

Polysiloxanes: Synthesis and Purification of Silicon Obtained from Iran's Domestic Micronized Sand

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ABSTRACT

Polysiloxanes are prime examples of inorganic polymers with unique combination of high temperature stability and excellent low temperature elastomeric properties. These materials have alternating silicon and oxygen atoms with organic groups linked to silicon atoms. There are two major routes to polysiloxanes: Kipping-Grignard and the catalytic reaction. The first step of both routes involves the reductive conversion of sand into silicon. In this paper, the main features and industrial routes of preparing polysiloxane are discussed and the results of preparation and purification of silicon using domestic micronized sand are reported. Silicon is a starting material for preparing dichlorodimethylsiloxane which is used extensively in manufacturing of silicones of numerous applications, such as silicone rubber.

Key words: polysiloxane, silicon, synthesis, purification, properties and application

INTRODUCTION

The area of high molecular weight polymers with inorganic elements in their backbone is attractive for those researchers who are interested in synthesizing new class of polymers with special properties not available with conventional organic polymers. In general, inorganic high polymers possess a unique combination of high temperature stability and excellent low temperature elastomeric properties [1-4].

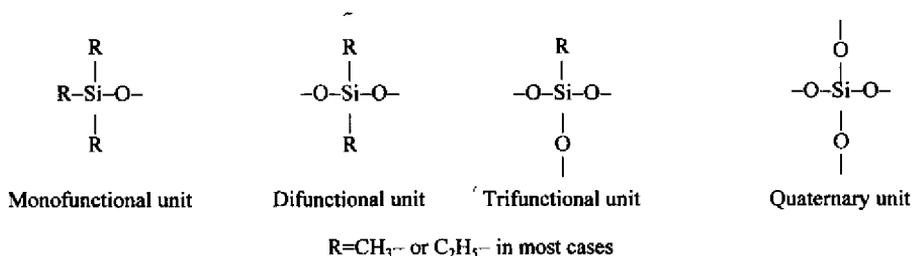
Polysiloxanes, frequently referred to as silicones, are commercially important high polymers which have found many applications. The polymer backbone consists essentially of silicon and oxygen

with organic groups linked to the silicon atoms [5, 6].

Polysiloxanes are considered as hybrid polymers, because they possess a combination of useful properties as both organic and inorganic materials. These compounds exhibit thermal stability, as shown by materials such as the silica and silicates, and stability and plasticity of organic polymers to some extent.

Organic groups can be small groups like methyl, alkyl, cyclic structures such as phenyl or unsaturated groups as vinyl, linked to silicon. So, the basic structure of silicones is a more or less complicated network of alternate Si and O atoms in which some valences are occupied by organic groups [7, 8].

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Scheme I

The structure of different silicones is basically composed of four repeating units presented as in Scheme I.

The backbone of the polymer obtained from these units contains silicon atoms bound to oxygen atoms, with organic groups linked to silicon atoms. The number of oxygen atoms bonded to a central silicon atom dictates whether a side chain or any cross-linking is possible.

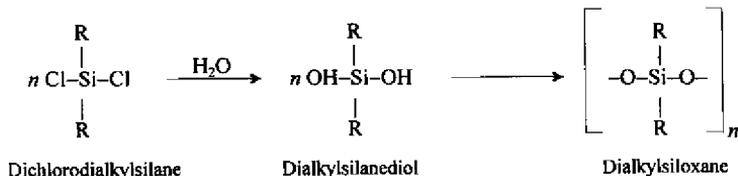
These repeated units are derived from the chloro-analogues, and the units are hydrolyzed to produce silanols, which are unstable and readily lose water to give polysiloxanes (Scheme II).

The properties of the polymer obtained depend on their average molecular weights and the degree of cross-linking. In the absence of cross-linking, if the number of monomer units is up to 3,000, the polymer product is a fluid, and if it is more than 4,000 a jelly-like polymer is obtained. A siloxane with minimum amount of branching would have an elastomeric properties and a typical peroxide cured silicone rubber would have about 13,500 monomer units in its chain [9, 10].

Silicone fluids, because of their unusual surface

activity, are used in many commercially important products. For example, dimethylsilicone fluid finds use as cleansing spray and of wipe-type for polishing the cars and furniture. It is shown that the addition of even small amount of silicones to polishes enhances the gloss and give added durability to the finish without any degradation of the original surface. The dimethyl fluids, because of their low surface tension, are extensively used as defoamers. Some silicone fluids are widely used as release agents in moulding of rubber and plastics mainly because of their low surface tension and non-stick properties. Another typical application of these fluids is in paints to improve the flow and surface structure and weather resistance under extreme condition of temperature and chemicals in the air.

The other interesting members of silicone family are thermosetting silicone resins, some of which are ideal resin constituents for easy flowing, low pressure moulding compounds. The combination of excellent electrical properties, high heat distortion temperature, flame, thermal, and moisture resistance of these compounds make them excellent materials for encapsulating delicate electronic components with



Scheme II

high standards of reliability. Silicone resins are preferred in paints and varnishes, where extreme service conditions are encountered [11].

The most important family of silicones are rubbers. Silicone rubbers exhibit a unique combination of inherent properties such as excellent weather and thermal stability, ozone and oxidation resistance, good electrical properties, extreme low-temperature flexibility, good release from organic materials, good solvent and oil resistance, physiological inertness, curability by variety of methods at both elevated and ambient temperatures. These properties, which make silicones quite different materials from all others, lead to their use in many applications where organic rubbers cannot perform satisfactorily. Today, silicone rubbers are extensively used in construction, medical, automotive, aerospace, mould making and electronics applications [12–14].

In this paper, the industrial route of preparing polysiloxane is discussed and the results of preparing silicon from domestic micronized sand and its purification are reported. The first stage in preparation of different silicones involves converting the sand into silicon.

EXPERIMENTAL

Materials

Silica powder was obtained from Alborz Co.(Iran) The particle size data are given as follows: Grades; AKA: 150–770 μ , CK: 150–1000 μ , and AKB: 150–770 μ .

Microsilica from Vand Chemie Co.(Iran) with particle sizes of 0.05–0.15 μ , powdered corundum (particle size: 0.15 mm), and aluminium powder and pellets, sulphur and other reagents were purchased from Merck Chemical Co.

Instruments

The instruments used in this study were Link, XR 300 X-ray fluorescent spectrometer (XRF), Philips Pu 9712 infra-red (IR) spectrophotometer, and Siemens, D5000 X-ray diffractometer (XRD), at Iran Polymer Institute.

Preparation Method

A mixture of silica powder, sulphur and aluminium powder were packed inside of a corundum bed in the reaction vessel (alumina crucible) in the following manner: The bottom of the vessel was filled to a height of about 1 cm with corundum powder, and a tube with a diameter of about 1 cm smaller than the diameter of the vessel was inserted vertically. The space between the tube and the vessel wall was filled with corundum powder. Then, the reaction mixture was packed inside the tube and the tube was pulled out of the vessel, and the surface of the reaction mixture was covered by aluminium pellets. Finally, a small portion of the charge in the reaction vessel was ignited with an hydrogen–oxygen torch. The reaction proceeded from top to bottom of the charge. After ignition, the reaction vessel had to be left to cool to allow setting out the metal droplets and eventual solidification. After cooling, the slag and the product block were easily dumped out, and the hard white slag and the product block were broken up with hammer. The block containing the product was physically disintegrated by water. The Si block was extracted for several days with boiling 1:2 hydrochloric acid, and then after washing it was again extracted with boiling hydrofluoric acid/sulphuric acid. The Si product was finally washed thoroughly with water and after drying, the purity of the product was examined with IR, XRF and XRD methods [15, 16].

RESULTS AND DISCUSSION

There are two industrial synthetic routes of preparing polysiloxanes, namely Kipping-Grignard process and Rochow catalytic process [9, 17]. As the first method has the disadvantage of producing a high quantity of waste chemicals, the second route, Rochow catalytic process, however, is preferred today.

The catalytic process involves converting sand (quartz) into silicon and preparing chloromethane either from natural gas or from methanol via coke and steam. Then, the ground silicon powder is reacted with chloromethane at 250–300 °C and 1–5 atm by using a metal, typically copper, as catalyst. Hot

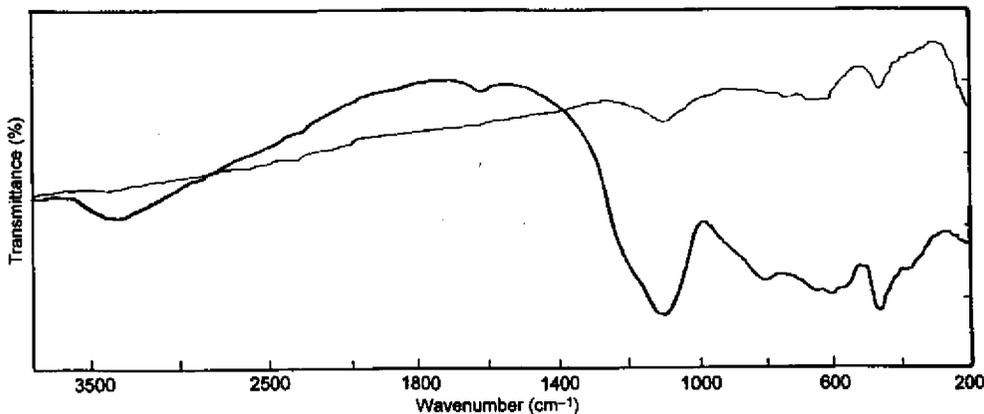
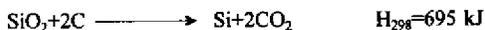


Figure 1. IR spectrum of the impure and purified silicon.

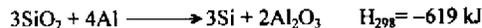
chloromethane vapour is passed upwards through a silicon-copper powder mixture. The reacted silicon powder is replaced. The products are separated by fractional distillation and after hydrolysis they are condensed to polysiloxanes.

As it was mentioned, the first stage in Rochow catalytic process is conversion of sand (quartz) to silicon. Silicon is produced by two methods: carbothermal reduction of silicon dioxide.



This reaction is carried out in electric-arc furnaces and is the industrial route of producing mass volume of this metal. In view of small tonnages involved, such productions usually occur only where an electric-arc furnace exists for other purposes.

Another way to produce silicon from SiO_2 is aluminothermal reduction [15];



This reaction is strongly exothermic over the entire temperature range. This reaction is usually carried out in steel pot lined with refractory or in a sand bed. The reaction mixture is fed into the vessel and a small portion of it is ignited. The reaction then

proceeds through the remaining charge. The speed of reaction can be controlled by varying the feeding rate. This reaction is fast with less heat loss and much less gas volume is produced, and also it requires small capital investment on a plant suitable for limited production.

In this work, aluminothermal process was employed to prepare silicon samples for two reasons: small production in bench-scale, and availability of the required equipment. The starting material was micronized sand with different particle sizes obtained from domestic manufacturings. The reaction was carried out in a corundum bed in an alumina crucible. The charge, including sand, sulphur and aluminium powders were placed in corundum bed. Corundum powder acts as an insulating material to prevent breaking of the alumina vessel by high exothermic heat of reaction and also to dispel air out of the reaction mixture, thus preventing the oxidation of silicon product. Sulphur is added to supply excess heat to the exothermic reaction mixture. So, there would be sufficient heat to shift the equilibrium to the desired direction and to produce fully liquid metal and a fluid slag, so as to permit good separation of slag and metal. The reaction mixture is ignited with a hydrogen-oxygen flame. After cooling, the slag is removed from the product as it was mentioned earlier

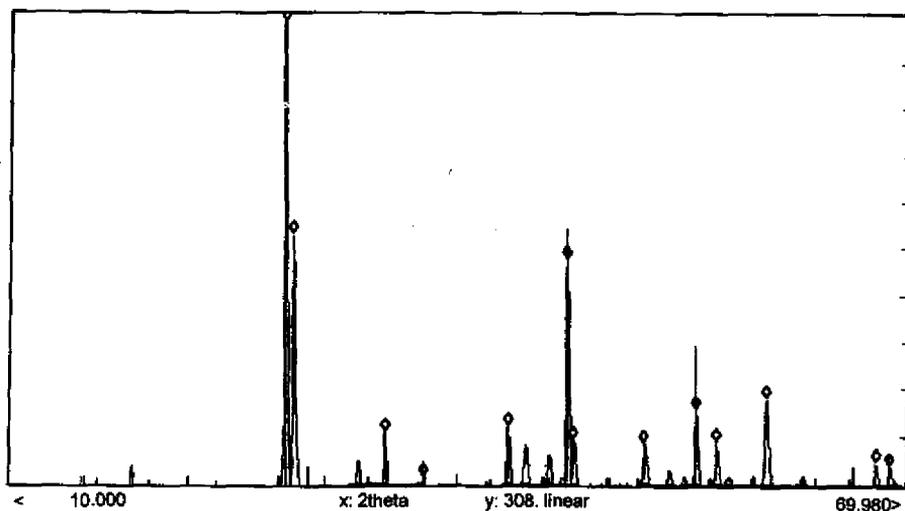


Figure 2. XRD spectrum of silicon after single purification step.

and the crude silicon was purified by an acid leaching process. In using this process the sample is granulated and then extracted with boiling hydrochloric acid to dissolve silicates and later in a mixture of hydro-

fluoric and sulphuric acids to remove aluminium and silica. After washing to eliminate residual acids and drying, the purity of the sample was examined by IR, XRF and XRD techniques.

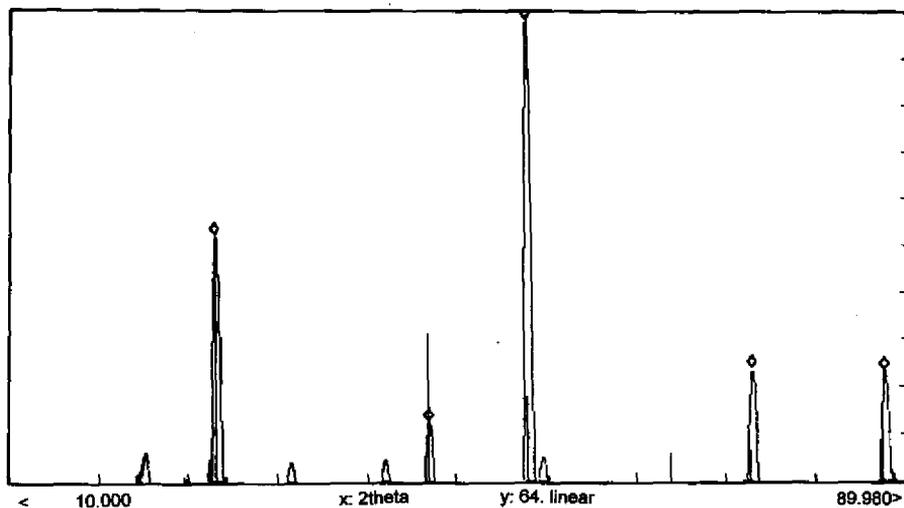


Figure 3. XRD spectra of purified silicon.

Comparison of IR spectra of the product before and after purification (Figure 1) indicates that the absorption bands of the oxide impurities (Figure 1a) either they are disappeared or weakend in the spectrum of the purified silicon (Figure 1b). Silicon is highly permeable to infra-red light.

The XRD spectra of crude and purified silicon are shown in Figures 2 and 3. The spectrum of impure sample shows the peaks corresponding to starting material, silica (SiO_2), and alumina (Al_2O_3) which are eliminated in the spectrum of purified sample (Figure 3). In this Figure the silicon peaks are clearly observed and superimposed on reference peaks of elemental silicon.

The XRF results are shown in Table 1. It is found that silicon purity is about 91.7%. Part of this residual impurity comes from domestic micronized sand which is used as received. Further purification of silicon is usually done by zone melting technique [6].

The next stage of this work will be conversion of silicon to dichlorosilane by Rochow process. As mentioned earlier, in this process the ground silicon is reacted with chloromethane. The dichlorosilane obtained is hydrolyzed to produce the unstable silanol which undergoes condensation to give cyclic siloxanes. The principle cyclic siloxane used for prepar-

ation of polysiloxanes is a tetramer.

CONCLUSION

The main features of polydimethylsiloxanes, silicones, their industrial synthetic routes, properties and the applications of these high inorganic polymers are discussed, and the preparation, characterization and purification of silicon from domestic micronized sand (silica) as starting material is presented. In this method, aluminium powder is used to reduce the silica. Sulphur provides the additional heat and corundum acts as insulating material. The advantages of this method is the short reaction time and less heat loss. Corundum is easily removed, washed and reused. The purification of the product is feasible using ordinary laboratory reagents. The characterization and purity of the silicon have been examined by IR, XRD and XRF instruments, available in Iran Polymer Institute, and satisfactory results have been obtained.

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Table 1. XRF data of purified silicon.

Z	Weight (%)	Standard error
9 F	<	-
11 Na	0.037	0.008
12 Mg	0.021	0.002
13 Al	6.800	0.100
14 Si	91.700	0.100
15 P	0.025	0.003
16 S	0.650	0.030
17 Cl	0.036	0.004
19 K	0.088	0.007
20 Ca	0.090	0.007
22 Ti	<	-
23 V	<	-
24 Cr	<	-
25 Mn	<	-
26 Fe	0.340	0.020

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