

Kinetics of swelling of natural thermoxidized rubber in benzene

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The kinetics of swelling of thermoxidized fractions of natural rubber in benzene was studied by measuring volumetrically the amount of incorporated solvent in a thin plate of the investigated sample. It has been found that the mean integral diffusion coefficient of benzene in a solid film of natural rubber varies with the time of destruction according to the equation $D = D_0 e^{k_1 t}$, where D_0 is the value of D in the nondestroyed sample and k_1 is an empirical constant. The thermal oxidation was carried out at 130°C.

Была изучена кинетика набухания термически окисленных фракций натурального каучука в бензоле. Количество впитанного бензола определялось волюметрически на образце тонкой пластинки. Было найдено, что средний взаимный интегральный коэффициент диффузии бензола в тонкой пленке натурального каучука зависит от времени деструкции по уравнению $D = D_0 e^{k_1 t}$, где D_0 — значение D в недеструированном образце и k_1 — эмпирическая постоянная. Термическое окисление проводилось при температуре 130°C.

Besides experimental conditions, the progress of transport processes in a system polymer—penetrant is significantly affected by the character of both components constituting the investigated system. The size and structure of the statistical kinetic segment, degree of branching or crosslinking of chains through bond interactions polymer—polymer represent the main factor [1] from the view-point of polymer material. The course of thermoxidative strain of natural rubber in a thin film is accompanied both by a change in chemical structure of the chain — the content of oxygen bonded in the form of carbonyl groups, hydroperoxides, peroxides, etc. increases [2] — and by breaking of the main chain [3].

Owing to the first change, the value of the thermodynamic interaction parameter changes with the degree of destruction while the second change results in the fact that the intensity of motion of the basic kinetic unit changes in the concomitant

process producing new vacancies necessary for transition of a solvent molecule from one interstitial position into another in the sense of flow coordinate. As the thermodynamic as well as kinetic factor is included in the value of D according to general theory of the diffusion processes [4], we have tried to find out to what extent the degree of thermoxidative destruction of the fractionated natural rubber influences the value of the diffusion coefficient D of a certain penetrant. The results presented in this paper are a continuation of our preceding study [5] dealing with the influence of relative molecular weight of natural rubber on its thermoxidative stability. The results of the preceding communication were obtained by the method of infrared spectroscopy without paying attention to the degree of crosslinking, solubility, etc.

Experimental

Preparation of samples

The samples of different molecular weight were prepared by fractional precipitation of the 1.5 wt % benzene solution with a precipitant (methanol) in dark and nitrogen atmosphere at laboratory temperature. The physical constants of the used natural rubber are listed in our preceding paper [5]. The precipitated fractions were dried in a vacuum drier to constant weight and characterized by determining the limiting viscosity numbers $[\eta]$ in benzene at 25°C. The limiting viscosity numbers of individual fractions are given in Table 1.

Table 1

Limiting viscosity numbers of individual fractions

Fraction	Lim. visc. number m ³ /kg	Fraction	Lim. visc. number m ³ /kg
1	0.010	8	0.080
2	0.020	9	0.111
3	0.031	10	0.190
4	0.042	11	0.332
5	0.050	12	0.391
6	0.060	13	0.673
7	0.071	14	1.044

Kinetics of swelling

The kinetics of swelling was investigated in films. These films were prepared by casting a ca. 1.5 wt % solution of the polymer fraction in benzene in nitrogen atmosphere on cylindrical test pieces at laboratory temperature. In order to obtain homogeneous structure

of the film, the test pieces regularly rotated about the axis of the cylinder. A thorough evaporation of the solvent molecules was achieved by drying the films in a vacuum drier for two days in dark.

During drying, the temperature was held at 30.5°C and the pressure was 133.3 Pa. The width of a film thus prepared was about 10^{-3} m. The thermal oxidation of the rubber films was carried out in air at $130 \pm 0.5^\circ\text{C}$.

The kinetic measurements were performed in an apparatus according to *Dogadkin* [6]. A sample of the polymer fraction on test piece precisely weighed and measured was dipped into benzene the temperature of which was $25 \pm 0.02^\circ\text{C}$. The amount of benzene incorporated into the sample was determined by measuring the change in volume of the coexisting liquid phase in certain intervals of the kinetic process.

The accuracy of determination of the volume change was $\pm 1 \times 10^{-3}$ ml.

Results and discussion

The kinetics of sorption of a low-molecular penetrant into the solid polymer phase is controlled by the diffusion process provided the mobility of the segments of macromolecular chains is sufficient [7—9]. A characteristic feature of these measurements is a linear dependence of the amount of penetrant sorbed by unit amount of sorbent Q on the square root of time $t^{1/2}$ and reciprocal value of the width of sorbent.

In our case, the isotropic samples exhibited the shape of thin plate. For the initial intervals of sorption, the experimental relationships between Q_t/Q_∞ and $t^{1/2}$ are not significantly different from those resulting from the curves for the processes with constant diffusion coefficient. The symbol Q_t stands for the amount of solvent bound in a weight unit of the swollen sample in the time moment t and Q_∞ is the

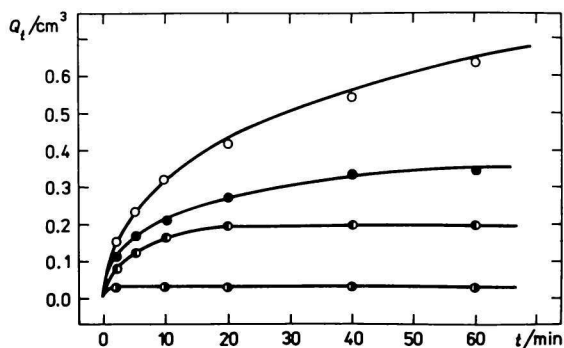


Fig. 1. Amount of the incorporated benzene Q in the film of natural rubber in particular time intervals of the kinetic process.

Fraction 3. Oxidation time in min: \circ 0, \bullet 80, \bullet 110, \bullet 170.

amount of solvent bound in the sample in the equilibrium state of swelling read from the kinetic curves of swelling.

The results presented in this paper are of this type. The kinetic curves of swelling of the samples of rubber fractions in benzene are represented in Figs. 1—3 (for fractions prepared by fractionation in nitrogen atmosphere and in dark; the constant parameter for individual curves is the time of oxidation).

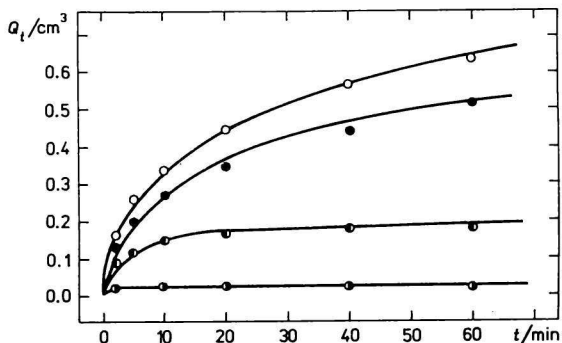


Fig. 2. Amount of the incorporated benzene Q in the film of natural rubber in particular time intervals of the kinetic process.

Fraction 7. Oxidation time in min: \circ 0, \bullet 50, \bullet 80, \bullet 110.

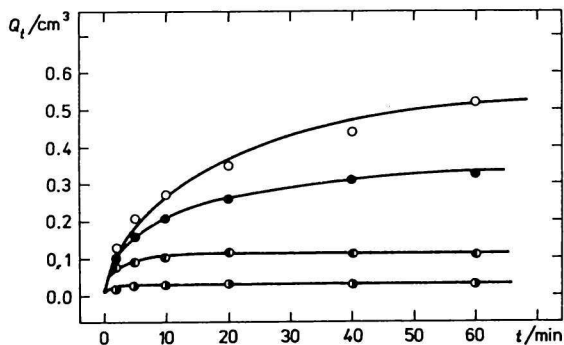


Fig. 3. Amount of the incorporated benzene Q in the film of natural rubber in particular time intervals of the kinetic process.

Fraction 9. Oxidation time in min: \circ 0, \bullet 40, \bullet 80, \bullet 135.

The models suggested for the description of diffusion processes in the solid phase are based on the idea that the rate of diffusion is controlled by the rate of formation of the free holes which leave room for translational motion of the molecules of penetrant in the negative sense of the gradient of its chemical potential [10—12].

The differential equation for an unidirectional unsteady diffusion process has the following form

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D \left(\frac{\partial c}{\partial x} \right) \right] \quad (1)$$

If the diffusion coefficient D is a function of concentration, the solution of eqn (1) necessitates analytical expression of this relationship. However, *Crank* [13] has shown that the sorption curves for a plane plate are not significantly different whether $D = D(c)$ or $D \neq D(c)$. The second condition allows to write eqn (1) in the form

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (2)$$

According to *Crank* [13], the solution of eqn (1) for diffusion along a half-line gives the following equation

$$\frac{Q_t}{Q_\infty} = \left(\frac{4}{l} \right) \left(\frac{Dt}{\pi} \right)^{1/2} \quad (3)$$

where l is the width of film in the sense of the flow coordinate. The validity of eqn (3) is limited. It holds with satisfactory precision only if $Q_t/Q_\infty < 0.6$ and necessitates the fulfilment of the following conditions:

- a) Penetrant enters the sample only by diffusion;
- b) infiltration of penetrant into the solid phase is not accompanied by any mechanical or physical changes in the system;
- c) entire wetting of the external surface of the sample occurs immediately after its coming into contact with liquid penetrant;
- d) penetrant enters only through the surface of the sample and the surface is large enough so that the flow along the edges in the direction perpendicular to the vector of width may be neglected. These conditions were, especially in the initial stage of incorporation, fulfilled.

It may be assumed that the transport of penetrant obeys the Fick's laws in the first moments of sorption owing to a great packing of the polymer coils in the solid phase. It proceeds through the free holes arising as a consequence of thermal vibrations of polymer segments. The evaluation of the kinetic curves of swelling has been based on the assumption that a limited swelling exists in the first approximation even in the noncrosslinked samples. This simplification may be considered

plausible only if a substantial difference (of a few decimal orders) between the values of the partial diffusion coefficient of polymer and solvent exists.

As evident from Fig. 4, the value of the mean integral diffusion coefficient of the benzene molecules in polyisoprene exponentially increases with increasing time of thermal oxidation of the fractions of natural rubber in the investigated time interval. The rapid increase in the values of D_{benzene} may be explained by an increase in mobility of polymer segments due to a decrease in molecular weight caused by the breaking of chains in the first stage of degradation. The change in molecular weight of natural rubber during the induction period of oxidation was already studied [14].

It results from Fig. 4 that the value of the mean integral diffusion coefficient of benzene in the destroyed natural rubber is governed by the equation

$$D = D_0 e^{k_1 t} \quad (4)$$

where D_0 is the value of the diffusion coefficient in a nondestroyed sample and k_1 is an empirical constant.

According to *Barrer* [15], the formation of free holes in the diffusion of simple organic substances in the solid polymer phase is due to the motion of polymer segments. Therefore, a certain relaxation time of the relaxation mechanism of segment motion corresponds to each value of D . Since the time necessary to reach a certain degree of saturation Q_t/Q_∞ is always proportional to square power of

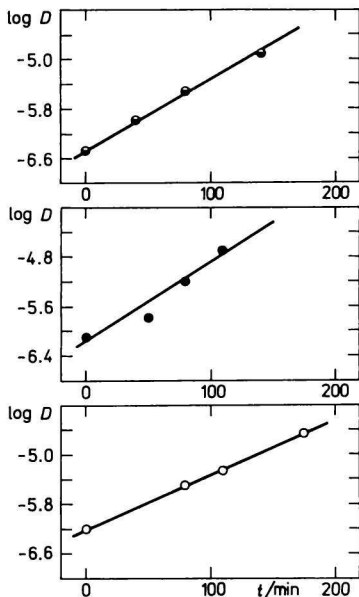


Fig. 4. Variation of $\log D$ with destruction time for the fractions of natural rubber (D is the mean integral diffusion coefficient of benzene in natural rubber).

○ Fraction 3, ● 7, ● 9.

width, i.e. $t/l^2 = \text{const}$ [16, 17] and τ_{rel} is inversely proportional to D , Kanamaru and Sugiura [18] put forward the following equation for calculation of the relaxation time

$$\tau_{\text{rel}} = \frac{l^2}{\pi^2 D} \quad (5)$$

The relaxation times corresponding to the diffusion coefficients D of individual destroyed and nondestroyed samples of natural rubber which are represented in Figs. 5 and 6 show that the relaxation time τ_{rel} for the nonoxidized fractions is

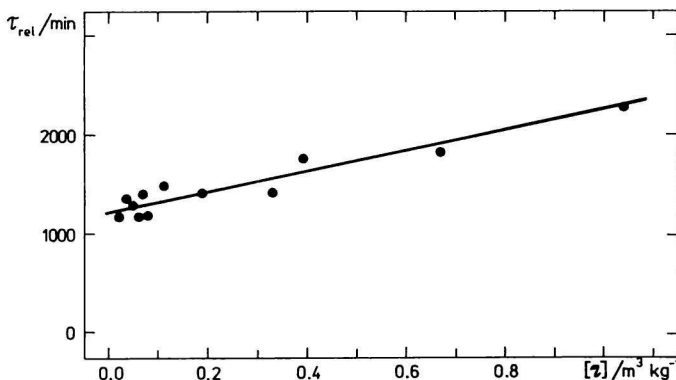


Fig. 5. Variation of relaxation time τ_{rel} with $[\eta]$ for the relaxation mechanism in the nonoxidized fractions of natural rubber.

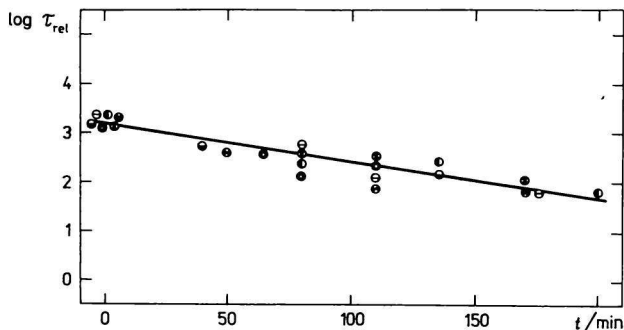


Fig. 6. Variation of $\log \tau_{\text{rel}}$ with time for thermoxidative destruction of the fractions of natural rubber.

poorly sensitive to a change in molecular weight or limiting viscosity number. An appreciable decrease in the amount of benzene bound in the swollen fractions of natural rubber Q_1 with increasing time of oxidation may be justified by increasing polarity of the polymer with time.

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