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Abstract

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THE INFLUENCE OF THE CHEMICAL NATURE OF SOLVENTS ON THE OXIDATION OF RUBBER IN SOLUTIONS

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Many investigators (1–5) use rubber solutions for modeling oxidative processes that develop in rubber in the solid state. In doing so, the main attention is directed to the transformation of the polymers themselves. As for the solvent,* its role in the process of rubber oxidation in solutions is not considered at all. Meanwhile, the participation of the solvent in the indicated process follows from the radical-chain mechanism of hydrocarbon oxidation now generally accepted.

The aim of the present investigation was to study the influence of the chemical nature of solvents on the oxidation of rubber in solutions.

Purified sodium-butadiene rubber was subjected to investigation. Aromatic hydrocarbons (benzene, toluene, xylene, ethylbenzene, and isopropylbenzene), naphthenic and naphtheno-aromatic hydrocarbons (decalin and tetralin) were used as solvents. The hydrocarbons selected differed in their reactivity toward oxidation.

For the oxidation of rubber solutions, as well as of the solvents, a special apparatus was constructed in which provision was made for vigorous shaking of them during the reaction in order to eliminate diffusion retardation of oxygen.

The kinetic oxidation curves of 1% rubber solutions shown in Fig. 1 indicate that the oxidation rate of the solutions increases in the following series of solvents: toluene < xylene < decalin < ethylbenzene < isopropylbenzene < tetralin. In terms of oxidation rate the aromatic hydrocarbons themselves are arranged in the same series: toluene < xylene < ethylbenzene < isopropylbenzene.**

In a separate series of experiments*** it was shown that 1% rubber solutions in benzene oxidize at a lower rate than in toluene (Fig. 2).

The observed difference in the oxidation rates of rubber solutions can be caused only by the unequal action of the solvent on the development of the radical-chain process of rubber oxidation.

The question arises as to which elementary steps of the rubber oxidation reaction are most substantially affected by the solvent, and how its chemical nature is

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

manifested in this.

In the course of the initiation reaction of the oxidative chain of rubber,

$$\underset{\text{(rubber hydrocarbon)}}{\mathrm{R-H}^{*}} + \mathrm{O_2} \rightarrow \mathrm{HO_2^{\cdot}} + \mathrm{R^{\cdot}} \qquad (1)$$

radicals $R^{\cdot}$ arise, which may or add oxygen with the formation of peroxide radicals, $ROO\cdot$, or enter into interaction with the solvent molecule^{+}. If the radicals are capable of abstracting an H atom from the solvent molecule, then in this case new radicals must arise, with which oxygen can react, thereby transferring the chain from the rubber macromolecule to the solvent molecules.

Fig. 1. Oxidation kinetics of 1% solutions of sodium-butadiene rubber at 90°: 1 —in toluene, 2 —in xylene, 3 —in decalin, 4 —in ethylbenzene, 5 —in isopropylbenzene, 6 —in tetralin

Frank (7) points to the occurrence of chain-transfer reactions during oxidation of a mixture of two low-molecular hydrocarbons. However, solvents can serve not only as chain-transfer agents; some of them, such as, for example, aromatic hydrocarbons (benzene, toluene, xylene, etc.), show a tendency toward radical addition (7-11). Thus, Stockmayer and Peebles (11) showed that the retardation of the polymerization of vinyl acetate in benzene is associated with the addition of the latter to the polymer radical according to the reaction:

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* By the term solvent here should be understood various low-molecular hydrocarbons in which rubber dissolves.

** This agrees with the generally known proposition (6) that, in the oxidation of hydrocarbons, in most cases the C—H bond of a tertiary carbon atom is most readily attacked by oxygen, that of a secondary atom less readily, and that of a primary carbon atom least readily.

*** Owing to the considerable vapor pressure of benzene at 90°, in these experiments the oxidation process was observed not by oxygen absorption, but by the accumulation of peroxide compounds.

Fig. 2. Kinetics of peroxide accumulation during oxidation of 1% solutions of sodium-butadiene rubber at 90°: 1 —in benzene, 2 —in toluene

$$R(CH_2CHOAc)_x\cdot + C_6H_6 \rightarrow R(CH_2CHOAc)_x\overline{H}$$

According to these authors, deactivation of radicals occurs under the action of oxygen during the operations of precipitation and dissolution of the polymer.

* What is meant is abstraction of the hydrogen located at the α-methylene carbon atom.

According to the concepts developed in work ([8]), the act of stabilization of the low-activity radical

$$\mathrm{R(CH_2CHOAc)_x - \underset{H}{C}\!-\!C_6H_5\cdot}$$

can occur by abstraction of hydrogen from it by some other radical present in the system, according to the reaction:

$$\mathrm{R(CH_2CHOAc)_x - \underset{H}{C}\!-\!C_6H_5\cdot + R_1\cdot \rightarrow R_1H + R(CH_2CHOAc)_x - C_6H_5},$$

where $\mathrm{R_1}\cdot$ is a polymer radical.

In an analogous manner, radicals R·, formed during the initiation reaction of the oxidative chain of rubber in solution, can be captured by molecules of aromatic hydrocarbons, namely:

$$\mathrm{R\cdot + C_6H_6 \rightarrow \overset{R}{\underset{H}{C}}\!-\!C_6H_5 \xrightarrow{X\cdot} XH + R - C_6H_5},$$

where X· may be R·, ROO·, RO·, ·OH, etc.

If, however, the radical R· has time to react with oxygen, then the peroxide radical thereby formed may either isomerize* with rupture of the molecular chain of the rubber, which is detected by the decrease in the relative viscosity of the oxidized solutions, or become stabilized. The probability of the stabilization act of the ROO· radical depends on the chemical nature of the solvent and on the concentration of rubber in the solution. During oxidation of rubber in benzene, the ROO· radical is not capable of abstracting an H atom from a solvent molecule, since even the more reactive radical $\cdot\mathrm{CH_3}$ cannot do this ([8]). Therefore stabilization of the peroxide radical may proceed either through its capture by benzene molecules, with the eventual formation of a stable peroxide

$$\mathrm{ROO - C_6H_5},$$

Fig. 3. Accumulation of phenol in the course of oxidation of a 4% solution of sodium-butadiene rubber in benzene at 110°: 1 —peroxides, 2 —phenol

Figure 3: Fig. 3. Accumulation of phenol in the course of oxidation of a 4% solution of sodium-butadiene rubber in benzene at 110°: 1 —peroxides, 2 —phenol

or by abstraction of hydrogen from rubber molecules with formation of the hydroperoxide ROOH and a free radical. The latter circumstance explains why, with increasing concentration of rubber in solution, the rate of oxidation of the solution increases.

In the course of oxidation of the solution, rubber hydroperoxides ROOH may decompose with the formation of the reactive radicals RO· and ·OH, which, as a result of their capture by benzene molecules, are capable of giving several compounds, among which we shall indicate

$$\mathrm{RO} - \mathrm{C_6H_5}$$

and

$$\mathrm{HO} - \mathrm{C_6H_5}\,:$$

Indeed, during oxidation of a 4% solution of rubber in benzene at 110°, the formation of phenol was detected (Fig. 3). It should be noted that the formation of phenol may also be attributed to the decomposition of peroxides

$$\mathrm{ROO} - \mathrm{C_6H_5}.$$

Fig. 3. Accumulation of phenol in the course of oxidation of a 4% solution of sodium-butadiene rubber in benzene at 110°:
1 —peroxides, 2 —phenol

Thus, capture of radicals R· and ROO· by benzene molecules should lead to termination of the primary oxidative chain, while capture of radicals RO· and ·OH should lead to termination of the secondary chain.

On going from benzene to toluene, a new possibility appears for stabilization of the polymer radical ROO·—by abstraction of a hydrogen atom from the methyl groups of toluene ([12]), with formation of a low-activity benzyl radical according to the reaction:

* What is meant is migration of the free valence within the peroxide radical, analogous to that which occurs during oxidation of low-molecular-weight hydrocarbons ([12]).

$$ROO\cdot + C_6H_5CH_3 \rightarrow ROOH + C_6H_5\dot{C}H_2.$$

The benzyl radical can interact comparatively easily with oxygen, forming the radical $C_6H_5{-}\dot{C}H_2OO$. If this radical is not captured by a toluene molecule, it can be stabilized by abstraction of hydrogen either from rubber molecules or from solvent molecules, with formation of toluene hydroperoxide, $C_6H_5CH_2OOH$. The course of the reaction involving transfer of the oxidative chain from the rubber macromolecule to solvent molecules leads to an increase in the length of the oxidative chain.

On going from toluene to xylene, ethylbenzene, and isopropylbenzene, the mobility of hydrogen in the side chain increases.

This factor favors still more strongly the occurrence of oxidative-chain transfer reactions, which leads to an increase in the rate of oxidation of rubber solutions in this series of solvents (see Fig. 1).

In the oxidation of rubber solutions in tetralin and decalin, the influence of the different chemical nature of the solvent molecules is also manifested. Owing to the ease of abstraction of an H atom from tetralin molecules, intermediate products—peroxides of the solvent molecules and of the rubber—accumulate comparatively rapidly in solution. Under the action of the free radicals present in the system, these products decompose, promoting the development of an autocatalytic process of oxidation of rubber solutions in tetralin. The course of autocatalysis is favored by the lower thermal stability of tetralin hydroperoxide in comparison with isopropylbenzene hydroperoxide.

In decalin at 90°, the oxidation of rubber develops at a very low rate because the peroxide radicals are not able to abstract an H atom from the solvent molecule. These radicals could be stabilized with chain propagation through abstraction of hydrogen from rubber macromolecules, but in a dilute solution the probability of this act occurring is small. With an increase in temperature to 100°, a sharp jump is observed in the rate of oxidation of rubber in decalin, which can be explained by the possibility under these conditions of chain transfer with the participation of solvent molecules.

Consequently, in the oxidation of rubber in solutions, solvents may retard (curves 1, 2 in Fig. 1), accelerate (curves 4–6), and also not participate in the process—act as diluents. In terms of the accelerating action, the rubber solvents used by us may be arranged in the following order: tetralin > isopropylbenzene > ethylbenzene; in terms of retarding action: benzene > toluene > xylene.

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