

A Review Study on the Development of Silicone Resin Polymer

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Abstract

This article reviews industrial status and applications of silicone resin polymer. The background of silicone resin is introduced in this article to explain the production costs and supply availability of various silicones. Just around the time of the Second World War, various silicone polymers were synthesized on a large scale and widely commercialized. They are available as electric insulator coatings, surface treatments for glass materials and heat resistant oils. Silicone resins are able to accept various kinds of fillers, plasticizers, blowing agents and cross-linking agents. Silicone can be utilized for the construction of a wide variety of medical devices owing to its superior stability as well as its outstanding rubber elasticity. In this work, thermal degradation of linear silicones is also discussed.

Keywords: Silicones, Silicon Chemistry, Thermal Degradation, Industrial Applications and High Temperature Reaction.

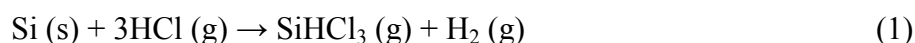
Introduction

Silicon is an element whose atoms have similar linking properties to those of carbon, but it is stable at much higher temperatures. To utilize the properties of silicon, certain plastics, called silicones have been developed based on the element. Although they are much more expensive, they contain excellent properties. These super materials are available as oil, plastics and rubbers. The stability of silicones under widely varying service conditions make them valuable materials for applications such as laminates in the aerospace industry, gaskets and seals for engineering purposes and cable insulation for aircraft electrical systems. Silicones can be used for a lot of things. Silicones are inorganic polymers, i.e., there are no carbon atoms in the backbone chain. The backbone is a chain of alternating silicon and oxygen atoms. Each silicone

has two groups attached to it, and these can be any organic groups. Silicones can stand high temperatures without decomposing, but they have very low glass transition temperatures. Silicone Resin is a colorless to light gray, transparent or translucent and viscous liquid. It is almost odorless. Just around the time of World War II, various silicone polymers were synthesized on a large scale and widely commercialized.

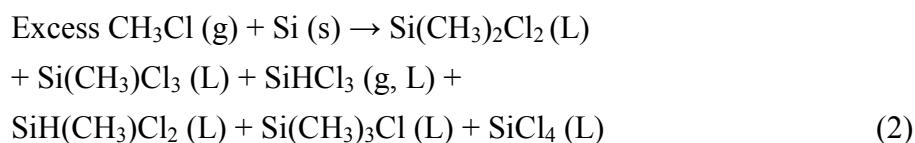
Background of Silicone Resin

Silicon is industrially produced at present on a tremendous scale. The origin of silicon is high purity mineral silica sand. Such silica sand is typically reduced by carbon in an electric arc furnace at 3,000 °C. The silicon obtained, of 98–99% purity, is called metal-grade silicon. It is used as a component in various alloys of Fe and Al and also in the electronics and silicone polymer industry. For the uses in electronics, the metal grade silicon is reacted with SiCl₄ and hydrogen to yield HSiCl₃. This compound is a transparent liquid with a boiling point of 31.8 °C. The liquid nature of HSiCl₃ means that the compound can be distilled for purification. After the distillation, reduction by hydrogen and the Czochralski process, a single crystal of silicon with extreme high purity is obtained. The unique properties of the pure silicon, such as its semi conductive nature, acceptance of doping and formation of insulating silica layers on the surface during oxidation, are presently well known. The application of Si for solar cells is increasing its importance in recent times. SiCl₄ is an important recycled product in the pure silicon industry. SiCl₄ is also useful for the synthesis of various organosilicon compounds. Kipping systematically investigated organosilicon monomers and polymers derived from SiCl₄. The first silicone resin, reported by Kipping as a glue-like product, did not however attract any kind of industrial attention but the polymeric nature of these glue-like silicones attracted the attention of Hyde and related groups at Corning Glass Works. The company developed the industrial process for silicone resin production on the basis of the SiCl₄—Grignard reagent combination and opened the doors to silicone resin commercialization. The silicone resins were found to be highly compatible with glass materials. Utilization as binders for glass fibers and scratch resistant coatings on glass plates was promoted. The main silicone investigated by Hyde was a kind of polyethylphenylsiloxane (PEPhS). The synthesis of PEPhS with using Grignard reagent is, however, a multi-step process. Grignard reagents are highly flammable, and the synthesis requires a large amount of metallic magnesium. The silicone thus obtained is rather special and a little far from conventional plastic, like polyethylene, polyamide or phenolic resins, widely produced from petroleum industry raw materials. In order to overcome such economical and industrial problems, Rochow developed a direct synthesis process for organosilicon monomers without the aid of Mg in 1940. This was essential progress in the silicone industry. According to Rochow, SiHCl₃ is formed from Si and HCl as

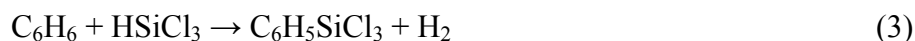


In the Rochow process, CH₃Cl was introduced in a reaction column instead of HCl, and grains of Cu-Si alloy were loaded in the column. Cu was expected to act as a catalyst. A liquid product i.e., mixture of methylchlorosilanes is obtained by the

following reaction:



This is intrinsically a gas-solid reaction. Thus, continuous operation is possible by adjusting the rate of introduction of CH₃Cl gas, Si, and Cu powders into a reactor. By fractional distillation, each compound can be isolated with high purity. Si(CH₃)₂Cl₂ has the highest boiling point, while Si(CH₃)₄ has the lowest boiling point, except for the starting CH₃Cl. Si(CH₃)₂Cl₂ is the most valuable component in the obtained mixture, because it forms linear Si-O-Si chains after the hydrolysis. However any kind of methylchlorosilanes is useful for tailoring silicone resins, oils, greases, rubbers and varnishes. On the other hand, phenyl chlorosilanes are also useful monomers in the silicone industry. It is possible to synthesize phenyl chlorosilanes by direct reaction of chlorobenzene (C₆H₅Cl) and the Si-Cu alloy. Higher temperature (400–500 °C) and a larger amount of Cu content (30 mass %) are however required. Compared to such direct synthesis using the Si-Cu alloy, the following dehydration or dehydrochloration reaction is more efficient and widely available for the production of phenyl chlorosilanes and vinyl chlorosilanes:



The introduced HSiCl₃ is obtained by the fractional distillation of the product of Rochow process, or is obtained from the products in the pure silicon industry. From a cursory glance at such chemical processes, we can get a sense of how polymers so unique as the silicones have been widely produced at relatively low cost, and what kind of silicone is more popular from the viewpoint of the industry [1].

Thermal Degradation of Linear Silicones

Silicone is superior in heat and chemical resistance as compared with ordinary polymers. Silicone oils are necessary component in high vacuum systems. Elastic silicone rubber materials are used in medical and chemical applications. In most cases, linear polysiloxane or partly cross-linked polysiloxane are used in commercialized products. Si-O bonds in siloxane chain are flexible as compared with C-C bonds, and silicones intrinsically maintain their liquid nature over a wide temperature region. For example, glass transition temperatures of polydimethylsiloxane (PDMS) or polymethylphenylsiloxane (PMPhS) are –127 °C and –86 °C, respectively [2-3]. Thermal degradation of PDMS with complete linear structure proceeds at 290–600 °C with formation of cyclic oligomers. In an inert atmosphere or vacuum, a trimer (Si₃O₃(CH₃)₆) and tetramer (Si₄O₄(CH₃)₈) are the major components in the decomposition gas. Chemical species with higher molecular weight, like a hexamer and an octamer, are also found as components [4]. The low

activation energy (40 kcal/ mol) suggests the existence of a stable transition state, which promotes the degradation of the silicone resin. The linear siloxane chains can easily make intermolecular contact because of the flexible nature of the chains and the Si d-orbital interactions. Thus, the degradation proceeds by simultaneous rearrangement of Si-O bonds with expulsion of cyclic oligomers. It is interesting that PDMS is obtained not only from hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ but also from ring opening polymerization of the cyclic tetramer $(\text{Si}_4\text{O}_4(\text{CH}_3)_8)$. In other words, the decomposition process of PDMS is a kind of depolymerization. In the presence of oxygen, the degradation process of linear silicones becomes complex.

Industrial Status of Silicone Resin

Nowadays, a few kinds of silicone resins are commercialized under the PMSQ name. Wacker-Belsil PMS MKTM is available from Wacker Chemie AG. It is white powder with the proposed chemical structure $(-\text{CH}_3)_2\text{Si}(\text{O}_{3/2})_n$ [5]. YR 3370TM is a transparent hard resin. Kim et al. used polymer blend or filler loaded YR 3370TM as starting materials for SiC or silicon oxycarbide based porous ceramics [6-7]. The ceramization of YR3370TM was also well characterized [8-9]. Figures 1 (a) and (b) show a TG curve and ²⁹Si-NMR spectrum of YR3370TM during the pyrolysis. SR 350TM, which is a kind of silicone resin with low carbon content and with highly branched structure is available from General Electric Silicone Products. The resin is softened at 30 °C and becomes fluid at 90 °C. It is also soluble in most organic solvents like toluene, ketones, alcohols and ether. Some resins with the PMSQ name are available mainly in the field of cosmetics.

Applications of Silicone Resin

Polydimethylsiloxane (PDMS) or silicones have been utilized extensively for the construction of a wide variety of medical devices owing to its superior stability as well as its outstanding rubber elasticity. At present, silicone finds its way into an extremely wide range of medical and industrial applications. Silicone resin is an inorganic polymer, having properties depending on the molecular weights and alkyl groups in its structure [10]. The utilization of poly silsesquioxanes (PSQ) in the field of ceramic matrix composites has been reported [11-12]. The synthesis of heat resistant ceramic foams by using the viscoelastic nature of silicone resins was widely examined. Colombo et al. reported Si-O-C ceramic foam synthesis from the mixtures of SR350, monomers of polyurethane and a blowing agent (CH_2Cl_2) [13]. Silicone resins are thus able to accept various kinds of fillers, plasticizers, blowing agents and cross-linking agents. Control of cell size, density and connectivity of foamed cells are intrinsically possible by using various methods developed in the plastic foaming industry field. Since commercialized silicone resins with high ceramic yield usually conserve some amount of silanol groups in their molecular structures, the resins often accept chemical modification by various alkoxides. The uses of the alkoxides as cross-linking agents guarantee the atomic level distribution of introduced elements in the starting resin networks, and homogeneous structure evolution during the pyrolysis

is expected. In particular, high temperature properties of pyrolyzed materials, like oxidation resistance, corrosion resistance or creep resistance, are probably influenced by additional elements.

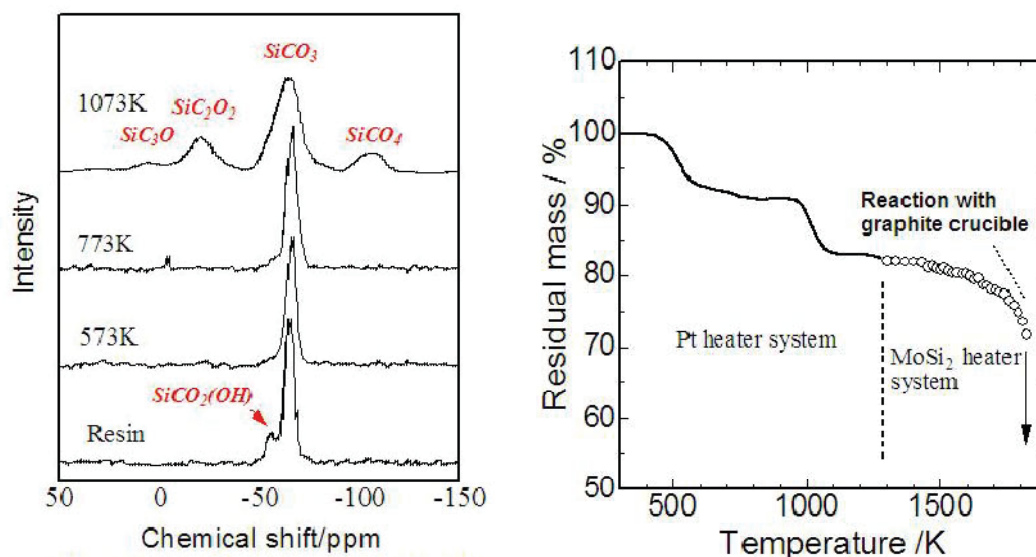


Figure 1: (a) Results of TG analysis on YR3370TM resin in carbon rich atmosphere (10 K/min up to 1473 K, 3 K/min beyond 1473 K and holding at 1873 K for 3 h) [8]; (b) ^{29}Si -NMR spectrum of YR3370TM pyrolyzed at various temperatures [9].

Conclusions

This review article is mainly focused on background, industrial status and applications of silicone resin. Thermal degradation of linear silicones is also included in this work. Silicone resins have been used as supporting players in ceramic synthesis processes. Silicone resins are old and classic materials developed at the early years of the 20th century. In future, Silicone resin can be used as a promising material for promoting the precursor method availability in wide industrial applications.

Acknowledgement

The authors thank Prof. A.P. Tiwari, Department of Chemistry, D.A.V. (P.G.) College, Bulandshahr (U.P.) India, for the valuable discussions and guidance without which this review article would not have come up.

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