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THERMAL INVESTIGATION OF SILICONE RUBBER CONTAINING IMIDE-SILOXANE COPOLYMERS

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Abstract

Dynamic mechanical thermal analysis and isothermal thermogravimetry yield useful information on the temperature dependence of the mechanical properties and thermal stability of silicone rubbers.

In the thermal mechanical relaxation spectra, only one characteristic phenomenon may be observed.

Isothermal thermogravimetry reveals that the thermal degradation is a first-order reaction. 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-time values.

Keywords: imide-siloxane copolymers, isothermal thermogravimetry, silicone rubber

Introduction

The widespread application of silicones was made possible through such properties as their hydrophobic character, their thermal stability, their resistance to oxidation, and their applicability in a wide temperature range (from –55 to +180°C), etc. [1, 2].

On the basis of earlier work [3], it was presumed that isothermal thermogravimetric measurements would permit the characterization not only of silicone elastomers in the uncured state, but also of the finished products.

Further, the viscoelastic properties (e.g. relaxation) of silicone rubbers can be described by dynamic mechanical thermal analysis [4].

In the present study, similar data are reported for methylvinylsilicone rubber (containing two types of imide-siloxane copolymers as additives).

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Experimental

Two types of imide-siloxane copolymers were prepared [5], from pyromelliticdiimide-siloxane as copolymer I, and from benzophenonediimide-siloxane as copolymer II. These copolymers were mixed with methylvinylsilicone polymer in 5–50 wt% ratios, and with 40% fumed silica and 20% anti-crepe agent. The reaction mixture was then vulcanized with 2,4-dichlorobenzoyl peroxide as initiator.

The produced rubbers were investigated by the following methods:

Dynamic mechanical thermal analysis

The purpose of the present investigation was to shed light on the temperature dependence of the mechanical properties of the methylvinylsilicone rubber as standard and methylvinylsilicone rubbers containing different types of imide-siloxane copolymers (I and II) in different ratios. The measurements were made with a Polymer Laboratories Thermal Sciences Mark II dynamic thermal analyzer (DMTA) [6], at 0.3, 1. and 3 Hz, and a heating rate of 3 deg·min^{-1}, between –100 and 50°C.

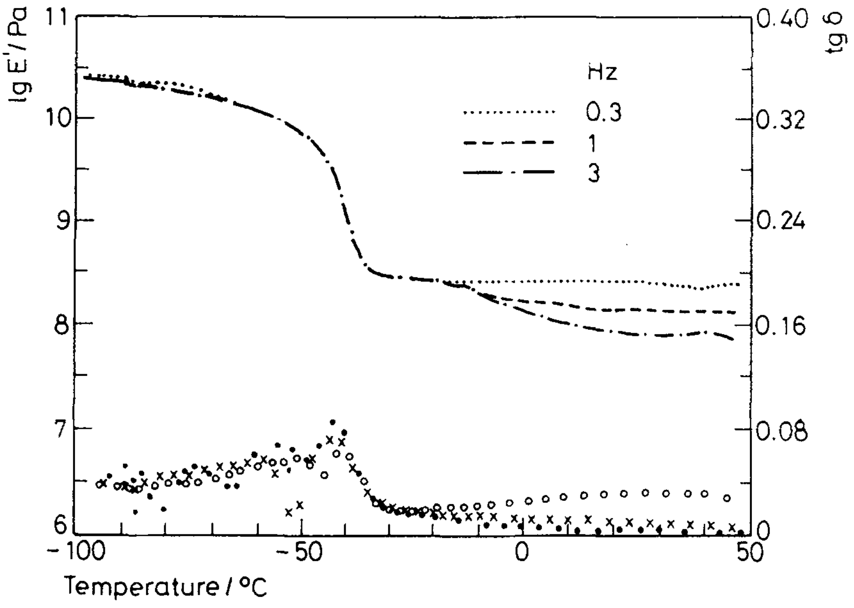

Fig. 1 DMTA analysis curve for methylvinylsilicone rubber

In the thermal mechanical relaxation spectra, only one characteristic phenomenon may be observed: the peak between –40 and –50°C (as shown in

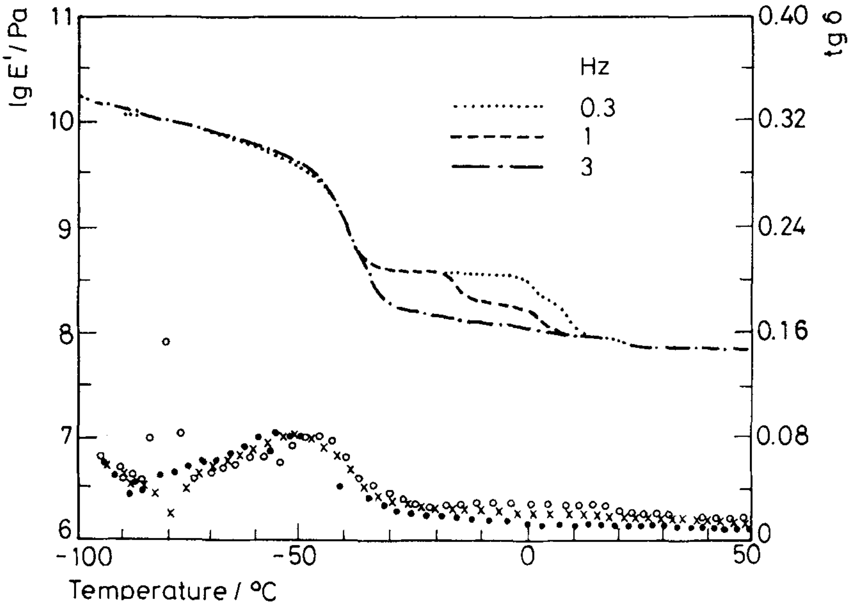

Fig. 2 DMTA analysis curve for methylvinylsilicone rubber containing 50 wt% imide copolymer I

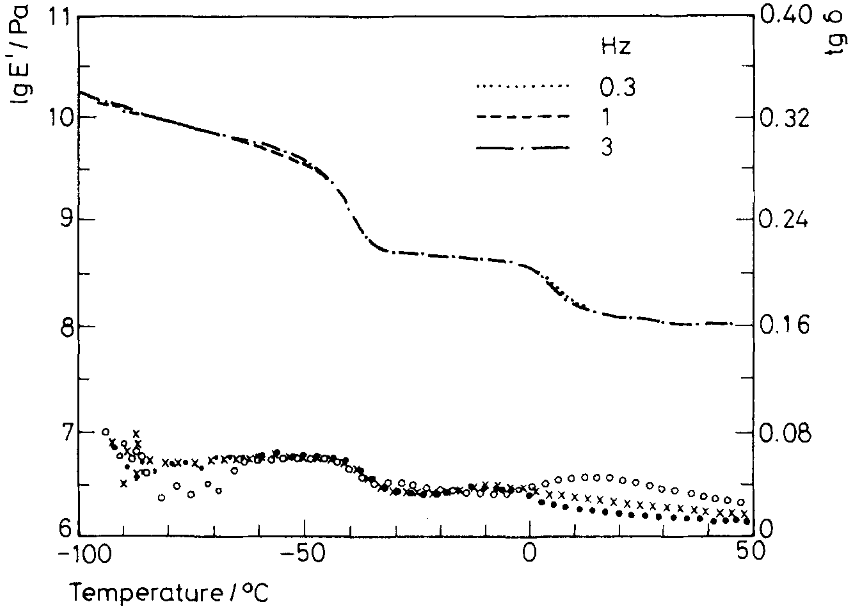

Fig. 3 DMTA analysis curve for methylvinylsilicone rubber containing 50 wt% imide copolymer II

Figs 1–3), which may be assigned to an aerosil-siloxane chain motion. It is shown that secondary bonds are formed between the active filling material and the chains.

The silica particles are built into the polymer network and are held by either hydrogen-bonded dimer or Si–O–Si linkages. The increase in the mechanical properties of the pure silicone elastomer is explained on this basis [7].

The temperature of this relaxation is independent of the imide content of the polymer. This may be explained with the help of Fig. 4:

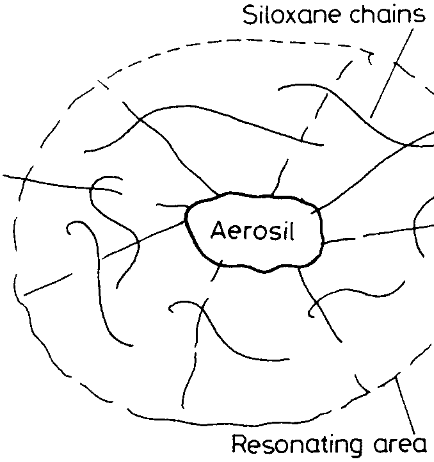

Fig. 4

According to this hypothesis is the mechanical energy will dissipate on the aerosil areas, which are coupled only weakly to the siloxane chains. On increase of the exciting frequency, the size of the co-vibrating siloxane coat decreases, so relaxation temperature does not change.

On introduction of copolymer I into the methylvinylsilicone rubber, the same relaxation between –40 and –50°C was observed, as shown in Fig. 2.

However, in the case of copolymer II, a second relaxation was also observed between 20 and 35°C, as shown in Fig. 3. This second relaxation may be explained in that copolymer II has a more active C=O group, which is probably able to form secondary bonds with the aerosil particles. This saturation process will cause a similar relaxation as the first one, but at higher temperatures.

Of course, much experimental work is needed to confirm this hypothesis.

Isothermal thermogravimetry

In polymers, degradation in an inert atmosphere or in vacuum is caused exclusively by heat. Thermoanalytical methods are suitable for following degradation processes proceeding in an inert atmosphere or in vacuum, and also for the investigation of thermooxidative reactions proceeding in parallel with degradation in the presence of air. Variation of the conditions 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. It has been proved experimentally that isotherms obtained from the results of isothermal thermogravimetric analysis are suitable for the characterization of silicone rubber. The mass loss of the samples was observed versus time at different temperatures. Differences between the various methylvinyl silicone rubbers and methylvinylsilicone-imide-siloxane rubber mixtures were found on the basis of the dynamic method (using a derivatograph), but these differences scarcely surpassed the limit of measurement error. Isothermal thermogravimetric investigations, however, proved to yield more information.

Method of measurement

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 [8].

The mass loss of the sample was observed over 24 h at 180, 220, 200 and 250°C. 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.

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 stability and thermal properties), the cured rubber was subjected to thermal aftertreatment at 200°C for 4 h.

Processing of the 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. 5).

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.

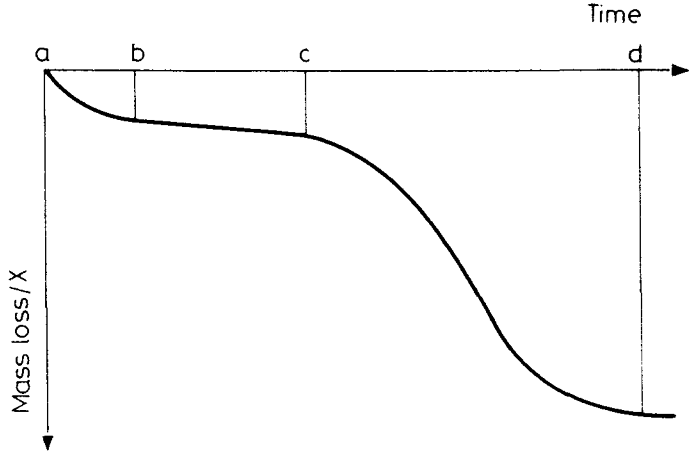

Fig. 5 General representation of isothermal thermogravimetric curves of silicone elastomers

The evaporation of the volatile components is complete in 10–15 h in the case of silicone polymers [8]. Mathematical relationships valid for first-order reactions could be used to calculate the reaction rate and the reaction rate constants of thermal degradation [9].

For evaporation:

$$v_d = \frac{dN_o}{dt} = k_e \cdot N_o = RTe^{-\lambda_b / RT} \tag{1}$$

where v_e is the rate of evaporation, k_e is the rate constant of evaporation, N_o 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 mole fraction of the degradation product.

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

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

where x is the mole fraction of the degradation product.

On integrating Eq. (1), we obtain

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

Since the mass losses are small:

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

i.e. $x = kt$.

Therefore, k can be calculated in the following way:

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

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

$$s\% = x_{24} - x^{o}_{24} \tag{6}$$

where x_{24} is the mass loss measured after 24 h, and x^{o}_{24} is the mass loss calculated from

$$x^{o}_{24} = (1 - e^{-k_d t}) \cdot 100 \tag{7}$$

where k_d is the reaction rate constant, and t = 24 h. From the overall reaction rate constant (k), the half-times characteristic of the durations for the various polymers can also be calculated via the relationship holding for first-order reactions:

$$t_{1/2} = \frac{\ln 2}{k} \tag{8}$$

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.

The isotherms of samples of methylvinylsilicone as standard and methylvinylsilicone rubbers containing imide I and II were recorded at 250°C for 24 h, as shown in Figs 6 and 7. The aim of our investigations was to clarify the effects of the different imide-siloxanes as additives on the thermal properties of silicone rubber. A comparison of the mass losses as a function of the imide copolymer quantity in the rubber at 250°C may be of great help in determination of the optimum value of imide-siloxane copolymer in the rubber that showed minimum loss mass. In the curves taken during this period in the cases of pure methylvinylsilicone and methylvinylsilicone rubbers containing copolymer I, section c–d of the thermal process can be observed, but in the case of methylvinylsilicone rubber containing copolymer II section c–d can not be distinguished. It can also be concluded from the curves that the weight loss has a minimum at 25 wt% imide II content.

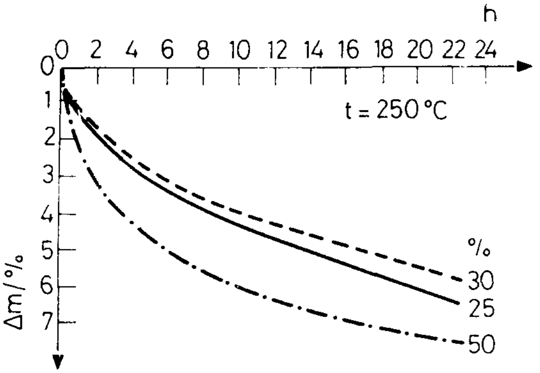

Fig. 6 Isothermal thermogravimetric curves of methylvinylsilicone rubbers containing imide I

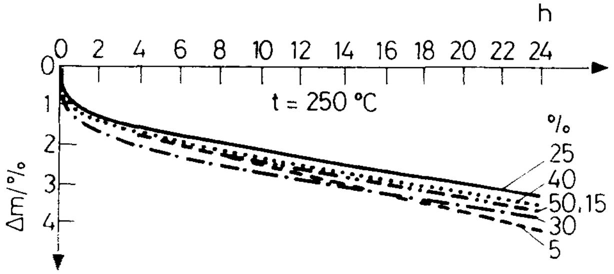

Fig. 7 Isothermal thermogravimetric curves of methylvinylsilicone rubbers containing imide II

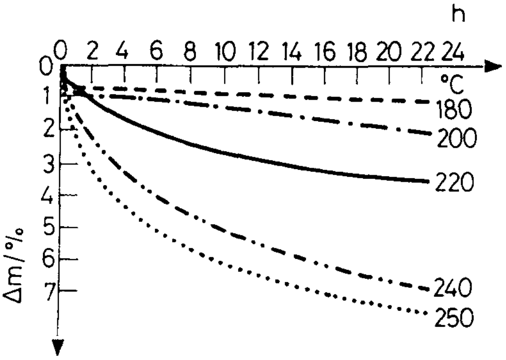

Fig. 8 Isothermal thermogravimetric curves of pure methylvinylsilicone rubber at different temperatures

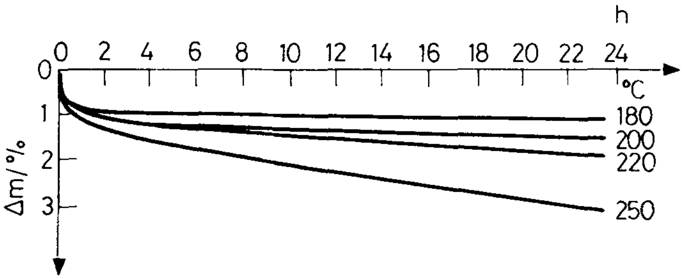

Fig. 9 Isothermal thermogravimetric curves of methylvinylsilicone rubber containing 25 wt% imide II

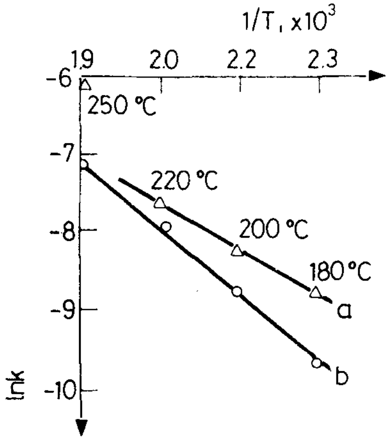

Fig. 10 ln k vs. $1/T$ diagram of (a) methylvinylsilicone rubber and (b) methylvinylsilicone rubber containing 25 wt% imide copolymer II

To follow the effects of 25 wt% imide copolymer II, isothermal thermogravimetric analysis was carried out on pure methylvinylsilicone rubber and methylvinylsilicone rubbers containing imide copolymer II. Their isotherms were recorded at 180, 200, 220 and 250°C (Figs 8 and 9). After this, mathematical relationships were used to determine the reaction rate constants of degradation and the half-times at different temperatures from the experimental isotherms.

The values of reaction rate constants, half-time and quantity of volatile part (s%) are listed in Table 1.

Table 1 Overall (apparent) reaction rate constants and half-times for pure methylvinylsilicone and methylvinylsilicone rubbers containing 25 wt% copolymer II at 180, 200 and 250 °C

		Methylvinylsilicone rubbers	Rubber containing 25 wt% imide II
180 °C	$k\cdot10^4$ [h^{-1}]	1.5	0.62
	$t_{1/2}$ [h]	4600	11129
	s%	0.995	0.9
200 °C	$k\cdot10^4$ [h^{-1}]	2.5	1.56
	$t_{1/2}$ [h]	2760	4423
	s%	1.02	0.98
220 °C	$k\cdot10^4$ [h^{-1}]	4.77	3.43
	$t_{1/2}$ [h]	1446	2011
	s%	2.36	1.08
250 °C	$k\cdot10^4$ [h^{-1}]	32.68	7.5
	$t_{1/2}$ [h]	211	920
	s%	2.45	1.31

k: overall reaction rate constant;
$t_{1/2}$: half-time
s: volatile part arising from the degradation process

The results in Table 1 prove that a 25 wt% imide copolymer II content increases the half-time of methylvinylsilicone rubber. In the knowledge of the overall (apparent) reaction rate constants and the respective temperatures, a ln k *vs.* $1/T$ diagram can be constructed (Fig. 10). Since the 25 wt% imide copolymer II decreases the decomposition and hence the reaction rate, the points arising from the experimental results for the sample containing the 25 wt% imide copolymer II lie below the straight line corresponding to the original sample (in the range of lower values). The ln k *vs.* $1/T$ values relating to the methylvinylsilicone sample also lie on a straight line, with the exception of the k value for 250 °C. In contrast, in the case of the methylvinylsilicone-imide sample the $k_{250°C}$ value lies on the straight line given by the other k values. This fact proves that thermal degradation may be accompanied by thermal oxidation in the case of methylvinylsilicone rubber, which was not expected for the rubber with 25 wt% imide copolymer II. It may be noted that k measurements were included in earlier studies [3, 8, 9] of thermal degradation and oxidation of silicone rubbers.

Conclusions

It can be stated that the imide-siloxane copolymer I influences the properties of methylvinylsilicone rubber to only a small degree, but copolymer II has a larger effect. The greatest influence in the case of copolymer II is at 25 wt%. In the case of the latter imide-siloxane copolymer, the lifetime and thermal stability are very favourable as compared with pure methylvinylsilicone rubber.

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Zusammenfassung — Dynamische mechanische Thermoanalyse und isotherme Thermogravimetrie lieferten nützliche Informationen über die Temperaturabhängigkeit der mechanischen Eigenschaften und der Thermostabilität von Silikongummi.
Im thermischen mechanischen Relaxationsspektrum kann nur 1 charakteristische Erscheinung beobachtet werden.
Ausgehend von der isothermen Thermogravimetrie ergibt sich für den thermischen Abbau eine Reaktion erster Ordnung. Die experimentellen Resultate bringen die Möglichkeit zur Berechnung der Gesamt- (scheinbaren) Reaktionsgeschwindigkeitskonstante des thermischen Zersetzungsprozesses und von Halbzeitwerten mit sich.