Melt rheology and structure of silicone resins

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Abstract Rheological investigation and X-ray analysis of silicone resins have been performed to get a fundamental understanding of the relationship between melt rheology and structure. Rheological properties of the melts of silicone resins were characterized by dynamic shear measurements. Samples were a series of silicone resins having different side groups, such as methyl, phenyl, methylenphenyl, and propylphenyl. A time-temperature superposition based on the WLF rule was successfully applicable. The free volume fraction at the glass transition temperature and the free volume expansion coefficient were estimated from the C1 and C2 values of the WLF-equation. The loss modulus G" was found to be proportional to the angular frequency in a double-logarithmic plot over a wide frequency range. However, the storage modulus G' exhibited a bending in an intermediate frequency region for all silicone resins. The shape of the G' curve is unexpected from the results of gel permeation chromatography (GPC) and differential scanning calorimeter (DSC), which demonstrate that the silicone resins are amorphous polymers of relatively low molecular weight. To get more insight into the rheological properties of the silicone resins which indicate a heterogeneous structure, X-ray analysis was carried out. The X-ray measurement displayed two peaks, one broad peak around 4.5 Å of d-spacing which corresponds to a random amorphous structure, and the other higher intensity peak from 8.5 Å to 12 Å. This peak strongly depends on the size of organic side groups. From the rheological characterization and the X-ray analysis, it can be concluded that the silicone resins consist of two components; one of them shows a random amorphous and the other a regular structure even in the molten stage.

Key words Silicone resins · Melt rheology · Dynamic mechanical behavior · Structure · X-ray analysis

Introduction

The development of ceramic materials in the system Si-C-O from polymers as precursors has attained a considerable interest, since the breakthrough by Yajima et al. (1975, 1976) making silicon carbide (SiC) based fibers from polycarbosilane. The Si-C-O ceramics could be obtained from the conventional ceramic technology. Rice (1983) and Greil (1995) mention that one of the main advantages of the route using polymers as precursors over the conventional ceramic manufacturing method is wider possibilities of product shaping, such as fibers, films, membranes, bulk components, and foams. Such examples can be found in the papers by Greil (1995) and Colombo and Modesti (1999), and in the book of Bill et al. (1999).
Because of easy handling characteristics in the ambient atmosphere, silicone polymers as precursors, usually referred to as silicone resins, have been frequently studied among various polymers used as precursors since the reports of White et al. (1987a, b). General characteristics of silicone resins have been published by Baney et al. (1995) and Tanimura (1993). Silicone resins have been commercialized for many years and utilized with solvents for heat resistant coatings. Monomers of silicone resins are mostly three functional alkoxyl silicates. Silicone resins are, thus, known to be nonlinear polymers containing large amounts of silsesquioxanes, which have the formula RSiO$_{3/2}$ where R is a hydroxyl, alkoxyl, alkyl, or aryl group, etc. This feature is quite different from polydimethylsiloxane, which has a linear structure.

It is described by Baney et al. (1995) and Tanimura (1993) that silicone resins generally include a small amount of reactive groups, such as hydroxyl and alkoxyl groups, which start cross-linking reactions induced by temperature. White et al. (1987a, b) have first demonstrated that silicone resins can become useful ceramics through shaping processes in the molten stage, followed by a cross-linking reaction, and a subsequent pyrolysis. In spite of the importance of melt rheology for the shaping processes, however, investigations about the melt rheology of silicone resins were not reported until now. The further development of ceramics from polymers as precursors requires an interdisciplinary approach from various fields including rheology. The necessity of melt rheology studies for the development of ceramics from polymers as precursors was also emphasized by Baney and Chandra (1988).

This paper deals with the melt rheology of a series of silicone resins. The aim is to understand their fundamental rheological properties. Furthermore, the structure of silicone resins is discussed by combining rheological properties with molecular weight, thermal properties, and X-ray analysis.

### Experimental

**Samples**

The tested samples were commercially available silicone resins, which were all kindly supplied by Wacker-Chemie GmbH, Germany. These silicone resins were methyl, phenyl, methylphenyl, and propylphenyl silicone resins. They are summarized in Table 1. Samples were stored in a refrigerator at around 2 °C to prevent a further condensation reaction, which very slowly proceeds even at room temperature during one year’s storage. All samples are solid at room temperature and they are either in the form of powders or flakes. According to the manufacturer, remaining hydroxyl and ethoxy groups can act as functional groups for further cross-linking reactions, which generate water and ethanol by increasing temperature:

\[
\text{Si-OH} + \text{CH}_3\text{CH}_2\text{O-Si} \rightarrow \text{Si-O-Si} + \text{CH}_3\text{CH}_2\text{OH} \tag{1}
\]

The weight percentage of the functional groups and the gases generated during cross-linking are summarized in Table 1 based on the manufacturer’s catalog. All samples were characterized and investigated as received.

**Molecular and thermal characterization**

Molecular properties were characterized by GPC (gel permeation chromatography). The GPC columns were calibrated with 12 narrowly distributed polystyrene (PS) standards with molecular weights ranging from $5.8 \times 10^2$ g/mol to $2.18 \times 10^4$ g/mol. It should be noted that the obtained molecular weight results are based on the assumption that silicone resins are linear polymers, though it is well known that they have non-linear structures. Thermal properties were characterized by DSC (differential scanning calorimetry, TA Instruments) and TGA (thermal gravimetric analysis, TA Instruments). The heating and cooling speed of DSC measurement is 5 °C/min. The weight loss in air at 100 °C for 2 h was evaluated with TGA.

**Melt rheological measurement**

The dynamic mechanical shear behavior of the silicone resins was measured using a strain-controlled rheometer (ARES, Rheometrics Scientific) under air between 60 °C and 110 °C where no cross-linking reaction and no degradation occurs. The experimental window with respect to temperature and time where cross-linking and degradation do not occur was determined from dynamic shear rheology for every sample.

**X-ray diffraction (XRD) analysis**

The effect of temperature (30, 90 °C) was examined using a diffractometer of CuK$_\alpha$ radiation (X-PERT-MPD, Philips with a temperature control). The influence of types of silicone resins on the microstructure was studied with another diffractometer of CuK$_\alpha$ radiation (Diffractometer-5000, Siemens). The intensity of XRD was measured between 5° and 40° as a function of the diffraction angle of 2θ.

**Results and discussion**

**Thermal property and molecular properties**

Silicone resins start cross-linking reactions as the temperature increases. In the temperature range showing no reaction, the first and the second heating of DSC was measured for all silicone resins. A step transition but no melting peak was observed for all resins in the temperature range between –50 °C and 100 °C. The DSC curves support the assumption that the silicone resins are typical amorphous polymers. It is known that the glass transition temperature for amorphous polymers is slightly influenced by prehistory and cooling rate. The glass transition temperature was, thus, determined from the curve of the second heating. Table 1 summarizes the glass transition temperatures. The DSC analysis suggests that the silicone resins can be considered as amorphous with glass transition temperatures between 40 °C and 46 °C. Table 1 also lists the weight loss of silicone resins observed from TGA. The weight losses at 100 °C for 2 h under air are very small.