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Improving Heat Ageing, Mechanical Properties, and Thermal Conductivity of Silicon Rubber by Surface Modification of Iron Oxide and Field Testing of Silicon Rubber O-rings

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Abstract

Silicone rubber (SR) compounds were prepared to apply O-ring at high temperatures. Silane surface modified Fe_2O_3 and unmodified Fe_2O_3 were added to the SR compounds, and the compounds were assessed by analyses of FESEM (Field-Emission Scanning Electron Microscopy) (for morphology) and TGA and tests of thermal conductivity at different temperatures, thermal aging, hardness, tensile and compression set. Moreover, O-rings were prepared and field tested in an online Gas Chromatograph (GC) of Chemical Analysis in one Petrochemical Company under the pressure of 7 bar and temperature of 180 °C. The obtained results show that the thermal conductivity, aging resistance, thermal stability, and mechanical properties of SR decreased in the following order: surface-modified Fe_2O_3-filled SR, unmodified Fe_2O_3-filled SR, and SR without Fe_2O_3. Overuse of Fe_2O_3 reduced mechanical properties and hardened processability. The thermal conductivity of SR filled with varying volume percent of modified and unmodified Fe2O3 decreased as the temperature increased. Using surface-modified Fe_2O_3 increased thermal conductivity and improved aging resistance, ultimately enhancing thermal resistance. It is particularly beneficial for the production of O-rings resistant to high temperatures. The field-test results confirmed that the O-rings were compatible with high-temperature conditions. Furthermore, after testing, the O-rings exhibited low volume swelling and a smooth surface without any cracks, blisters, or unevenness.

Keywords: Silicon Rubber, Fe_2O_3, Surface Modification, Thermal Aging, Thermal Conductivity, O-ring.

Introduction

Silicones, consisting of silicon, oxygen, hydrogen, and carbon, are a group of rubber materials known for their excellent thermal, ozone, and chemical resistances, low compression set, and high flexibility. These properties make silicones attractive for various applications [1-2]. O-rings, made of rubber, are used to prevent fluid leakage in joints, fittings, and valves. Since they are in direct contact with fluids and exposed to aggressive media, the chemical resistance and properties of the base rubber of O-rings are crucial, particularly at high temperatures and pressure [3].

Numerous studies have focused on improving the properties of silicone rubber, especially its thermal and mechanical properties [2-4]. For example, Ramirez et al. [4] investigated the thermal conductivity and erosion resistance of silicone rubber composites filled with a mixture of fumed micro-nanosilica and a surfactant, finding that increasing the filler amount increased thermal conductivity, especially with the addition of nanofillers. Silva et al. [5] studied the thermal stability, morphology, and swelling of polydimethylsiloxane (PDMS)/Titanium dioxide (TiO_2) composites, observing that TiO_2 particles were evenly distributed in the silicone matrix. Furthermore, the anisotropic properties of silicone rubber composites with titanium oxide particles randomly distributed within the silicone matrix were examined by Kashani et al. [6].

Fillers such as Fe_2O_3 and carbon nanotubes (CNTs) have been shown to improve the thermal properties of silicone rubber and other properties. For instance, the noncovalent functionalization of CNTs with poly(dimethyl-co-methyl phenyl)siloxane (PMPS) was found to enhance mechanical properties, particularly after thermal-oxidative aging [7]. The combined effect of iron oxide and CNT on the thermal stability of silicone rubber has also been reported [8]. Other researchers have attached iron oxide particles to the surface of CNTs, leading

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to higher degradation temperatures and fewer degradation products [9]. Different crystalline forms of iron oxide and CNTs have been employed to study the thermal stability of silicone rubber, with CNTs shown to delay degradation and iron oxide preventing degradation of methyl groups on silicone rubber chains [10].

The effects of crystalline forms of iron oxide and the bond between Fe_2O_3 and carbon nanotubes (CNTs) on the thermal oxidative stability of silicone rubber were investigated by Li et al. [11]. Their results indicated that CNTs affected the crystalline form of attaching Fe_2O_3, and γ-Fe_2O_3 − CNTs are a more effective thermal resistant additive.

In previous studies by Xie et al. [12], the optimization of filler dispersion and enhancement of mechanical properties in silicon rubber were explored by adding iron oxide. Their findings indicated that incorporating iron oxide as a masterbatch improved dispersion and higher mechanical performance compared to direct addition methods. Meanwhile, Lu et al. [13] studied silicone rubber's curing system, highlighting the addition of iron oxide and other additives, including high-resistant agents and vinyl content, as significant factors. They also raised concerns regarding the insufficient thermal stability of silicone rubber as a sealing material in the oil and gas industry. As a result, the development of formulation considerations for highly thermally stable silicon rubbers in oil and gas environments became necessary. Furthermore, several researchers [14] have investigated the effects of Fe_2O_3 and surface-modified Fe_2O_3 particles on enhancing thermal conductivity, thermal stability, and aging properties of silicon rubber, providing valuable insights in this area.

Silane can be used as a surface modifying agent to improve nanoparticles' interaction with silicone rubber (SR); for example, hexagonal boron nitride (h-BN) nanoparticles were surface modified with varying concentrations of vinyltrimethoxysilane (VTMS) to improve their interaction with silicone rubber (SR) [15]. The modified nanoparticles were then incorporated into SR at different weight percentages. The nanocomposites were characterized for curing, thermal, mechanical, and morphological properties, as well as hydrophobicity. Silane grafting improved crosslink density but decreased the curing rate index and increased water contact angle. The enhanced nanoparticle-rubber interaction led to improved dispersion and properties of the nanocomposites.

By aligning fillers in the SR composites, the thermal conductivity of SR can be improved, for example in the study by Xue et al. [16], silicone rubber (SR)/vertically aligned boron nitride (BN) composites were prepared, and their thermal conductivity was investigated. The SR/ABN composites demonstrated significantly higher through-plane thermal conductivity than the non-orientated SR/BN composite. The through-plane thermal conductivity of SR/ABN150 reached 5.4 W m−1 K−1, which was much higher than SR/BN150 and pure SR. Additionally, the surface thermal infrared analysis indicated excellent heat transfer capacity of the vertically aligned SR/ABN composites. These results highlight the potential of designing high through-plane thermal conductivity thermal interface materials (TIMs) for thermal conductive and electrical insulating applications. Several other research studies have also shown that silane-treated fillers and other fillers can improve the thermal conductivity and thermal properties of silicone rubbers, including the following research studies. Utilization of silane-treated fillers has been proven to enhance the mechanical, thermal, and electrical characteristics of silicone rubber. Lee et al. [17] conducted a study to explore the creation of composites with low dielectric loss and high thermal conductivity through the combination of silane-treated reduced graphene oxide (rGO) and boron nitride (BN). Additionally, they utilized the sintering of silver nanoparticles (AgNPs) on the surface of two-dimensional fillers and infiltration of poly(dimethylsiloxane) (PDMS). Applying a silane coupling agent on the rGO surface decreased interface resistivity between the filler and matrix, leading to strengthened thermal, electrical, and mechanical properties. In their study, Farahani et al. [18] integrated pure and exfoliated boron nitride nanosheets (BNNSs) into nanocomposites of silicon rubber and conducted an assessment of their thermal and electrical performances. The findings revealed a marked enhancement in thermal conduction for both h-BNs and exfoliated BNs, with the latter exhibiting insignificant changes in thermal properties. However, exfoliation contributed significantly to enhancing the electrical volume resistivity. In their work, Han et al. [19] highlighted the use of metal oxide-containing compounds (such as CeO_2, Al_2O_3, and Fe_2O_3) and carbon nanomaterials (including carbon black, carbon nanotubes, and graphene) as functional additives that are commonly employed to improve the high-temperature resistance of silicone rubber composites.

Silanes can be used to improve the adhesion properties of polymer to steel. In a previous research work [20], we used the chemical modification of the metal surface with a type of organic silane compound to increase the adhesion of the maleated polyethylene layer to the metal (carbon steel sheets). The results showed that silane has improved the adhesion properties of maleinated polyethylene to steel. Increasing polymer adhesion to filler can increase the thermal conductivity of the composite.

Despite these studies, research on the effects of surface modification of Fe_2O_3 on the thermal conductivity at different temperatures and aging properties of silane-modified Fe_2O_3-filled silicone rubber is scarce. Furthermore, the mechanical properties of these composites before and after aging have not been extensively explored. Therefore, this investigation is unique in evaluating changes in tensile strength, elongation at break, and thermal conductivity of silane-modified Fe_2O_3-filled silicone rubber after aging.

Therefore, this investigation is unique in the following senses. First, the knowledge of the changes in the tensile strength and elongation at break after aging; second, the knowledge of the changes in the thermal conductivity gives an insight into the ability of modified Fe_2O_3 to improve the thermal resistance of SR compounds. If surface-modified Fe_2O_3-filled SR is resistant to heat, it can be used as sealing rubbers (for example, o-rings) at high temperatures.

In the present work, chemically modified iron oxide was used as filler for SR to improve its thermal conductivity, aging resistance, and thermal stability.

The thermal resistance of the compounds vis-à-vis Fe_2O_3 filled SR and SR without Fe_2O_3 were assessed by analyses of FESEM (for morphology) and TGA and tests of thermal conductivity at different temperatures, thermal aging, hardness, tensile, and compression sets. Mechanical properties have been compared before and after aging. It is to ascertain whether the incorporation of modified Fe_2O_3 can increase the thermal conductivity and thermal aging resistance of SR compared to Fe_2O_3-filled SR and SR without Fe_2O_3. After that, it will be concluded that silane-modified Fe_2O_3-filled SR can be applied as sealing rubbers (for example, O-rings) in high temperatures. Finally, as a unique study, O-rings were made from one of the above silicone rubber compounds. They were field tested in contact with mono ethylene glycol (MEG), diethylene glycol (DEG), and triethylene glycol (TEG) gases under high pressure and high temperature.

Materials and Methods

Materials

Compounded (C-SR) and non-compounded silicon rubber (N-SR) with a commercial brand of SILMIX were obtained from Wacker Company of Germany. N-SR contained fumed silica and silicon oil, while C-SR contained all additives (fumed silica, Fe_2O_3, titanium oxide, and silicon oil) except for peroxide. The selected silicon rubber was vinyl methyl silicone; this type of silicon rubber was selected because the vinyl group has higher resilience, lower compression set, and more oil resistance, which also accelerates curing compared to other groups. In addition, Fe_2O_3 was used as the additive that promotes thermal properties, e.g., thermal resistance and thermal conductivity. It was purchased from the German Lanxess Company with the Bayferrox® 130 M brand name (predominant particle size 220 nm). Titanium oxide, a product of Evonik Company with the brand of Aeroxide TiO_2, was used in this research (average primary particle size is 21 nm). The peroxide used for the type 2 & 5 Base (Tert-butyl proxy) -2, 5-dimethyl hexane with Luperox 101 was prepared from American Company Arkema. The fumed silica produced by Evonik Company with the Aerosil 200 brand was used to regulate properties and hardness.

Methods

Surface Modification of Fe_2O_3 Particles

First, 20 cc of Vinyl Trimethoxyvinylsilane (VTMO) (18%) was mixed with 90 cc Heptane (82%) then 10 gr of Fe_2O_3 particles was added. The obtained mixture was put under the temperature of 70 °C with severe reflux and stirred for 4 hours. In the next step, Fe_2O_3 particles were isolated from a mixture using a centrifuge and washed through ethanol several times to isolate unreacted VTMO from the surface of Fe_2O_3. Then, these modified iron dioxide particles were put in a vacuum oven at room temperature for 24 hours to be dried. This procedure was obtained from several research studies [21-23], and some other research studies used to obtain this procedure are: [14, 24-28].

Silicon Rubber Compound Formulations

Selected formulations are called H-FS[1], L-FS[2], L-P[3], and optimum; their components are listed in Table 1.

Silicon Rubber Compound Mixing

Mixing base silicon rubber with additives was carried out using a laboratory scale two-roll mill at 36 rpm for the front roll and 44 rpm for the rear roll (ratio from 1:1.4 to 1:1.2). The rolls were kept cool during mixing by cold water circulation to keep the temperature of mixture low. The roll distance was adjusted to 0.3 mm, and base silicone rubber in the above composition was supplied to the open roll. A uniform band was formed while rolling cuts from each side of the mill were made, making the polymer homogenous and sufficiently warm. The band was transferred from low-speed nip to high-speed nip when the base materials softened enough. At this time, the base was ready to add additives. First, the silica was mixed with silicon oil and added uniformly into the gum, and then, the mixture of Fe_2O_3 and TiO_2 was added to ensure fine distribution and color matching as pre-mixture. When the dispersion of fillers was completed, then peroxide was added over 2 minutes. After adding peroxide over 5 minutes, extra mixing was done to gain a good distribution of additives. The total time of mixing was usually 18-20 minutes. Then, the mixture was supplied to the open roll to form sheets. During mixing, the temperature increase should be prevented, but the cooling should not be so high that it could increase viscosity [29]. Mixing was done for C-SR mixtures as follows: rubber was softened on nips for about 2 minutes, and then peroxide was added to this rubber gradually for 2 minutes.

Table 1 Component values of formulations.

Formulation Components	H-FS (g)	L-FS (g)	L-P (g)	Optimum (g)
Silicon rubber	100	100	100	100
Fumed silica	32	7	-	-
Fe_2O_3	2.50	2.50	1.75	1.75
TiO_2	1.80	1.80	1.26	1.26
Silicon oil	3	1		
Peroxide	0.60	0.60	0.3	0.6

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1. High Fumed Silica
2. Low Fumed Silica
3. Low Peroxide

Analysis

The curing curve of the compounded rubbers was obtained by cure Rheometer, Zwick Co., Germany, at 177 °C. The optimum curing time was calculated from this curing curve. With this curing time, samples were compressed, molded, and cured in a hot press with the dimensions required for each of the following tests and analyses. The hardness of cured rubber was measured by a Hardness Shore A tester from Shimadzu Company Japan according to ASTM D 2240 using tablets with a diameter of 13 mm and thickness of 6 mm. For the tensile test, the dumb-bell shape specimens were cut from the molded rubber sheet using Wallace (UK) type C. Tensile properties were determined according to ASTM D 412 standard at room temperature using universal testing machine, 500 kg Zwick (Germany) at a cross-head speed of 500 mm min^{-1}. A minimum of six specimens were tested, and the data reported averaged at least four reproducible results. Tear test specimens were cut from the molded rubber sheet, and the test was done according to ASTM D 624 using the same tensile machine at 500 mm min–1. A compression set test was performed on specimens like the hardness test according to ASTM D 395 at 175 °C for 24 hours. Thermal aging was done according to ASTM D 573 standard for 70 hours at 225 °C on the specimens with the same shape and size as tensile test specimens.

O-ring Preparation and O-ring Field Test in Gas Chromatograph of Maron Petrochemical Co.

O-rings manufactured from the silicone rubber compound called Optimum, listed in Table 1, underwent field testing. The dimensions of the O-ring were as follows: Inner diameter - 15.85 mm, outer diameter - 19.43 mm, and thickness - 1.7 mm.

These prepped O-rings were installed in the liquid injection valves of three gas chromatograph devices owned by Maron Petrochemical Co., located in the south of Iran. The devices contained Monoethylene Glycol (MEG), Diethylene Glycol (DEG), and Triethylene Glycol (TEG) gases. Testing was conducted at a pressure of 7 bar and a temperature of 180 °C. The samples were left in the line for one month, after which the pressure was released, the part was opened, and the O-rings were examined for their dimensions and appearance. Before examination, the O-rings were allowed to sit in the environment for one hour to allow any trapped gas to escape. After examination, the O-rings were re-installed in part and placed back in the line for an additional two weeks to confirm their reusability.

Results and Discussion

Silicon Compound Testing

Curing Rheometry

The curing rheometry chart of the C-SR is illustrated in Fig. 1. According to Figure 1, a scorching time of about 1 minute is seen at 177 °C and the optimal curing time can be calculated as follows (Equation 1)

$$t_{90\%} = 0.9 \times (tmax - tmin) + tmin \qquad (1)$$

which comes to a value of 9.5 minutes. Therefore, a curing time of 10 minutes was used to mold all the samples and O-rings.

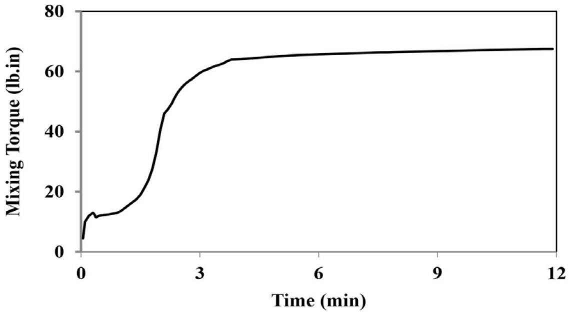


Fig. 1 The cure rheometry chart of C-SR.

Tensile and Tear Properties

The mechanical properties of silicone rubber prepared with various formulations were studied, and the results are shown in Fig. 2.

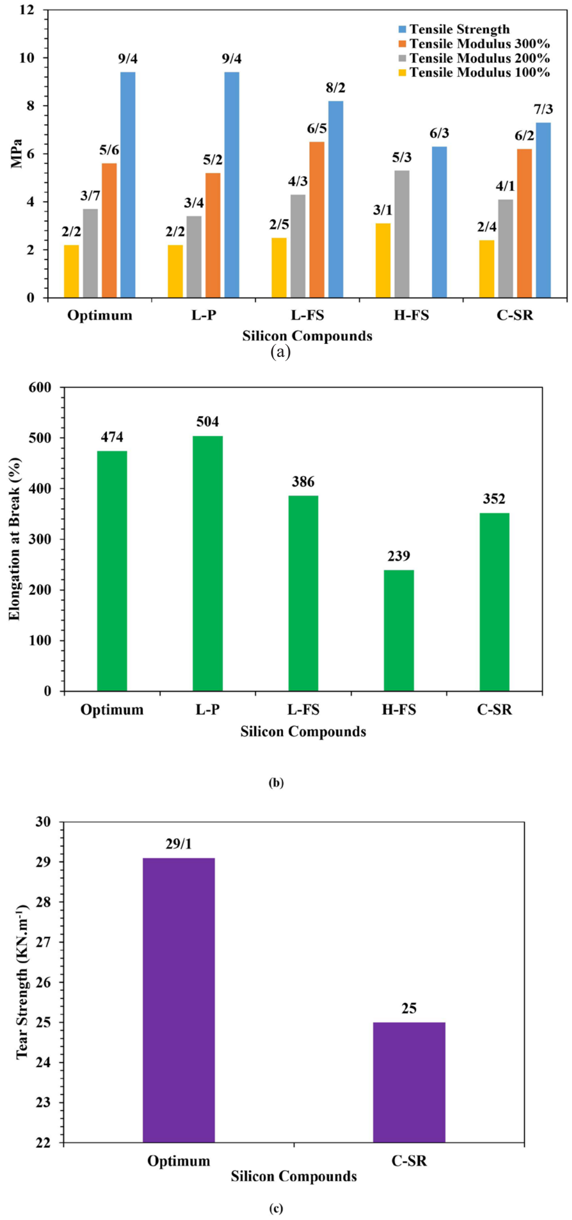


Fig. 2 The tensile strength (a) and (b), as well as tear strength (c) of the silicon compounds.

According to Fig. 2, The C-SR has shown relatively high tensile strength, elongation, and tear strength, indicating good distribution and reinforcement of used fillers and proper curing [11]. A lower fumed silica amount leads to an increase in tensile strength and elongation to the failure point. The obtained properties of the L-FS mixture are higher and better than the C-SR mixture. Decreasing the fumed silica amount would improve distribution and increase interactions between fumed silica particles and the matrix [23,30]. The tensile strength of crosslinked rubbers as a function of crosslink density usually accompanies a maximum value, i.e., there is an optimum value for the crosslink density and peroxide concentration to obtain the highest tensile strength [31]. The higher tensile strength of L-P compared to those of H-FS and L-FS shows that the peroxide content in the L-P compound has reached the optimum value. On the other hand, the lower silica content in L-P might be another reason for its higher tensile strength and elongation at break. Elongation at break usually decreases with increased crosslink density [31], accounting for higher elongation at break of L-P with lower peroxide content and crosslink density. The lower the density of crosslinks is, the higher the Molar (Mc) volume between two connections is; in this case, polymeric chains would move, leading to increased chain flexibility and elongation to the failure point.

Hardness Assessment of Silicone Compounds

The hardness of the H-FS compound was measured to be 73.75 ±0.25 Shore A, which is higher than that of the C-SR, i.e., 64.5 Shore A. Hardness depends on crosslink density and filler content. Therefore, a lower hardness of 71.5 ± 0.5 Shore A was obtained for the L-FS compound due to lower amount of silica than the H-FS compound. High hardness values are not appropriate for high-temperature applications due to thermal degradation's further increase in hardness [2]. The L-P compound with a hardness of 65±1 Shore A seems more appropriate. In fact, a lower peroxide amount reduces crosslink density and hardness. The optimum compound indicates 64.5 ± 5 Shore A. In this range of hardness, properties, including compression set and heat resistance, have been suggested as suitable for use as O-rings [2, 3].

Compression Set

The value of the compression set indicates the state of proper curing and resilience of a rubber compound. The compression set depends on the type of rubber, curing system, curing time, and other compound components such as filler. Crosslinks with –C-C- type have lower flexibility than crosslinks with –S-S- type, while the former has higher resistance against pressure [2]. A compression set value of 6.76±0.2 was obtained for the C-SR.

The compression set of H-FS is 9.96 ± 0.35% higher than the base due to the large amount of fumed silica in H-FS. The amount and distribution of filler particles influence the compression set. It means that a large increase in fumed silica due to its hard and uncompromising nature leads to the formation of aggregates that prevent the movement of silicone flexible chains. Due to the high hardness and compression set, relatively low mechanical properties, and low aging resistance of the L-FS compound compared to those of C-SR, the amount of fumed silica in the L-FS compound decreased. The compression set of L-P was 3.4 ± 0.2%. With the reduction in density of the crosslink, the percentage of compression set will be reduced, and it is because of the increased flexibility of silicon chains. In this optimized formulation, mechanical properties such as elongation and tensile strength have been increased, indicating good mixing of compound ingredients and the proper amount of used fumed silica. The compression set of optimum formulation was 4.14 ± 0.2%. The compression set is the main factor in the design of the O-ring. In static applications, the recommended compression set for O-rings is equal to 15-30% [3], and the maximum of this amount for silicon O-rings with a hardness of 60-70 Shore A and high thermal strength is equal to 35% [32]; in our research, the obtained compression set amount for the optimum sample is lower than this limit. Therefore, the optimum sample can be used as an O-ring.

Aging Assessment of Silicone Compounds

Figure 3 shows the physicomechanical properties of silicone compounds before and after aging. Usually, an acceptable range is considered for changes of properties after aging to prevent degradation and premature failure of the seal [3]; this acceptable range, in accordance with AMS-3304G standard, is equal to -25%, -40%, and ±10 for tensile strength, elongation at break and hardness, respectively. Change in hardness is controlled to prevent too much softening that leads to seal extrusion because of pressure or too much hardening that leads to crack. According to Fig. 3(a), all the compounds have fulfilled these acceptable ranges.

Chemical Modification of the Surface of Fe2O3

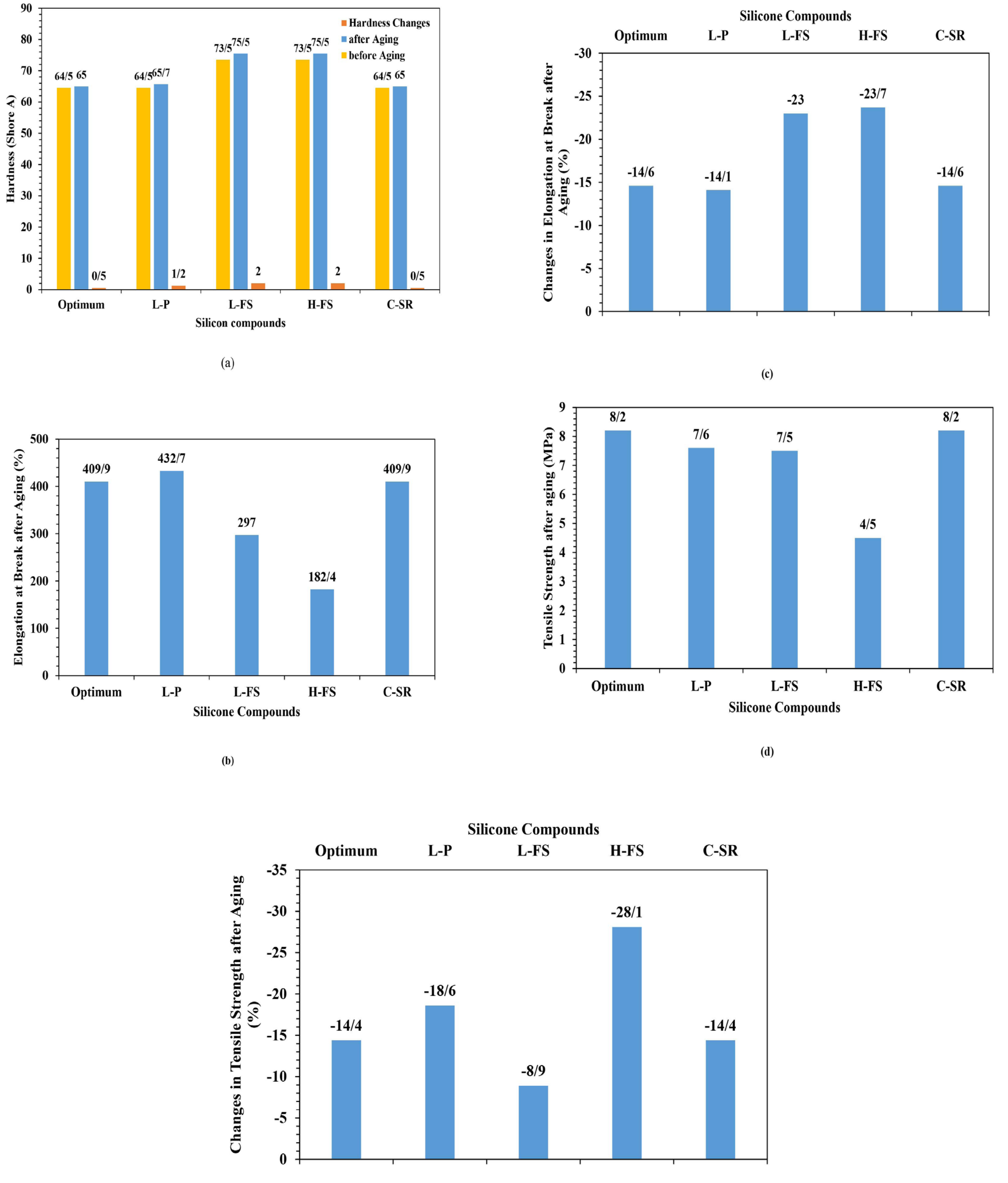
Impact of Surface Modification and Content of Fe_2O_3 on Mechanical Properties

Fig.s 4(a-c) and Fig. S1 show the effect of modified and unmodified Fe_2O_3 at varying amounts on the mechanical properties of silicone rubber compounds. Fig. 4(a) shows that an increase in Fe_2O_3 would increase the tensile modulus of silicon rubber composite up to 40%. The tensile modulus of silicon rubber filled with modified Fe_2O_3 in all composition percentages is slightly higher than silicon rubber filled with unmodified Fe_2O_3.

Modifying Fe_2O_3 particles with VTMS would increase crosslink density, leading to an increase in modulus. Also, modified Fe_2O_3 particles would have been well distributed in the silicon rubber matrix; therefore, hard Fe_2O_3 particles would directly reinforce the silicon rubber matrix. Modulus depends on the geometry, particle size distribution, and the amount of filler. Figures 4(b and c) indicate an increase in tensile strength and elongation at the break of the composites by adding 0.5 vol%, then a reduction in tensile strength and elongation at break for higher loadings. Tensile strength and elongation at break are slightly higher for the compounds with modified Fe_2O_3.

Impact of Surface Modification and Content of Fe2O3 on Thermal Aging Properties

Fig.s 4(b and c) also compare the mechanical properties of the compounds under study before and after aging. As these figures show in comparison to the state before aging, changes in the tensile strength of modified samples are significantly lower than in the tensile strength of silicon rubber filled with unmodified Fe_2O_3.



(a)

(b)

(c)

(d)

(e)

Fig. 3 Comparative analysis of the hardness and elongation at break of silicon compounds before and after aging, as well as the changes observed in these properties after aging. Specifically:

(a) Hardness of the silicon compounds before and after aging.

(b) Elongation at Break after aging of the silicon compounds.

(c) Changes in Elongation at Break after aging of the silicon compounds.

(d) Tensile Strength after aging of the silicon compounds.

(e) Changes in Tensile Strength after aging of the silicon compounds.

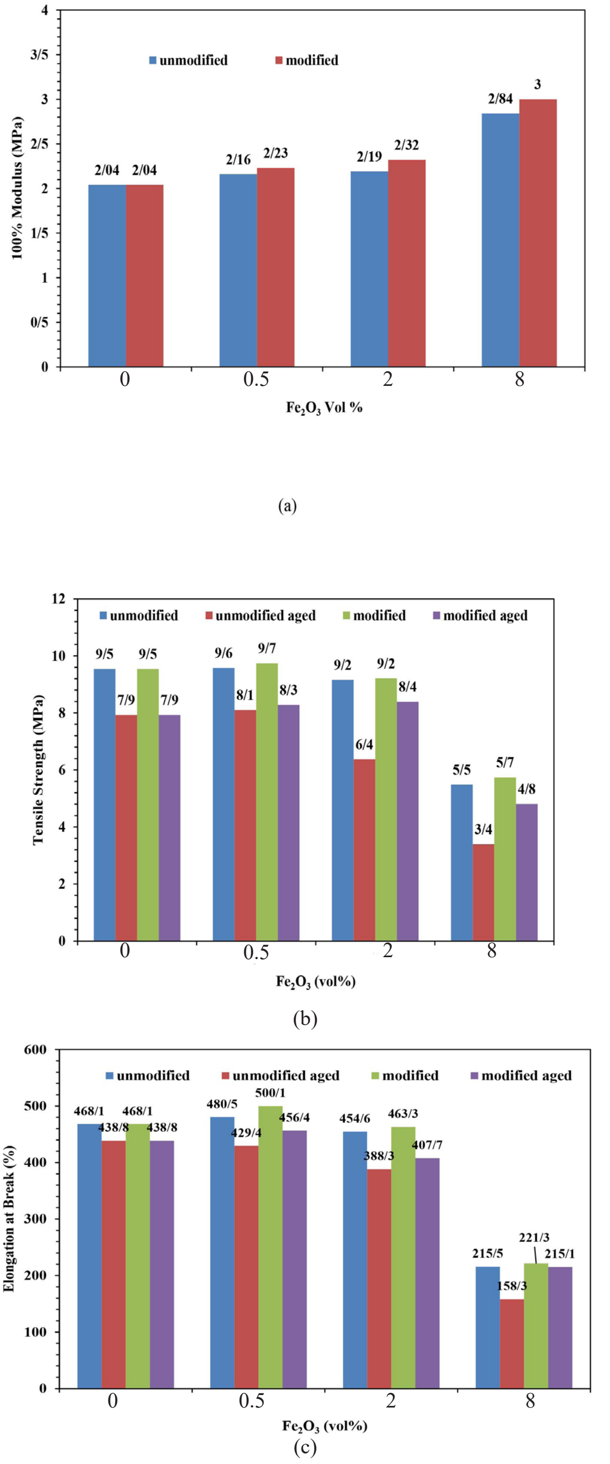


Fig. 4 (a) Modulus comparison with different quantities of modified and unmodified Fe_2O_3. (b) Comparison of tensile strength before and after aging, with varying amounts of modified and unmodified Fe_2O_3. (c) Comparison of elongation before and after aging, with different quantities of modified and unmodified Fe_2O_3.

In other words, modification of the surface of Fe_2O_3 particles would increase the efficiency of these particles in increasing the thermal stability of silicon rubber. Furthermore, Fe_2O_3 particles would trap free radicals released by thermal oxidation in the silicon matrix and act as a barrier to prevent the matrix from higher degradation and breakage of the chains [21].

The changes in the elongation at break of the modified Fe_2O_3 samples are lower than those of unmodified samples at all volume percentages due to the better dispersion of particles, which can prevent thermal degradation by trapping radicals. Therefore, the incorporation of modified Fe_2O_3 can increase the thermal aging resistance of SR compared to Fe_2O_3-filled SR and SR without Fe_2O_3, which will result in increased thermal resistance of SR. It will be concluded that silane-modified Fe_2O_3-filled SR can be applied as sealing rubbers (for example, O-rings) at high temperatures.

Morphology Observations

Fig.s 5 and 6 show the FESEM images of the fractured surface of the silicon rubbers without Fe_2O_3 and filled with unmodified and modified Fe_2O_3 in various amounts of Fe_2O_3. According to Fig. 5, with an increase in unmodified Fe_2O_3 particles, aggregates and agglomerates increasingly appear in the matrix. In comparison, the formation of such agglomerates is suppressed in the composites containing surface-modified Fe_2O_3 particles with VTMS (Fig. 6). Better improvement in the dispersion of iron oxide particles is responsible for the observed better mechanical properties after aging.

Effect of Surface Modification and Content of Fe_2O_3 on Thermal Properties

Thermal Gravimetric Analysis (TGA) of Silicone Rubber Filled with Surface Modified or unmodified Fe_2O_3

Fig. 7 shows the TGA curves of silicon rubber filled with various amounts of unmodified and modified Fe_2O_3. The remaining weight at an equal temperature is higher for the silicon rubber filled with Fe_2O_3 than for silicon rubber without Fe_2O_3. Furthermore, a higher weight remains due to the increase in iron oxide. The higher remaining weight indicates improved thermal resistance of silicon rubber by iron oxide particles. Moreover, silicon rubber filled with 0.5 and 8% volume of modified Fe_2O_3 has higher remaining weights than silicon rubbers filled with unmodified Fe_2O_3 at the same amounts. It is due to better dispersion distribution of modified iron oxide particles, which provides higher interface area, better interface adhesion, and better attraction of silicon chains on iron oxide particles, and therefore, higher thermal stability by entrapping more radicals formed from thermal oxidative reactions.

On the other hand, solid particles are considered stearic barriers that prevent destructive reactions [29, 33]. Asadi et al. [34] verified the thermal-oxidative degradation of three different types of polymers by TG and DTG. Thermo oxidation is a process that occurs when these polymers are heated in the presence of oxygen, leading to their degradation over time. It was found that the degradation rate increases significantly with an increase in temperature.

Thermal Conductivity of Silicon Rubber Filled with Various Volumes of Surface Modified or Unmodified Fe_2O_3

Fig. 8(a) and Fig. S2 show the thermal conductivity of silicon rubber filled with various volumes of Fe_2O_3. As seen, the thermal conductivity of silicon rubber has increased by 0.1W/mK with the addition of 8%vol Fe_2O_3. The observed increase at this amount is significant compared to previous studies trying to increase the thermal conductivity of silicon rubber by different particles [4, 35-37] and some other previous studies [33, 38-41].

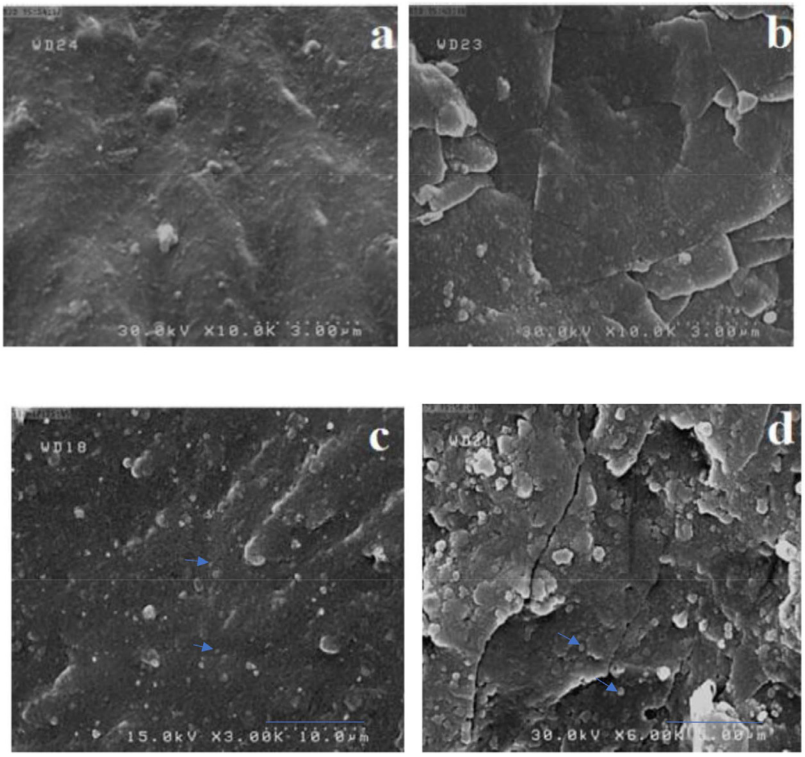


Fig. 5 FESEM images of the fracture surface of silicon rubber with varying Fe_2O_3 concentrations. Arrows indicate the presence of Fe_2O_3 particles. (a) Silicon rubber without Fe_2O_3, Scale Bar: 3 µm. (b) Silicon rubber with 0.5vol % of unmodified Fe_2O_3, Scale Bar: 3 µm. (c) Silicon rubber with 2vol % of unmodified Fe_2O_3, Scale Bar: 10 µm. (d) Silicon rubber with 8 vol% of unmodified Fe_2O_3, Scale Bar: 5 µm.

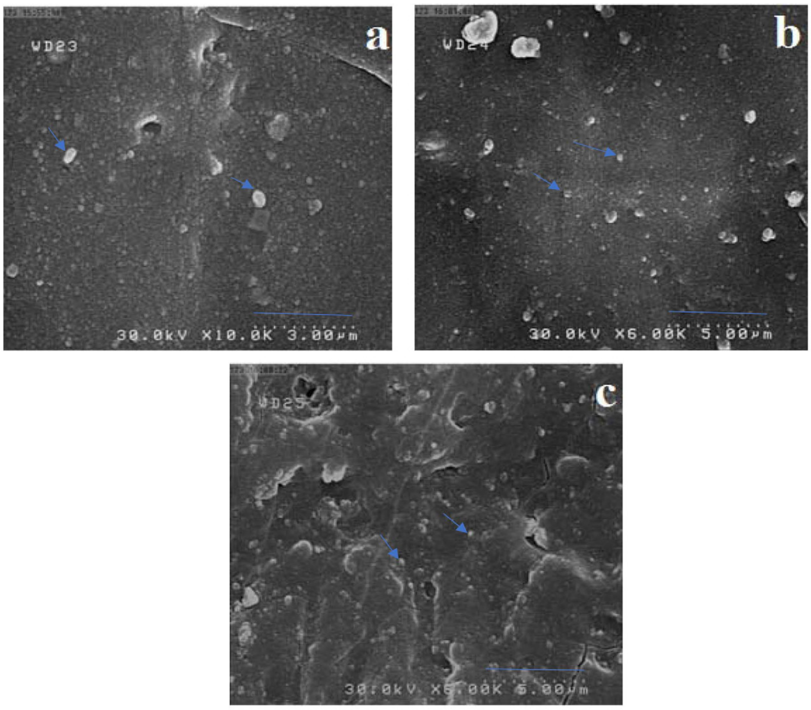


Fig. 6 FESEM images of the fracture surface of silicon rubber with varying concentrations of modified Fe_2O_3. Arrows indicate the presence of Fe_2O_3 particles, (a) Silicon rubber with 0.5 vol % of modified Fe_2O_3, Scale Bar: 3 µm, (b) Silicon rubber with 2 vol % of modified Fe_2O_3, Scale Bar: 5 µm, (c) Silicon rubber with 8 vol % of modified Fe_2O_3, Scale Bar: 5 µm.

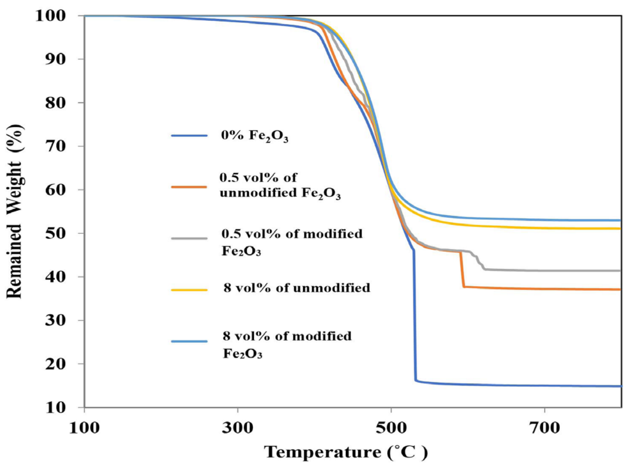
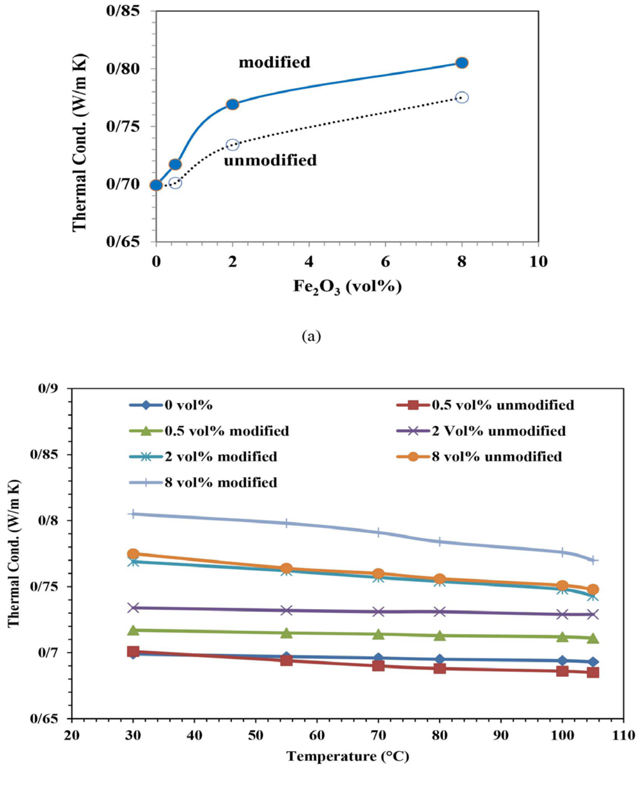


Fig. 7 TGA Curves of silicon rubber filled with varying amounts of modified and unmodified Fe_2O_3.



(a)

(b)

Fig. 8 Comparison of thermal conductivity between silicon rubber filled with different volumes of modified and unmodified Fe_2O_3 (a). Comparison of the change in thermal conductivity of silicon rubber filled with various volumes of modified and unmodified Fe_2O_3 at different temperatures (b).

Effect of Fe_2O_3 Surface Modification on Thermal Conductivity of Silicon Rubber

Fig. 8(a) also compares the thermal conductivity of silicon rubber filled with modified and unmodified Fe_2O_3. The thermal conductivity of silicon rubber filled with modified Fe_2O_3 is higher than silicon rubber filled with unmodified Fe_2O_3; in this case, the thermal conductivity of silicon rubber in 2% volume of modified Fe_2O_3 is approximately equal to the thermal conductivity of silicon rubber in 8% volume. It indicates that the thermal resistance of the interface is eliminated, and silicon rubber's thermal conductivity is improved through particle modification and better dispersion [42].

Change in Thermal Conductivity of Silicon Rubber Containing Surface Modified or Unmodified Fe2O3 with Temperature

Fig. 8(b) compares the thermal conductivity of silicon rubber filled with varying volume percent of modified and unmodified Fe_2O_3 at several temperatures. The thermal conductivity of the silicon compounds decreases with increasing temperature. The dependence of conductivity on temperature is more considerable at higher filler loading. At low filler loading, by increasing temperature, the polymer matrix expands, and conductivity decreases. However, at high filler loading, the matrix expansion leads to the disconnection of particle networks, which have a significant share in thermal conduction in the composite [33]. In conclusion, the incorporation of modified Fe_2O_3 can increase the thermal conductivity of SR compared to Fe_2O_3-filled SR and SR without Fe_2O_3, resulting in increased thermal resistance of SR. As a result, silane-modified Fe_2O_3-filled SR can be applied as sealing rubbers (for example, O-rings) at high temperatures.

Field Test of O-ring Made from Silicone Rubber Compounds

To ensure the performance of the produced O-ring, volume changes 6 weeks after installation of the O-ring were measured with Gas Chromatography devices under 7 bar pressure and 180 °C temperature using optimum formulation. The O-rings have been tested in an online Gas Chromatograph (GC) of Chemical Analysis in Maroon Petrochemical Company in the south of Iran in contact with mono ethylene glycol (MEG), Diethylene Glycol (DEG), and Triethylene Glycol (TEG) gases; the obtained 30% volume of swelling shows that materials selection, formulation, and processing for obtaining required specifications for O-ring should be compatible with high-temperature conditions. Furthermore, as Fig. 9 shows, after the test, the surface of the O-ring was smooth. There were no cracks or blisters on the surface, and the surface was not uneven.

Conclusions

The results of this study indicate that the thermal conductivity, aging resistance, thermal stability, and mechanical properties of SR compounds decrease in the following order: surface-modified Fe_2O_3-filled SR, unmodified Fe_2O_3-filled SR, and SR without Fe_2O_3. The thermal properties of a sample containing 2%vol of modified Fe_2O_3 are approximately equal to those of 8%vol of unmodified Fe_2O_3. Mechanical properties are better, and processability is simpler in lower amounts of Fe_2O_3. Therefore, using modified Fe_2O_3 with lower volumes can preserve mechanical properties and processing simplicity while obtaining good thermal properties. The thermal conductivity of SR filled with varying volume percentages of modified and unmodified Fe_2O_3 decreased by increasing temperature.Using surface-modified Fe_2O_3 resulted in increased thermal conductivity and improved aging resistance, ultimately leading to enhanced thermal resistance. Therefore, the final conclusion is that silane-modified Fe_2O_3-filled SR can be applied as sealing rubbers at high temperatures.

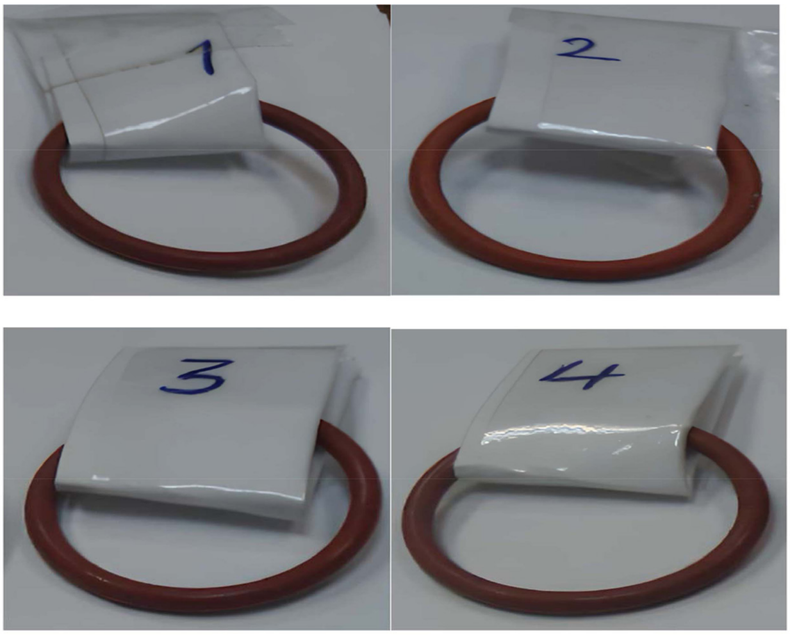


Fig. 9 O-rings made from silicone rubber compounds after Field Tests: (a), (c), and (d) made from Optimum compound; (b) made from C-SR.

The field-test O-ring results show that the O-ring was compatible with high-temperature conditions. After the test, it had a low swelling volume, and its surface was smooth without any cracks, blisters, or unevenness.

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