TOPICAL REVIEW

Research status and development trend of ceramifiable silicone rubber composites: a brief review

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Abstract

Ceramifiable silicone rubber composites (CSR) are one of the most important industrially produced elastic technical materials. At present, there is a strong demand for CSR in the high-tech fields of high-speed rail, nuclear power, rocket and aerospace, which are still to be met. Many scholars have committed to the research work of improving the thermal stability, flame retardant, mechanical properties by changing the silicone rubber (SR) matrixes and filler, tremendous advances in CSR have been made for over the last decades where CSR intended for the high technology fields has evolved through different generations. In summary, the first-generation research is based on matrix reaction, the second-generation research is on reaction products, and the third-generation research is on fillers effects. In this review, the evolution of CSR and the synthesis routes, reaction mechanism, and degradation mechanism are introduced and analyzed; fillers, various types of CSR based composites as well as the flame retardancy and mechanical properties are reviewed. Finally, the problems of developing high-performance CSRs are proposed and discussed. This review provides a theoretical basis and supporting data for the application of high-performance CSR, as well as provides details on the fire prevention mechanism of CSR.

1. Introduction

New polymer materials have been developed at a high speed, while the fires become increasingly complicated, causing larger explosion and damage due to the resulting fire, which is difficult to extinguish. Especially, fire resulting from electrical equipment can cause financial and property losses and injuries may occur. With the development of science and technology, high-power electromechanical equipment has become increasingly common. Use of electrical equipment increases the risk of fire. Therefore, to keep the fire from spreading, flame-retardant materials are required. Magnesium oxide mineral insulation, mica powder [1], and other refractory materials are applied to the fire retardant wires and electrical fields to improve the fire resistance grade of wire. However, traditional materials are difficult to produce; the production process is complicated and expensive. The yield can only partly meet the needs of the high-tech fields. CSR is a type of polymer-refractory material. It is applied in the fields of decoration, safety cables, aerospace, and other fields owing to its safety, flame retardancy, low smoke, and nontoxicity. The application of CSR in these fields provides a new method for fire prevention. Compared with the traditional fire-retardant materials, CRS has excellent mechanical properties and corrosion resistance at room temperature, ensuring work and operation in a normal temperature environment. When a fire occurs, the temperature increases. CSR protects equipment from fire owing to the high strength of ceramic body [2, 3]. The ceramic body will not melt and drop in the fire environment, which acts as a safety feature that ensures power transmission in the case of a fire breakout and provides time for fire rescue.

The concept of polymer-ceramic composites was proposed by Professor Hanu [4], who found that the liquid phase spread into the surrounding matrix and the eutectic liquid phase penetrates into the SR matrix region as temperature and exposure time increases. Prof. Hanu et al [4] reported that when the firing temperature
increases to 1100 °C, SR with inorganic fillers undergoes a eutectic reaction to generate ceramics which possess good mechanical performance and flame retardancy. Based on which, it was concluded that CSR could be achieved by the ceramic reaction of SR and the addition of minerals according to the mechanism. Different fillers provide different CSR performances [4–6]. CSR fillers include porcelain fillers, melting aids, reinforcing agents, and flame retardant agents [2, 6]. The CSR content is optimized. The SR matrix and filler were improved during the experiment. Pędzich et al [7] studied the effect of wollastonite, bentonite, and kaolin on the properties of CSR when three minerals were used as fillers. Yang et al blended gaseous SiO₂ and silica gel matrices to study the influence of the change in the matrix on the CSR.

A low ceramization temperature, good flame retardancy, and excellent mechanical CSR are required. Many scholars have contributed to the research work on CSR. These studies have been carried out to improve the thermal stability, flame retardancy, and mechanical properties by changing the SR matrices and fillers [8]. However, this topic is not yet adequately understood, and a detailed review is also not presented in the literature [9–17]. This review first summaries the reaction mechanism, including the degradation mechanism of SR, flame retardancy mechanism, fire prevention mechanism of ceramics, and then the development process of the CSR is described in detail, the performance and application of CSR are presented, and finally, the problems and prospects of CSR are listed. In addition, the procedure of selecting the fillers for CSR, thermal stability, flame retardant, and mechanical properties, and the properties of CSR are also presented. This review is expected to lay the experimental foundation and provide a theoretical basis and supporting data for the development and application of high-performance CSR. This brief review also provides details about the fire prevention mechanism of CSR.

2. Reaction mechanism in high-temperature atmosphere

CSR is a new revolutionary material [12]. When applied in industrial production and daily life, its properties are non-toxicity, temperature resistance, excellent electrical insulation performance, and good processing performance of ordinary SR [13]. Because of the chain of organosilicon, when the temperature is lower than 500 °C, CSR begins to crystallize, forming self-supporting ceramic products with a small specific heat capacity. After crystallization, the crystallized material gains high strength, can withstand a higher impact force and resist the ablative of open flame above 1200 °C while maintaining the integrity of the product [18, 19]. It can be divided into the degradation, ceramic, and flame retardant mechanism of the SR according to the reaction of the CSR at temperature.

2.1. Degradation mechanism of SR

The basic unit of the main chain of SR is the main chain (–Si–O–). The organic groups are on the side chain. These organic groups on the side of the main chain constitute group Sr figure 1. Illustrates a detailed representation of the SR structure, where the side and main chains constitute the CSR [20].

For each side unit, the SR type shows a different specialty. The structure of the SR has confirmed this difference. These side groups affect the degradation behavior of the SR in a high-temperature environment and determine the strength of the SR. The SR whose side group with silanol end group (Si–OH) undergoes a condensation reaction between the molecular chains in the high-temperature environment during degradation, resulting in the viscosity average molecular content of the polymer. For example, when the polysiloxane was at normal temperature, during the process of polysiloxane degradation, the side produced a silanol condensation reaction; viscosity molecular weight increased, silicone hydroxyl produced a bite phenomenon in the internal module of polysiloxane in the high-temperature environment, and the high-molecular-weight polysiloxane fracture breaks and the breakage spawns main chain ring siloxane with low-molecular-weight. The mechanism of this reaction is illustrated in figure 2. This is the reason why the degradation mechanism of SR was named the release degradation mechanism.

The inert group on the side chain (–Si–(CH₃)₃) can lead to a random chain-breaking reaction of the Sr. This is because random intermolecular or intramolecular rearrangement reactions occur at the terminal of the inert

![Figure 1. Molecular formula of SR.](image-url)
group of polysiloxane at high temperatures. Polydimethylsiloxane (PDMS) was used to describe the random chain breaking reaction. The groups of PDMS have the structure –\([Si-(CH_3)_3]\), and the random rearrangement mechanisms at high temperatures cause the formation of hexamethyldisilane [20]. The reaction mechanism is shown in figure 3 [17]. Random chain-breaking reactions react to the surroundings of sufficient flexibility and high molecular polarity on the polymer backbone. Compared with the link degradation mechanism, the molecular weight of SR decreased sharply, and the molecular weight distribution increased sharply when the degradation temperature was reached. This is because a random chain-breaking reaction can occur at any position of the molecule. According to the study of Radhakrishnan [17], it was found that random chain-breaking degradation reactions occurred during the degradation of alkenyl capped PDMS. Random chain breaking and buckling reactions occurred during the degradation of hydroxy-terminated PDMS.

When SR contains catalysts and polar additives, the catalytic reaction of substances in a high-temperature environment intensifies the degradation of SR This degradation mechanism is called the external catalytic degradation mechanism [18]. According to Grassie [19], the presence of KOH (ring-opening polymer or polycondensation catalyst) in SR accelerates the fracture of the SR backbone, degrades and generates oligomers or silicon ions, as shown in figure 4.

The pyrolysis process of SR is related to the heating conditions and the gas atmosphere environment in which it is located [19]. This phenomenon reveals that there are two pyrolysis mechanisms and the interplay between the two mechanisms in the pyrolysis process: molecular mechanism and free radical mechanism.
Grassie et al. [19] studied the thermal degradation products of trimethylsiloxy terminal PDMS under different heating rates and gas atmospheres and proved that different heating rates and gas atmospheres would affect the generation of SR degradation products, indicating that the oxidative degradation and crosslinking of PDMS are competitive during pyrolysis. For example, when the heating rate of PDMS is 10° C min⁻¹, the main products are cyclic oligomers and trimers; at 80° C min⁻¹, they are cyclic oligomers and tetramers. The specific conditions for the oxidative and inert degradation of PDMS are shown in figure 5.

The free radical degradation mechanism of SR is used to explain the cracking of the –[Si–CH₃] chemical bonds in a high-temperature environment. During this process, methane is produced due to oligomerization. SR in a high-temperature environment generates macromolecular radicals I and II; these two kinds of macromolecular radicals can produce a crosslinking reaction, reduce the flexibility of the main chain of the PDMS, decompose cyclic polymers, and enhance the thermal stability of PDMS [4, 20]. In this process, two kinds of macromolecular radicals are accompanied by the fracture of the old chemical bonds, the formation of new chemical bonds, and the generation of black Si–O–C ceramic compounds [4, 20]. The specific radical reaction mechanism is illustrated in figure 6.

2.2. Mechanism of flame retardant
CRS fire-resistant materials possess the SR specialty of good thermal stability, and high corrosion residue has gradually attracted great attention. As shown in figure 7, CO₂ and H₂O were the main flue gases produced by the SR matrix after combustion. It is non-toxic and does not pollute the environment.

Under high temperatures, the SR matrix will break and decompose to generate silica.

As temperature increases, the fillers penetrate into the matrix region, followed by the reaction between the inorganic fillers and the silica from the decomposed polymer matrix, which forms a eutectic liquid phase. The extent of eutectic formation was further influenced by the particle size and chemical composition of the fillers. For example, calcium carbonate fillers decompose at high temperatures, as shown in Formula 1. Halogen flame
retardants produce toxic gases, as shown in Formula 2. Aluminum silicate ceramic fibers and some calcium silicate fiber fillers generate silica in the multi-empty ceramic layer of the composite material. A dense ceramic body was formed at high temperatures, as shown in Formula 3 [21, 22].

\[
R\text{CO}_3\text{R}\text{SiO}_3 \xrightarrow{\text{HEAT}} \text{RO} + \text{CO}_2 \uparrow + (\text{SiO}_2) \downarrow
\]  

\[
\text{X}_2 + \text{O}_2 \xrightarrow{\text{HEAT}} \text{X}_2\text{O} \uparrow
\]  

\[
\text{Fiber}[\text{SiO}_2\text{Al}_2(\text{SiO}_3)\text{m}] \xrightarrow{\text{porous structure} \text{HEAT}} \text{Ceramic}
\]

In the research on flame retardants, the flame-retardant mechanism can be divided into three theories [23–26]: 1. Gas-phase flame retardant mechanism; 2. Condensed-phase flame-retardant mechanism; and 3. Co-effective flame-retardant mechanism. While using a microscopic perspective to observe the phenomenon, the combustion process can be divided into several steps. (1) Fuel and oxygen are excited after decomposition. (2) These free radicals form a relatively stable state of matter. The intense luminescence and heating phenomenon during this process is combustion. Finally, (3) the gas-phase mechanism reduces and interrupts the combustion of fuel by reducing the content of the free radical of O. According to the reaction principle of the SR matrix provided in figure 7, Non-flammable gases can be generated by CSR at high temperatures. In a high-temperature environment, the chemical bonds break and generate free radicals, which reduces the oxygen concentration around the combustion and blocks the free radical reaction. However, under high temperature conditions, CSR produces a hard ceramic layer. After generating the ceramic layer, the condensed phase delays and terminates combustion. The mechanism of the reaction shows the performance of the condensed phase in the CSR. The flame-retardant mechanism of CSR is reflected by the addition of different flame retardants.

2.3. Ceramization and fire prevention mechanism

The concept of ceramifiable fire prevention for silicone rubber was proposed in 2004 [4], which was followed by a quick shift of the fire prevention research of SR from the traditional flame-retardant method to ceramifiable fire prevention method. Changing the organosilicon substrate and mineral powder filler [27] produces different types of CSR. The main chain of the polymer material is key to [Si–O]–, and the alkyl side chain is composed of vinyl, phenyl, and other organic groups. Owing to the high energy of the silica key, the material exhibits good fireproof performance. The theoretical mechanism confirms the fire prevention of CSR. In addition, CSR forms a hard ceramic body at high temperatures, ensuring the safety of the material. As the of [Si–O]– key breaks, SiO₂ is generated, and the three-dimensional network structure changes at high temperature, which further improves the thermal stability of the composite material, as shown in figure 8. The matrix degrades; a eutectic reaction occurs with the filler to form a new solid or liquid phase, and a bridge phase will arise [28], as shown in figure 8. After cooling and curing, a hard ceramic body is formed to protect the internal structure. According to the porcelain-forming process and physical properties of CSR [29], the reaction process of CSR can be divided into six categories, and the specific levels are shown in figure 9.
2.4. Mechanism comparison between traditional fire prevent and ceramization

The traditional flame-retardant mechanism involves the addition of halogen flame retardants such as chlorine and bromine to achieve good combustion resistance; however, large amounts of toxic gases such as CO, SO₂, H₂S, HCN, and black smoke are produced during rubber combustion. The release of poisonous smoke poses a serious threat to human health, and it is strictly prohibited because of heavy environmental pollution [30–33]. With the continuous improvement of environmental protection awareness, the toxicity and environmental pollution of halogen flame retardants have been widely studied. In addition, the mechanical properties of the traditional rubber materials will decline rapidly during the combustion process, so it is very easy to produce a structural collapse, which poses a major threat to personal safety. Therefore, it is theoretically and practically important to develop environment friendly and halogen-free flame retardants with low-toxicity, and high-efficiency for SR materials [32–35]. Ceramization is an efficient way to improve the fire resistance of rubber which can help to obtain a hard, durable, and porous ceramic structure during the process of burning at high temperature [32]. The flame retardant mechanism of CSR involves the addition of inorganic fillers to form a self-supporting ceramic material at high temperatures, and the ceramic layer has the properties of flame retardant,
fireproof, and high-temperature resistance. CSR decomposes into silicon dioxide during combustion, and a molten eutectic is formed between silicon dioxide and porcelain filler in the matrix through the eutectic reaction. At high temperatures, with the extension of time, the eutectic diffuses around, and the filler particles are continuously filled by the eutectic, and a dense ceramic shell is formed on the surface of the matrix which can isolate oxygen and heat and prevent further combustion of the matrix. Because the ceramic layer has high mechanical strength, the ceramic shell can withstand external impact and vibration [34–37].

2.5. The economic feasibility of using ceramifiable

The emergence of CSR meets people’s needs for safety and environmental protection. It can be widely used in places with high public fire protection and fire safety requirements owing to its excellent characteristics. For example, CSR simplifies the production, processing, laying, installation, and application of fire-proof wires and cables. Compared to the previous fire-proof and fire-resistant cables, the cost has been greatly reduced and the fire-resistant performance has been greatly improved, which has made great contributions to the wide popularization and promotion, especially for ordinary civil use [31–37].

The successful development and application of CSR has improved the scientific and technological levels of fire-protection products. It provides a revolutionary new idea and development direction for the advancement of flame retardant products, and provides a reliable, feasible, economic, safe, and cost-effective solution for the flame-retardant industry.

3. The composition of CSR

The composition of the composite material determines its characteristics. When CSR was proposed, the physical and chemical properties of the CSR were optimised by changing the matrix and filler of the CSR.

3.1. Matrix materials

The SR is a silicone crosslinked skeleton, as shown in figure 10, which ensures that CSR has both organic and inorganic polymer properties [38]. Compared with rubber, whose main bond is the –C–C– bond, the chemical key of the main chain of SR is the –Si–O– bond. Because the bond energy of the –Si–O– bond (451 kJ mol⁻¹) is greater than that of the –C–C– bond (345 kJ mol⁻¹), the thermal stability of SR is more stable than that of other rubber. In addition, the macromolecular chain of SR is a helical molecule with a small intermolecular force, ensuring that SR has a certain resilience [39]. The helical structure of the alkyl ensures that SR has unique surface properties such as hydrophobicity, surface anti-viscosity, physiological inertia, and biocompatibility [40, 41]. SR can not only work between −200 °C and 400 °C [6], but also has good flame retardancy with thermal stability [42] when burning.

The intramolecular structure of SR ensures low-and high-temperature resistance. However, different vulcanisation mechanisms have a slight impact on the internal molecular structure [43]. According to vulcanization methods, SR can be divided into normal temperature vulcanization (RTV) and high-temperature vulcanization (HTV), which can be divided into several types, as shown in figure 11. Because the relative molecules of the active end groups of the SR are different at different curing temperatures, the molecular weight of the active end groups of RTV is lower and can be prepared at normal temperature, while the active end group molecules of HTV are higher and can be prepared at high temperature [44, 45].

3.2. Ceramifiable filler

SR has excellent physical and chemical properties. However, SR is easy to decompose during application, and SR is not easy to extinguish when it burns. To broaden the application of SR, it is necessary to add different fillers to the SR. Fillers can be divided into porcelain fillers, fluxes, reinforcing fillers, flame retardants, and other categories.
The ceramic filler supports the decomposition of SR, which can improve the thermal stability of the CSR. To meet this requirement, a porcelain filler with a high melting point is required. From the perspective of composition, the ceramic filler is either silicate or other inorganic powders. Common porcelain fillers include mica, kaolin, and calcium carbonate. Mica, which possesses excellent electrical and thermal insulating properties, is used as a porcelain filler for CSR. Zhang Xi et al prepared CSR by adding mica as a ceramic filler. The thermal properties of the composites were tested at different temperatures. The products were analysed by thermogravimetry-differential scanning calorimetry, Fourier transform infrared spectroscopy, and X-ray diffraction. The results show that mica powder can produce a phase transition ceramic reaction with SR at high temperatures (above 600 °C). The higher the temperature, the better is the ceramic performance. Thus, it can be speculated that the silica produced by the decomposition of SR reacts with mica powder to form a eutectic mixture with a bridging structure, and the ceramization product is formed after cooling [46]. The decomposition of calcium carbonate at high temperatures absorbs a certain amount of heat. The decomposition of CaO and SiO2 at high temperatures creates a calcium silicate ceramic layer which is a common porcelain filler. Wang et al [47] developed a type of CSR which contains calcium carbonate decomposed at a high temperature, and finally released carbon dioxide and generated calcium silicate. The release of carbon dioxide was synchronized with ceramization. Ceramization can effectively prevent cracking of calcium silicate. The conversion chemical equation is shown in equations (4–7) [47].

\[
\begin{align*}
\text{PDMS} & \rightarrow \text{SiO}_2 + \text{VOC}(>500 \, ^\circ\text{C}) \\
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 (>600 \, ^\circ\text{C}) \\
\text{CaO} + \text{SiO}_2 & \rightarrow \text{CaSiO}_3 (>800 \, ^\circ\text{C}) \\
2\text{CaO} + \text{SiO}_2 & \rightarrow \text{CaSiO}_4 (>800 \, ^\circ\text{C})
\end{align*}
\]

Kaolin, whose chemical composition is aluminum acid, is also a common filler for porcelain formation. Rybiński, Przemysław et al [48] prepared porcelainable refractory SR composites with clay minerals that were used as porcelain fillers. It was analyzed by TG/DSC, and the thermal stability of the materials was tested. The results show that the thermal stability of SR can be improved by adding clay minerals. The decomposition temperature can be increased by approximately 100 °C. By XRD analysis and SEM observation, it was found that, except for a small number of impurities, the SR phase after ablation at 600 °C is cristobalite, and the phase after ablation at 1200 °C is mullite and cristobalite. The micro-morphology characteristics are a compact flocculent structure. The porous structure was connected by the liquid phase after ablation at 1200 °C. The conversion equation is shown in equations (8–10) [48].

\[
\begin{align*}
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} & \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}(>600 \, ^\circ\text{C})
\end{align*}
\]
In addition, the addition of fibre fillers such as carbon, aluminium silicate ceramic, and calcium silicate, can also improve the mechanical properties and thermal stability of CSR. Imielia et al. [21] studied the effect of carbon fibres on the thermal properties and mechanical strength. They changed the filler ratio and produced different CSRs with different properties. The results show that adding different ratios of carbon fibre can effectively enhance the mechanical properties of the ceramic structure of SR [49–51]. The addition of carbon fibres can increase the compressive strength of the composite. During the low-speed heat treatment phase, the flammable carbon fiber provides additional heat energy, which enables the flux to form a more solid connection with the mica powder and silica particles. In the high-speed heat treatment phase, most of the carbon fibers remain unburned, which can significantly enhance the ceramic strength of the composites. Yu et al. [22] studied the thermal properties and ablative resistance of SR prepared using aluminium silicate ceramic and calcium silicate fibres as ceramic fillers. The morphology, composition, and ablative resistance of the residue were analyzed after ablation using an oxyacetylene torch. The results show that there are three different ceramic layers in the composite ablative residue. In the porous ceramic layer, SR is decomposed to produce trimer, tetramer, and silica powder, while aluminium silicate ceramic fibers and some calcium silicate fibers exist in the compact layer.

3.3. Lacquer solvent

The liquid phase was formed when the flux melted SR, which reacted with the decomposed SR to generate a ceramic body with a certain strength. Therefore, the melting point of the flux was lower. Common fluxes [21] are low-melting-point glass powder, boron oxide, and zinc borate. The low eutectic theorem means that in a multi-binary system, two components can melt into a liquid phase at any ratio during the heating process. If two components are mixed in appropriate proportions, both solid components can melt at a temperature usually below the melting point of each pure component. According to the low eutectic theorem, it can be seen that the eutectic temperature of porcelain-forming materials decreases when the component systems are formed in CSR. The melting point of the ceramic fillers (mica, kaolin, and wollastonite at approximately 1800 °C, 1735 °C, and 1450 °C) is high. According to the low eutectic theory, substances with low melting points are added to reduce the melting point of porcelain-forming materials. In the preparation process of CSR, first, the flux of silica and filler reaches the melting point; second, the flux forms the molten liquid phase, and the fillers flow between the porcelain and the pores of the SR; as the temperature increases, a more liquid phase is formed. When the temperature decreases, the bridging effect occurs with the surrounding substances to increase the strength [6]. Glass powder has a low melting point flux. According to Hanu et al. [4, 20, 52], fractions can promote the ceramicification process. However, it reduces the thermal stability of CSR. Mica and FeO can reduce the heat release rate of CSR and improve the stability of the matrix. Wu et al. [53] used scanning electron microscopy and found that an increased ratio of Frits would weaken the internal density of the porcelain products. Some boron-containing oxides can be used as a CSR flux. According to Ying-Chieh. Lee [34], Jeong-Ryeol Kim [55], Siska Hamdani [56], zinc borate glass, and zinc borate have low melting points. Alexander G [57] et al found that zinc borate has good stability after dehydration and can replace glass as a filler. In addition, it can be used as a flame retardant and plays a role in flame retardancy.

3.4. Flame retardant

Based on its composition, flame retardants can be divided into halogen-and halogen-free flame retardants. Halogen-free flame retardants are further classified as phosphorus-based flame retardants, nitrogen-based flame retardants, metal oxides, and compound flame retardants [58–60]. The metal oxide flame retardants used in CSR fillers are Al(OH)₃ and Mg(OH)₂ [61–63]. Flame retardants undergo exothermic decomposition and release a large amount of water during combustion, which can reduce the temperature of combustion and dilute the concentration of combustible gases. In addition, the decomposition of Al(OH)₃ and Mg(OH)₂ generates dense compounds Al₂O₃ and MgO, which cover the surface of the polymer and can play a role in heat isolation and oxygen. However, the flame-retardant efficiency of metal hydroxide is low. In order to improve it, Metal oxide flame retardants are usually used to improve the crosslinking effect between SR and filler. A silane coupling agent was added to the metal oxide to improve the hot-vulcanized SR/aluminum hydroxide flame retardant system. The study found that a silane coupling agent added to the hot vulcanized SR-aluminum hydroxide flame retardant system of aluminum hydroxide can be evenly dispersed in rubber, improve the flame retardancy of the material and mooney viscosity of rubber [7].

In addition to increasing the flame-retardant performance of CSR, substances that promote the expansion of SR can also be added. This flame retardant expands in a high-temperature environment through CSR, isolating the contact between the protected material and the flame. The specific flame-retardant process is illustrated in figure 1.2. The process of expansion into porcelain is illustrated in figure 1.3. According to the figure, Li Jianhua [64] prepared modified CSR by adding expandable graphite (EG) to the filler and tested the performance of

\[
2(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \rightarrow 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{SiO}_2 (950 °C \sim 1050 °C) \quad (9)
\]

\[
3(2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2) \rightarrow 2(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) + 5\text{SiO}_2 (>1095 °C) \quad (10)
\]
oxygen index, vertical combustion performance, thermogravimetric analysis, and expansion test. The oxygen index effect was found to be the best when the ratio of expandable graphite and aluminum hypophosphate was 1:1. This is the reason why the combination of the two causes the carbon layer to become dense and improves its strength, isolating air and heat. When ten parts of expandable graphite and aluminum hypophosphate are added, the oxygen index increases from 30.6 to 40.8, and the vertical combustion reaches the V-0 grade from no grade and reaches the self-extinguishing from the fire. This is the reason for the rapid expansion of graphite at the initial stage of heating. When the two are combined, the pHRR decreases from 455 kW m$^{-2}$ to 259 kW m$^{-2}$, and the decrease in pHRR is determined by the condensed phase. When the expandable graphite expands, it produces a large amount of carbon residue, which mainly affects the condensed phase. Block air and heat. Phosphine generated by the decomposition of aluminum hypophosphate can be oxidized in air to form

**Figure 12.** Protection schematic of power cable tray by the expandable CSR.

**Figure 13.** The process schematic of expanding into ceramics for CSR.
polyphosphate. The experimental data are listed in table 1. The thermal degradation analysis of SR shows that the addition of aluminum hypophosphate has a good effect on increasing the thermal stability of the material. With the addition of aluminum hypophosphate, the residual carbon increased. Moreover, the strength increased.

3.5. Reinforcing filler

The mechanical properties of ordinary SR are poor. The Shore hardness, tensile strength, and elongation at break (%) were found to be 31, 1.7 Mpa, and 332.5, respectively [65]. High-temperature vulcanization and SiO₂ modification are required before common use. To solve the problem of poor mechanical properties of SR, it is important to add a certain reinforcing agent to the Sr Silica, carbon black, and calcium carbonate are commonly used [66–68].

SiO₂ is commonly used as a reinforcing agent to improve the mechanical properties of CSR. Wang [13] enhanced the mechanical properties of CSR by changing the proportion of silica in CSR. The mechanical properties, flame retardancy, thermal stability, and combustion properties of different proportions of CSR were tested. The experimental results show that the mechanical properties of the composite can be improved by using silica. When silica was added at 40 phr, the mechanical properties of the composite reached the maximum value, the tensile strength was 9.35MPa and the elongation at break was 614.7%. This occurs due to the hydrogen bonds being formed between the hydroxyl group on the surface of silica and the SR polymer which strengthens the interface bonding force between various components of CSR. However, when the ratio of silica is too high, agglomeration occurs, which reduces the mechanical properties. The experimental data for the above are listed in table 2. When the amount of silica reached 50 phr, the limiting oxygen index of the composite reached 25.0%.

The specific data are presented in table 1. Through thermogravimetric (TG) and thermogravimetric (DTG) analyses of different proportions of CSR, it was found that the addition of silica could improve the thermal degradation temperature of CSR, and the addition of silica could significantly improve the initial thermal decomposition temperature and high-temperature carbon formation rate of the composites. The initial thermal decomposition temperature was 495.4 °C. When the amount of silica was 40 phr, the high-temperature carbon residue rate was 31.4%, the specific data for which are shown in table 1. A cone calorimeter was used to test the
combustion performance of different proportions of CSR, and it was found that silica was being added, as shown in table 1. This could reduce the heat release rate, total heat release, total smoke generation, and carbon dioxide generation in composite materials. In addition, white carbon black also affects the expansion of CSR after it gets converted into a charcoal (figure 14). This proves that when heated white carbon black migrates to the surface to form a carbon layer, it traps the heat transfer, protects the internal matrix, and reduces the internal matrix decomposition. At the same time, the volatile gas produced by pyrolysis of SR leads to the expansion and foaming of the carbon layer. The addition of silica promoted the formation of an expanded carbon layer. The
carbon layer is not continuous and compact. Therefore, the addition of silica can effectively reduce the heat release rate of the composite.

4. Performance and application of CSR

Compared with traditional fireproof materials, CSR functions as a flame retardant in a high-temperature environment. With the exception of good performance in a high-temperature environment, CSR can play a corresponding role in a low-temperature environment.

Since the 1990s, research on CSR began [67]. This is because the flue gas generated by the combustion of the SR matrix was CO$_2$ and H$_2$O. Their combustion properties are non-toxic and they do not pollute the environment. CSR has been used as a ceramic fire-refractory material. After combustion, organosilicon exhibited excellent high-temperature resistance. The preparation of a porcelainable flame-retardant refractory with silicon has advantages in both the selection of the process and raw materials [68]. However, SR reacts in a high-temperature environment and has defects in its mechanical properties after high-temperature porcelain formation. CSR needs to be optimized. By analyzing the mechanism of CSR in a high-temperature environment, the properties of CSR can be changed by changing the type of CSR filler [69].

To obtain the ideal CSR, many scholars have conducted studies on the matrix of CSR to the filler (figure 14). At present, the research field is focused on improving the mechanical properties, thermal stability, flame retardancy, and other fire protection fields of CSR by changing the types of fillers. It is expected to improve the mechanical properties as well as the flame-retardant properties, table 3 shows the expansion performance of SR was improved by adding EG and AHP [64].

In addition to the application of CSR in the daily flame retardant field, SR has a wide range of applications in aerospace, nuclear power plants, military, and so on. It is important to improve the resistance of Sr Nano titanium dioxide was used as the radiation-resistant additive of Sr It was found that the mechanical property storage modulus and glass transition temperature of the SR with the radiation-resistant additive were less than those of the ordinary Sr Hanu [72] et al chose tungsten carbide and boron carbide as shielding materials for γ-rays. In the presence of barium sulfate, diamond, pile, and other substances prepared with a high radiation resistance at room temperature, vulcanized SR is used in aerospace and military nuclear weapons fields. At present, there are many methods to improve the resistance of a material, including the addition of rare earth metals and radiation resistance additives. Radiation-resistant SR can be prepared by adding radiation-resistant additives. However, the compatibility of additives and the organic matrix is poor, which can easily cause a decrease in the mechanical properties. The other aspect is the preparation of SR containing irradiation-resistant groups by adding benzene rings to the main side chain. There are many disadvantages in that the chemical reaction is too complex to control. Currently, there is a lack of research on improving the irradiation-resistant performance of CSR Adding irradiation-resistant agents is a feasible scheme for improving irradiation-resistant performance.

5. Problems and prospects

Research on the modification of CSR has achieved significant results, and CSR with certain characteristics has been successfully developed. The CSR specialty can meet the needs of specific fields. However, at present, there are still some problems.

1) As CSR performance improves, CSR modification is often accompanied by other performance degradations. This is because the preparation methods cannot guarantee the stoichiometric ratio, nor manufacturing techniques can guarantee the uniform distribution of dispersed phases in the matrix [70]. It is necessary to use the preparation method of CSR or to add different fillers to increase the cross-linking effect between each filler and matrix. In addition, it can improve the performance of CSR synergistic fillers.

2) Depending on its chemical composition and crystallization characteristics, the material exhibits different performances. The microstructure of materials is related to performance [75–77]. The macroscopic properties of a material are determined by its microstructure. According to previous studies, the relationship between the microstructure and pyrolysis, expansion and contraction, and elastic mechanics has not been revealed. When heated, the microstructural change of the material affects the thermal behavior of the material. Changes in the thermal properties of materials directly affect the thermal response characteristics of materials during service, which is very important for the service reliability of high-performance CSr. To meet the requirements of CSR in high-tech equipment, it is necessary to conduct research to improve the radiation resistance performance and reliability of CSR.
(3) Research focuses on the formula design and properties. There is less research on the systematic theory of CSR, which limits the development of CSR.

6. Conclusion

High-end equipment manufacturing fields, such as high-speed rail, nuclear power, rocket, and aerospace, have increasingly high requirements for flame-retardant refractory materials. Traditional fire-retardant materials fail to meet the requirements of ablative resistance and thermal protection of high-end equipment. Currently, the ablative structure of CSR is uncertain. This limits the development of the CSR. Therefore, it is important to understand the internal relationship between the CSR formula and porcelain flame retardancy, and it is necessary to clarify the structure and chemical reaction of CSR.

In this review, the mechanism, composition, application, and problems of CRS are discussed. The development and methods for producing new CSR are described in detail. The procedure for selecting the fillers in CSR, thermal stability, flame retardancy, and mechanical properties and properties of CSR are also presented. The CSR performance is shown in the table. The reaction mechanism of CSR has analysed the reaction of the filler at different temperatures, and the reasons for the performance changes in CSR were proved. However, most of the SR matrices used in current studies are RTV and studies on other types of SR. In the research direction of CSR packing, the influence of a single substance on CSR performance has been gradually extended to the coupling effect of multiple fillers. With the expansion of the CSR research field, research on CSR will gradually move from a single direction to multi-field and multi-level research. By changing the types and proportions of the SR matrix and filler, the CSR will show different performances. Therefore, it is necessary to clarify the ablative mechanisms of CSR. The ceramic structure and the mechanism of flame retardancy were systematically investigated for effective control of the ceramic temperature, expansion temperature, and degree. The correlation and internal regularity were revealed by observing the changes in the microstructure and the evolution of the thermal properties.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest/Competing interests

The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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