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THERMOANALYTICAL INVESTIGATION OF SILICON RUBBER SYSTEMS.I.

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ABSTRACT

Silicon rubbers have great industrial importance because of their outstanding thermostability. Some types of silicon rubber produced by Wacker Chemie GmbH were investigated by the method of isotherm-thermogravimetric analysis. The first section of weight loss was the result of the evaporation of the volatile components. The second part was characteristic for the degradation, the third one, the thermooxydation was rarely measured during 24 hours. From the experimental data the rate constant (k) characterising the all-over process was calculated.

INTRODUCTION

The isotherm-thermogravimetric analysis is a useful method for investigating the heat resistance feature of different material. Namely the "lifetime" is a very important factor for consumer at the industrial application. We have tried to find the fundament kinetic and thermodynamic characteristics for thermodegradation (ref.1).

EXPERIMENTAL

Material and method

Silicon rubber samples of series VP-R 3003/30-40-50-60 in heat-tempered condition and without heat treatment were produced by Wacker Chemie GmbH (ref.2). All the patterns were examined by a reconstructed analytical balance at 180, 200, 225, 250 °C temperatures. The appropriate temperature was regulated with ± 0.2 °C deviation by regulator "Programik" produced by the Research Institut for Measuring Instrument Hungary. The investigation run always lasted for 24 hours.

DISCUSSION

The experimental data of the weight loss (values in weight percentage) were plotted against time (time values in hour).

The isothermal degradation curves seemed to consist of two or

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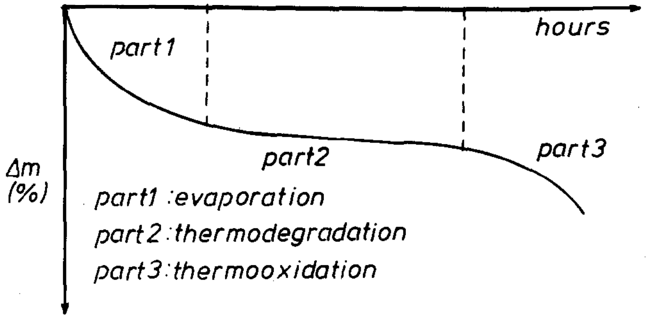
sometimes of three elementary parts (Fig.1).



The evaporation process could be characterized according to the theory of reaction kinetic as a process of first order

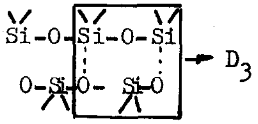
$$v_v = \frac{dN_o}{dt} = k_v N_o \qquad (1)$$

where v_v was the evaporation reaction rate; $\frac{dN_o}{dt}$ was the evaporation rate and k_v was the evaporation rate constant.

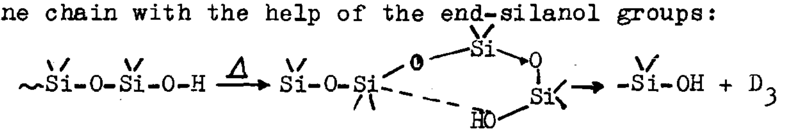
The next part of the experimental curve was characteristic for the thermodegradation. This process caused the destruction of the long polysiloxane chains:

$$HO[(CH_3)_2SiO]_nH \xrightarrow{\Delta} [(CH_3)_2SiO]_x$$

where n was 300 and x was 3. The hexamethylcyclotrisiloxane (D_3) occurred very easily due to the dipole-dipole orientation of the polysiloxane chain of helix structure.



Parallell to this process there is a "cut back" reaction of siloxane chain with the help of the end-silanol groups:



This reaction-step might be declared by the "zip" effect of the silanol group.

This process was characterized by the following relationship

$$v_d = k_d(1-x) = -\frac{dx}{dt} \qquad (2)$$

where $v_d = -\frac{dx}{dt}$ was the degradation rate; k_d was the degradation rate constant, x was the quantity of degradation product.

The integrated form for relationship (2) was the following:

$$\ln \frac{1}{1-x} = k_d t \tag{3}$$

where t was the time.

It could be proved that when $x \longrightarrow 0$ at that time:

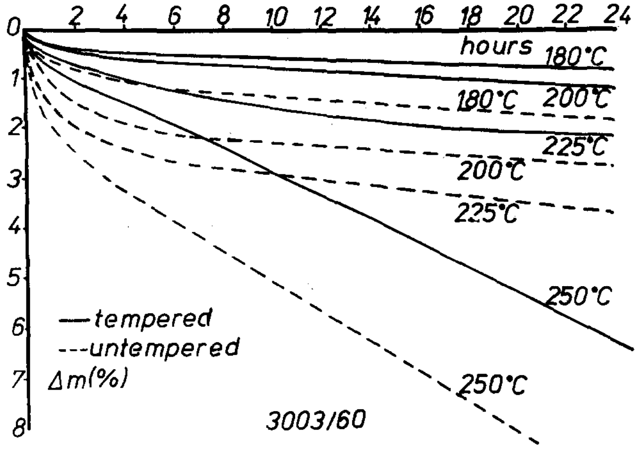
$$\ln \frac{1}{1-x} = k_d t \tag{4}$$

and then $\frac{x_2-x_1}{t_2-t_1} = k_d$. (5)

The all-over reaction rate constants were calculated from the weight loss value pairs belonging to 10 hours and 24 hours, respectively. The "half-life time" was obtained according to equation:

$$t_{1/2} = \frac{\ln 2}{k_d} \tag{6}$$

Fig. 2 shows a curve serie of silicon rubber system VP-R 3003/60.



From the data of Table 1 is to be seen, that the reaction rate constants of heat-tempered silicon rubbers are smaller than the k_d values of the patterns without heat treatment because of the removal of volatile components during the producing process. Otherwise the reaction rate constant values are greater at 250 °C than at the other three temperatures, because of thermooxydation of higher rate. In this case the order of the all-over process was changed too.

RESULTS

The isotherm-thermogravimetric investigation of some silicon rubber types gave the possibility to compare the thermostability of these systems with each other at the same temperature also the dependence of heat-stability vs. temperature. It was proved, that the all-over thermodegradation process investigated by us was a reaction of first order. So it was possible to characterize kinetically the silicon rubber system by the numerical values of reaction rate constant. Our intention is to use this calculations for getting more information about the behaviour at higher temperatures of other silicon rubber systems, about which we are going to report in the future.

TABLE 1

Isothermal degradation kinetic values of the serie VP-R 3003/

		30	40	50	60
180 °C	k	$1.4.10^{-4}$	$1.4.10^{-4}$	$2.1.10^{-4}$	$2.5.10^{-4}$
	k^*	$3.6.10^{-4}$	$2.9.10^{-4}$	$2.9.10^{-4}$	$2.1.10^{-4}$
	$T_{1/2}$	4900	4900	3200	2800
	$T^*_{1/2}$	1900	2200	2400	3200
200 °C	k	$2.5.10^{-4}$	$3.2.10^{-4}$	$2.5.10^{-4}$	$2.9.10^{-4}$
	k^*	$3.6.10^{-4}$	$3.2.10^{-4}$	$3.2.10^{-4}$	$3.3.10^{-4}$
	$T_{1/2}$	2800	2200	2800	2400
	$T^*_{1/2}$	1900	2200	2200	2100
225 °C	k	$4.2.10^{-4}$	$5.0.10^{-4}$	$4.6.10^{-4}$	$5.7.10^{-4}$
	k^*	$5.4.10^{-4}$	$4.2.10^{-4}$	$4.6.10^{-4}$	$6.4.10^{-4}$
	$T_{1/2}$	1700	1400	1500	1200
	$T^*_{1/2}$	1300	1700	1500	1100
250 °C	k	$28.6.10^{-4}$	25.10^{-4}	$17.9.10^{-4}$	$26.3.10^{-4}$
	k^*	30.10^{-4}	$23.9.10^{-4}$	$17.1.10^{-4}$	$23.6.10^{-4}$
	$T_{1/2}$	250	280	390	260
	$T^*_{1/2}$	230	290	400	290

REFERENCES

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2 Wacker Silicone. Wacker Chemie GmbH, München, Mai 1983, Merkblatt SM 11-174.835

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[*] The reaction rate constants belonging to the patterns VP-R 3003/30-40-50-60 in heat tempered condition and without heat curing were listed in Table 1. The appropriate values of the latter ones are marked with a star.