Stability of ozonide rings in unsaturated polymers during latex ozonisation

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Earlier, an examination was made of the process of ozonolysis of unsaturated rubbers, and also certain inherent positive properties of rubbers and latexes based on butadiene, its copolymers with styrene, methacrylic acid, or natural rubber, modified in a microheterogeneous system – latex – by controlled ozonisation [1–6]. It was established that this process is accompanied with a reduction in pH to 4.0–6.0 and can lead to partial or complete coagulation of latexes stabilised with salts of carboxylic acids or rosin. The recommended introduction of additional sulfonate-type emulsifiers, resistant to ozone, prevents coagulation of the latex but complicates considerably the formation of rubber by saline coagulation and the biological purification of the waste waters [7].

Uncontrolled reduction in pH to the neutral or acid region during ozonisation of latexes also entails, in our opinion, an increase in the amount and stability of intermediated formed ozonide rings in the chain of the ozonised polymer, which cause structure formation of the rubber, much like peroxides, by a free radical mechanism. Ozonide rings can retain stability at reduced ozonisation or storage temperatures of the polymer. Conducting ozonolysis at higher temperatures, for example at 20°C and above, leads to partial or complete transformation of ozonide rings (with a yield of over 80 wt% of the theoretical) into organic compounds or fragments of rubber macromolecules with end aldehyde and carboxylate groups [3, 5]. Ozonides in a weakly acid or neutral medium are more stable than in an alkaline medium [8].

The similarity of ozonides to peroxides is confirmed by a number of chemical reactions typical of them. Like most peroxides, they react with potassium iodide with the formation of free iodine.

We developed conditions for modifying elastomers in latex by the action of ozone, by which the presence of non-broken-down ozonides in the system is eliminated to the maximum degree or entirely, and intermolecular branching and crosslinking of macromolecules of the elastomer during ozonisation and its subsequent processing are limited [9]. However, to establish the influence of factors such as temperature and alkalinity on the formation and retention of ozonide rings in the polymer chain during ozonolysis of the latex, subsequently determining the stability of the prescribed properties of modified latexes and rubbers, it was necessary to conduct an additional study of certain kinetic parameters – the order of the reaction, the rate constants, and the activation energy of decomposition of ozonide rings – during the ozonolysis of latexes.

For this investigation, use was made of butadiene latex produced by the polymerisation of butadiene at a temperature of 5–6°C in an aqueous emulsion stabilised by potassium salts of synthetic fatty acids (C₁₂–C₁₆ fraction) and disproportionated rosin (1.1 and 4.2 parts per 100 parts butadiene). Polymerisation was initiated using a system consisting of pinane hydroperoxide, sodium formaldehyde sulfoxylate, and an iron–trilon complex. In the latex obtained, the solids concentration amounted to 30 wt%, the polymer content was 24.5 wt%,
the pH was 9.6, the surface tension was 62 mN/m, the solubility of the formed polymer in toluene was 98.2 wt%, and the Mooney viscosity was 68 nominal units.

The ozonisation of latex was carried out in a thermostatically controlled three-necked flask equipped with a mechanical stirrer, a thermometer, and a bubbler for feeding the ozone–air mixture. In the unit there were devices for controlling the feed rate and measuring the volume of ozone–air mixture fed for ozonisation, and also for controlling the pH. The ozone concentration in the ozone–air mixture before and after the reaction with polybutadiene and the amount of intermediate ozonides formed were determined by iodometric titration. A non-ionogenic emulsifier – oxyethylated m-nonylphenol (average degree of oxyethylation 10) – was introduced beforehand into the latex to stabilise it, in a quantity calculated to be 4.0 wt% of the solids of the latex.

To eliminate possible error, the latex sample before analysis was blown with argon for 20 min to remove traces of ozone.

It was established that the equilibrium concentration (i.e. the equilibrium established at a certain instant of ozonolysis under prescribed conditions between the expected concentration of ozonide rings formed in the polymer and the number of ozonide rings that have already decomposed) and the stability of intermediate ozonide rings depend on the pH of the latex. The transformation of ozonides into aldehyde carboxylate derivatives of the modified polymer is most active at pH > 8. It was important to clarify how the time factor affects the stability of the ozonide rings in the polymer chain as a result of ozonolysis of latexes at a temperature of 20 ± 1°C and a different pH. The isotherms and effective rate constants of change in the concentration of ozonide acid in the polymer (Figure 1)

\[ K' = \frac{2.303}{t} \log \frac{c_0}{c_t} \]

(where \( t \) is the ozonolysis time, \( c_0 \) is the initial concentration of ozonide oxygen (mol/dm³), and \( c_t \) is the concentration of ozonide oxygen at instant of time \( t \)) confirm the considerably higher rate of reduction in the equilibrium content of ozonide rings during the holding of ozonised latex in an alkaline medium.

The concentration of ozonide oxygen (in relation to the polymer) at pH > 10.5 and a temperature of 20 ± 1°C after 2 h decreases to 0.001 mol/dm³, which causes practically no steric changes or crosslinking of the rubber during drying or processing in rubber mixes at elevated temperatures. The conditions found were used in the method for producing unsaturated elastomers modified with terminal aldehyde and carboxyl groups. Positive results were obtained when they were tested in rubber mixes filled with active silica without the use of special coupling agents between the rubber and the indicated filler [5, 6].

A study was also made of the temperature dependence of the stability of polybutadiene ozonides in the latex (Figure 2). It was established that the amount of ozonide oxygen in the polymer during holding of ozonised latex with a constant pH of 7.5–8.0 regularly decreases in the temperature range 15–65°C. Here, the logarithm of the current concentration of residual ozonide oxygen in the polymer chain depends linearly on time, which is characteristic of first-order reactions. The first order of

**Figure 1.** Dependence of the content of ozonide oxygen on the ozonolysis time of polybutadiene (temperature 20.0 ± 1°C, amount of ozone absorbed by latex 1.5 wt%) with different pH values (the effective rate constants of decomposition of ozonide rings \( K' \times 10^{-3}, \text{min}^{-1} \), are given in parentheses): 1 – pH 4.5–5.0 (6.7); 2 – pH 6.5–7.0 (18.0); 3 – pH 8.5–9.0 (44.0); 4 – pH 9.5–10.0 (77.0); 5 – pH 10.5–11.0 (1050.0)

**Figure 2.** Dependence of the content of ozonide oxygen on the ozonolysis time of polybutadiene (pH of latex 7.5–8.0, amount of ozone absorbed by latex 1.5 wt%) at different temperatures (the effective rate constants of decomposition of ozonide rings \( K' \times 10^{-3}, \text{min}^{-1} \), are given in parentheses): 1 – 15 ± 1.0°C (1.4); 2 – 25 ± 1.0°C (2.3); 3 – 35 ± 1.0°C (4.7); 4 – 45 ± 1.0°C (8.1); 5 – 55 ± 1.0°C (15.5); 6 – 65 ± 1.0°C (31.9)
the reaction of thermal transformation of ozonide rings into the most probable fragments of macromolecules of ozonised polybutadiene with aldehyde and carboxyl terminal groups was also determined according to the well-known integral method [10] by means of the formula

\[
n = 1 + \frac{\lg \tau_1 - \lg \tau_2}{\lg c_{01} - \lg c_{02}}
\]

where \(\tau_1\) and \(\tau_2\) are the times of 50% transformation of ozonides with initial concentrations of ozonide oxygen \(c_{01}\) and \(c_{02}\).

At a temperature of 35.0 ± 1 °C and a pH of 7.5–8.0, \(c_{01} = 0.025\) mol/dm³ and \(c_{02} = 0.0125\) mol/dm³, and \(\tau_1 = 152\) min and \(\tau_2 = 149\) min, and the calculated order of the reaction of breakdown of ozonide rings in polybutadiene at the latex stage is equal to 1.02 (with respect to the ozonide) with an effective rate constant of decomposition of \(4.5 \times 10^{-3}\) min\(^{-1}\). The found value of the order of the reaction of breakdown of ozonide rings in an unsaturated polymer in the form of an ozonised butadiene latex is in good agreement with the previously investigated reaction of breakdown of hexene-1 ozonide, which is also first order [8].

On the basis of the experimental data and found values of the effective rate constants \(K'\) (see Figure 2) of thermal transformation of ozonide rings into decomposition products, a linear dependence of \(\lg K'\) on \(1/T\) was established, characteristic of the reactions proceeding in the kinetic region. The activation energy of thermal breakdown of ozonide rings in the butadiene latex polymer under the given experimental conditions, equal to 108.02 kJ/mol, was determined by means of the formula

\[
E_a = 2.303R \frac{\alpha}{n}
\]

where \(R\) is the gas constant, equal to 1.985, \(\alpha\) is the slope of the obtained line to the abscissa axis, and \(n\) is the scale ratio along the abscissa and ordinate axes.

The found activation energy approaches the activation energies for reactions of homolytic decomposition of a typical peroxide such as benzoyl peroxide (139.42 kJ/mol) [9], which once again confirms the possibility of structure formation of ozonised polymers by a radical mechanism when undecomposed residual ozonide oxygen is present in them.

Thus, on the basis of the presented kinetic results of ozonisation of unsaturated polymers in microheterogeneous aqueous systems for the case of butadiene latex, it is possible to predict, as a function of the latex ozonolysis conditions, the content of the equilibrium quantity of intermediately formed ozonide rings, and to control this quantity by changing the temperature, alkalinity, and holding time of ozonised latex for their maximum breakdown before formation of the rubber. The residual trace concentrations of ozonides, as shown by the results of experimental tests, can be finally removed by the additional introduction into the ozonised latex of small quantities of active agents binding ozonide oxygen.

The kinetic data obtained from the investigation of the factors influencing the formation and stability of ozonide rings during the ozonolysis of butadiene latex can be applied fully to the ozonisation of latexes of copolymers of butadiene with styrene, acrylonitrile, unsaturated acids, and other comonomers.

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