

TRIMETHYLSILYLATED SILICA AS RHEOLOGY MODIFIER FOR SILICONE RESINS

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Abstract Trimethylsilylated silica was synthesized through hydrolytic condensation of tetraethoxysilane followed by trimethylsilylation. Rheological properties of the silicone resin with trimethylsilylated silica as modifier were studied. It turned out that the particle size of silica was important to the rheological behavior of the modified resin. Trimethylsilylated silica of medium particle size shows the strongest tendency of forming physical network in the resin.

Keywords Silica, Trimethylsilylation, Rheology modifier, Silicone resins

INTRODUCTION

Silicone resins possess excellent electrical properties and thermal resistance. They are used as electrical insulating coatings and adhesives in highly demanding areas. The resins consist of multifunctional prepolymers of low molecular weight, the curing becomes effective at high temperatures through condensation of the silanol groups^[1]. As the melt viscosity of silicone resins drops sharply with increasing temperature, a rheology modifier is required in order to make consistent coating layers, or to avoid starved adhesive bond lines. Minerals and metal oxides can be added to the resin to modify the rheological properties. However, they are not suitable for the preparation of very thin coatings.

Silica of different particle size can be easily made through the hydrolysis of tetraethoxy-silane^[2], and the property of the particle surface can be modified by trimethylsilylation^[3-5]. It has been found that trimethylsilylated silica is compatible with silicone resins. In the present article the rheological properties of the silicone resins with trimethylsilylated silica as modifier are studied.

EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS), ethanol, aqueous ammonia solution (28%) and toluene were of analytical reagent quality produced by the Beijing Chemical Factory. Hexamethydisilazane, methyl-trichlorosilane and dimethyldichlorosilane were chemical reagents from the Second Chemical Factory of Beijing.

Synthesis of Trimethylsilylated Silica

Nearly mono-dispersed silica was synthesized through the hydrolysis of TEOS in ethanol, using ammonia as the catalyst as reported by Stöber, Fink and Bohn^[2]. To 570 mL ethanol, 62.4 g TEOS and 30 g aqueous ammonia solution were added, the mixture was stirred at room temperature for 4 h to effect the hydrolytic condensation. By changing the concentration of ammonia, silica samples of different particle sizes were prepared (Table 1).

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Table 1. Particle size of silica

Code	Silica-20	Silica-40	Silica-80
Concentration of ammonia (mol/L)	0.185	0.37	0.74
Particle size (nm)	20	40	80

The ethanol dispersions of silica were concentrated to ca.10% by distillation. An equal amount of hexamethyldisilazane based on the content of silica was added, and the mixture was stirred at room temperature for 10 h to effect the trimethylsilylation. Then toluene was added, and ethanol was removed by distillation. Stable dispersions of trimethylsilylated silica in toluene were thus obtained. The particle size of the silica did not change during the above treatment (Fig. 1). Trimethylsilylated silica samples of particle sizes 20 nm, 40 nm and 80 nm are designated as Silica-20M, Silica-40M and Silica-80M, respectively.

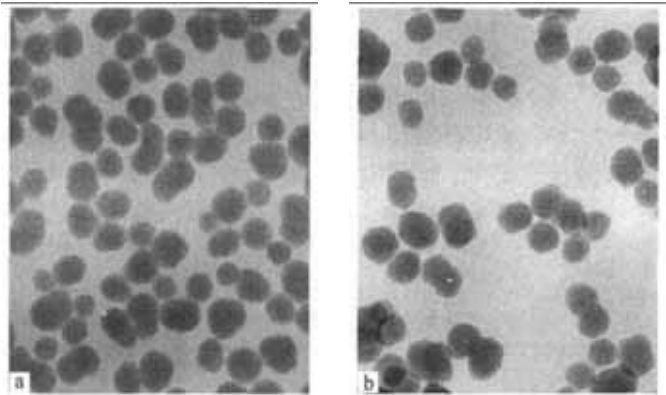


Fig. 1 Electron micrographs of a) Silica-80 and b) Silica-80M
a) $\times 60000$, b) $\times 60000$

Preparation of Silicone Resins

The silicone resin used in this study was prepared through hydrolytic condensation of methyltrichlorosilane and dimethyldichlorosilane in toluene. The gel time of the resin at 250°C was 3 min. To prepare the modified silicone resins, the toluene dispersions of trimethylsilylated silica were slowly added to the toluene solution of silicone resins while stirring.

Characterization

The particle size of silica was estimated from the electron micrographs. The concentration of trimethylsilyl group on the silica surface was determined by solid ^{29}Si -NMR on a Bruker-AM 300 instrument at 59.6 MHz with $t_d = 20$ s. SiO_2 was used as the standard to measure the chemical shift of ^{29}Si . The unit ratio of $(\text{CH}_3)_3\text{Si}-\text{O}-$ to SiO_2 was calculated according to the integrated signals in the spectra as shown in Fig. 2.

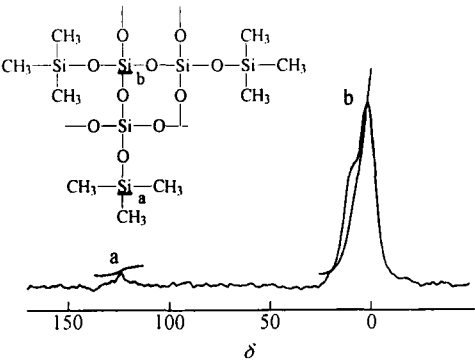


Fig. 2 ^{29}Si -NMR spectrum of Silica-20M

For the characterization of rheological properties of the silicone resins, the included solvent was removed in vacuum at 80 °C. The rheological measurement was carried out at 100 °C, using a Rheometer DSR 200 (Rheometric Co.). The parallel plates with 25.000 mm diameter and 1.000 mm gap were used. The accuracy of experimental temperature is ± 0.1 °C. The specimen loaded between the plates was allowed to stand for 2 min after adjusting the gap in order to release the residual stress. The rheological characterizations including steady stress and dynamic stress at a frequency of 1 Hz ramp tests were performed on the same sample.

For the measurement of sag during the curing, a strip of the resin having a size of 50×5×0.1 mm (thickness) was coated on a glass sheet. The sheet was vertically placed in an oven, and cured at 250 °C for 4 h. The dripping distance was recorded.

RESULTS AND DISCUSSION

The Characteristic of Trimethylsilylated Silica

Silica particles formed by the hydrolytic condensation of TEOS in basic medium have a dense core with silanol groups on the surface. According to Iler^[6], the number of silanol group can be calculated:

$$N = 24.6 d^2 - 17.6 d + 4.18$$

where d is the diameter of the particle. The area occupied by each silanol group can be calculated likewise. For Silica-20, Silica-40 and Silica-80, each silanol group accordingly occupies ca. 0.13 nm².

Even if the reaction between hexamethyldisilazane and silanol is very fast at room temperature, owing to the steric hindrance induced by the bulky (CH₃)₃Si—O— group which has a dimension of about 0.45 nm², only a part of the silanol groups on the silica particles can be tri-methylsilylated. From the integrated signals of (CH₃)₃Si—O— and SiO₂ in the ²⁹Si-NMR spectrum (Fig. 2), the concentration of the (CH₃)₃Si—O— group was calculated. For Silica-20M, about 32% of the silanol group was trimethylsilylated. Although this method is not precise enough to allow us to make a statement on the influence of the particle size on the degree of trimethylsilylation, we are convinced that roughly 2/3 of the silanol groups is still retained on the silica particles.

Rheological Behavior of Silicone Resins Modified with Trimethylsilylated Silica.

The silicone resin without filler behaved as a Newtonian fluid. In the presence of trimethylsilylated silica, the change of the shear stress or the viscosity with the shear rate deviated from linearity. The non-Newtonian behavior is attributed to the interaction of silica particles in the fluid. Based on an equal level of the additive, Silica-40M showed the most significant effect, as shown in Figs. 3 and 4.

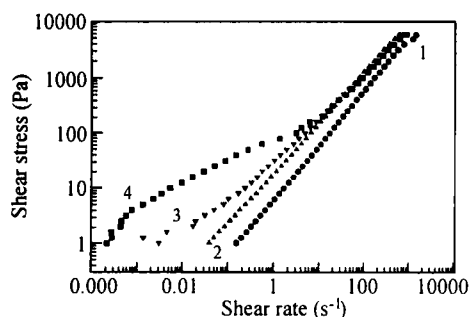


Fig. 3 Stress versus shear rate at 100 °C for the silicone resin containing 20 phr of trimethylsilylated silica of different particle size
1) control, 2) Silica-80M, 3) Silica-20M, 4) Silica-40M

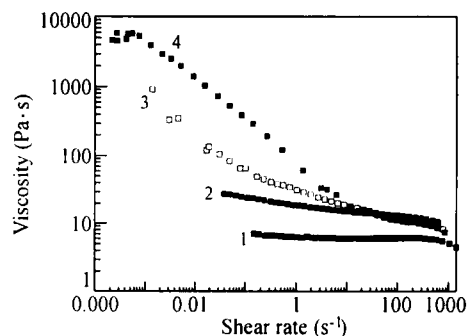


Fig. 4 Viscosity versus shear rate at 100 °C for the silicone resin containing 20 phr of trimethyl-silylated silica of different particle size
1) control, 2) Silica-80M, 3) Silica-20M, 4) Silica-40M

In the rheological curve for the resin containing 20 parts of Silica-40M per 100 parts of resin (phr), three flow regions are obvious. There is a Newtonian region at very low shear rates, where the aggregates of filler particles are not disturbed. In the next region the viscosity reduces with the increase of shear rate as a result of

breakdown of particle aggregation. As the shear rate increases further, the curve enters the second Newtonian region, where the particle aggregation is completely disrupted.

The low-shear Newtonian region is not shown in the rheological curves for the resins modified with 20 phr of Silica-20M or Silica-80M in the shear rate range of the measurement.

Through dynamic measurements in linear visco-elastic regime, the storage modulus G' and the loss modulus G'' can be separated. $G' = G''$ is characteristic for a system in the critical gel state^[7].

It was found that G' was negligible for the neat resin. For the resin with 20 phr of Silica-40M as modifier, G' and G'' crossed over at a shear stress of ca. 2 Pa (Fig. 5). Under a stress lower than this value, the resin behaved as a gel. For the resins modified with 20 phr of Silica-20M or Silica-80M, the gel state did not show up in the stress range of the measurement.

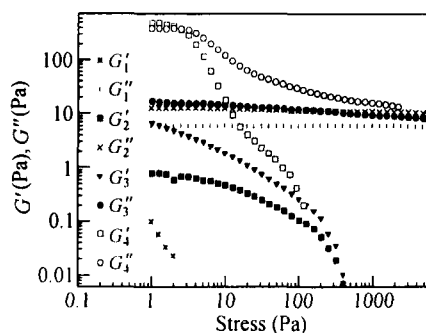


Fig. 5 G' and G'' versus shear stress at 100°C for the silicone resin containing 20 phr of trimethylsilylated silica of different particle size, frequency 1 Hz

Subscript: 1) control, 2) Silica-80M, 3) Silica-20M, 4) Silica-40M

Sag of the Silicone Resin upon Curing

On use of silicone resins for adhesive and coating purposes, they should be able to flow in order to facilitate complete wetting of the substrates yet their fluidity should be appropriate in order to avoid the formation of starved glue line. Therefore, careful adjustment of the sag resistance is of critical importance to the success of the application.

Table 2. Sag of the silicone resin cured at 250°C (mm)

Level of silica (phr)	0	10	20	30	40
Silica-80M	56	45	18	7	0
Silica-40M	56	13	0	—	—
Silica-20M	56	37	10	0	—

It is seen in Table 2 that the sag of the silicone resin can be modified with trimethylsilylated silica. Silica-40M was most effective in improving the sag resistance as expected on the basis of the rheological data given above, and Silica-80M was least effective. In the presence of 20 phr of Silica-40M, particles formed a physical network, therefore, the resin became sag free upon curing.

Influence of the Particle Size

Trimethylsilylated silica-modified silicone resins are disperse systems. It is interesting to note that the influence of the particle size was not monotonic. According to the G' values of the modified silicone resins under a definite shear stress and the sag of the resin upon curing, it can be concluded that the influence of the trimethylsilylated silica on the rheological behavior based on an equal weight percentage declined in the following order:

Silica-40M > Silica-20M > Silica-80M.

Silica-40M of medium particle size showed the strongest effect on the rheological behavior of the resin.

The effect of the particle size is two fold. Small particles have a greater particle number and higher specific

surface area. Therefore, they should exert a greater influence on the rheological properties. On the other hand, the small particles have less steric hindrance in the trimethyl-silylation. Therefore, fewer silanol groups would be available for the inter-particle interaction.

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