High and Low Temperature Resistance of Phenyl silicone rubber

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Abstract: Methyl Phenyl and diphenyl silicone rubbers were synthesized from octamethyl cyclotetrasiloxane (D₄), methylphenyl cyclosiloxane, octaphenyl cyclotetrasiloxane, etc. Compared with the commercial methylvinyl silicone rubber, the high and low temperature resistances of methyl vinyl silicone rubber were studied in this paper. The results showed that the introduction of phenyl groups can improve the thermal properties of silicone rubber, and the thermal stability of diphenyl silicone rubber is better than that of methyl phenyl silicone rubber. But there is little difference of mechanical properties in high temperature environment for three silicone rubber. DMTA analysis showed that there were still a small amount of crystals in diphenyl silicone rubber, while methylphenyl silicone rubber was amorphous rubber. The mechanical properties at low temperature indicated that the tensile strength of diphenyl silicone rubber was 4.1Mpa higher than that of methylphenyl silicone rubber at -70°C due to the existence of low-temperature crystallization.

1. Introduction

Silicone rubber is a kind of organic-inorganic hybrid polymer material with Si-O bond as the main chain. Due to the large bond energy (422.5kj/mol), large bond Angle, large orientation degree of freedom and good flexibility, Si-O-Si has super high and low temperature resistance and is widely used in aviation, aerospace, machinery and electronics industries [1]. Commercial methylvinyl silicone rubber generally can work at -55~180°C for a long time. The phenyl silicone rubber obtained a small amount of Ph₂SiO or MePhSiO has better resistance to high and low temperature. Generally, it can work at -70~200°C for a long time, and can withstand elasticity for several weeks over 200°C or above 300°C in an instant. At present, the commercial diphenyl silicone rubber is not easy to widespread application for its complex synthesis process, poor batch stability and the higher price. With the improvement of synthesis technology of methylphenyl cyclosiloxane, methyl phenyl silicone rubber has become a research hotspot due to its simple synthesis process and low cost [2-4]. In this study Methyl Phenyl and diphenyl silicone rubbers were synthesized from octamethyl cyclotetrasiloxane, methylphenyl cyclosiloxane, octaphenyl cyclotetrasiloxane, etc. The high and low temperature properties of
silicone rubber were studied by thermogravimetry analysis (TGA), DMTA (dynamic mechanical thermal analysis) and material high and low temperature testing, which provides reference for the development and use of phenyl silicone rubber.

2. Experimental

Materials

D₄(≥ 99.5%) and tetravinyltetramethylcyclotetrasiloxane(D₄Vi, ≥99.5%), were purchased from Wake Co., Ltd. Methylphenyl cyclosiloxane (≥ 99.9%) was purchased from Xiantao Green Chemical Co., Ltd. Octaphenyl cyclotetrasiloxan (≥99%) was supplied by Dalian Yuanyong Silicone Co., Ltd. Methylvinyl silicone rubber, 110-2VT, was supplied by of China National BlueStar (Group) Co Ltd, Chengrand Research Institute of Chemical Industry Co. Ltd.

Sample Preparation

Synthesis of methyl Phenyl silicone gum

The ring-opening reaction of methylphenyl cyclosiloxane, D₄ and D₄Vi were catalyzed by tetramethyl ammonium hydroxide base rubber under nitrogen protection. At the end of the reaction, the catalyst was destroyed, and the small molecules were removed by vacuum decompress. Colorless and transparent methyl phenyl silicone gum (MePhSiO mole fraction 5%, 121-1) was synthesized according this method.

Synthesis of diphenyl silicone gum

The high purity dimethyl diphenyl cyclosiloxane mixture was prepared by catalytic rearrangement of octaphenyl cyclotetrasiloxan and D₄. The mixture cyclosiloxane were catalyzed by tetramethyl ammonium hydroxide base rubber under nitrogen protection with D₄ and D₄Vi. Diphenyl silicone gum (Ph₂SiO mole fraction 5%, 120-1) was synthesized according the above method.

Preparation of silicon rubber

According to the literature [1], silicone gum, SiO₂, Fe₂O₃ were compounded and then vulcanized at 160°C for 15 min under 9.8 MPa of pressure. The vulcanized samples were post cured at 200°C for 4 h. All the results are taken as the average of 5 samples for each testing.

Measurements

Mechanical tensile tests under various environments were performed on a universal testing machine (Instron3366), at 25°C and around 60% RH. The samples were tested at ambient temperature for 20min, and the stress-strain curve was automatically drawn. The loading speed of the test was 500mm/min. TGA was performed using Q600SDT thermal analysis at a heating rate of 5°C/min in an atmosphere of nitrogen. DMTA were done using IV dynamic mechanical thermal analysis at a heating rate of 2°C/min (frequency, 1 Hz).

3. Results and discussion

Mechanical property. Mechanical properties, hot air aging properties and compression cold resistance coefficient of methyl vinyl silicone rubber (110-2VT), diphenyl silicone rubber (120-1) and methyl phenyl silicone rubber (121-1) are shown in table 1.

| Testing                        | 1   | 2   | 3   |
|-------------------------------|-----|-----|-----|
| Tensile strength/MPa          | 10.6| 10.5| 10.3|
| Elongation at break/%         | 184 | 113 | 121 |
| Hardness (shore A)            | 60  | 61  | 63  |
| 225°C×72h thermal air aging test| -20 | -12 | -14 |
From Table 1, it can be found that, methyl phenyl silicone rubber 121-1 and diphenyl silicone rubber 120-1 have similar tensile strength and slightly lower elongation at break compared with the methyl vinyl silicone rubber 110-2VT. It also showed that a small amount of phenyl structure has a little influence on the tensile strength of silicone rubber, but as for rigid phenyl groups, the flexible order is Me2SiO > MePhSiO > Ph2SiO for dimethyl silica link or greater acuity diphenyl methyl phenyl silicone oxygen link link, the higher flexible is corresponding to the bigger elongation performance. The thermal air aging test shows that the phenyl structure improves the thermal resistance of silicone rubber, and the thermal resistance of 120-1 is slightly better than that of 121-1. The compression cold resistance coefficient test shows that the phenyl structure greatly improves the cold resistance of silicone rubber, and the cold resistance of 121-1 is significantly better than that of 120-1.

TGA analysis.

The TG curves of the three silicone rubbers are shown in Fig. 1. It can be seen from Fig. 1 that the initial thermal decomposition temperature curves of the three silicone rubber are almost identical, which indicated that the thermal resistance is not significantly different. With the increase of temperature, the heat resistance 120-1 and 121-1 showed higher heat resistance than 110-2VT, and 120-1 is better than that of 121-1. It also can be seen from Fig. 1 that phenyl structure may prevent main chain crosslinking or degradation [3] caused by oxidative decomposition of the side groups, which improved the thermal stability of silicone rubber. The thermal stability of Ph2SiO is better than that of MePhSiO.

|                           | 110-2VT | 120-1 | 121-1 |
|---------------------------|---------|-------|-------|
| **Rate change of Elongation at break (%)** | -36     | -27   | -31   |
| **Rate change of Hardness (%)** | +3      | +2    | +2    |
| Compression cold resistance coefficient |         |       |       |
| -50℃                     | 0.55    | 0.64  | 0.71  |
| -70℃                     | 0       | 0.45  | 0.61  |

Figure. 1 Thermogravimetric curves for the thermal degradation of silicone rubber samples

Table 2 compares the mechanical properties of 110-2VT, 120-1 and 121-1 at high temperatures. From Table 2 it can be seen that with the increase of temperature, the tensile strength and elongation at break of the three silicone rubber samples decreased significantly. This may be due to the fact that the molecular chains of silicone rubber are very flexible and the interaction between the chains is weak. When stretched at high temperature, under the influence of heat effect and volume expansion effect, the motion of polysiloxane molecular chain segment is accelerated, which weakens the force between SiO2 and polysiloxane molecular chain, resulting in lower tensile strength and elongation at break. And a few phenyl groups have little effect on the mechanical properties of silicone rubber at high temperature.
Table 2. Mechanical properties of samples at high temperature

| Samples   | Temperature /°C | Tensile strength /MPa | Rate change of Tensile strength /% | Elongation at break /% | Rate change of Elongation at break /% |
|-----------|------------------|------------------------|-----------------------------------|------------------------|---------------------------------------|
| 110-2VT   | 30               | 10.6                   | -                                 | 184                    | -                                     |
|           | 60               | 9.6                    | -9.4                              | 159                    | -13.5                                 |
|           | 90               | 8.7                    | -17.9                             | 130                    | -29.3                                 |
|           | 120              | 6.3                    | -40.1                             | 99                     | -46.2                                 |
|           | 150              | 4.4                    | -58.4                             | 94                     | -48.9                                 |
|           | 200              | 3.3                    | -68.9                             | 72                     | -60.8                                 |
| 120-1     | 30               | 10.5                   | -                                 | 113                    | -                                     |
|           | 60               | 8.3                    | -20.9                             | 100                    | -11.5                                 |
|           | 90               | 7.2                    | -31.4                             | 90                     | -20.4                                 |
|           | 120              | 5.6                    | -46.7                             | 72                     | -36.3                                 |
|           | 150              | 4.7                    | -55.2                             | 58                     | -48.7                                 |
|           | 200              | 3.1                    | -70.5                             | 51                     | -54.8                                 |
| 121-1     | 30               | 10.3                   | -                                 | 121                    | -                                     |
|           | 60               | 8.0                    | -22.3                             | 106                    | -12.4                                 |
|           | 90               | 6.7                    | -35.0                             | 93                     | -23.1                                 |
|           | 120              | 5.2                    | -49.5                             | 73                     | -39.7                                 |
|           | 150              | 4.8                    | -53.4                             | 64                     | -47.1                                 |
|           | 200              | 2.9                    | -71.8                             | 54                     | -55.4                                 |

Low temperature resistance. DMTA analysis of low temperature resistance of silicone rubber samples is shown in Fig. 2. Elastic modulus (E') is an important index of rubber elasticity. It can be seen from figure 2, 110-2VT begins to produce crystallization near about -35°C. As the temperature decreases, the crystallinity increases and the elastic modulus increases. 110-2VT belongs to crystalline rubber 120-1 destroyed the regularity of methyl vinyl silicone rubber, resulting in a decrease in crystallization temperature. From -50 degrees, a small amount of tension-oriented crystallization produced, and the elastic modulus increased first and then decreased. 121-1 does not have any crystalline transition, and it performs better at low temperature.

Figure. 2 DMTA analysis of low temperature resistance of silicone rubber samples

The polymer chain structure is the main factor to determine the basic properties of the polymer, while
the polymer aggregation structure is the main factor to determine the properties of the polymer. The aggregation form of molecular chain in silicone rubber has great influence on the properties of silicone rubber, and the main factor that affects the aggregation form of silicone rubber is temperature. Figure 3 shows the stress-strain curves of 110-2VT, 120-1 and 121-1 at low temperature, respectively.

It can be seen from the tensile stress-strain diagram of the three silicone rubber samples that the tensile strength and elongation at break of phenyl silicone rubber increase gradually with the decrease of temperature in the range of -70°C to 30°C. When stretched at low temperature, with the decrease of temperature, the thermal motion energy of polysiloxane molecular chain decreases, and the activity of the motion unit decreases, which is the crystallization effect and volume contraction effect of polysiloxane molecular chain at low temperature. Due to the phenyl structure, the regularity of molecular chain is destroyed and the crystallinity of silicone rubber (120-1 and 121-1) is greatly reduced in the range of -70°C~30°C. In the range of -30°C~70°C, the slope of the curve increases obviously, and low temperature crystallization is the main reason leading to the increase of 110-2VT. Affected by the combined influence of crystallization and volume shrinkage of silicone rubber, the mechanical properties of 110-VT increased first and then decreased. The mechanical properties of 120-1 and 121-1 showed obvious enhancement (Table 3). 120-1 is greatly affected by low-temperature crystallization effect, and it shows higher tensile strength (20.7 MPa) at -70°C, which is 4.1MPa higher than 121-1 (16.6 MPa).

![Figure 3 The stress-strain curves of 110-2VT, 120-1 and 121-1 at low temperature](image-url)
Table 3. Mechanical properties of samples at low temperature

| samples  | Temperature /℃ | Tensile strength /MPa | Rate change of Tensile strength/% | Elongation at break/% | Rate change of Elongation at break /% |
|----------|-----------------|------------------------|----------------------------------|-----------------------|---------------------------------------|
| 110-2VT  | 30              | 10.6                   | -                                | 184                   | -                                     |
|          | -10             | 13.4                   | +26.4                            | 209                   | +13.6                                 |
|          | -30             | 15.1                   | +42.5                            | 202                   | +9.8                                  |
|          | -50             | 17.4                   | +64.2                            | 167                   | -9.2                                  |
|          | -70             | 16.9                   | +59.4                            | 84                    | -54.3                                 |
| 120-1    | 30              | 10.5                   | -                                | 113                   | -                                     |
|          | -10             | 12.8                   | +21.9                            | 125                   | +10.6                                 |
|          | -30             | 15.4                   | +46.7                            | 132                   | +16.8                                 |
|          | -50             | 16.9                   | +61.0                            | 130                   | +15.0                                 |
|          | -70             | 20.7                   | +97.1                            | 138                   | +22.1                                 |
| 121-1    | 30              | 10.3                   | -                                | 121                   | -                                     |
|          | -10             | 12.5                   | +21.4                            | 135                   | +11.6                                 |
|          | -30             | 13.5                   | +31.1                            | 137                   | +13.2                                 |
|          | -50             | 14.2                   | +37.9                            | 141                   | +16.5                                 |
|          | -70             | 16.6                   | +61.2                            | 145                   | +19.8                                 |

4. Conclusion

The reliability of steel structural roof is computed under big data loads. According to the safety rules of the building and serviceability objectives, the Monte Carlo method is used to consider the uncertainty of roof load and the big data loads on the roof. The reliability of the steel structural roof under the big data loads was obtained. However, it should be noted that this reliability assessment is usually less than 25-45%. Although the reliability is similar, even if the roof design has the same load exceeding 50 years of the load, the substantial difference in probability shape will result in the distribution of the maximum snow load per year. Producing different reliability results, these are important for roof snow loads.

In addition, the application of this analysis method should be fully consider the difference climate and geological distribution. The annual maximum snow load has a great impact on the reliability analysis. At the same time, changing the physical characteristics of the roof has little effect on the reliability index. Secondly, there is a strong correlation between the reliability and maintainability of steel roofs. Finally, for the steel structural roof, the design of the deflection limit results in a larger cross-sectional dimension, resulting in considerable improvement in safety, maintainability and reliability.

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