УДК 678.4.023

Yu. F. Shutilin, D. Sc. (Engineering), professor (VSUET);
A. S. Kazakova, PhD (Engineering), assistant lecturer (VSUET);
O. V. Karmanova, PhD (Engineering), assistant professor (VSUET);
A. V. Kasperovich, PhD (Engineering), assistant professor (BSTU)

SIMULATION OF POLIDIENE OXIDATION KINETICS

Synthetic isoprene rubber (SIR) is similar in structure and to the properties of natural rubber (NR). Currently, it can almost completely replace NR in the production of automobile tires and rubber products. An urgent task is to study the aging processes of polymers and their products, assess the impact of various factors on the oxidative stability of polymers and the selection of effective ways to protect polymers from aging. We simulated aging of inhibited (commodity) and reprecipitation (purified) polyisoprene.

Introduction. Changes of commodity (filled with antiageing reagents) polydiene presents practical interest for assessment of rubber inhibited ageing at temperatures of storage, service (20°C) and processing (up to 100°C). It is ascertained that the presence of antiageing reageints in commodity rubber lowers (reduces) the possibility to obtain objective results in assessing the ageing effects. It is accounted for by their unmonitored impact on chemical reactions of commercial (industrial) rubber stabilizers and leads to the difficulty to get reproducible and reliable results.

Main part. The objects under investigation were samples of commodity (commercial) and purified (reprecipitated) rubber SKI-3. They were 20 μm films on sodium-silicate glasses, obtained from toluene 1 % rubber solutions. The samples were subject to heating in the thermostat at 100°C during 0.1–45.0 hours and in the air at 20°C during 1–40 days, the samples (glasses with films) being periodically tested. The capillary viscosimeter was used for assessing the characteristic viscosity of the film toluene solutions.

Fig. 1 presents changes in typical (characteristic) viscosity of sample films of commodity polyisoprene SKI-3 oxidated at 20 and 100°C.

Analysis and discussion of the obtained experimental data were based on the following viscosity values: change of characteristic viscosity as a result of the first drop in characteristic viscosity $\Delta[\eta]_1$, change of characteristic viscosity as a result of the second drop in characteristic viscosity $\Delta[\eta]_2$, overall drop in characteristic viscosity $\Delta[\eta]_{all}$.

The experimental data indicated in Fig. 1 correlate to the previously-discussed [1, 2, 3] five zones of characteristic viscosity changes and occur in commodity polydienes at 20°C and 100°C:

I – induction period, when apparent addition of oxygen isn't observed;

II – first drop in characteristic viscosity related to intermonomer breakage of macrochains along weak "defective" bonds but not to oxygen addition;

III – transfer of curves onto the plateau – preservation or small change of molecular weight – compensation of destruction processes by structurization at weak oxygen addition and CH_2-group consumption (depletion);

IV – repeated drop in characteristic viscosity accompanied by (associated with) active addition of oxygen and simultaneous reduction of CH_2-group share-oxidative destruction;

V – transfer of curves onto the plateau after the repeated drop of characteristic viscosity – stabilization of the samples structure.
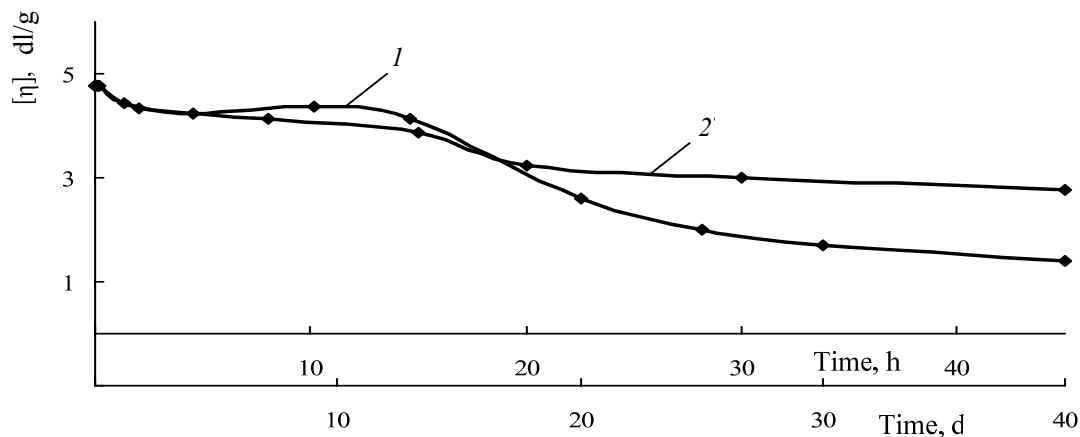

Fig. 1. Dependence of characteristic (typical) viscosity of commodity rubber films SKI-3 on heating time:
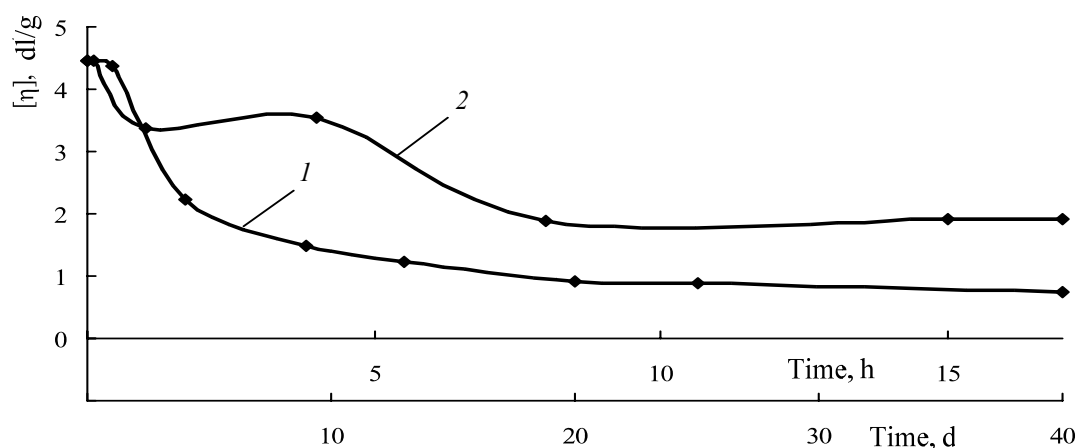*1* – days at 20°C; *2* – hours at 100°C

Fig. 2. Dependence of characteristic viscosity of reprecipitated rubber films SKI-3 on heating time:
1 – days at 20°C; *2* – hours at 100°C

The kinetics of reprecipitated polydiene oxidation at 100°C is described in a similar way.

Reprecipitated polydienes accurately simulate the behavior of rubber films at thermostating under conditions of storage and processing. Fig. 2 indicates changes in characteristic viscosity of sample films of reprecipitated rubber SKI-3 oxidated at 20 and 100°C, respectively.

All reprecipitated polydienes displayed somewhat different kinetics of ageing. Thus, we distinguished the following three stages of oxidation (Table 1):

1 – induction period;

2 – continual drop in characteristic viscosity with addition of oxygen-containing groups and CH_2-group consumption (depletion) at its beginning. This stage can be described by the general effect of zones II–III–IV display;

3 – plateau – stabilization of the molecular weight equivalent to zone V.

In analyzing and summarizing the results we took into account the following extrapolation parameters of rubber ageing kinetics in zones I–V:

$\tau_{f1} = \tau_{s2}$ (f – final; s – start) – extrapolation period corresponding to the time of the induction period (I) termination and the intermonomer destruction (II) starting;

$\tau_{f2} = \tau_{s3}$ – termination of period II and starting of period III;

$\tau_{f3} = \tau_{s4}$ – termination of period III and starting of period IV;

$\tau_{f4} = \tau_{s5}$ – termination of period IV and starting of period V;

τ_x – time of loss of film solubility in toluene.

The following extrapolation parameters are established for the process of three-stage oxidation:

$\tau_{f1} = \tau$ – induction period;

τ_{f2-4} – intermonomer-oxidative decomposition of chains;

τ_5 – transfer onto the plateau corresponding to $\Delta[\eta]_{pre}$, as in the process of films ageing at 20°C loss of their solubility at τ_x wasn't achieved.

Any curve of characteristic viscosity dependence on oxidation time can be divided into five parts (commodity polydienes at 20°C and 100°C, reprecipitated polydienes – at 100°C): three linear and two non-linear ones (Fig. 3). Each part indicates a definite stage in characteristic viscosity change at oxidation and it can be represented in the form of the function. For linear sections the function is

$$f = ax + f_0,$$

for non-linear sections

$$f = e^{ax} + f_0.$$

Table 1

Changes of characteristic viscosity in periods depending on the polymer type

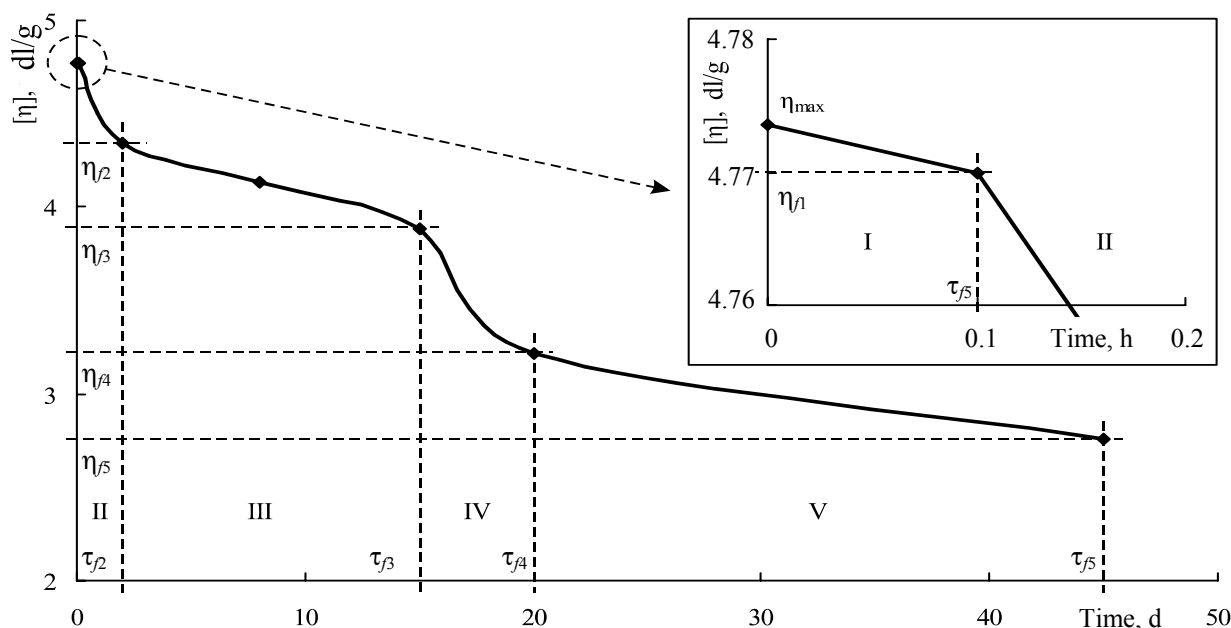| Rubber	20°C			100°C		
	$\Delta[\eta]_1$	$\Delta[\eta]_2$	$\Delta[\eta]_{all}$	$\Delta[\eta]_1$	$\Delta[\eta]_2$	$\Delta[\eta]_{обш}$
Tradable						
SKI-3	0.47	2.90	3.37	0.77	1.25	2.02
Re-precipitated						
SKI-3		3.60		0.91	1.64	2.55

Fig. 3a. Graphic material processing

The sections of the curve described in this way are characterized by parameter a defining the drop in characteristic viscosity, i. e. speed of polymer destructurization in some time periods.

Parameter a for each section of the curve can be received with the help of approximation. Thus, there appears a possibility to make a quantitative comparison of inhibited and commodity polydienes. It should be noted that the first section representing the induction period is a segment joining two or more points, and parameter a is equal to the tangent of the angle of this section slope. The parameters of the other sections are calculated by the proposed function approximation.

Imagine a general form of the function describing the curve of characteristic viscosity (Fig. 3b–3e) as the sum of viscosity value at the starting moment of time and values of five functions in the corresponding sections:

$$y = \eta_{max} + f_1 + f_2 + f_3 + f_4 + f_5,$$

but the form of function f_1 being known and each of functions f_2–f_5 approximates the viscosity curve in the corresponding time interval but the other time moments being equal either to zero or to the value in the extreme point.
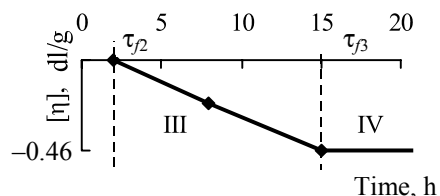
$$f_1 = \begin{cases} ax, & \text{when } x < \tau_{f1}, \\ a\tau_{f1}, & \text{when } x \geq \tau_{f1}. \end{cases}$$
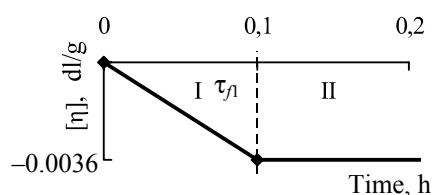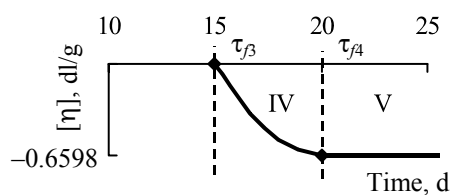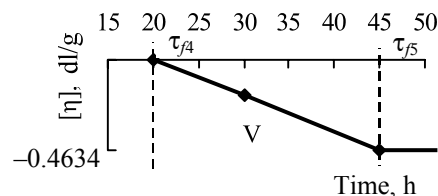

Fig. 3b. Graphic form of function f_1

$$f_2 = \begin{cases} 0, & \text{when } x < \tau_{f1} \\ \left(\eta_{f1} - \eta_{f2}\right)\left(e^{b(x-\tau_{f1})} - 1\right), & \text{when } \tau_{f1} < x < \tau_{f2} \\ \left(\eta_{f1} - \eta_{f2}\right)\left(e^{b(\tau_{f2}-\tau_{f1})} - 1\right), & \text{when } x \geq \tau_{f2} \end{cases}$$
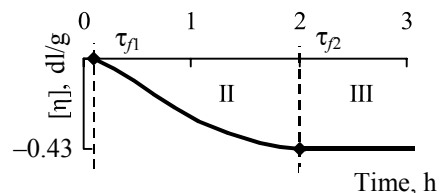
Fig. 3c. Graphic form of function f_2

$$f_2 = \begin{cases} 0, & \text{when } x < \tau_{f2} \\ c(x - \tau_{f2}), & \text{when } \tau_{f2} < x < \tau_{f3} \\ c(\tau_{f3} - \tau_{f2}), & \text{when } x \geq \tau_{f3} \end{cases}$$

Fig. 3d. Graphic form of function f_3

$$f_2 = \begin{cases} 0, & \text{when } x < \tau_{f3} \\ \left(\eta_{f3} - \eta_{f4}\right)\left(e^{d(x-\tau_{f3})} - 1\right), & \text{when } \tau_{f3} < x < \tau_{f4} \\ \left(\eta_{f3} - \eta_{f4}\right)\left(e^{d(\tau_{f4}-\tau_{f3})} - 1\right), & \text{when } x \geq \tau_{f4} \end{cases}$$

Fig. 3*e*. Graphic form of function f_4
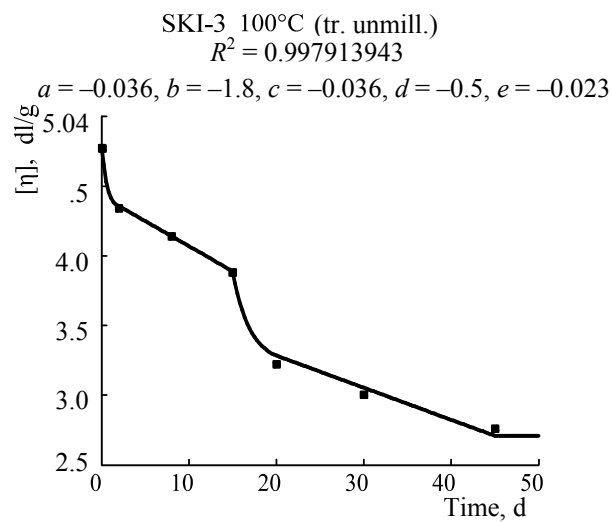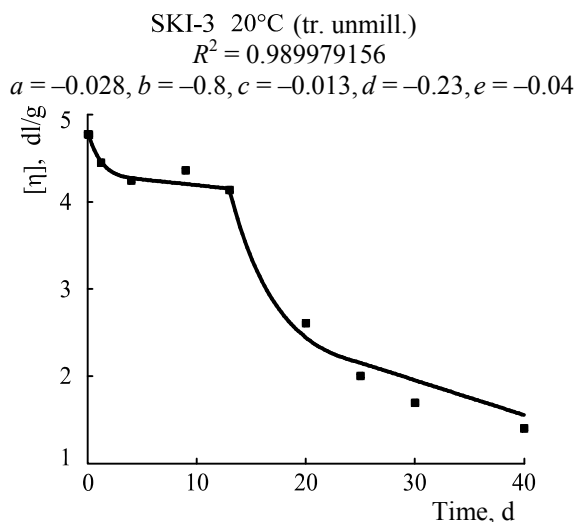

Fig. 3*f*. Graphic form of function f_5

$$f_2 = \begin{cases} 0, & \text{when } x < \tau_{f4} \\ \mathrm{e}(x - \tau_{f4}), & \text{when } \tau_{f4} < x < \tau_{f5} \\ \mathrm{e}(\tau_{f5} - \tau_{f4}), & \text{when } x \geq \tau_{f5} \end{cases}$$

With the help of the mathematical package of analyzing experimental data **Table Curve** we carried out approximation of the curves of characteristic viscosity (Fig. 4) and calculated parameters of the corresponding segments (Table 2).
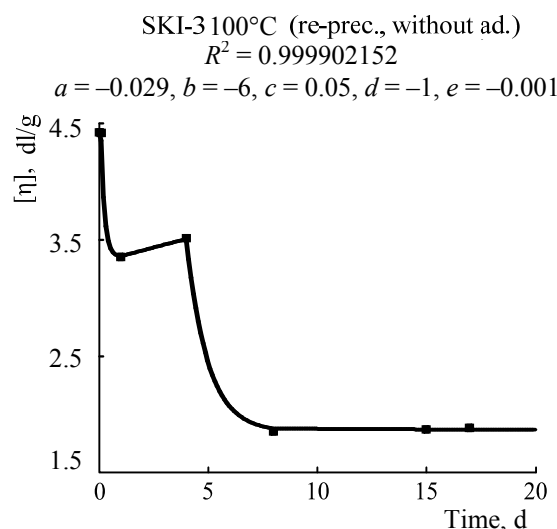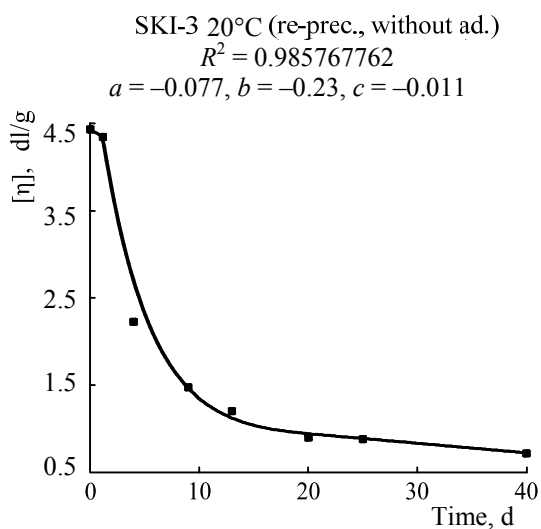
Table 2

Parameters of segments of curves of rubber SKI-3 heating

Type SKI-3	20°C					100°C				
	a	*b*	*c*	*d*	*e*	*a*	*b*	*c*	*d*	*e*
Tradable	−0.028	−0.8	−0.013	−0.23	−0.04	−0.036	−2.2	−0.035	−0.76	−0.018
Re-precipitated	−0.077	−0.23	−0.011	−	−	−0.029	−6	0.05	−1	−0.001

SKI-3 20°C (tr. unmill.)
$R^2 = 0.989979156$
$a = -0.028, b = -0.8, c = -0.013, d = -0.23, e = -0.04$

SKI-3 100°C (tr. unmill.)
$R^2 = 0.997913943$
$a = -0.036, b = -1.8, c = -0.036, d = -0.5, e = -0.023$

a

SKI-3 20°C (re-prec., without ad.)
$R^2 = 0.985767762$
$a = -0.077, b = -0.23, c = -0.011$

SKI-3 100°C (re-prec., without ad.)
$R^2 = 0.999902152$
$a = -0.029, b = -6, c = 0.05, d = -1, e = -0.001$

b

Fig. 4. Dependence of characteristic viscosity of commodity (*a*) and reprecipitated (*b*) rubber SKI-3 films on heating time at 20 and 100°C

Conclusion. The study of polydiene ageing at 20°C and 100°C allowed to determine principal tendencies and directions of polydiene film oxidation. Objective data can be obtained only in comparing chemical processes and their consequences in samples with clearly established parameters of their structure and composition.

Differences in kinetics of inhibited and repricipitated polydiene ageing are established. According to the experimental data it is proved that antiageing reagents in rubber composition reduce the effect of ageing which is associated with their unmonitored presence in commodity elastomers.

References

1. Барабин, С. С. Свойства окисленных полидиенов в пленках различной толщины: дис. ... канд. техн. наук: 05.17.06 / С. С. Барабин. – Воронеж, 2010. – 190 л.

2. Чичварин, А. В. Изучение термоокислительных процессов в эластомерных системах: дис. ... канд. техн. наук: 05.17.06 / А. В. Чичварин. – Воронеж, 2005. – 121 л.

3. Шутилин, Ю. Ф. Справочное пособие по свойствам и применению эластомеров: монография / Ю. Ф. Шутилин. – Воронеж: Воронеж. гос. технол. акад., 2003. – 871 с.