Silicone fire-resistant composite material modification

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Abstract. The effect of the thermally expanding flame retardant dosage as well as its combination with the modifier - the product of silicone rubber waste destruction - on the properties of cold-cured compositions based on low-molecular-weight silicone rubber was studied. It was shown that equal mass substitution of aluminum hydroxide for thermally expanding graphite in an amount of 5% by weight results in sealants with a swelling ratio of 5.8, which is sufficient for fire retardant systems used in nuclear and thermal power plants. It was established that the use of an optimal amount of destructive material (5% by weight) in combination with thermally expanding graphite leads to an increase of the conditional strength at break of silicone flame-resistant cold-curing compositions by 35%. The use of thermally expanding graphite and the silicone waste destruction product in the formulation of a silicone sealant reduces the cost of the composites obtained by 6% in terms of raw materials.

1. Introduction

Composite materials based on low molecular weight silicone rubbers have a complex of unique properties: heat resistance (from -60 to +250°C), bio inertness, resistance to radiation and ozone exposure. This is due to the nature of their chemical bonds of the main molecular chain of the polymer. Thus, the Si – O bond energy in silicone polymers is 450 kJ / mol, while the bond energy of fluorinated carbon atoms in fluor elastomers is only 356 kJ / mol, the C – C bond in hydrocarbons is 336 kJ / mol [1].

Nonetheless, the each year growing fire safety requirements are forcing new ways to improve the flame retardant properties of silicone composites. These requirements are particularly high in the nuclear industry, aerospace, construction, automotive and shipbuilding.

One of the solutions is the creation of silicone fire-resistant sealants that form mechanically strong vulcanite foam (swelling effect) under the action of high temperatures (fires), which can significantly reduce the thermal conductivity of the coating [2-4].

The aim of the work is to increase the flame retardant properties of silicone composite materials (sealants, mastics) by modifying them with intumescent additives.

2. Research methods

Characteristics of the components used in the preparation of the prototypes of silicone flame-retardant sealant:

1. Low-molecular silicone rubber «107 RTV» - viscosity 20000 mm²/s (at 25°C), ρ = 0.975 g / cm³ (at 25°C), volatile matters 0.67% (at 150°C, 3 hours) (China).
2. Polymethylsiloxane 100 - a clear, colorless liquid, viscosity 100 mm²/s (at 25°C), volatile matters 0.65% (at 150°C, 3 hours), the refractive index 1.4030, the flash point 315°C (China).

3. Aluminum hydroxide special «FRAMIAL» - white powder, Al(OH)₃ content = 99.5%, ρ = 2.4 g/cm³, Mohs hardness 2.5-3.5, refractive index 1.56 -1.58, humidity <0.3%, electrical permeability (ISO 787-14) <100 µS/cm, pH = 8-10, loss on ignition > 34% (800°C, 1 hour), average particle size 15 microns. 1711-015-40705684-2006 Standart (Russia).

4. Thermo-expanding graphite - carbon content 99%, expansion ratio 350 ml/g, average particle size 177 microns, volatile matters content <10%, pH = 5-7 (China).

5. Diethylaminomethyltriethoxysilane (ADE-3) - a clear, colorless or yellowish liquid, the content of the basic substance is 90.02% (China).

6. Ethyl silicate-32 - a clear, colorless liquid, the SiO₂ content 32.47% wt., ρ = 0.9810 g/cm³, the content of chlorine ions is 0.001% wt. (China).

7. Silicone rubber waste destruction product - a grey suspension with a typical smell, pH = 6-7, the proportion of the solid phase is 50% wt, the chemical composition of the liquid fraction is 30% wt. oligodimethylsiloxane, 70% wt. oligoethoxysiloxane [5,6].

Standard physio-mechanical tests of sealants were carried out in accordance with State Standards: 21751-76, 21981-76.

The coefficient of expansion of vulcanizates was determined according to the method of VSK-04-2001 (Ministry of Emergency Situations of Ukraine). Two steel plates (50x50x2 mm) were uniformly applied with a sample of fire-resistant sealant. After complete vulcanization, the plates with the vulcanizer were thermostatically controlled for 3 hours at T = 70°C. Then the thickness of the applied coating of both plates was measured (L₁, L₂). Next the sample was placed in a muffle furnace for 30 minutes at T = 340°C, after which the thickness of the expanded coating was determined (L₁, L₂). The coefficient of expansion of the vulcanizates was determined by the formula:

\[ K = 0.5 \times \frac{L_{m1}}{L_{m1} + L_{m2}} / L_{m2} \]

(1)

3. Experimental results and their discussion

There is a huge amount of flame-retardant additives in the world, which can be classified as follows (Figure) [7-13].

Figure 1. Main types of fire retardants
In order to give the silicone sealants the effect of expansion under the action of high temperatures (fires), thermally expanded (thermo-oxidized) graphite was introduced into the silicone sealant formulation. The choice of this intumescent additive is determined by the lower cost (160 rubles/kg) and simplicity of introduction into the system compared to, for example, a system consisting of ammonium polyphosphate (165 rubles/kg) and pentaerythritol (130 rubles/kg). It should be taken into consideration that the amount of thermally expanding graphite in the composite, to achieve the desired coefficient of expansion, is less by 50-60%.

A series of physico-mechanical and fire tests made it possible to determine the optimal dosage of thermally expanding graphite in the composition of the sealant - 5.0% wt. (Table 1). This optimum is determined based on the fact that the required coefficient of expansion for silicone fire-resistant sealants used in fire-retardant systems at nuclear and thermal power plants is at least 5.

| Components                          | Content, % wt. |
|-------------------------------------|----------------|
| Low molecular weight silicone rubber| 30.0           |
| Polymethylsiloxane                  | 15.0           |
| Aluminum hydroxide                  | 55.0 - 51.0    |
| Thermally expanding graphite        | 0 - 4.0        |
| Curing composition (based on the finished paste): | 3.0 / 3.2 |
| ADE-3/Ethyl silicate-32             |                |

Table 1. Composition and technical characteristics of silicone flame-retardant sealant samples with different content of thermally expanding graphite

The name of indicators | Test results |
|-----------------------|-------------|
| Shore A hardness      | 35 - 37     |
| Conditional strength at break, MPa | 2.25 - 1.5 |
| Elongation at break, % | 210 - 165  |
| Swelling coefficient  | 1.3 - 5.8   |

However, the replacement of part of aluminum hydroxide by graphite led to a significant decrease in the physical and mechanical properties of the vulcanizate. This may be due to the poor distribution of the intumescent additive in the composition due to the larger volume of graphite compared to aluminum hydroxide.

The next step was to use the silicone rubber waste destruction product upon receipt of silicone sealant to improve the strength characteristics of the composite [14].

An efficient and cost-effective technology for processing silicone rubber wastes, developed at the «Vesto» LTD [15], allows to obtain liquid products of destruction, which can later be used as a water-repellent additives in water-dispersion paints [16]. In the course of further destruction products processing, which consists in their vacuum degassing [17], an «oligomeric» fraction is formed. It is used at «Vesto» LTD as a polyfunctional additive in the production of one-component industrial and household silicone sealants [14], as well as two-component potting and building mastic.

A complex of physical and mechanical tests showed that the optimal content of «oligomeric» fraction in the formulation was 5% wt. (table 2). The increase of the strength characteristics with the introduction of a destruction product into the system is primarily associated with the filler nanoparticles contained in it (particle size from 1 to 70 nm [5]), which, as is known [18,19], significantly increases the physical and mechanical properties of silicone rubber based products. The presence of oligodimethylsiloxane in the amount of 30% wt. in the liquid fraction [5,6] has a plasticizing effect on the process of obtaining a silicone flame-retardant sealant, allowing to replace part of the expensive imported plasticizer -
polymethylsiloxane, which ultimately will lead to a decrease in the cost of the final product (Table 3-4).

Table 2. Composition and technical characteristics of silicone flame-retardant sealant samples with different contents of the silicone rubber waste destruction product

| Components | Content, % wt. |
|------------|----------------|
| Low molecular weight silicone rubber | 30,0 |
| Polymethylsiloxane | 15,0, 14,0, 13,0, 12,0, 11,0, 10,0, 9,0, 8,0 |
| Destruction product | 0, 1,0, 2,0, 3,0, 4,0, 5,0, 6,0, 7,0 |
| Aluminium hydroxide | 50,0 |
| Thermally expanding graphite | 5,0 |
| Curing composition (based on the finished paste): ADE-3/Ethyl silicate-32 | 3,0 / 3,2 |

The name of indicators | Test results |
|-----------------------|--------------|
| Shore A hardness | 37 |
| Conditional strength at break, MPa | 1,5, 1,7, 1,8, 2,0, 2,2, 2,3, 2,1, 2,1 |
| Elongation at break, % | 165, 165, 160, 160, 155, 155, 155, 150 |
| Swelling coefficient | 5,8 |

The use of a destruction product as a technological additive does not change the production technology of silicone flame-retardant sealant.

A comparative analysis of tables 3-4 shows that an optimized formulation will reduce the cost of sealant production by 16,500 rubles (6%) per 1000 kg of finished product.

Table 3. Cost calculation of silicone fire-resistant sealant obtained by the control recipe

| Raw materials name | Raw materials amount, % wt. | 1 kg raw materials cost, rubles | 1 t of product price, rubles |
|--------------------|-----------------------------|-------------------------------|-----------------------------|
| Low molecular weight silicone rubber | 30,0 | 390,0 | 117000,0 |
| Polymethylsiloxane | 15,0 | 400,0 | 60000,0 |
| Destruction product | 0 | 70,0 | 0 |
| Aluminium hydroxide | 50,0 | 60,0 | 30000,0 |
| Thermally expanding graphite | 5,0 | 160,0 | 8000,0 |
| Curing composition (based on the finished paste): ADE-3/Ethyl silicate-32 | 3,0 / 3,2 | 1800,0 / 190,0 | 60080,0 |
| Total | | | 275080,0 |

Table 4. Cost calculation of silicone fire-resistant sealant obtained by the experienced recipe

| Raw materials name | Raw materials amount, % wt. | 1 kg raw materials cost, rubles | 1 t of product price, rubles |
|--------------------|-----------------------------|-------------------------------|-----------------------------|
| Low molecular weight silicone rubber | 30,0 | 390,0 | 117000,0 |
| Polymethylsiloxane | 10,0 | 400,0 | 40000,0 |
| Destruction product | 5,0 | 70,0 | 3500,0 |
| Aluminium hydroxide | 50,0 | 60,0 | 30000,0 |
| Thermally expanding graphite | 5,0 | 160,0 | 8000,0 |
| Curing composition (based on the finished paste): ADE-3/Ethyl silicate-32 | 3,0 / 3,2 | 1800,0 / 190,0 | 60080,0 |
| Total | | | 258580,0 |
4. Conclusion

Thermally expanding graphite introduction to the basic formulation of silicone flame-retardant cold-curing sealant in an amount of 5% by weight allows to get composites with a high temperature exposure coefficient of expansion equal to 5.8. At the same time there is a decrease in physical and mechanical properties. However, the combination of thermally expanding graphite in the same dosage with the silicone rubber waste destruction product leads to leveling of the strength properties, reaching the level of the indicator of tensile strength at break for the basic formulation at a dosage of modifier 5% by weight. Equal-mass replacement of expensive and scarce polymethylsiloxane liquid to the silicone rubber waste destruction product in the formulation of a sealant leads to a reduction in the cost of the finished product by 6% (in terms of raw materials).

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