



The research progress of silicone rubber

Silicone rubber is a linear, high Mr (relative molecular mass) polysiloxane, its Mr generally more than 1.5×10^5 , the molecular backbone consists of silicon atoms and oxygen atoms alternately (-Si-O-Si-), the bond energy of the Si-O bond (422 kJ/mol) is higher than the C-C bond (240 kJ/mol). Silicone rubber is non-toxic and tasteless, and has a good resistance to high and low temperature (without losing the original strength and elasticity at temperature of 300 °C and -90 °C), electrical insulation, light aging resistance, aging resistance, mildew resistance and chemical stability, and thus in the aerospace industry and agriculture, medical and health and electrical and electronic industries and other fields are widely used.

Silicone rubber can be divided into heat vulcanized (HTV) type silicone rubber and room temperature vulcanization (RTV) type silicone rubber according to its vulcanization characteristics. The vulcanizing agent can crosslink the linear silicone rubber into a three-dimensional network structure (reduced plasticity, elasticity). Besides of some thermoplastic silicone without vulcanization, the natural rubber and a variety of synthetic rubber are usually required to use vulcanizing agent vulcanization (After the vulcanization of silicone has a value, its mechanical properties greatly improved.). To meet the special needs, special properties of silicone rubber should be used, such as conductive silicone rubber, thermal silicone rubber, heat-resistant silicone rubber, oil-resistant silicone rubber, shielding silicone rubber, flame-retardant silicone rubber, damping silicone rubber, silicone rubber insulation and sponge silicone rubber.

With the rapid development of high-tech, people has put forward higher requirements on the use of silicone rubber performance, such as good mechanical properties, heat resistance, anti-radiation performance, adhesive properties and weathering resistance, etc., so the modification of silicone rubber (physical modification, chemical modification, etc.) is imperative.

Classification of silicone rubber

HTV silicone rubber

HTV silicone rubber (high temperature vulcanized silicone rubber) with large output, and it is widely used, the Mr $(4.0 \sim 6.0) \times 10^5$. HTV silicone rubber can be divided into methyl silicone rubber, dimethyl vinyl silicone rubber, methyl vinyl phenyl silicone rubber, nitrile silicone rubber and fluorinated silicone rubber. Adding reinforcing filler, curing agent and other additives into the HTV silicone rubber, after mixing that can be used for molded products, extruded products. For HTV silicone rubber, organic peroxide is used for curing, and dibenzoyl peroxide (BPO) is widely used as organic peroxides. HTV silicone rubber has excellent resistance to high and low temperature performance, physiological inertia, electrical insulation properties, ozone resistance, weather resistance, hydrophobicity and moisture resistance.





Dimethyl silicone rubber

Dimethyl silicone rubber referred to as methyl silicone rubber, silicone rubber is the oldest type, it can maintain good flexibility at the temperature of $-60 \sim 250^{\circ}\text{C}$. The raw rubber is a colorless transparent elastomer, usually with high activity of organic peroxide vulcanization. Dimethyl silicone rubber vulcanization activity is low, there will be permanent deformation under high temperature compression. It 's not suitable for the preparation of thick products (this is because the curing is more difficult for thicker product , bubble will appear inside). The methyl vinyl silicone rubber obtained after the introduction of vinyl is easy to crosslink, the mechanical properties of the prepared product are good, so the dimethyl silicone rubber has been gradually replaced by methyl vinyl silicone rubber.

Methyl vinyl silicone rubber

Methyl vinyl silicone rubber (referred to as vinyl silicone rubber), that is a mixture of dimethylsiloxane and a small amount of vinyl siloxane. This kind of rubber contains a small amount of vinyl side chain, so it is easier to vulcanize than dimethyl silicone rubber, and there are more types of peroxide for its vulcanization, which can greatly reduce the dosage of peroxide. To compare with dimethyl silicone rubber, silicone rubber with a small amount of vinyl can effectively improve the anti-compression and permanent deformation of the product (low compression deformation endow good high temperature support for sealing elements , which is the performance of O-ring and washers, etc.). Methyl vinyl silicone rubber process performance is good, easy to operate, can be made of thick products, the surface of semi-finished product by calender is smooth, meanwhile, methyl vinyl silicone rubber coated fiberglass fabric, with high strength, anti-aging, long service life , it's currently commonly used silicone rubber.

RTV silicone rubber

RTV silicone rubber is a terminal hydroxyl or acetoxy silicone rubber, its Mr is lower, and it is viscous fluid, which can be vulcanized at room temperature. The vulcanizing agent is ethyl orthosilicate. This type of rubber by adding the appropriate amount of reinforcing agent, vulcanizing agent and catalyst (or impacted by the moisture in the air), which vulcanize at room temperature to form an elastomer. Fully vulcanized products have good heat resistance, cold resistance and dielectric properties, but the mechanical strength is low, which can be used for casting and coating compounds.

Single component RTV silicone rubber

One-component RTV silicone rubber consists of end-based silicone-containing silicone rubber, reinforcing agent and other additives; it is necessary to add a catalyst without using a single-component RTV-type silicone rubber, you can get the elastomer (this is because it can be associated with moisture in the air cross-linking reaction). This silicone rubber has good adhesive properties on the metal, glass and plastic and so on, the drawback is that the process of





vulcanization with acetic acid generation [acetic acid can spread from the vulcanized rubber, but it has corrosive effect on the contacting objects (especially metal)] One-component RTV silicone rubber is easy to use, especially for sealing, caulking and other materials.

Two-component RTV silicone rubber

Two-component RTV silicone rubber consists of hydroxyl-containing silicone rubber, reinforcing agent and vulcanization agent and other preparation, the use of additional catalyst. Commonly used vulcanization agent is organic tin salts, the condensation reaction takes place between the silicone rubber containing the hydroxyl group and the vulcanizing agent when vulcanizing, and form crosslinked structure. By changing the vulcanizing agent and catalyst content, the rate of vulcanization can be adjusted (the alcohol produced during the vulcanization process gradually escapes from the vulcanized rubber).

Silicone rubber modification

Silicone rubber modification method is physical modification and chemical modification: the former is modified by blending or modified by filling, the latter through chemical grafting, copolymerization and other methods to achieve the purpose of modification. Blending modification is helpful to compensate for the deficiency of single component. Filling modification can improve the mechanical properties of the polymer, reduce the cost of raw materials or endow new function to the material. The blending modification and filling modification which is simple and flexible.

Blending modification

Blending with polyurethane rubber (PUR)

PUR has high strength and good elasticity, with excellent wear resistance, but its molecular structure contains a large number of -NCO, hydroxyl, urea groups and other strong polar groups, resulting in relatively large surface material, high friction factor and poor heat resistance, so the working life of PUR is short. PUR and silicone rubber blends, can significantly improve the heat resistance. In addition, due to the large difference between the two material, the blending system is poor, if the two material interpenetrated to network structure, can significantly improve the compatibility of the system.

Blending with fluoros rubber

FPM has good oil resistance, solvent resistance, chemical resistance, strong oxidizing agent resistance, high temperature resistance and flame resistance and many other advantages, but its flexibility, low temperature resistance and processing performance are poor, the silicone rubber and FPM can improve the system of cold resistance and processing performance after blending. The polarity of FPM and silicone rubber is different, the two material is incompatible system, it's technical difficulties to improve the compatibility of the two material.





The co-vulcanization of rubber blends has a great effect on its properties. Silicone rubber is used as a vulcanizing agent, and a number of FPMs with peroxide as vulcanizing agents have been developed so that peroxide can be used as co-vulcanizing agent. When $V(\text{FPM}): V(\text{silicone rubber}) = 80:20$, the brittle temperature of the system is about $10\text{ }^{\circ}\text{C}$ lower than FPM, the low temperature performance is obviously improved and the cost is reduced.

The blending modification of silicone rubber is an effective way to improve the performance of the single material and has made significant progress, but how to make the phases of the blend achieve synchronic crosslinking, or co-crosslinking a reasonable distribution aid, and how to choose the right compatibilizer, there are still many problems.

Filling modification

Nano filling modification

Nanoparticles have quantum size effect, small size effect, surface effect and macroscopic quantum tunneling effect, which show many special properties. It has a good prospect in the fields of catalysis, light absorption, magnetic media and new materials, and also has great development space for the modification of polymer materials.

Nano-TiO₂ can improve the anti-radiation properties of silicone rubber, which is due to the nano-TiO₂ has the nano-ion properties, and it can effectively increase the physical or chemical crosslinking point of silicone rubber, so that can effectively improve the cross-linking density of silicone rubber. When the system is subjected to external force, due to the interaction of the stress field, the micro-deformation zone in the matrix can absorb part of the energy, so the anti-radiation ability of the system is good.

With the rapid development of nano technology, more and more new nano-materials will have huge impact on the silicone rubber industry. Nano-materials is used for the modification of the silicone rubber, so that the properties is been developed. Therefore, it's significant to develop new nano materials to modify traditional silicone rubber products, improve its development space and market competitiveness.

Fill modification of white carbon

Fumed white carbon black is high purity amorphous silica, the particle size is $4 \sim 10\text{nm}$ (most is $10 \sim 30\text{nm}$), the density is very small, it's light blue transparent particles when in the very thin layer, and it is mainly used In the reinforced HTV silicone rubber.

Some researchers have investigated the effect of silica fillers on the properties of silicone rubber CKTB-6 (Ukrainian production). The results show that the strength and hardness of the vulcanized rubber is improved and the elasticity decreases with the increasing content of the silica in the





compound. Adding a certain amount of titanium dioxide during introducing the fumed white carbon black, which can effectively improve the strength and elasticity of vulcanized rubber.

At present, fumed white carbon black as the main reinforcing agent, which endow silicone rubber good mechanical properties. However, the large amount of hydroxyl groups contained on the surface of the gas-phase silica can react with the end groups of the silicone rubber molecules and are susceptible to structural effects, resulting in hardening of the compounds, difficulty in processing and expensive price.

Modification of mineral powder

Many mineral fillers are rich in Lewis, Bronsted acid point and other active sites, due to these characteristics of mineral powder, through a series of physical or chemical methods, so that it has the ability to combine with silicone rubber, which can effectively enhance the silicone rubber mold quantity, improve the mechanical properties of products. Mineral powder was used to take place of fumed white carbon black as silicone rubber enhancer, that can reduce the cost of products, but also increase the added value of mineral powder.

The modification of mineral powder filler can not only reduce the processing cost of rubber industrial products, but also improve the performance of rubber products, but there are few reports in this area. In order to better play the role of mineral materials, and improve the comprehensive utilization of mineral resources, it is necessary to increase the research in this area.

Conductive modification

The composite conductive material prepared by adding the conductive filler with silicone rubber as the base material, which has good resistance to high and low temperature resistance, aging resistance, molding processability and electrical conductivity. Therefore, it has been widely used in anti-static materials, electromagnetic shielding materials, and its application areas have been all over the aerospace, electrical and electronic, computer, construction, medical and food and other industries.

The development of conductive silicone rubber is mainly focused on the development of anti-static materials and electromagnetic shielding products, the development trend is mainly to improve the conductivity, reduce the filler filling, improve the processing performance and mechanical properties. Therefore, the development of new conductive varieties, the development of multi-functional conductive silicone rubber, is also one of the important areas of the research.





The application of silicone rubber

Medical

Medical equipment

Over the past 20 years, silicone rubber with its excellent performance (good biocompatibility, stability and comfort, etc.), it has become one of the development trend of medical materials. According to the different contact time, medical silicone rubber can be divided into long-term implantation and short-term contact type. Which implanted in the body more than 29d of the device called long-term implantation, otherwise known as short-term contact type.

Drug release system

Prolong the efficacy of drugs, improve the specificity and safety of drugs, which is an important issue in pharmaceutical research. The method of silicone rubber to control the release of drugs are mainly encapsulation and particle dispersion.

Silicone rubber film has a good permeability of O₂ and CO₂, and its moisture permeability and human skin moisture evaporation is similar, while its non-toxic to the human body, harmless, no allergies, easy to cause foreign body reaction or rejection and so on. In addition, silicone rubber film with nylon, polyester fiber reinforced, can be used as artificial film.

Auto industry

Silicone rubber has good resistance to flexibility, high temperature resistance and aging resistance, since the 1950s, it has been used in many important rubber seal products, the rapid development of the automotive industry , and the demand of silicone rubber is significantly increased. Automotive engine with silicone rubber sealing products can meet the requirement of service life of more than 10a and 150000km. In recent years, the heat resistance temperature of the silicone rubber without secondary vulcanization is increased by 50 °C , the adhesive property and the mechanical strength are improved.

Silicone rubber is widely used for the sealing products. The main sealing products are automotive engine crankshaft seals, fuel pump seals, air conditioning compressor seals, potentiometer insulation bushings and potting materials.

Market expectation

In 2006, the total market volume of silicone rubber in the developed countries and areas was about 328kt (in terms of polysiloxane). The US market was about 156,000 t, the European market was about 138,000 t and the Japanese market was about 34,000 t.

With the rapid development of the world economy, the future demand for silicone rubber materials will be greatly increased. With deep research of silicone rubber, and modification, a variety of modified silicone rubber is bound to the new, high-performance, diversification and multi-functional direction.

