THERMAL ANALYSIS OF SILICONE CAOUTCHOUC POLYMERS AND SILICONE RUBBERS, II

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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:

\[ X[(\text{CH}_3)_2\text{SiO}]_n\text{H} \rightarrow [(\text{CH}_3)_2\text{SiO}]_y \]

where \( X \) is an OH or CH\(_3\) group,

\( n \) is the number of (CH\(_3\))\(_2\)SiO units, and

\( y \) is the number of (CH\(_3\))\(_2\)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°C, 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>
<thead>
<tr>
<th>Samples</th>
<th>( k ), hour(^{-1})</th>
<th>( k_{\text{relative}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPR-3003/50 + thermal stabilizer</td>
<td>( 2.6 \cdot 10^{-4} )</td>
<td>0.7</td>
</tr>
<tr>
<td>VPR-3162</td>
<td>( 2.6 \cdot 10^{-4} )</td>
<td>0.7</td>
</tr>
<tr>
<td>VPR 3003</td>
<td>( 3.1 \cdot 10^{-4} )</td>
<td>0.9</td>
</tr>
<tr>
<td>VPR 3176 C 1</td>
<td>( 3.3 \cdot 10^{-4} )</td>
<td>0.9</td>
</tr>
<tr>
<td>Polymer V 1400</td>
<td>( 3.6 \cdot 10^{-4} )</td>
<td>1</td>
</tr>
<tr>
<td>VPR 3175 C 1</td>
<td>( 6.4 \cdot 10^{-4} )</td>
<td>2</td>
</tr>
</tbody>
</table>

*J. Thermal Anal. 32, 1987*