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THERMOANALYTICAL INVESTIGATIONS OF SILICONE CAOUTCHOUC POLYMERS AND SILICONE RUBBERS, I.

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The investigations proved that isothermal thermogravimetry yields useful information on the thermal stability of silicone caoutchouc and silicone rubber. It was established that the thermal degradation is a first-order reaction. Measurements and calculations verified that in multicomponent systems the resultant degradation curve obtained by isothermal measurements is formed additively from the degradation curves of the components, i.e. the thermal decompositions of the components proceed independently of one another.

Silicones are inorganic polymers with chemical structures similar to those of inorganic silicic acids and silicates. The basic skeleton is the polymer chain, built up from Si–O–Si bonds, which has a high resistance to chemical and thermal action.

Inorganic (e.g. H) or organic (e.g. alkyl or aryl) groups are attached to the remaining bonding sites of the silicon atoms. The natures of the substituents and the steric structure of the polymer formed (chain or network) influence the properties of the silicones.

Silicone products for industrial use are:

(a) silicone oils, which are chain molecules containing methyl, phenyl, etc. groups as substituents on the silicon atom;

(b) silicone caoutchoucs or rubbers, which are long macromolecules with branches in the chain at some places;

(c) silicone resins or varnishes, which are cross-linked polymers.

In the latter two kinds of polymers, the organic substituents are the same as the groups mentioned for the oils.

The widespread application of silicones was made possible through their properties, which differ appreciably from those of other polymers, e.g.

—their low surface tension,

—their hydrophobic character,

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—their thermal stability,
—their resistance to oxidation,
—their gas (O_2; N_2) and vapour permeability,
—their resistance to chemicals,
—their applicability in a wide temperature range from (−55 to +180°),
—their biological neutrality.

Processes proceeding in silicones at higher temperatures, or with increasing temperature, can be investigated in several ways:

(a) Degradation caused exclusively by heat can be followed through experiments in an inert atmosphere or in vacuum. During degradation induced only by heat, the chain is fragmented and chemical bonds are split, and this requires rather high energy. According to Pauling, these values are

$$E_{\mathrm{Si-C}} = 69.3 \text{ kcal/mol}$$

and

$$E_{\mathrm{Si-O}} = 88.2 \text{ kcal/mol.}$$

Thermoanalytical methods are suitable for following degradation processes proceeding in an inert atmosphere or in vacuum, as well as for the investigation of thermooxidative reactions proceeding in parallel with degradation in the presence of air. Variation of the mode of thermoanalytical measurements and of the experimental parameters can yield information to industrial specialists interested in thermal stability, which is observed as the resultant of thermal degradation and thermooxidative processes.

(b) If thermal action and an air atmosphere are applied simultaneously, then chain fragmentation may be accompanied by oxidative processes at higher temperatures.

(c) As concerns its duration, thermal action can be applied over a long time, or periodically, i.e. pulse-wise.

Due to the increasing interest in heat- and cold-resistant materials, the importance of silicones surpasses that of other plastics.

Literature survey

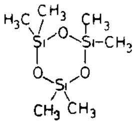
The development of the methods and instruments of thermal analysis offered a possibility for the investigation of the degradation processes induced in silicones by thermal action. In recent decades much experience and numerous results have been gained in this field of research, giving information primarily on dimethylpolysiloxanes (DMS), which are used in the largest quantities for technical purposes.

Depolymerization studies have been carried out partly under dynamic, and partly under isothermal conditions.

Patnode and Wilcock [1] and Thomas and Kendrick [2] established that the thermal decomposition products of DMS are mainly cyclic products, i.e. hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) are formed in the largest quantities, but small quantities of pentamers, hexamers, and even cyclic "mers" with higher numbers of members are also observed.

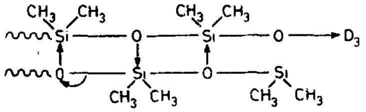
Adrianov [3] and Alexandrova [4] investigated the thermal degradation of DMS with hydroxy end-groups and, in contrast with the authors mentioned above, also detected the formation of methane. As concerns the mechanism of degradation, the opinions of Adrianov [3] and Rode [5] differ. Rode [5] considers that degradation proceeds with the participation of the hydroxy end-group, while Adrianov [3] attributed the thermal degradation to the effect of residues of the catalyst used during the preparation. In any case, it is incontestable that the thermal stability is sensitively influenced by the nature and quantity of the residual catalyst [6, 7]. To clarify these inconsistencies, Grassie and Macfarlane [8] investigated the thermal degradation of DMS in a nitrogen atmosphere, under dynamic conditions. They found that the reaction rate is highest at 443°. The degradation products are cyclic compounds, from trimers up to decamers. The thermal stability of the polymer increases when the hydroxy chain end-groups are replaced by trimethylsilyl groups, but there is no change in the nature of the volatile products. Degradation is strongly accelerated when pure DMS contamined by potassium hydroxide, and methane is also formed in substantial quantities. Thermogravimetric measurements indicated that polymers with hydroxy end-groups are decomposed in a stepwise manner, starting from the hydroxy end-group. The hydroxy end-groups react with one another in condensation reactions even before the beginning of evaporation of volatile components, which results in an increase in the average molecular mass of the product.

This process does not affect the decomposition mechanism. The degradation products in this case too are cyclic oligomers, of which the trimer comprises the main part:



No chain-splitting occurs during the thermal degradation, but processes taking place in the preparation from octamethylcyclotetrasiloxane proceed in the opposite direction.

According to Thomas and Kendrick [2], in the case of chains with trimethylsilyl terminal groups disintegration proceeds in the following way:



In this case too, cyclic oligomer is formed: the hydrogen of the hydroxy group is substituted by a trimethylsilyl group during the formation of the four-centred cyclic intermediate. This process too causes a decrease in the average molecular mass, while an intensive loss by evaporation can be observed.

Thermoanalytical investigations

The results discussed in the literature survey suggested that experimental results measured by means of thermoanalytical methods may possibly yield numerical data on the thermal stabilities and life durations of silicone rubber varieties used industrially in large quantities. However, as a difference from the cases discussed above, silicone rubbers do not consist only of silicone caoutchouc (DMS), but contain other additives (e.g. plasticizer, filler, etc.). The question arose as to how the thermal stabilities of the basic polymer and the finished product are influenced by these additives.

The derivatograph was first used for our investigations. Differences between the various silicone rubber mixtures were found with the dynamic method, but these differences scarcely surpassed the limit of measuring error. We then thought that isothermal thermogravimetric investigations would perhaps be more suitable for the systematic solution of the given problem.

Measuring method

A modified analytical balance was used for the experiments. The left arm of the balance was equipped with a porcelain rod, the upper end of which carried the sample holder. This extended into the interior of a furnace kept at constant temperature. Constant temperature was provided by a program controller within an accuracy of ±0.2 deg.

The mass loss of the sample was observed over 24 hours at three different temperatures: 160, 180 and 200°.

Since the results depend on the mass/surface ratio of the sample [9], a quartz crucible of identical diameter was used in each experiment. The weight of the sample was in each case 1.0000 ± 0.0002 g.

Investigations were deliberately carried out in an air atmosphere, because application generally occurs under such circumstances, and our aim was the collection of data relating to practical use.

Processing of data

Isotherms for different temperatures were obtained by plotting mass loss data (mass fraction or mass percentage) as a function of testing time. When measurements were continued for an appropriately long time, S-shaped curves were obtained (Fig. 1).

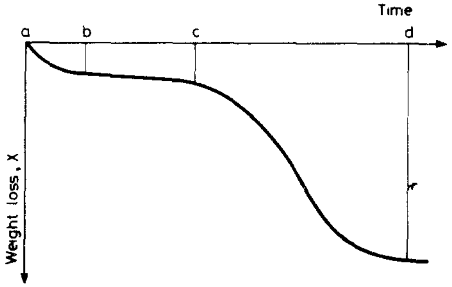


Fig. 1 General representation of isothermal thermogravimetric curves of silicone elastomers

Three sections of the thermal process can be distinguished:

a–b: evaporation of volatile components;

b–c: thermal degradation;

c–d: thermal degradation simultaneously with thermal oxidation, the latter process predominating.

The overall reaction rate observed is the sum of the reaction rates of the partial processes.

Experimental samples

To establish how the thermal stabilities of finished silicone rubber products are influenced by the thermal properties of the various components, the thermal properties of the substances present in a given silicone rubber were investigated separately by isothermal thermogravimetry. Following this, systems with mass ratios corresponding to those of the manufacturing formulations were prepared from the components, and their isotherms were also recorded at 160, 180 and 200° [10]. Data measured on these samples are given in Table 1. The substances for the experiments were supplied by Wacker Chemie GmbH (München).

Table 1 Qualitative and quantitative compositions of the systems investigated

Sample no.	Qualitative composition	Quantitative composition, %
1	Polymer FD 80	100
2	Polymer FD 80 Plasticizer 100	74.1 25.9
3	Polymer FD 80 Plasticizer 100 Filler HDK 15	68.5 23.9 7.6
4	Polymer FD 80 Plasticizer 100 Filler "Aerosil R 972"	68.5 23.9 7.6
5	Polymer FD 80 Filler HDK 15	90.1 9.9
6	Polymer FD 80 Filler "Aerosil R 972"	90.1 9.9
7	Plasticizer 100	100

Evaluation relationships

The duration of the isothermal investigations was 24 hours. During this period, thermal degradation occurred corresponding to section b–c of the curve (Fig. 1), but oxidation was not observed in any of these cases at the experimental temperatures. Evaporation and thermal degradation processes are reflected by the isotherms (e.g. Fig. 2). The "resultant" curve reflecting the two kinds of processes was separated into two rate sections by computer processing. We found that the evaporation of the volatile components is complete in 10–15 hours in the case of silicone polymers. After this, mathematical relationships valid for first-order reactions could be used to calculate the reaction rate and the reaction rate constants of thermal degradation [10].

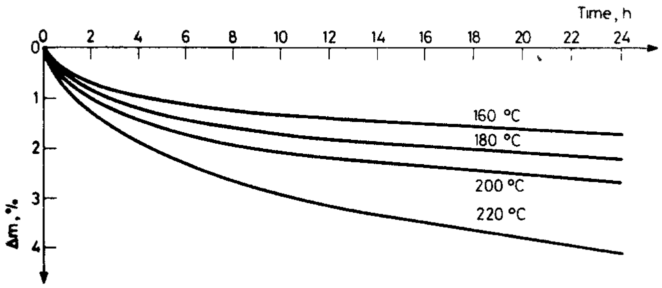


Fig. 2 Isothermal thermogravimetric curves of Polymer FD 80 at 160, 180, 200 and 220°

For evaporation:

$$v_e = \frac{dN_0}{dt} = k_e \cdot N_0 = RTe^{-\lambda b/RT} \tag{1}$$

where v_e is the rate of evaporation,
k_e is the rate constant of evaporation,
N_0 is the number of particles evaporating from unit surface,
λ_b is the internal heat of evaporation,
R is the universal gas constant, and
T is the temperature.

For degradation:

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

where v_d is the rate of degradation,
k_d is the degradation rate constant, and
x is the molar fraction of the degradation product.

Since the mass losses observed are small, certain simplifications were used in our calculations.

The rate of the overall reaction (v_b), characteristic of the total process, can be written as:

$$v_b = k(1-x) \tag{3}$$

On integrating Eq. (3), we obtain

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

Since the mass losses are small:

$$\ln\frac{1}{1-x} \cong x$$

that is $x = kt$.

Therefore, k can be calculated in the following way:

$$k = \frac{x_2-x_1}{t_2-t_1} \tag{5}$$

The quantity (m%) of the volatile part arising from the degradation process can be determined from

$$m = x_{24}-x_{24}^0 \tag{6}$$

where x_{24} is the mass loss measured after the 24 hour, and x_{24}^0 is the mass loss calculated from

$$x_{24}^0 = (1-e^{-k_d t})100 \tag{7}$$

where k_d is the reaction rate constant, and t = 24 hours.

If the mass loss caused by thermal degradation is subtracted from the overall mass loss, the mass loss due to evaporation is obtained, from which the rate constant of evaporation can be calculated:

$$k_e = \frac{1}{t}\ln(x_e^0/x_e^0-x_e) \tag{8}$$

From the overall reaction rate constant (k), the half-times characteristic of the durations of the various polymers can also be calculated via the relationship holding for first-order reactions:

$$t_{1/2} = \frac{\ln 2}{k} \tag{9}$$

Reaction-kinetic calculations

With the above relationships, the reaction rate constants of evaporation and degradation and the half-times for various components (Polymer FD 80, Plasticizer 100) were determined at different temperatures from the experimental isotherms.

In the 24-hour isothermal investigation of fillers, no loss in mass was observed.

Overall mass losses were determined from the respective isotherms.

Characteristic data for Polymer FD 80 and Plasticizer 100 are listed in Tables 2 and 3.

Table 2 Disintegration kinetic data for Polymer FD 80

160°	h^{-1}	$t_{1/2}$, h
$x_d^0 = 0.98945$	$k_d = 3\cdot 10^{-4}$	2310
$x_e^0 = 0.01051$	$k_e = 0.41$	1.7
180°		
$x_d^0 = 0.98636$	$k_d = 3.5\cdot 10^{-4}$	1980
$x_e^0 = 0.01364$	$k_e = 0.41$	1.7
200°		
$x_d^0 = 0.98305$	$k_d = 4\cdot 10^{-4}$	1732
$x_e^0 = 0.01695$	$k_e = 0.36$	1.87
220°		
$x_d^0 = 0.96480$	$k_d = 4.6\cdot 10^{-4}$	1507
$x_e^0 = 0.0352$	$k_e = 0.16$	12.5

Table 3 Disintegration kinetic data for Plasticizer 100

160°	h^{-1}	$t_{1/2}$, h
$x_d^0 = 0.99099$	$k_d = 3\cdot 10^{-4}$	2310
$x_e^0 = 0.00801$	$k_e = 0.6$	1.16
180°		
$x_d^0 = 0.98647$	$k_d = 5\cdot 10^{-3}$	1386
$x_e^0 = 0.01353$	$k_e = 0.55$	1.26
200°		
$x_d^0 = 0.98367$	$k_d = 1.6\cdot 10^{-3}$	433
$x_e^0 = 0.01633$	$k_e = 0.5$	1.4
220°		
$x_d^0 = 0.9680$	$k_d = 2.85\cdot 10^{-3}$	243
$x_e^0 = 0.032$	$k_e = 0.4$	1.73

It can be stated from the data in Table 2 that the loss by evaporation increases, while the evaporation rate constant decreases with increasing temperature. This contradiction can be attributed to the fact that, as the temperature increases, less volatile components influence the rate of evaporation. The degradation rate constants increase with increasing temperature, while the half-time decreases, in accordance with expectations.

The isotherms demonstrate that the evaporation and degradation processes can be separated from one another rather well (see Fig. 2). This is indicated by the difference of three orders of magnitude between the values of the evaporation and degradation rate constants.

Similar tendencies are observed for Plasticizer 100 as for Polymer FD 80 (Table 3). There is only one essential difference between the two polymers: the reaction rate constants are higher for Plasticizer 100.

Calculation of thermodynamic constants

The reaction rate constants calculated from the isothermal thermogravimetric data permitted determination of the activation enthalpies (ΔH^*) characteristic of the thermal degradations of the individual components (Polymer FD 80, Plasticizer 100) via the Arrhenius equation

$$k = Ae^{-\Delta H^*/RT}$$

A plot of ln k *vs* $1/T$ gave a straight line from the slope of which $(\Delta H^*/R)\Delta H^*$ was calculated by the method of least squares.

When the activation enthalpy is known, the activation entropy can be calculated in the following way [11]:

$$\Delta S^* = 19.150\left(\log k + \frac{\Delta H^*}{19.150 \cdot T} - \log 2.08 \cdot 10^{10}\, T\right)$$

In the knowledge of the activation entropy, the free activation enthalpy was obtained with the Gibbs equation:

$$\Delta G^* = \Delta H^* - \Delta T S^*$$

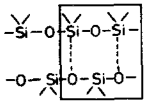
Thermodynamic data characteristic of the two kinds of components are shown in Table 4.

It can be established from the data in Table 4 that the activation enthalpy of Polymer FD 80 is lower than that of the other component. The difference between the ΔH^* values can be explained by the fact that Polymer FD 80 contains hydroxy

Table 4 Thermodynamic characteristics of Polymer FD 80 and Plasticizer 100

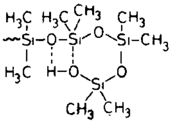
Polymer FD 80	k_1	$= 0.009038 \cdot \exp(-1474.53 \cdot T^{-1})$
	ΔH^*	$= 12.3$ kJ $\cdot$ mol^{-1}
	ΔS^*	$= -268.7$ J $\cdot$ mol^{-1} deg^{-1}
	ΔG^*	$= 139.4$ kJ $\cdot$ mol^{-1}
Plasticizer 100	k_2	$= 93661 \cdot \exp(-8522.1 \cdot T^{-1})$
	ΔH^*	$= 69.6$ kJ $\cdot$ mol^{-1}
	ΔS^*	$= -153.6$ J $\cdot$ mol^{-1} deg^{-1}
	ΔG^*	$= 142.3$ kJ $\cdot$ mol^{-1}

groups at the end of the polysiloxane chains, and during degradation a relatively stable intermediate may be formed via these groups:



This is supported by the high negative activation entropy, that is, the intermediate with cyclic structure has a higher order.

In Plasticizer 100, the polysiloxane chains are terminated by trimethylsiloxy groups. Accordingly, the intermediate formed in the degradation process is less stable, as indicated by the substantially lower activation entropy than that of Polymer FD 80.



Investigation of the degradation kinetics of Polymer FD 80, Plasticizer 100 and active silica gel systems

A) Polymer FD 80 + Plasticizer 100 system

The investigation of the systems listed in Table 1 was begun after the evaluation of the investigations and results discussed above, to decide whether the thermal properties of mixture systems, e.g. their thermal stability, are formed in an additive or synergistic way from the respective properties of the components.

Degradation kinetic investigations were carried out by plotting the isotherms of various systems, using the isothermal thermogravimetric method. The results obtained in this way proved that the total quantity of volatile components and thermal degradation products arose additively from the corresponding quantities of the components (Fig. 3). Calculations relating to these investigations were performed as described previously. The respective calculated overall mole fractions of volatile and degradation products agreed with the experimental values within the limits of measuring error (Table 5).

Table 5 contains separately the mole fractions of the degradation products of the component, and the sum of the mole fractions of the volatile products, obtained from Tables 2 and 3. The Table also contains the rate constants of the overall degradation reaction.

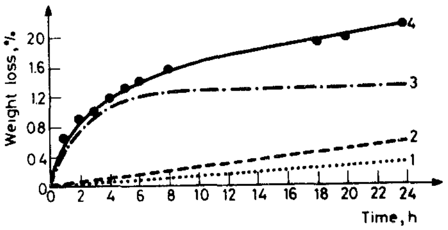


Fig. 3 Change in mass of the volatile components of Polymer FD 80 (1) and Plasticizer 100 (2), sum of the thermal degradation products of Polymer FD 80 and Plasticizer 100 (3), and isotherm values measured from the curves (4) and calculated

Table 5 Overall disintegration rate constants of the system Polymer FD 80+Plasticizer 100, disintegration products of the components, and volatile components of the system, expressed in mole fraction

°C	k_d [h^{-1}]	x_0, FD 80	x_0, L 100	x_e^0
160	0.32	0.7313	0.2556	0.0131
180	0.40	0.7300	0.2552	0.01488
200	0.42	0.7277	0.2543	0.0180
220	0.20	0.7114	0.2486	0.0400

B) Polymer FD 80, Plasticizer 100 and active silica gel systems

When it had been proved that the thermal evaporation and degradation processes of methyl polysiloxanes proceed independently of one another, and that the overall process observed is the sum of each of two corresponding partial processes, the question arose of whether these findings are affected by the fillers used? Our experimental results proved that the reaction kinetic parameters discussed in point *A)* are not influenced either by hydrophilic or by hydrophobic silica gels.

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Zusammenfassung — Die isotherme Thermogravimetrie liefert nützliche Informationen über die thermische Stabilität von Silkonkautschuk und Silikongummi. Der thermische Abbau verläuft nach einer Reaktion erster Ordnung. Messungen und Berechnungen haben bestätigt, daß in Vielkomponentensystemen die resultierende isotherme Zersetzungskurve sich additiv aus den Zersetzungskurven der Komponenten zusammensetzt, d. h., daß die thermische Zersetzung der Komponenten unabhängig voneinander verläuft.

Резюме — Исследования показали, что изотермическая термогравиметрия дает полезную информацию о термической устойчивости силиконового каучука и силиконовой резины. Установлен первый порядок реакций их термического разложения. Проведенные измерения и вычисления подтвердили, что в многокомпонентных системах результирующая кривая распада, получаемая в изотермических условиях, дополнительно состоит из кривых разложения отдельных компонент, т. е. термическое разложение компонентов протекает независимо друг от друга.