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THERMOANALYTICAL INVESTIGATIONS ON CURING AND DECOMPOSITION OF METHYL SILICONE RESIN

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ABSTRACT

Methyl silicone resins, $(CH_3SiO_{1.5})_n$, containing alkoxy and hydroxy end groups are cured by heating. It will be shown that thermal analysis is a helpful tool to investigate curing conditions and pyrolytic decomposition in silicone resins, e.g. in Wacker Silicone Resin MK. DSC, TG/DTG and EGD measurements in air und N_2 up to 1000 °C were conducted and the formed products analyzed with the help of IR, GLC and $^{1}H/^{29}Si/^{13}C$ NMR. The composition and structure of the uncured and cured resin and of the solid residues obtained by heating to 1000 °C in air or N_2 will be discussed.

INTRODUCTION

Silicone resins are common technical products, used in different fields of application [1]. Although known for some ten years, only little has been published about the resins' structure. Derived from chemical composition, the resins are organosilsesquioxanes, $(RSiO_{1.5})_n$, R = CH_3, C_6H_5. Within this class of compounds well-defined and characterized species of polyhedral shape with n = 8, 10, 12 are known [2]. The industrially produced resins consist of a variety of structural subunits as has already been proved by ^{1}H and ^{29}Si NMR spectroscopy [3]. But there are only a few, partially controversial, publications dealing with the description of the resins' structure in general [4-6] or discussing their thermal properties [7-9]. One recently published paper [10] describes the decomposition of

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Owens-Illinois GR 650, a pure methyl silicone resin. Our investigations were focused on Wacker Silicone Resin MK, a methyl silicone resin of comparable composition but with different chemical properties.

In general, silicone resins are produced via hydrolysis of the appropriate organotrichlorosilanes [1]. Precursor of Wacker Resin MK is CH_3SiCl_3, which is reacted with ethanol and water in toluene as solvent. In a multi-step process of conditioning and purification we get the relatively low molecular resin containing OH and OC_2H_5 end groups. Resin MK shows a glass transition at about 40 °C.

RESULTS AND DISCUSSION

From analytical data (elemental analyses, ^1H NMR) we have calculated the average composition of Resin MK:

$$[CH_3SiO_{1.45}(OC_2H_5)_{0.067}(OH)_{0.033}]_{30}.$$

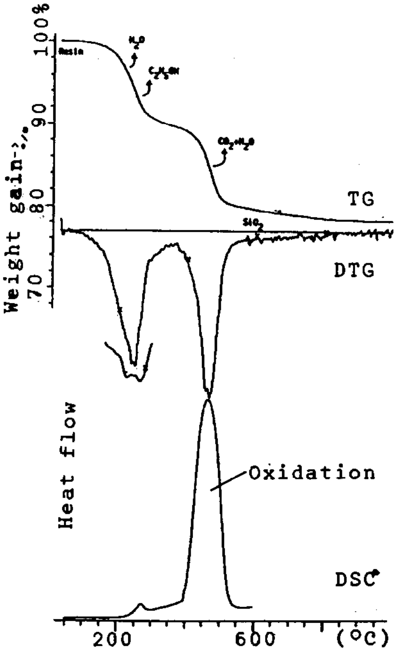
Some structural units in the resin network can be identified by silicon nuclear magnetic resonance spectroscopy [3]. The ^{29}Si NMR spectrum shows two broad signals centered at about -66 ppm and -55 ppm relative to TMS.

These signals show that the resin predominantly consists of ladder- and cage-type T unit structures with ring subunits containing 4 siloxy units (signals at -66 ppm) resp. 3 siloxy units (-55 ppm). Siloxanes bearing end groups such as OH and OC_2H_5 appear at about -57 ppm.

For technical application, methyl silicone resins are thermally cured - usually by addition of a catalyst. Thus thermal analysis is the prefered method for examination of curing as well as for thermal stability of the resin. We used thermogravimetry (TG), differential scanning calorimetry (DSC) and evolved gas detection (EGD) for thermal analysis of Wacker Resin MK. Fig. 1 shows DSC, TG, DTG curves of Resin MK in air. Heating rate in all experiments was 10 K/min.

Two exothermal peaks can be seen at 270 °C and 470 °C in the DSC diagram. The peak at 270 °C does <u>not</u> show thermal curing of the resin but a consecutive reaction (chemical or physical transformation) <u>after</u> curing. This peak cannot be attributed - as described in a publication - to oxidation of the ethoxy end groups [7]. This interpretation is supported by the TG analysis. The mass loss on curing which is caused by cleavage of the resin end groups will come to an end <u>before</u> appearance of the DSC peak.

According to TG measurement, there are at least two chemical processes between 200 and 300 °C. This can be concluded from the DTG graph. We analyzed the split off products in order to support the TG measurement and we found that at first SiOH end groups have reacted and water is set free. At slightly higher temperatures (approx. 250 °C), ethoxy end groups are involved in the reaction and ethanol is produced as additional volatile product [11].



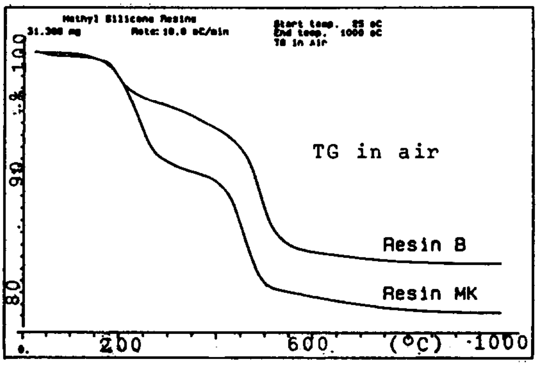


Fig. 1 (left). TG, DTG and DSC of Wacker Resin MK in air, heating rate 10 K/min.

Fig. 2 (right). TG of methyl silicone resins in air.

If all chemically analyzed end groups react under condensation and release of water and ethanol, a mass loss of approx. 4% should be expected in this curing step. We found, however, a mass loss of 10.5%!
The main reason for this high mass loss is the formation of isolated cage-like $(CH_3SiO_{1.5})_n$-structures, which sublimate and lead to a loss of resin. We found no diethly ether which is expected to be the volatile compound formed on condensation of two $SiOC_2H_5$ end groups, nor did we find ethene, which formally could be formed as an elimination product from $SiOC_2H_5$.
The second step of cleavage shown by TG between 400 and 550 °C can be easily explained. The Si-bound methyl groups in the resin are oxidized, CO_2 and H_2O are released. SiO_2 remains in the crucible. This strongly exothermal oxidation reaction (about 5000 J/g) is responsible for the peak with a maximum at 470 °C in the DSC measurement.

To demonstrate that especially thermogravimetry is a helpful tool to distinguish between resins with identical chemical composition, e.g. type and content of end groups resp. molecular weight but with different curing behavior or cross-linking in the siloxane network, we have done TG in air with another methyl silicone resin. Resin B is a laboratory product with an identical composition to Resin MK.
TG (Fig.2) detects that

- o Curing is faster in resin B.
- o Lower mass loss between 200 and 300 °C in resin B. Only end groups are given off, but no volatile methyl silsesquioxanes.
- o Thermal stabilities of siloxane structures formed on curing are different.
- o After oxidative processes took place in the resins, the yield of SiO_2 at 800 °C is higher for resin B.

In inert gas atmosphere, pyrolysis reactions will start from 500 °C in Resin MK (TG, two steps, Fig.3). Step 1 with a mass loss of approx. 3% leads to a product with slightly reduced C-content. Inspite of the pyrolysis, the resin is still colorless and transparent. Severe decomposition reactions start about 650 °C which will gradually darken the resin. Eventually, at a temperature of 1000 °C a porous black solid remains. Mass loss

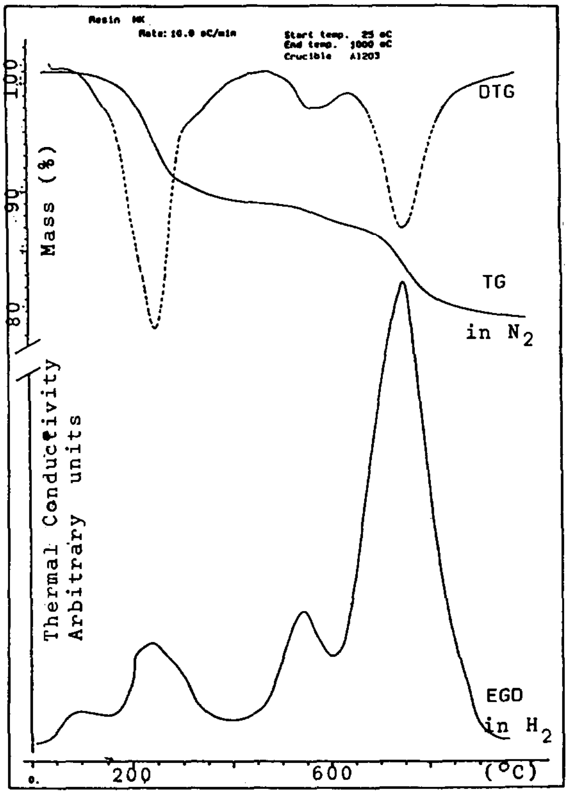


Fig. 3. Separately measured TG in N_2 and EGD in H_2 of Resin MK.

of this second pyrolysis step is around 8.5%. For examination of the evaporating gaseous substances we used EGD (H_2) as a thermal method. Fig. 3 summarizes the EGD curve as well as the - separately taken - TG/DTG curves. The EGD shows a peak in the curing step (200 - 300 °C) which detects the release of two volatile substances (water and ethanol). The released cage-like siloxanes condense before reaching the detecting device and are not registered. The two EGD peaks of pyrolysis at 570 and 750 °C are nearly symmetrical.

Additional pyrolysis-GLC-measurements show that methane is released at 570 °C, and at 750 °C methane, H_2 and traces of ethane are set free.

Based on thermal analyses and the complementary elemental and GLC analyses we propose the following compositions for the volatiles and the remaining solids on pyrolysis.

- On pyrolysis between 500 and 600 °C, one molecule of methane is removed from 8 $CH_3SiO_{1.5}$-units. As the isolatable solid residue formed in this pyrolysis step we formulate a methyl silicone with Si-CH_2-Si-grouping.
- In the second step of pyrolysis between 650 and 850 °C, CH_4 and H_2 is evolved in a ratio of approx. 1:2 mol; a black solid with composition $SiO_{1.5}C_{0.6}(H_x)$ remains in the crucible. Although the C,H-analysis does no longer show any hydrogen content for this product, the IR spectrum - as one can see from the CH-absorption band - still proves a residual H-content bound to carbon.

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11 Solid-state NMR spectroscopy of the tempered resins also leads to the result that the $SiOC_2H_5$ end groups will only react at higher temperatures compared to condensation of SiOH end groups. O.Schneider, manuscript in preparation.