The progress of high temperature vulcanization addition reaction silicone rubber

Silicone rubber has many unique and excellent features, such as high and low temperature resistance, UV resistance, radiation resistance, weather resistance, electrical insulation, high permeability, physiological inertia. Silicone rubber has been widely used in aviation, aerospace, electrical, electronics, chemical, instrumentation, automobile, machinery and other industries as well as medical and health, daily life in various fields, which has become indispensable new materials in modern chemical industry. Silicone rubber can not only do mold products, but also can composite with fabric, such as silicone coated fiberglass cloth, which widely used in the production of modern industry. Therefore, the development and application of silicone rubber and organic silicone, and promote the transformation and development of many technical fields.

There are many types of silicone rubber, it can be divided into single-component and two-component type according to its packaging ; it can be divided into solid and liquid silicone rubber according to its material form; it can be divided into high temperature, Low temperature (room temperature) silicone rubber according to the vulcanization temperature ; it can be divided into peroxide-induced, condensation reaction and addition reaction type silicone rubber according to the vulcanization mechanism . High temperature vulcanization silicone rubber mainly refers to no extra high investment injection molding, using the peroxide high temperature vulcanized silicone rubber molding equipment and molding process, the silicone rubber can be produced directly. In recent years, with the increasing researches of silicone rubber, high temperature vulcanization silicone rubber research has become a hot topic in the rubber industry.

Features of high temperature vulcanization addition reaction silicone rubber

The addition reaction silicone rubber has many excellent features: There is no small molecule in the vulcanization process, the vulcanization process itself does not produce any by-products; the dosage of catalyst is less, and the vulcanized product is safe to the human body; Vulcanization process without the participation of extra ingredients, it can be done in depth vulcanization; can be vulcanization under atmospheric pressure (hot air); Vulcanized rubber with high transparency, flame retardant, excellent physical and mechanical properties; The linear shrinkage and compression set of the addition silicone rubber vulcanized products are the lowest in the three vulcanized silicone.

At present, for the research and application of room temperature vulcanization addition reaction silicone rubber, because the catalyst activity is too high, generally use two-component A / B packaging, this form is not only inconvenient during use, there is still the existence of residual

residue of the waste and processing problems. Compared with room temperature vulcanization addition reaction silicone rubber, the advantages of high temperature vulcanization silicone rubber is stable at room temperature or low temperature storage, vulcanize under high temperature, it can effectively avoid the disadvantages of room temperature vulcanized silicone rubber .

At present, the research focus of high temperature vulcanization addition reaction silicone rubber is mainly focused on the research of catalyst / inhibitor system, the key is the activity of inhibitor catalyst, especially the storage stability of catalyst.

At present, several manufacturers of have been formed series of mature products of high-temperature vulcanization addition silicone rubber, such as ELASTOSILplusR series of high temperature vulcanization addition silicone rubber from Wacker Company , which has developed high strength, impact, self-adhesive, single Component extrusion, fire retardant and other different products.

Progress of basic polymer and compounding agents

Basic polymer

The basic polymer of the addition silicone rubber is polymethyl vinyl siloxane, referred to as vinyl silicone rubber. The study found that silicone rubber molecules as long as they contain two or more vinyl, whether it is vinyl silicone rubber, phenyl silicone rubber, fluorosilicone rubber can be treated with addition vulcanization. At present, the research on vinyl silicone rubber mainly focused on the study of structure, the purpose is to produce high strength, especially high resistance addition silicone rubber.

Crosslinking agent

Polysiloxanes containing more than two Si-H groups in the molecule which can be used as the crosslinking component of the silicon-hydrogen-addition vulcanized silicone rubber. The structure and dosage of the crosslinking agent have a significant effect on the properties of the addition silicone rubber. After the addition reaction of vinyltrimethoxysilane with 1,3,5,7-tetramethylcyclotetrasiloxane, and reacted with 1,1,3,3-tetramethyldisiloxane in the presence of an acid catalyst to produce Si-H group-containing diblock siloxane as a crosslinking agent, the vulcanization activity and the performance of the vulcanized silicone rubber can be improved.

Reinforcing filler

Fumed silica is the most important reinforcing agent for silicone rubber. In order to achieve better reinforcement effect and processing performance, the need for silica treatment, there should be some treatment for fumed silica. Using the surface with a vinyl siloxane oligomer or vinyl siloxane-containing high specific surface area of fumed silica as a reinforcing filler, the tensile

strength and tear strength of addition reaction silicone rubber has improved. It has been reported that in the process of on-site treatment of white carbon black, the anti-tear properties of silicone rubber can be improved after dilution heat treatment process

Tackifier

Silicone Hydrogenated vulcanized silicone rubber is substantially unbonded to the substrate. In the case of bonding with a contact substrate, the substrate is previously subjected to a primer treatment or adding the tackifier in the compound. Phenyl-containing hydrosiloxane copolymer and methyl hydrogen cyclosiloxane and used as cross-linking and thickening ingredients, which can be dubbed on the plastic and metal, and have a good adhesion. An alkoxysilane containing an addition functional group, a siloxane oligomer containing an addition functional group-containing alkoxy group, a cyanuric acid ester containing an addition functional group and an alkoxy group as tackifier, which has good adhesion for plastic (PC, PPS, etc.), metal, glass, etc. , and rubber storage stability is good, the color of product does not change at high temperatures.

The reaction products of Silane coupling agent and titanate for the preparation of the adhesive agent have good adhesion on the plastic (PPS, PBT, etc.), metal (copper, aluminum, steel, etc.). Silane coupling agent can be selected from Methacryloxypropyltrimethoxysilane, glycidoxypropyltrimethoxysilane , titanate can be selected from butyl titanate, isopropyl titanate, diisopropoxide (Ethyl acetoacetate) titanium, etc. .Silane coupling agent and titanate mix at a mass ratio of 1: 1 and reacted at 50 to 80℃ for 50 to 100 hours to hydrolyze a part of the alkoxy ester exchanger to form an oligomer.

Other additives

The catalytic efficiency of platinum catalyst is high , but there is a fatal drawback of the platinum catalyst, that is, when the system containing N, P, S organic compounds, or containing Sn, Pb, Hg, Bi, As and other heavy metal ion compounds, and organic compound containing unsaturated bond such as an alkynyl group, the platinum catalyst is liable to be poisoned and loose the catalytic activity..

In the presence of Si-Vi and platinum catalyst, Si-H will produce side reactions to produce hydrogen, there will be bubbles, which affect the mechanical properties of silicone rubber and dimensional stability. In order to eliminate the influence of such side effects, adding hydrogen absorbing agent into the material.

The research progress of Catalyst / inhibitor system

Common catalyst

The vulcanization mechanism of the addition silicone rubber is hydrosilylation reaction, the catalyst for the hydrosilylation reaction can be used in principle. Till now, almost all of the transition metals such as Pt, Pd, Rh, Ru, Ni, Co and the like are suitable for the hydrosilylation catalyst.

The earliest use of the hydrosilylation catalyst is chloroplatinic acid (H2PtCl6 6H2O). Chloroplatinic acid solution catalytic system belongs to the inorganic chloride ion ligand, when used in chloroplatinic acid dissolved in solvent (such as isopropyl alcohol), can be directly used for catalytic hydrogen hydride addition reaction. The advantage is that the catalyst has a good compatibility with the reactant matrix and can be homogeneous, so that the activity and selectivity of the metal active center can be adjusted by changing the ligand to modify the stereoselective or electronic environment of the metal active center. It was found that the catalytic activity of platinum in the low valence state was higher than that in the high valence state. For the chloroplatinic acid-divinyltetramethylsiloxane catalyst, when the platinum is reduced to zero, the activity of the catalyst is high. For the chloroplatinic acid-isopropanol catalyst, the valence of platinum is higher, the catalytic activity relatively low. Meanwhile, Chloroplatinic acid and divinyltetramethylsiloxane complex catalyst in the reaction system, which is in the better dispersion, high activity, and with better catalytic effect.

At present, the most commonly used catalyst is high activity, soluble in organic polysiloxane chloride complex, such as platinum - vinyl siloxane complex and so on. There are two kinds of preparation of platinum-vinylsiloxane complexes: one is the reaction of chloroplatinic acid with vinylsiloxane, and then the Willing method of acid washing; the another method is chloroplatinic acid and vinyl siloxane alkane in an alcoholic solution, followed by acid removal with sodium bicarbonate. The former is also referred to as chloroplatinic acid vinyl siloxane complex; the latter called Karstedt catalyst, because the complex of chlorine has been basically removed, platinum in the zero-valence state, and catalytic activity is high.

The type of inhibitor

The vinyl silicone rubber, the crosslinking agent and the catalyst are mixed and reacted at room temperature. Therefore, in order to adjust the vulcanization rate and prolong the use time, it is necessary to use a reaction inhibitor to suppress the hydrosilation reaction of vulcanization. When the inhibitor is added to the compound, it can form a certain form of complex with the catalyst, so that the catalyst can not catalyze the crosslinking reaction at room temperature, so that the compound can be placed at room temperature for a long time, only heated to a certain temperature to vulcanize. It should be noted that the inhibition of the catalyst activity does not permanently deactivate the catalyst, and when the rubber is vulcanized, the inhibited activity must be completely released. Some of the organic matter containing S, N, Sn and other elements, which make the catalyst activity lower. However, when the temperature rises, the vulcanization can be carried out, but even at a relatively high temperature, the vulcanization rate becomes very slow, and even the vulcanized product is wrinkled. This type of inhibitor is undesirable.

Inhibitors are generally divided into two types: one is added as a additive in the compound, with platinum action to block its activity; the other is prepared in advance which contain the inhibitory ligand complex catalyst, thereby inhibiting the catalytic activity. Till now, has been found that there are six types of the inhibitor which can be reacted with platinum.

(1) Unsaturated compound inhibitors. Mainly containing alkynyl and polyvinyl compounds, at present, there are a variety of common alkyne compounds (mainly acetyl alcohol), containing vinylsiloxane, maleic acid and its derivatives, fumaric acid and its derivatives. Thus, many people consider to use acetylene and hydrogen-containing silicone oil in the platinum complex catalyzed reaction to form a new unsaturated alcohol, the above defects are eliminated by alcohol, and also have a better inhibitory effect on the platinum catalyst at a certain temperature.

(2) Sulfur-containing compounds inhibitors. Such as sulfoxides, including organic sulfoxides and silicone sulfoxides, the inhibitors can make the stock to be stored for 3 months at room temperature .

(3) Peroxide inhibitors. This inhibitor makes the active period of one-component addition vulcanized silicone compound from six months to one year, so that active period of the two-component is several weeks, so that there is sufficient safe operating time for high-temperature addition silicone rubber. For high temperature addition rubber, when the temperature below the curing temperature, the peroxide inhibits the reaction, When the temperature above the curing temperature, it can accelerate the addition reaction.

(4) Metal salt inhibitor. The metal ions in these metal salts are Sn2 +, Hg2 +, Bi2 +, Cu2 + and Cu +, among which Sn2 + salt is used more. The dosage of metal salt is twice of platinum, which can make rubber curing cycle extended to more than 3 months.

(5) Nitrogen compound inhibitor. This is the most species of inhibitor, and it's widely used to medium and high temperature vulcanized silicone rubber. Including acrylonitrile, tetramethylguanidine carboxylate, hydrazine, aminosilicon, silamines.

(6) Phosphorus compound inhibitor. There are triphenylphosphine compound, divalent platinum - phosphorus compound and zero-valent platinum-phosphorus compound. The platinum-phosphorus compound is a kind of composite catalyst, when the temperature is lower than the vulcanization temperature, the ligand compound has an inhibitory effect on the activity of platinum in the central atom. When the temperature is higher than the vulcanization temperature, the ligand dissociates, platinum restore the catalytic activity, addition reaction is going on, and the rubber will vulcanize. The main drawback of the divalent platinum-phosphorus compound is that it can not be subjected to closed heating vulcanization.

New catalyst / inhibitor system

Improvement of platinum catalyst

Although there are many kinds of inhibitor compounds, the inhibitory effect is not satisfactory. In order to achieve a reduction in the activity of the catalyst without inactivation, it can be achieved

by improving the platinum catalyst. The method of improving the platinum catalyst is mainly to further complex the catalyst to limit its activity, such as using Carbene to complex the common platinum catalyst. Karstedt catalyst or maleate complex catalyst and carbene complexation of the catalyst, the gel time at room temperature greatly increased. The drawback of this method is that the production of Carbene is more troublesome, requiring very low temperatures in very dry conditions, it's difficult to achieve the conditions for conventional laboratories.

Microencapsulated platinum catalyst

Microencapsulated platinum catalyst refers to using thermoplastic resin or thermoplastic siloxane (softening point of 50 ~ 200℃) encapsulation of platinum complexes, made into microcapsules, as a hydrogen hydride catalyst. Using microencapsulated platinum catalyst prepared by the rubber material in the resin or silicone softening point below, the storage is stable, when the temperature rose to above softening point of the resin or silicone, the resin or silicone soft (melt), release Platinum catalyst, and then with addition reaction, cross-linked into elastomers. Preparation of microencapsulated platinum catalyst methods are spray drying, hot melt and water dispersion method, can be used for the packaging of many materials, such as polyvinyl alcohol, polyacrylate, polystyrene, silicone and so on. This is the best way to inhibit the activity of the catalyst, which can significantly increase the shelf life of the compound, and some even up to 1 year. There are prominent problems while using microencapsulated platinum catalyst, the most critical issue is the dispersion. The catalyst capsule must be in a phase-separated state with the silicone rubber system, and its dispersion must be uniform. Otherwise the vulcanization of the catalyst distribution is uneven, will inevitably lead to uneven vulcanization, get unqualified products. In addition, the storage time is too long, the catalyst capsule is liable to precipitate. Therefore, how to solve the dispersion of capsules, the particles should be small enough, ans the size is uniform, which is the key to this method. At present, this research has not made significant progress.

Preparation of platinum-inhibitor complexes

Using commonly used inhibitors and catalysts to form compounds to produce ready-made catalytic/inhibitory mixtures, which is also one of the most promising methods to inhibit platinum catalyst activity. The compound that have been reported are complexes of platinum and alkynes, complexes of cycloaliphatic platinum and alkynes, complexes of triorganophosphine and alkynyl compounds, and so on. The complexed silicone rubber formulated with platinum halide and alkynol catalyzed by alkali catalysis, that has the characteristics of long operation time and good anti-toxicity. The cyclopentadienyl platinum and alkynyl alcohol are catalyzed by alkali catalyst under the reaction of the formation of complex catalyst, the composition of the additive silicone rubber has a long storage life, high catalytic activity when heated. However, the conditions of preparation of platinum-inhibitor complexes is difficult, and it's also difficult to achieve the conditions for conventional laboratories.

Other methods

In addition to the above from the catalyst/inhibitor system to solve the catalyst activity inhibition and achieve high temperature addition vulcanization, currently it has been proposed another solution ideas. That is starting from improving the structure of silicone rubber. A large group is introduced into the main chain (especially the silyl group and the silyl group) to produce a steric hindrance to prevent the progress of the hydrosilylation reaction.

Conclusion

As high temperature vulcanization addition reaction silicone rubber has easy storage and transportation, easy to use, excellent performance and other characteristics, so that the addition silicone rubber is gradually to the direction of high temperature vulcanized silicone rubber development. Meanwhile, the catalyst / inhibitor system for high temperature vulcanization addition silicone rubber plays a vital role, which showing a good research and development prospects. The development of a higher activity, high selectivity, and easy control of the catalyst inhibitor system will promote the renewal and development of high temperature vulcanization addition silicone rubber.