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

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

*DEPARTMENT OF INORGANIC CHEMISTRY, TECHNICAL UNIVERSITY OF BUDAPEST, H-1521 BUDAPEST, HUNGARY
**WACKER CHEMIE GMBH, MÜNCHEN D-8000, G.F.R.

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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 multi-component 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,
—their thermal stability,
—their resistance to oxidation,
—their gas (O₂, N₂) 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

\[ E_{\text{Si-C}} = 69.3 \text{ kcal/mol} \]

and

\[ E_{\text{Si-O}} = 88.2 \text{ kcal/mol}. \]

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.

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