infty^{init} + \alpha_\infty^{*} = \alpha_\infty^{oz} \qquad (3)$$

2) In an ozone-treated rubber particle, the organic matter unaffected by ozone is transformed into liquid products according to the same mechanism as that for the initial OMR, that is, temperature of the maximum of the rate of thermal dissolution determined for the initial OMR remains the same, only its fraction $z$ changes.

3) On the basis of the above considerations, we may calculate the degree of conversion of the initial OMR:

$$\alpha^{init} = \alpha z \text{ and } \alpha_\infty^{init} = \alpha_\infty z \qquad (4)$$

and ozone-modified OMR:

$$\alpha^{*} = \alpha^{oz} - \alpha z \text{ and } \alpha_\infty^{*} = \alpha^{oz} - \alpha_\infty z \qquad (5)$$

Thus determined amount of the organic matter modified by ozone accounts for about 15–20 % of OMR, which is due to the heterogeneous character of ozonation, when ozone affects only the external surface of rubber particle and the inner volume remains unaffected.

The efficient activation energy $E_{ef}$ of thermal dissolution process was determined by means of the least squares from the Arrhenius plot for the initial and ozone-modified OMR, respectively:

$$\ln\left(\frac{d\alpha}{dT}\frac{1}{(\alpha_\infty - \alpha)}\right) = \ln\frac{k_0}{q} - \frac{E_{ef}}{RT}$$

$$\ln\left(\frac{d\alpha^*}{dT}\frac{1}{(\alpha^*_\infty - \alpha^*)}\right) = \ln\frac{k^*_0}{q} - \frac{E^*_{ef}}{RT} \qquad (6)$$

The $E_{ef}$ value for the initial and ozone-modified OMR was 80 and 96 (±5) kJ/mol, respectively.

The products of thermal dissolution of the initial OMR consist of a mixture of resin, oil and trace amounts of pyrobitumen. With an increase in temperature, the fraction of resin in the liquid products decreases as a result of secondary cracking, while the fraction of oil and the yield of gases increase. The transformation of rubber during ozonation, which involves rupture of some C–C and C–S bonds, saturation with oxygen and the formation of additional cross-links between the macromolecules in OMR [13], causes changes in the products of thermal dissolution. In particular, the fraction of tarry matter substances increases and the yield of gases decreases substantially (Fig. 3).

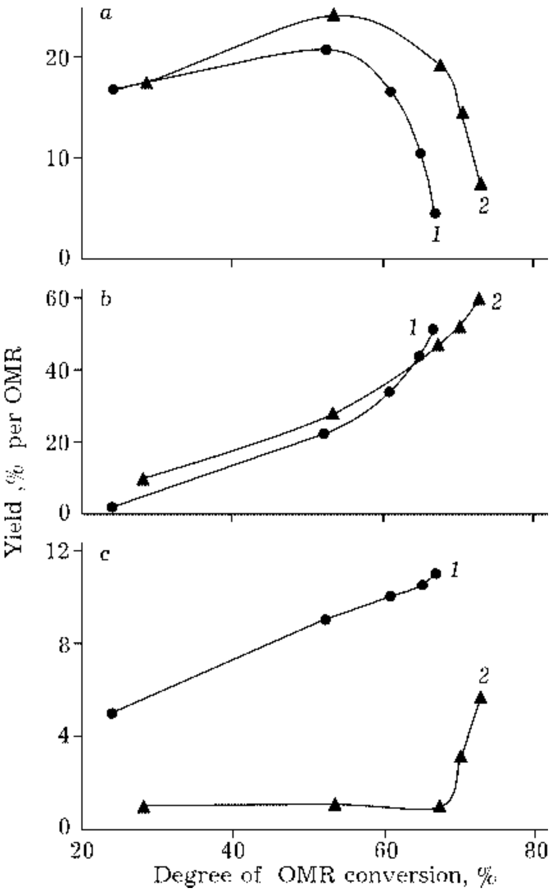

Fig. 3. Dependence of the yield of resin (*a*), oil (*b*) and gaseous products (*c*) on the degree of conversion of the initial (*1*) and ozone-treated (*2*) rubber during thermal dissolution.

## CONCLUSIONS

In our opinion, the results obtained in the investigation can be considered as a basis of the new economically efficient technologies of processing worn-out tyres and other rubber-containing wastes resulting in valuable products for different purposes. Tarry matter isolated from the products of thermal dissolution of ozone-treated rubber can be used as a valuable raw material in the production of paint-and-lacquer materials, waterproofing and corrosion-proof compositions possessing good adhesion and cohesion characteristics.

So, the use of non-isothermal dissolution procedure to estimate the reactivity of modified rubber allowed us to estimate the amount of the organic matter of rubber subjected to ozonation and to calculate the effective activation energy of the process that characterizes the strength of bonds subjected to thermolysis. It is demonstrated that ozonation of rubber results in a substantial decrease in the yield of gases and an increase in the fraction of tarry matter amount the liquid products of thermal dissolution.

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