

THERMAL ANALYSIS OF SILICONE CAOUTCHOUC POLYMERS AND SILICONE RUBBERS, II

*G. Liptay, J. Nagy, A. Borbély-Kuszmán and J. Ch. Weis**

DEPARTMENT OF INORGANIC CHEMISTRY, TECHNICAL UNIVERSITY
OF BUDAPEST, H-1521 BUDAPEST, HUNGARY

*WACKER CHEMIE GMBH D-8000 MUNICH, FEDERAL GERMAN REPUBLIC

It was proved experimentally that isotherms obtained from the results of isothermal thermogravimetric analysis are suitable for the characterization of silicone rubbers used in industry. The experimental results provide a possibility for the calculation of overall (apparent) reaction rate constants, characteristic of the thermal decomposition process, and for the calculation of half-life values in conjunction with the service life. Comparisons of the isotherms and of the characteristic calculated values demonstrated the effects of the parameters of silicone rubber preparation and of the conditions of application on the thermal stability.

It was presumed on the basis of earlier work [1] that isothermal thermogravimetric measurements permit the characterization not only of silicone elastomers in the uncured state, but also of the finished products. At a given temperature, the overall reaction rate constant calculated from the experimental results yields numerical values relating to the changes caused by heat in the original properties of the silicone rubber, and to its thermal stability. In the recorded results, the thermal decomposition processes are manifested as the sum of the partial decomposition processes of the rubber components [2].

On the basis of literature data and our own experiments, we earlier described [1] that decomposition isotherms determined by isothermal thermogravimetry are of S-shape, and, depending on the time of analysis, reflect three kinds of processes:

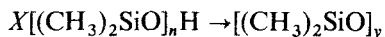
1. evaporation of volatile components,
2. thermal decomposition,
3. thermal oxidation.

The latter two processes are not always clearly separated from one another.

When our measurements were performed over 24 hours in the way described in [1], it was possible to follow only the first and second processes. Evaporation proceeds in a relatively brief time, in the initial section of the measurements.

The chemical changes of the substance are reflected by the second, approximately straight section of the isotherm. The thermal decomposition of silicone polymer can

be written in the following way:



where X is an OH or CH_3 group,

n is the number of $(\text{CH}_3)_2\text{SiO}$ units, and

y is the number of $(\text{CH}_3)_2\text{SiO}$ units in the cyclic products formed during decomposition, the value of which is most often 3, but it may also be 4, 5 or 6.

The formation of hexamethylcyclotrisiloxane (D_3 , if $y=3$) in large quantity can be attributed to the low activation enthalpy needed for its formation, which is a consequence of the helix structure of the polysiloxane chain. The helix structure is formed because of the dipole-dipole orientation of the Si—O bonds, and thus the splitting-off of cyclic D_3 is the preferential process.

The isothermal-thermogravimetric analyses and reaction kinetic calculations we have carried out permit the relative characterization of silicone rubbers used by industry through comparison of their overall (apparent) reaction rate constants. By way of example, the overall (apparent) reaction rate constants of a few silicone rubber types at 200° , and their relative reaction rate constants referred to type Polymer V 1400 are given in Table 1. The sequence of stability in Table 1 agrees with the experience of the users. Since the thermal decomposition is a first-order reaction, conclusions can be drawn on the life of silicone rubbers from the half-life values calculated with the aid of the overall reaction rate constants. Evidently, only reaction rate constants and half-lives relating to identical temperatures can be compared in the relative characterization of the products.

Effect of thermal treatment after curing

In the preparation of silicone rubber, to complete the curing process and to remove possible residual volatile products (which, if remaining in the rubber, unfavourably influence its form stability and thermal properties), the cured rubber

Table 1 Utilization of overall (apparent) reaction rate constants, characteristic of the thermal stability of silicone rubber, for qualification

Samples	k , hour ⁻¹	k_{relative}
VPR-3003/50 + thermal stabilizer	$2.6 \cdot 10^{-4}$	0.7
VPR-3162	$2.6 \cdot 10^{-4}$	0.7
VPR 3003	$3.1 \cdot 10^{-4}$	0.9
VPR 3176 C 1	$3.3 \cdot 10^{-4}$	0.9
Polymer V 1400	$3.6 \cdot 10^{-4}$	1
VPR 3175 C 1	$6.4 \cdot 10^{-4}$	2

Table 2 Losses in mass of thermally untreated silicone rubber type VPR 3003/60 in mass percents

Temperature, °C	Mass loss, % (under)			
	2 h	4 h	10 h	24 h
180	0.70	0.90	1.18	1.50
200	1.05	1.40	1.80	2.25
225	1.60	1.95	2.50	3.30
250	2.10	2.68	4.10	7.40

Table 3 Mass losses of thermally treated silicone rubber type VPR 3003/60 in mass percents

Temperature, °C	Mass loss, % (under)			
	2 h	4 h	10 h	24 h
180	0.37	0.48	0.60	0.92
200	0.50	0.62	0.94	1.35
225	0.78	1.15	1.67	2.47
250	1.25	1.80	3.60	7.21

is subjected to thermal after-treatment at a given temperature for a given time, depending on the curing method.

The data in Table 2 are the mass loss values of the Wacker Chemie GmbH product VPR 3003/60 without thermal after-treatment after 2, 4, 10 and 24 hours at 180, 200, 225 and 250°. Table 3 contains the mass loss values of the same product, measured under identical conditions as above, on a sample heat-treated at 200° for 4 hours. Isotherms plotted at different temperatures for the untreated and thermally treated VPR 3003/60 samples are shown in Fig. 1.

A comparison of the two sets of curves shows that the evaporation loss is considerably lower for the thermally treated samples, and thus the evaporation section of the isotherm is also shorter, and the isotherm more quickly attains the straight section characteristic of thermal decomposition. The advantageous effect of thermal treatment after curing is also proved by the overall rate constants and half-lives relevant to the untreated and thermally treated samples of the VPR 3003 series (Table 4).

These experimental results permit the conclusion that in the case of a given elastomer (batch) suitable instructions given by the manufacturer for curing should subsequently be maximally observed. If there is a change in the composition of the elastomer (batch), the quality and quantity of the curing agent included, isothermal thermogravimetric measurements may be of great help in the determination of both the optimum temperature and duration of curing and the optimum conditions of after-treatment.

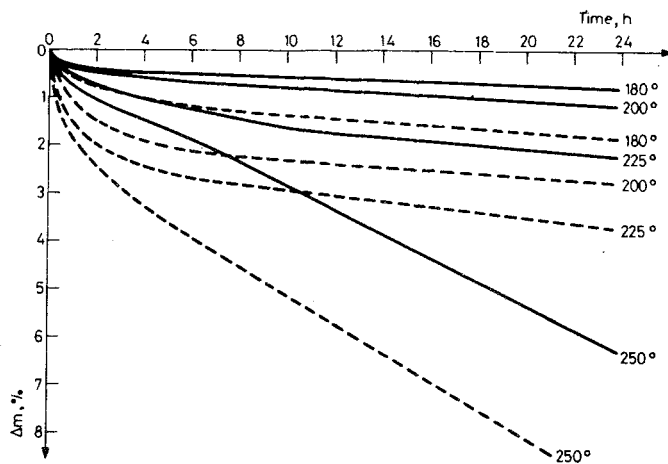


Fig. 1 Isotherms of VPR 3003/50 type untreated and heat-treated silicone rubber samples at different temperatures (--- untreated, — treated)

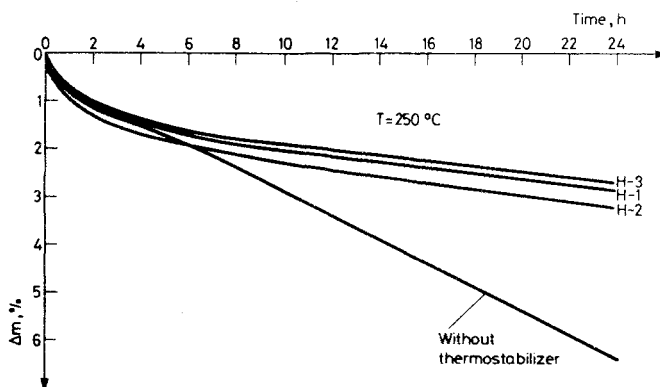


Fig. 2 Isotherms of VPR 3003/50 type silicone rubber sample in the presence of thermostabilizers and without thermostabilizer below 250 °C

Increase of thermal stability with additives

The increase of the thermal stability, and hence the life-time, of silicone rubber is of interest to the user. Similarly as for other polymers, in the case of silicone rubbers the use of certain additives in small quantities increases the period during which the product preserves the original properties required by the user. To follow the effects of thermostabilizer additives, isothermal thermogravimetric analysis was carried out on one of the samples of the VPR 3003 series we investigated: VPR 3003/50. Three kinds of stabilizers used by Wacker Chemie, GmbH, H-1, H-2 and H-3 were

Table 4 Overall (apparent) reaction rate constants and half-time values of silicone rubber types VPR 3003 at 180, 200, 225 and 250 °C

Temperature, °C		Thermal treatment, h			
		30	40	50	60
180	k^* , h ⁻¹	$1.4 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$
	k , h ⁻¹	$3.6 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$
	$t_{1/2}^*$, h	4900	4900	3200	2800
	$t_{1/2}$, h	1900	2200	2400	2400
200	k^* , h ⁻¹	$2.5 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$
	k , h ⁻¹	$3.6 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$
	$t_{1/2}^*$, h	2800	2200	2800	2400
	$t_{1 \infty 2}$, h	1900	2200	2200	2100
225	k^* , h ⁻¹	$4.2 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	$4.6 \cdot 10^{-4}$	$5.7 \cdot 10^{-4}$
	k , h ⁻¹	$5.4 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$	$4.6 \cdot 10^{-4}$	$6.4 \cdot 10^{-4}$
	$t_{1/2}^*$, h	1700	1400	1500	1200
	$t_{1/2}$, h	1300	1700	1500	1100
250	k^* , h ⁻¹	$28.6 \cdot 10^{-4}$	$25.0 \cdot 10^{-4}$	$17.9 \cdot 10^{-4}$	$23.6 \cdot 10^{-4}$
	k , h ⁻¹	$30.0 \cdot 10^{-4}$	$25.9 \cdot 10^{-4}$	$17.1 \cdot 10^{-4}$	$26.3 \cdot 10^{-4}$
	$t_{1/2}^*$, h	250	290	390	290
	$t_{1/2}$, h	230	280	400	260

* refers to the thermotreated samples

applied, consisting essentially of Fe₂O₃, colloidal carbon black and BaZrO₃, respectively.

The character of the isotherms recorded in the presence of the thermostabilizers was essentially similar to that for the basic product: considerable differences in mass loss values were observed only at higher temperatures. The effects of the thermal stabilizers are manifested by a decrease in mass loss. From the results after 24 hours at 250°, the following mass losses were found:

without thermostabilizer	5.6%
with thermostabilizer H-1 (Fe ₂ O ₃)	2.8%
with thermostabilizer H-2 (coll. carbon b.)	3.2%
with thermostabilizer H-3 (BaZrO ₃).	2.6%

Below 250°, there is no substantial difference between the isotherms. At the same time, the effects of the stabilizers can be better evaluated numerically at lower temperatures from the overall (apparent) reaction rate constants and half-lives calculable from the isotherms (Table 5).

The results in Table 5 prove that the stabilizers used hinder the thermooxidation process. Stabilizers H-1 and H-3 are most efficient than H-2. The first two types

Table 5 Overall reaction rate constants and half-time values of silicone rubber samples type VPR 3003/50 containing thermostabilizer additives

		Without stab.	H-1	H-2	H-3
180 °C					
[hour ⁻¹]	<i>k</i>	2.1 · 10 ⁻⁴	1.4 · 10 ⁻⁴	1.8 · 10 ⁻⁴	1.4 · 10 ⁻⁴
[hour]	<i>t</i> _{1/2}	3200	4900	3900	4900
200 °C					
[hour ⁻¹]	<i>k</i>	2.5 · 10 ⁻⁴	2.5 · 10 ⁻⁴	3.2 · 10 ⁻⁴	2.1 · 10 ⁻⁴
[hour]	<i>t</i> _{1/2}	2800	2800	2200	3200
225 °C					
[hour ⁻¹]	<i>k</i>	4.6 · 10 ⁻⁴	3.9 · 10 ⁻⁴	3.6 · 10 ⁻⁴	4.3 · 10 ⁻⁴
[hour]	<i>t</i> _{1/2}	1500	1800	1900	1600
250 °C					
[hour ⁻¹]	<i>k</i>	17.9 · 10 ⁻⁴	6.0 · 10 ⁻⁴	6.4 · 10 ⁻⁴	5.4 · 10 ⁻⁴
[hour]	<i>t</i> _{1/2}	390	1200	1100	1300

(H-1 and H-3) hinder the thermooxidative decomposition up to 310°, whereas type H-2 does so only up to 260°.

If the overall (apparent) reaction rate constants and the respective temperatures of the 3003/50 and stabilized 3003/50 samples, relating to the different temperatures, are plotted in a $\log k$ vs. $\frac{1}{T}$ diagram, the related points lie on straight lines parallel to one another (Fig. 3).

Figure 3 shows only the cases of one of the stabilizers and of the original sample.

Since the stabilizer decreases the decomposition, and hence the reaction rate, the points arising from the experimental results for the sample containing the stabilizer

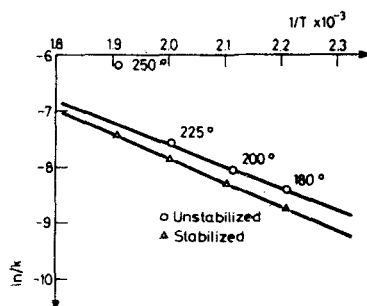


Fig. 3 $\ln k - \frac{1}{T}$ diagrams of stabilized and unstabilized VPR 3003/50 samples (○ unstabilized, △ stabilized)

lie below the straight line corresponding to the original sample, in the range of lower values. The $\ln k$ vs. $\frac{1}{T}$ values relating to the original unstabilized sample also lie on a straight line, with the exception of the k value for 250°. In contrast, in the case of the stabilized sample the k_{250° value lies on the straight line formed by the other k values. This fact too proves that the stabilizers used do not suppress the thermal degradation, but the process of thermal oxidation.

Effect of mass/surface ratio on thermal stability

The aim of our further investigations was to clarify the effect of the mass-surface ratio on the degree of thermal decomposition, as rubber products (e.g. sealing rings or rubber plates) of different thicknesses are applied, and their surface dimensions are also different. The effect of the mass-surface ratio on the thermal decomposition was studied by keeping the surface in contact with hot air at a constant value, and increasing the mass of rubber by increasing the number of test specimens. When these were superimposed, the mass of the experimental samples was multiplied [4]. In this way, a circular surface 16 mm in a diameter was in contact with hot air, while the mantle of the "cylinder" formed was protected by the walls of the sample holder from contact with air. These experiments proved that, with increasing mass, the thermal decomposition depends on the "free surface". Serial measurements are shown in Fig. 4.

When mass losses relating to given points of time of the isotherms in Fig. 4 are plotted as a function of the mass of the sample, the curves in Fig. 5 are obtained.

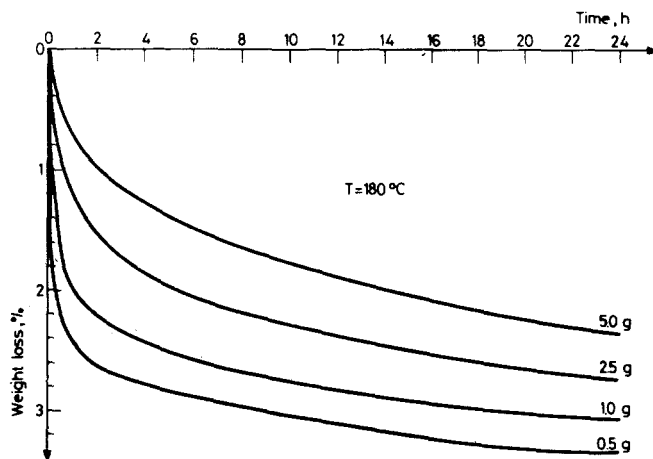


Fig. 4 Change of mass loss (%) of the sample investigated at 180 °C in dependence on the mass of the sample as a function of time (hour)

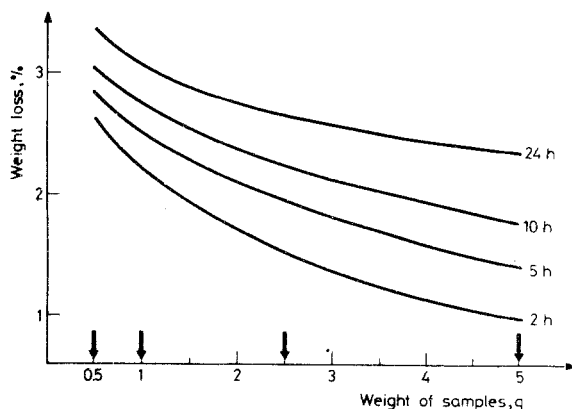


Fig. 5 Mass loss (%) of the sample investigated at 180 °C at selected points of time as a function of the mass of the sample

It may be noted from Fig. 5 that, with increasing mass/surface, the quantity of decomposition products decreases and approaches a limiting value. By numerical analysis of the curves at identical surface, an approximate evaluation can be made for “0” and “∞” substance quantities. On extrapolation to “0” substance quantity, the curves approach a common point. Extrapolation to “∞” quantity of substance is important from the point of view of the application technology, because the degree of decomposition is less and less with increasing sample quantity.

It can be established from the isotherms in Fig. 4 that, when silicone rubber is applied in a closed system, its thermal decomposition is lower than in an open space, because the loss of thermal decomposition products is hindered, i.e. in this case the life of the product is longer. On the other hand, in both open and closed systems, an increase in surface increases the thermal decomposition.

References

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Zusammenfassung — Es wurde experimentell nachgewiesen, daß die auf der Basis der Ergebnisse von isothermen thermogravimetrischen Untersuchungen gewonnenen Isothermen zur Charakterisierung von industriell angewandten Silicongummis geeignet sind. Die experimentellen Ergebnisse ermöglichen

einerseits die Berechnung einer für den thermischen Zersetzungsprozeß charakteristischen resultierenden Reaktionsgeschwindigkeitskonstanten und andererseits die Berechnung von Halbwertszeiten hinsichtlich der Gebrauchsdauer. Der Vergleich der Isothermen mit den errechneten charakteristischen Werten veranschaulicht den Einfluß der Parameter bei der Herstellung von Silicongummis und den Einfluß der Anwendungsbedingungen auf die thermische Stabilität.

Резюме — Экспериментально доказано, что изотермы, полученные на основе результатов термогравиметрического анализа, пригодны для характеристики силиконовых каучуков, используемых в промышленности. Экспериментальные результаты представили возможность вычисления кажущихся констант скорости полных реакций, характеристик процесса термического разложения и значений их полураспада в зависимости от срока их службы. Сопоставление изотерм и вычисленных характеристик показали, что термоустойчивость силиконовых каучуков затрагивается условиями их получения и использования.