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Synthesis of Cerium-containing Polymethylphenyl Silicone and Its Antioxidant Effect on Fluorosilicone Rubber

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Abstract As an essential elastomer used in edge technologies, fluorosilicone rubber (FSR) suffers serious oxidative ageing problem when serving at high temperature. Cerium oxide is generally used as an antioxidant additive but remains unsatisfactory. In order to obtain better antioxidant effect on improving the thermal stability of FSR, a kind of cerium-containing polymethylphenyl silicone (PSI-Ce) was synthesized and the structure was verified by Fourier-transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (¹H-NMR). Due to the homogeneous dispersion on molecular scale, PSI-Ce imposed much better antioxidant effect than the commercial CeO₂ did, no matter from isothermal degradation at 320 °C or thermal-oxidative ageing test at 230 °C. In particular, after ageing for 72 h, FSR/PSI-Ce (2 phr) maintained 82% of tensile strength and 63% of elongation at break, in comparison to the corresponding values of 48% and 42% for FSR/CeO₂ (2 phr). Moreover, 2 phr PSI-Ce was equivalent to 0.046 phr CeO₂ according to cerium element conservation.

Keywords Polymethylphenyl silicone; Cerium; Fluorosilicone rubber; Thermal stability

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INTRODUCTION

Fluorosilicone rubber (FSR) generally refers to the compound of poly[methyl(trifluoropropyl)siloxane] (PMTFPS) and nano-silica. Benefiting from the Si—O—Si backbone and fluorocarbon side chain of PMTFPS, FSR possesses excellent fuel and chemical resistance in a wide operating temperature range from −60 °C to 200 °C. Accordingly, it has been widely applied in petrochemical, astronaut navigation, and automotive industry.^[1–10] However, when FSR products are used at temperature above 200 °C for extended periods of time, they tend to be failed according to two main thermal degradation mechanisms:^[11–17] (I) rearrangement reactions of main chain to generate cyclic siloxane oligomers, and (II) the oxidative scission of side groups. Our previous work^[18–20] has indicated that mechanism II played the major role for the degradation at temperature below 300 °C. In order to inhibit such oxidative scission, the most common approach is to incorporate antioxidant additives.

Typically, metal oxides^[21] (including Fe₂O₃,^[22,24] CeO₂,^[25,26] ZnO,^[27] Al₂O₃,^[27,28] etc.) and organometallic compounds^[29,30] have been reported to act as antioxidant additives to improve the thermal stability of silicone elastomers

in many studies. Among these metal oxide additives, ceria oxide is one of the most frequently-used thermal stabilizers for polysiloxane due to its high efficiency in inhibiting oxidation scission of side groups.^[31] In our previous work,^[20] ceria particles of different shapes and sizes were studied as thermal stabilizers for FSR. The result indicated that surface modified ceria nanoparticles, which had larger specific surface area and higher dispersibility in matrix, significantly improved the thermal stability of FSR. For the improvement of dispersibility of metal-oxides or organometallic compounds, the commonly used organic agents are silicone compounds or polymers.^[32–34] Huang^[35] introduced a supercritical treatment for carbonyl iron powder (CIP) with silicone polymers containing reactive Si—OCH₃ groups. Li^[36] directly synthesized a polysilazane containing iron (PSZI) as an additive and improved the anti-oxidation property of silicone oil and rubber at 300 °C. Generally, increasing the dispersibility of antioxidants (such as Ce⁴⁺ and Fe³⁺) inside polymer matrix has become an effective way to improve the heat resistance of FSR.

In this work, a kind of cerium-containing polymethylphenyl silicone (PSI-Ce) was synthesized and used as antioxidant of FSR. The structure of PSI-Ce was characterized by FTIR and ¹H-NMR. The thermal stability of FSR incorporating PSI-Ce, PSI, and commercial CeO₂ was evaluated through TG, isothermal weight loss at 320 °C and thermal

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oxidative ageing at 230 °C. The results indicated that PSI-Ce possessed much better antioxidant property than commercial CeO₂ did because of its good dispersion inside FSR.

EXPERIMENTAL

Materials

Cerium(III) chloride (CeCl₃, 99.5%), 1,3-divinyltetramethyldisiloxane (DVTMDS, 98%), acetone (AR), and potassium hydroxide (AR) were supplied by Shanghai Taitan Co., Ltd. Cerium dioxide (99.99%, ≤ 5 μm), chlorodimethylvinylsilane (CDMV, 97%), and 2,5-dimethyl-2,5-di(*tert*-butyl) peroxyhexane (DBPH) were obtained from Aladdin Chemicals (Shanghai, China). 2,4,6,8-Tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane (P₄, 95%) was purchased from Changshu Changel Chemical Co., Ltd. Poly(3,3,3-trifluoropropyl)methylsiloxane (PTFPMS, $M_w = 8 \times 10^5$, $M_w/M_n = 1.5$, incorporated with 0.4 mol% methylvinylsiloxane units) and hydroxyl-terminated fluorosilicone liquid FSIR-301 ($\eta = 100$ mPa·s, hydroxyl value equal to 5–7 mg KOH/g) were obtained from FSIR Advanced Material (Zhenjiang, China). Hydrophobic fumed silica A200 (surface area equal to (200 ± 25) m²/g) was supplied by Evonik Degussa Specialty Chemicals (Shanghai, China). All of these reagents were used as received.

Synthesis of PSI-Ce

Firstly, the mixture of KOH (0.94 g), P₄ (54.5 g), and DVTMDS (2.33 g) were added into a 250 mL four-necked flask equipped with a reflux condenser and a stirrer. This reaction was conducted in oil bath at 120 °C for 1 h. Then, the bath temperature was cooled to 40 °C. CeCl₃ (2 g, dissolved in acetone) was added to the flask dropwise. After being stirred for 4 h, the obtained yellow sticky product was filtered and dried in a vacuum oven at 150 °C. The reaction scheme is depicted in Fig. 1. In comparison, compound PSI was prepared by P₄, KOH, and DVTMDS according to the same method above, but terminated by chlorodimethylvinylsilane (CDMV).

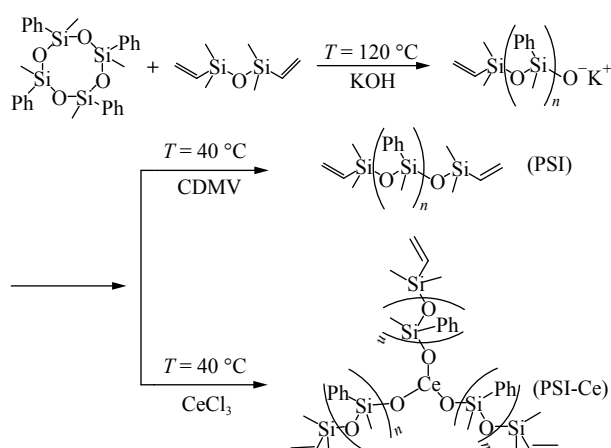


Fig. 1 Reaction scheme for the preparation of PSI and PSI-Ce

Preparation of FSR Specimens

The FSR composites were prepared by blending 60 g of PTFPMS, 21 g of A200, 4 g of FSIR-301, and specific loa-

ding of PSI-Ce, PSI, or CeO₂ (premixed with A200) in a torque rheometer (SU-70, Changzhou Suyan Science and Technology Co., China) at 170 °C for 10 min. Then, 0.8 g of DBPH was added into each composite using a two-roll mill (760, Jiangdu Xuanyu Experimental Machinery Plant, China). The resulting compounds were placed in a 130 mm × 170 mm × 2 mm mould for vulcanization, which was operated at 170 °C and 10 MPa for 10 min and then post-cured in an oven at 200 °C for 4 h.

Characterizations of PSI-Ce

FTIR spectra were obtained from a Nicolet 6700 infrared spectrometer (Thermo Electron Scientific Instruments Corp) using a KBr-pressed plate. Each spectrum was recorded at a resolution of 2 cm⁻¹ between 4000 and 400 cm⁻¹. ¹H-NMR spectra were recorded on a 600 MHz NMR spectrometer (Advance 600 NMR, Bruker) using deuterated dimethylsulfoxide as the solvent at ambient temperature.

Characterizations of FSR Composites

Scanning electron microscopy (SEM) images were taken by the S4800 (Hitachi, Japan) instrument at an accelerating voltage of 15 kV. The samples were gold-sputtered prior to the observation.

Isothermal ageing experiments were carried out in a TCXC-1700 muffle furnace (Shanghai Tongcoo Electric Equipment, China). The specimens cut into small sizes were placed into graphite crucibles and charged in the muffle furnace setting to 320 °C. The mass of each specimen was recorded at an interval of 20 min.

Thermal oxidative ageing treatment for FSR composites was performed at 230 °C in an ageing oven XY-401 (Jiangdu Xuanyu Testing Machinery Factory, China) for 72 h. Then, tensile strength (TS) and elongation at break (EB) of the FSR composites were measured using an electrical universal testing machine CMT-2203 (MTS, America) with a displacement rate of 500 mm/min according to ISO 37:2005. The specimens were shaped into dumb-bell type I.

Thermogravimetric analysis (TGA) was performed in air or nitrogen atmosphere between 25 and 700 °C at a heating rate of 10 °C/min using a NETZSCH STA409PC TA instrument (Netzsch, Germany).

MDR-2000 vulcameter (Wuxi Liyuan Electronic Chemical Engineering Equipment Co., Ltd. China) was applied to study the curing characteristics of the compounds. The swing frequency was fixed at 1.67 Hz and the swing angle was ± 0.5°. DBPH was used as the vulcanizer, and the test temperature was set as 170 °C.

RESULTS AND DISCUSSION

Characterization of PSI and PSI-Ce

Molecular structures of PSI and PSI-Ce were confirmed by FTIR and ¹H-NMR. Fig. 2 shows the FTIR spectra of PSI and PSI-Ce. For PSI, the absorption bands at 3070, 3050, 1591, 1483, 1428, and 730 cm⁻¹ are characteristic peaks of mono-substituted Si—C₆H₅ group, and 3009 cm⁻¹ is ascribed to stretching vibration of C—H of —CH=CH₂. The bands at 2962, 2905, 1261, 787, and 698 cm⁻¹ are attributed to Si—CH₃ groups, while those at 1127, 1095, and 1022 cm⁻¹

belong to S—O—Si.^[37,38] The spectrum of PSI-Ce is similar to that of PSI, except two significant differences. One is that the anti-symmetric stretching vibration of Si—O—Si (1095 cm^{-1}) shifts to 1083 cm^{-1} , which is probably due to the increase of mean Si—O distance caused by the substitution of small silicon by larger Ce^{3+} ;^[39–43] the other is that a new absorption band emerges at 595 cm^{-1} , corresponding to Ce—O group.

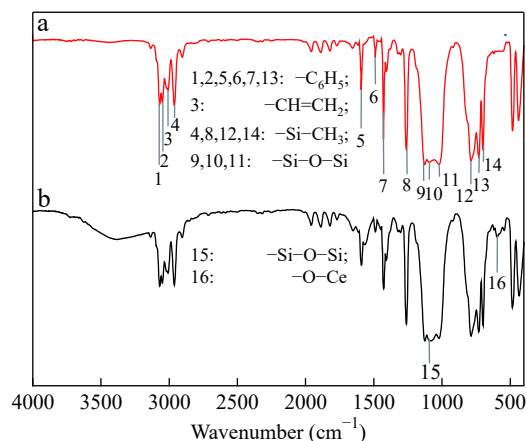


Fig. 2 FTIR spectra of (a) PSI and (b) PSI-Ce

$^1\text{H-NMR}$ spectra further validated the structures of PSI and PSI-Ce, as shown in Fig. 3. For PSI, the signals at 6.71–7.59 ppm are attributed to the protons on phenyl group. However, for PSI-Ce, the signals of protons on phenyl group shift to 6.86–7.68 ppm. This may be due to the fact that vacant orbitals on cerium attracted lone pair electrons of other atoms, reducing the electron cloud density of the hydrogen atoms on phenyl group, and then made the signals move to the lower field.

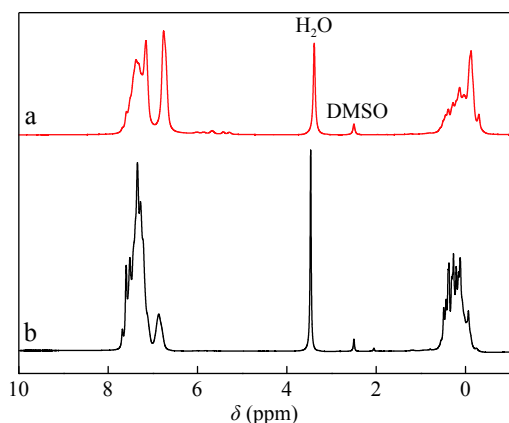


Fig. 3 $^1\text{H-NMR}$ spectra of (a) PSI and (b) PSI-Ce

Dispersion States of CeO_2 and PSI-Ce in FSR

Fig. 4 shows the SEM images of fracture section of FSR/ CeO_2 (2 phr) and FSR/PSI-Ce (2 phr). Plenty of microparticles and aggregates with dimension of several microns can be observed in the SEM image of FSR/ CeO_2 (2 phr), indicating that the commercial CeO_2 particles were difficult to be homogeneously dispersed in FSR matrix. In contrast, FSR/PSI-Ce (2 phr) specimen revealed a homogeneous phase,

suggesting PSI-Ce was much easier to disperse in the FSR matrix. As a result, the Ce of PSI-Ce had much more opportunities to contact with polymer matrix than commercial CeO_2 did.

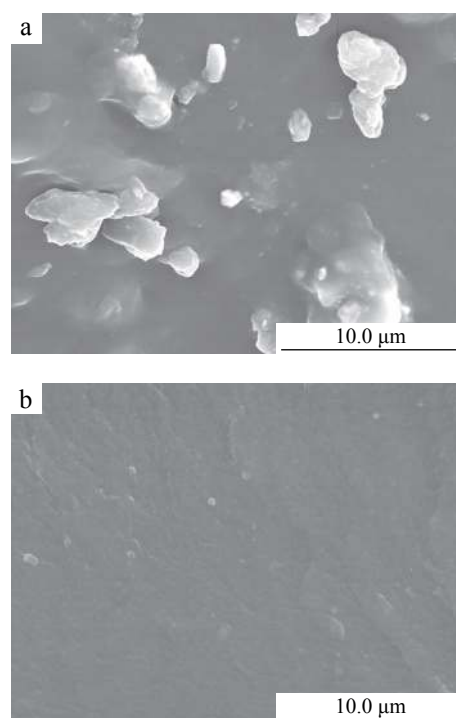


Fig. 4 SEM images of fracture sections of (a) FSR/ CeO_2 (2 phr) and (b) FSR/PSI-Ce (2 phr)

Thermogravimetric Analysis of FSR Composites

Fig. 5 presents the TG and DTG traces of FSR and FSR/PSI-Ce (4 phr) in air and nitrogen, and the detailed data are listed in Table 1. Herein we use T_{onset} (temperature at 5% of weight loss) and T_{max} (temperature at the minimum value on DTG trace) to indicate the initial decomposing temperature and the maximum decomposing temperature.

From the trace of neat FSR in nitrogen, it can be seen that FSR started to deteriorate from $445\text{ }^\circ\text{C}$ and rapidly degraded at around $493\text{ }^\circ\text{C}$. The residue weight (28%) was approximately equal to the addition amount of silica (25%). Therefore, the polymer of FSR, PMTFPS, degraded mainly into cyclic monomers by chain rearrangement (mechanism I) and volatilized. When the thermogravimetric analysis was performed in air atmosphere, FSR started to deteriorate from $338\text{ }^\circ\text{C}$ and revealed a two-step degradation: stage I ($338\text{--}397\text{ }^\circ\text{C}$) and stage II ($397\text{--}500\text{ }^\circ\text{C}$). According to the degradation mechanism of FSR,^[18,19] the weight loss in stage I should result from the oxidation scission of side groups (mechanism II), while the weight loss in stage II should be the joint effect of two mechanisms. When the side groups were oxidized, the polymer was likely to turn into inorganic silica rather than cyclic monomers. As a result, the residue weight (40%) was far more than that in nitrogen. In addition, T_{max} in air (380 and $417\text{ }^\circ\text{C}$) was much lower than T_{max} in nitrogen ($493\text{ }^\circ\text{C}$), demonstrating that oxidation degradation was the dominant factor to cause the decomposition of FSR.

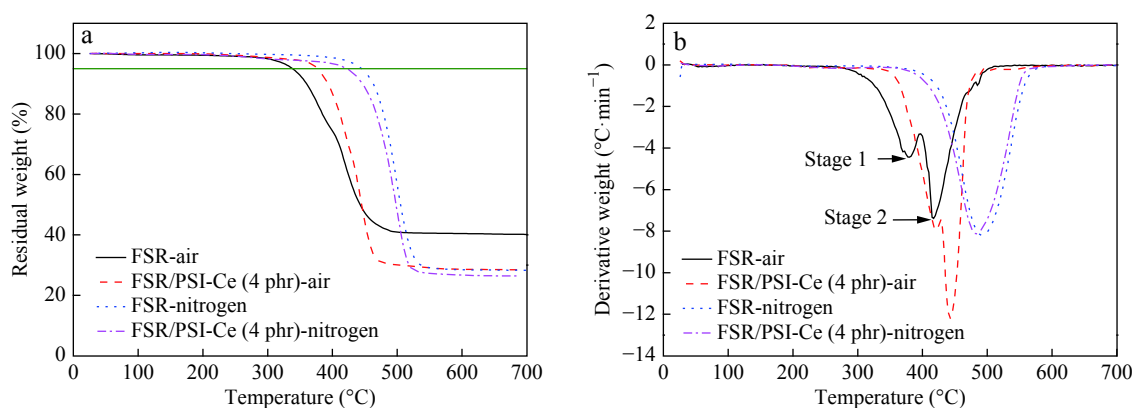


Fig. 5 (a) TG and (b) DTG curves of FSR/PSI-Ce composites in air and nitrogen atmospheres

Table 1 Detailed data from TG and DTG measurement for FSR and FSR/PSI-Ce composites

Sample	T_{onset} (°C)	T_{max} (°C)		Residual weight (%)
		Stage I	Stage II	
FSR-air	338	380	417	40
FSR/PSI-Ce (4 phr)-air	377	421	441	28
FSR-nitrogen	445	—	493	28
FSR/PSI-Ce (4 phr)-nitrogen	422	—	483	26

Compared with neat FSR, the addition of 4 phr PSI-Ce significantly improved the heat resistance of FSR in air, but slightly reduced the heat resistance of FSR in nitrogen. In our opinion, PSI-Ce would be decomposed into CeO_2 and hydroxyl-terminated organosilicone under high temperature conditions. In nitrogen, hydroxyl groups would promote rearrangement reactions of main chain,^[44] which reduced the T_{onset} and T_{max} of FSR. In air, the positive effect of CeO_2 (inhibiting the oxidation of side groups) was much greater than the negative effect of hydroxyl groups (promotion of rearrangement reactions), and therefore PSI-Ce can obviously improve the heat resistance of FSR in air.

Comparison of PSI, PSI-Ce, and CeO_2 on Antioxidant Effect

To further study the antioxidant effect of PSI-Ce, isothermal ageing tests of FSR and FSR/antioxidant were performed at 320 °C in air environment, and the results are shown in Fig. 6. According to TG results, at temperature of 320 °C, FSR was mainly degraded by oxidation scission of the side

groups. In order to specify the antioxidant effect of PSI-Ce, PSI and CeO_2 were used as control.

It was observed that neat FSR deteriorated intensively and sustained 51.2% of the initial weight after 12 h. However, the degradation rate of FSR was slowed down after incorporating 2 phr PSI, and the residual weight remained unchanged. PSI is a well-known heat resistant polymer because its repeated unit, methylphenylsiloxane, is difficult to be oxidized or cyclized. During the ageing process, it might reduce the mass (*i.e.* O_2 , radicals, volatile contents) transfer through shielding effect. However, the antioxidant effect of PSI was negligible. CeO_2 is a traditional antioxidant for silicone rubber. It indeed brought improvement to the thermal stability of FSR. According to previous studies,^[45–47] the thermo-oxidative ageing of polymer derived from the chain reaction of free radicals, and cerium could continuously eliminate free radicals by repeated conversion between Ce^{3+} and Ce^{4+} . It was easy to understand that only CeO_2 in touch with polymers could perform the antioxidant effect. In fact, the bulk of CeO_2 was deep inside the particles and had no impact on antioxidation.

In order to achieve the maximum antioxidant effect of Ce, Ce was assembled into PSI to obtain PSI-Ce. It can be seen from Fig. 6 that when 1 phr PSI-Ce was incorporated into FSR, the thermal degradation of FSR could be obviously inhibited. After isothermal ageing at 320 °C for 12 h, the weight loss of FSR/PSI-Ce (1 phr) was 17.4% less than that of FSR/ CeO_2 (2 phr). However, the cerium content of the former was nearly 1% of the latter. With the increase of PSI-Ce addition, the heat resistance of FSR was improved gradually. In addition, the corresponding visible changes in the appearance of FSR, FSR/PSI (2 phr), FSR/ CeO_2 (2 phr), and FSR/PSI-Ce (2 phr) are shown in Fig. 7. It could be observed that only FSR/PSI-Ce (2 phr) maintained its original morphology, while the rest turned into inorganic powders.

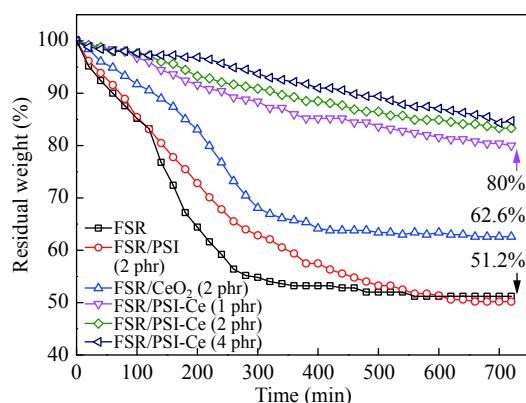


Fig. 6 Isothermal weight-loss curves of FSR incorporated with antioxidant additives in air atmosphere under 320 °C

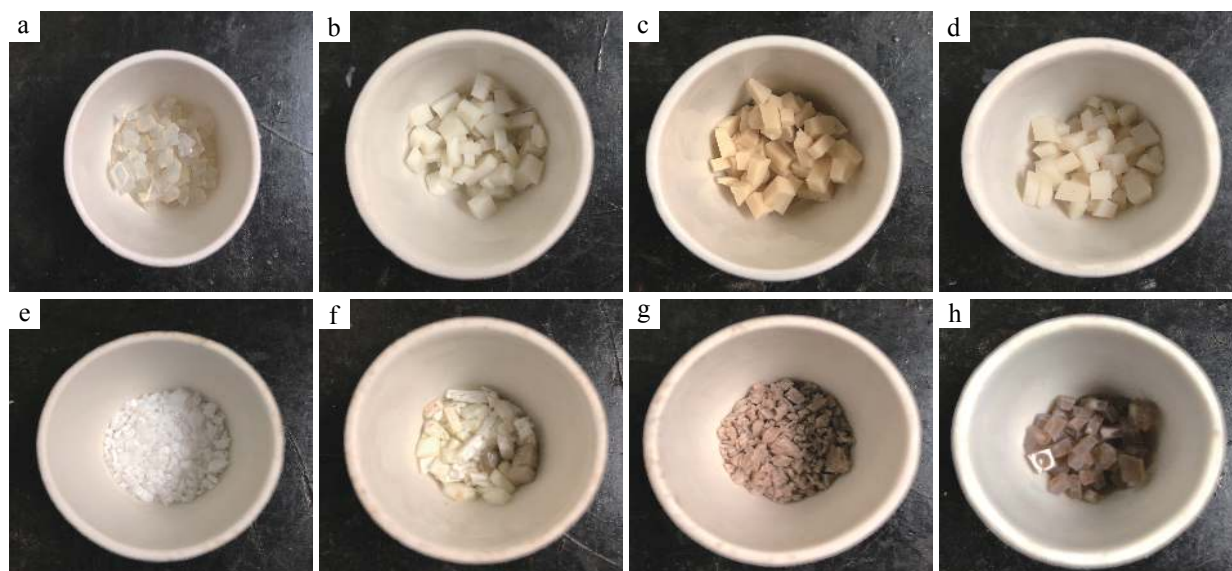


Fig. 7 Photographs of vulcanizates (a–d) before and (e–h) after ageing at 320 °C for 12 h: (a, e) FSR; (b, f) FSR/PSI (2 phr); (c, g) FSR/CeO₂ (2 phr); (d, h) FSR/PSI-Ce (2 phr)

Fig. 8 demonstrates the tensile strength (TS) and elongation at break (EB) of FSR and FSR composites before and after ageing at 230 °C for 72 h, with the data listed in **Table 2**. From the data of the initial performance (before ageing), it can be found that neat FSR exhibited good mechanical properties (TS = 10.4 MPa, EB = 936%, hardness = 54°). After incorporating 1–4 phr PSI-Ce, TS of the FSR compounds showed a slight decrease ($-\Delta\text{TS} \leq 1$ MPa), EB had a slight increase ($\Delta\text{EB} \leq 10\%$), and the hardness was dropped slightly. It seems that the FSR/PSI-Ce vulcanizates were

“softer” than neat FSR. **Fig. 9** presents the vulcanization curves of FSR and FSR/PSI-Ce (1, 2, and 4 phr). It can be seen that FSR/PSI-Ce compounds could be well vulcanized as T90 (the time to reach 90% of the maximum change in torque) of FSR/PSI-Ce (1, 2, and 4 phr) was approximately equal to that of FSR. However, Δtorque (the maximum change in torque) decreased with the increase of PSI-Ce addition. The phenomenon that the rubber became “soft” should be attributed to the plasticizing effect of PSI-Ce due to the lower molecular weight.

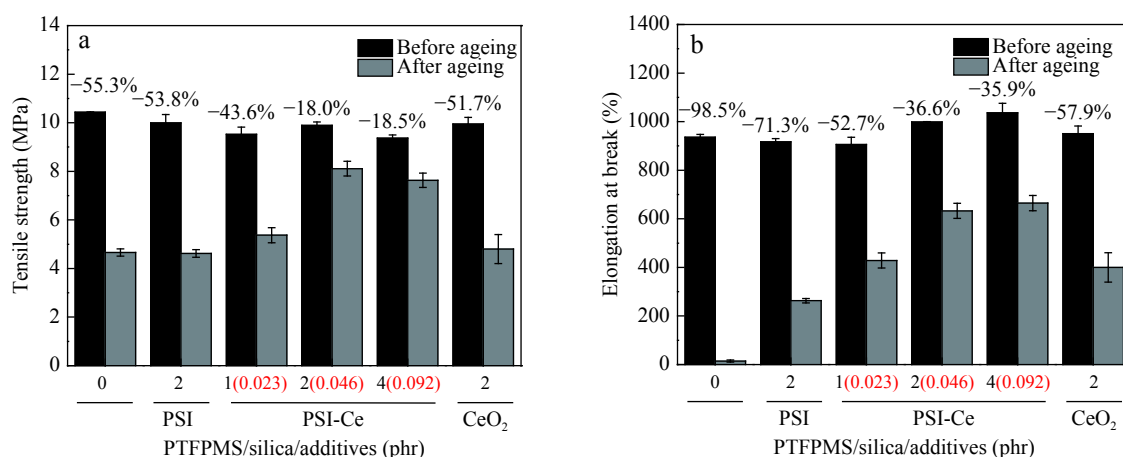


Fig. 8 Mechanical properties of FSR incorporating antioxidant additives before and after ageing at 230 °C for 72 h: (a) tensile strength; (b) elongation at break (The numbers in red represent the equivalent CeO₂ content.)

Table 2 Mechanical properties of FSR incorporating antioxidant additives before and after ageing at 230 °C for 72 h

Sample	Before ageing			After ageing		
	TS (MPa)	EB (%)	Hardness (Shore A) (°)	TS change rate (%)	EB change rate (%)	Hardness change (°)
Blank FSR	10.4	936	54	-55	-99	+41
FSR/PSI (2 phr)	10	917	53	-54	-71	+14
FSR/PSI-Ce (1 phr)	9.5	907	53	-44	-53	+9
FSR/PSI-Ce (2 phr)	9.9	999	52	-18	-37	+9
FSR/PSI-Ce (4 phr)	9.4	1037	51	-19	-36	+9
FSR/CeO ₂ (2 phr)	10.0	950	54	-52	-58	+9

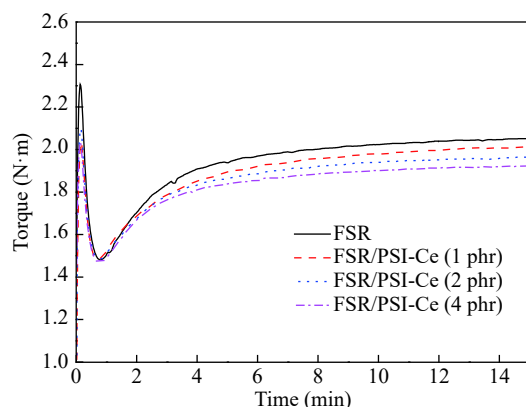


Fig. 9 Vulcanization curves of FSR and FSR/PSI-Ce composites using DBPH as vulcanizer

From the change rate of mechanical properties before and after ageing at 230 °C for 72 h, neat FSR became completely brittle and failed. When 2 phr PSI or CeO₂ was added, the heat resistance of FSR was improved to a certain extent, but the effect was far from comparable to that by adding PSI-Ce. Typically, after ageing at 230 °C for 72 h, TS and EB of FSR/CeO₂ (2 phr) dropped by 52% and 58%, respectively, while the corresponding values of FSR/PSI-Ce (2 phr) were 18% and 37%, respectively. More importantly, 2 phr PSI-Ce was equivalent to only 0.046 phr CeO₂, which was much lower than the addition of CeO₂ (2 phr). As expected, Ce was assembled into silicone oligomers and therefore improved its dispersibility in FSR matrix. It could be concluded that PSI-Ce was a potential antioxidant additive for FSR.

CONCLUSIONS

In this work, cerium-containing polymethylphenyl silicone (PSI-Ce) was successfully synthesized and used as antioxidant additive for FSR. PSI-Ce exhibited much better dispersibility than the commercial CeO₂, and therefore performed better antioxidant effect. Incorporated with 1–4 phr PSI-Ce, the FSR compounds could be well vulcanized and showed a little change on tensile strength and elongation at break compared with neat FSR, but the thermal stability was significantly improved. In particular, after having been thermal oxidative aged for 72 h at 230 °C, FSR/PSI-Ce (2 phr) maintained 82.0% of tensile strength and 63.4% of elongation at break, while neat FSR completely failed.

ACKNOWLEDGMENTS

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