Research Progress of Heat Resistance of Silicone Rubber

Silicone rubber is a special synthetic rubber, places an important position in the rubber family. Because of its special structure, it has excellent performance, such as high resistance, low temperature, high voltage resistance, ozone resistance, radiation resistance, weather resistance, physiological inertia and high air permeability, as well as lubricants and other media show excellent chemistry inert, its application is very extensive.

Although the silicone rubber has excellent heat resistance, with the rapid development of science and technology, it has been unable to meet the requirements of harsh conditions, therefore, how to improve the heat resistance of silicone rubber, that the research is the current hot topic.

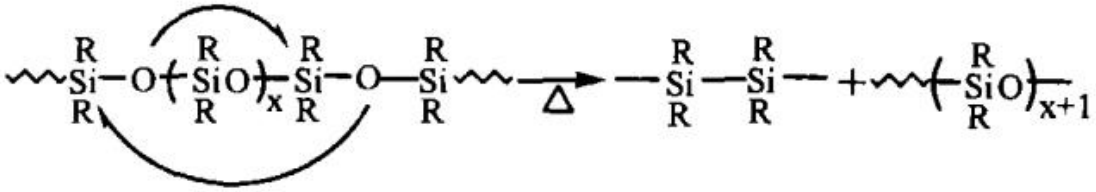
Thermal aging of silicone rubber

Thermal aging is the most important form of silicone rubber aging. The using environment of silicone rubber is in high temperature air, due to the combination of two factors of heat and oxygen to cause thermal aging. In the process of thermal oxygen aging, heat promotes the oxidation of silicone rubber, and oxygen promotes the thermal degradation of silicone rubber.

The structural changes of silicone rubber in the process of thermal oxygen aging can be divided into two categories: one is the degradation of the molecular chain of thermal oxygen aging reaction; the another one is the molecular chain of cross-linking between the thermal aging reaction. The molecular chain breakage-based rubber was sticky after aging; the main cross-linked rubber was hardening and crisp after aging, both will make the mechanical properties of rubber decreased or lost, and will be useless. The vulcanized silicone rubber are crosslinked when the air heats up, and the rate of elongation at break is much greater than the reduction in tensile strength. Methyl vinyl silicone rubber as the based vulcanized rubber, the cross-linking was reduced at 350℃, there is no change at 30℃, increased at 205℃, the cross-linking is independent of temperature after the continued aging.

Factors and Mechanism of Silicone Rubber Aging

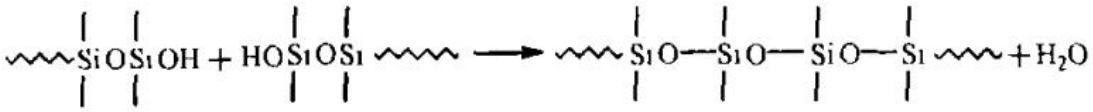
Silicone rubber molecular chain structure and composition are to determine the level of heat resistance of the main factors. silicone rubber main chain has Si-O atoms only, because of its flexibility, easy to curl, some trace impurities (such as water, silicon hydroxyl or residual catalyst) can quickly lead to degradation of the main chain. The difficulty in degradation not only depends on the structure of the silicone rubber, but also on the nature and content of the impurities. The high polarity of the Si-O bond also determines that it is susceptible to polar attack and rapidly causes thermal rearrangement degradation of the backbone.



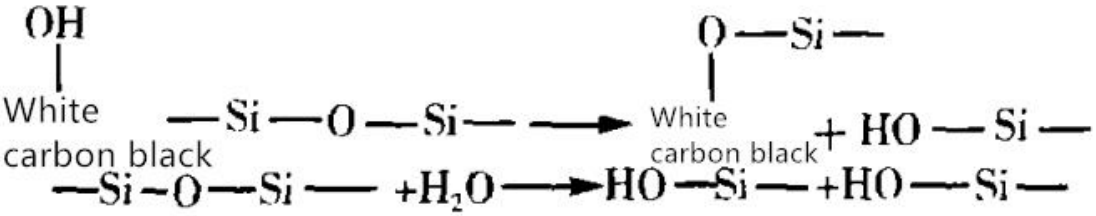
In addition to the thermal rearrangement degradation of the above main chain, there is also the oxidation of the pendant groups to make the reaction more complicated.

Oxygen can only interact directly with organic groups of silicon atoms. Obviously, the chain structure around the main chain has a great impact on the thermal stability, alkyl groups of side chain increased, the thermal stability of silicone rubber decreased. For example, dimethyl silicone rubber oxidize at 20℃, diethyl silicone rubber at 138℃, butyl silicone rubber was significantly oxidized at 120℃. Substituting methyl groups with vinyl also slightly reduces the thermal stability of the silicone rubber.

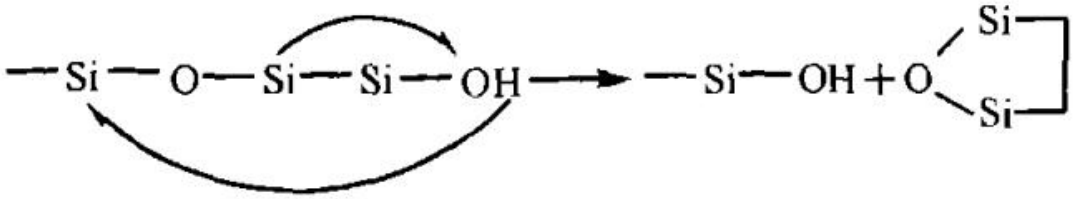
The end of silicone rubber will be with -OH during the synthesis, which is to promote the cross-linking use of silicone rubber in the using process, increase the molecular weight, and causing aging.



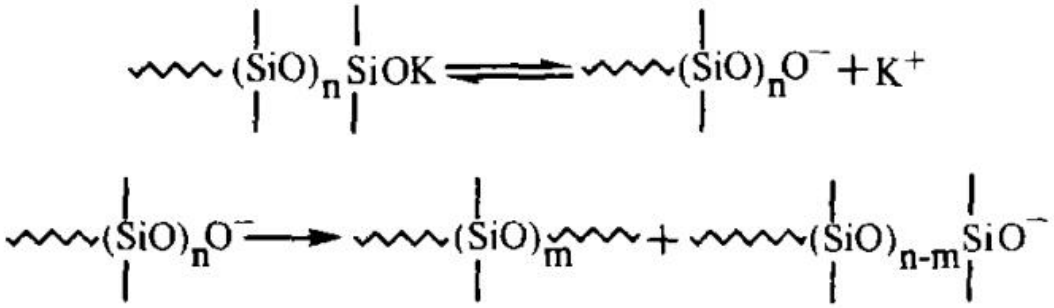
White carbon black is almost used in silicone rubber processing to strengthen, and there is a certain amount of active silicon hydroxyl groups on the surface of white carbon black, while the surface residual adsorbed water and water produced by the base condensation, so that the heat resistance of silicone rubber decreased.



The greater the amount of white carbon black used in the silicone rubber, the more active hydroxyl, the more adverse heat resistance will be.



In most cases, there will be catalyst left inevitably during the silicone rubber synthesis process. Both the acidic or alkaline catalyst impact the thermal stability of silicone rubber. The vinyl silicone rubber prepared by the acidic catalyst was heated at 305℃ for 2 h in vacuum and 25% of loss weight; while the same weight loss was achieved at 256℃ prepared with basic catalyst. Examples of catalytic synthesis of silicone rubber by KOH:



Therefore, avoiding residual monomers and catalysts helps to improve the thermal aging resistance of silicone rubber.

The way to improve the aging resistance of silicone rubber

For the silicone rubber vulcanized thermal aging mechanism, there are several ways to to improve its heat aging performance as following: ① Change the structure of silicone rubber side chain groups, such as the introduction of phenyl, etc., to prevent the silicone rubber due to the decomposition of side chain groups caused by molecular chain crosslinking or degradation. This is because the phenyl itself is not easy to oxidation, forming steric hindrance in the silicon chain, so that the silicone chain is more difficult to ring degradation. And because of its conjugate effect, the block effect is greater, so the thermal decomposition temperature is higher. (2) The thermal stability of the crosslinked bonds of vulcanized rubber was improved by introducing large volume segments, such as carbon decaboryl, phenylene, phenylene ether and cyclodiilazinyl groups in the molecular chain of silicone rubber. ③ Add heat-resistant additives to the compound To prevent side chain oxidation crosslinking and backbone cyclization degradation., such as ferric oxide, dioxane, hexaphenyl cyclotrisilane, etc.

As ①, ② two methods need to be achieved in the process of synthesis of silicone rubber, the process is difficult, the cost is high. The most commonly used method is ③ at present, which is

effective, low cost, easier to achieve. This article is briefly introducing several commonly used measures of the method ③.

Add metal oxide antioxidant

From the the aging mechanism of silicone rubber, silicone bond oxidation is mainly caused by the free radical scavenging reaction of pendant groups. If this chain reaction is destroyed, the oxidation process will be prevented. Fe_2O_3 is the most commonly used antioxidant, the amount is generally 3 to 5.

Relevant studies have reported that the composite metal oxide prepared by liquid phase coprecipitation method can significantly improve the heat resistance of silicone rubber. The study suggests that the iron-tin composite metal oxide is more effective than the single iron oxide and tin oxide in improving the heat resistance of silicone rubber. This is because the prepared composite metal oxide crystal structure has changed, they will play a role in addition to their own, there is synergistic effect.

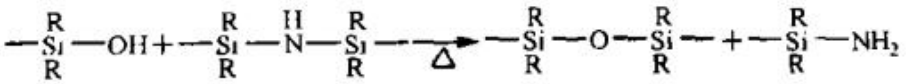
$$2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+}$$

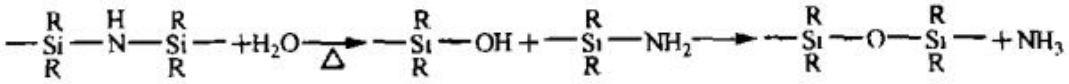
$$ROO\cdot + Fe^{2+} \longrightarrow ROO:Fe^{3+}$$

There is inhibit oxidation, and improve the heat resistance of silicone rubber.

Add silazane

The addition of silazane to silicone rubber can significantly improve the heat resistance of silicone rubber, the principle is: silazane can effectively inhibit the end of the main chain of the deduction degradation, the elimination of silicone rubber in the trace moisture and silicon light , so that the temperature resistance of silicone rubber up to 350℃.





And the hydrolytic apparent activation energy of silazane, the higher the hydrolytic stability, the better thermal stability of silicone rubber will be. Commonly used silazanes are: hexamethyldisilazane, hexamethylcyclotrisilazane and so on.

Add silicone resin

Silicone is highly crosslinked reticular structure of polyorganosiloxane, which is a kind of thermosetting resin. Its skeleton consists of siloxane bonds having the same structure as quartz and glass, and one of the most prominent properties is excellent thermal oxidation stability. After heating at 205℃ for 42h, the lose weight of silicone resin is only 2% to 8% of weight, and after heating at 350℃ for 24 hours, the weight loss of silicone was less than 20%.

Direction of development

With the development of high-tech, the use of silicone rubber will be further expanded, the performance requirements of silicone rubber will be higher and higher, silicone rubber heat resistance research will also enter a new stage. At present, the main filler material of silicon rubber is fumed white carbon black, because of its complex preparation process, the cost is very high, especially it has a negative impact on the heat resistance of silicone rubber, so looking for a suitable filler to reinforce the silicon rubber, which will be the main direction of future development. It is reported that by changing the surface energy of mineral fillers, that is expected to achieve mineral filler on the silicone rubber reinforcement. With mineral filler for silicone rubber filler, not only can reduce the cost of silicone rubber products, what' more, the heat resistance of silicone rubber has no negative impact, and even some mineral filler contributes to the heat resistance of silicone rubber. With the improvement of heat resistance of silicone rubber and the development of new filler, it will be hot topic of silicone rubber research in the field.

At present, there is a lot of research on the heat resistance of silicone rubber, and the use of special treatment of high-fine mineral filler instead of white carbon black, which developed a high hardness of silicone rubber (Soher A 58), not only with heat resistance and excellent mechanical properties, and greatly improve the thermal conductivity, mainly used for hot stamping with silicone version, the production of silicone roller.