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Effect of gamma radiation and modified CeO_2 on the physico-mechanical properties of silicon rubber nanocomposites

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HIGHLIGHTS

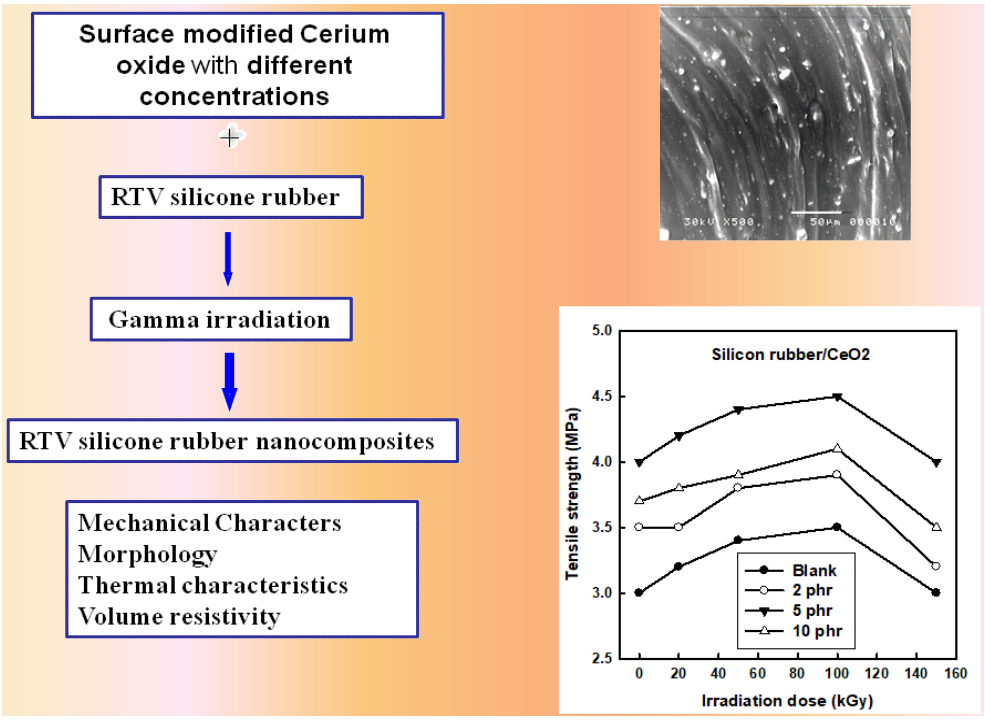
1- For all compositions, tensile strength increased with increasing irradiation dose up to 100 kGy, and then decreased.

2- The addition of cerium oxide increased the thermal properties and volume ressistivity

3- The composites containing 5 phr cerium oxides and exposed to 100 kGy radiation dose have the best thermo mechanical, and volume resistivity properties.

4- silicon rubber composites containing 5 phr cerium oxide and exposed to 100 kGy radiation dose have a wide range of industrial uses as effective thermal and electrical insulating materials.

GRAPHICAL ABSTRACT



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ABSTRACT

One of the most significant synthetic functional elastomers is silicone rubber (SR), which has special properties like thermal and chemical resistance, high weathering and oxidation resistance, low-temperature toughness, electrical insulation, and high optical transparency. Elaboration thermal and mechanical capabilities however are needed for the SR's ever-expanding applications. The effect of modified CeO_2 powder loaded in silicon rubber composites on the thermal and mechanical properties was investigated. The impacts of surface modification of CeO_2 powder content on silicon rubber composite characteristics were discussed. Silicon rubber nanocomposites were prepared by inclusion different concentrations of 2, 5 and 10 phr of the surface modified cerium oxide. The effect of radiation on the mechanical properties (TS, E %) at different doses was investigated. The thermogravimetric analysis (TGA) of the nanocomposites was studied. The volume resistivity was also measured. The results indicated that the nanocomposite contains 5 phr of CeO_2 and irradiated to 100 kGy has the best properties and it has a wide range of industrial uses as effective thermal and electrical insulating materials.

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1-INTRODUCTION

Rubber Silicones are widely recognized for having superior thermal and thermo-oxidative stability when compared to other polymers. Though silicone rubber has some combustion resistant characteristics, when ignited in the air, it can continue to burn. Room temperature vulcanized silicone rubber (RTVSR) utilizes innumerous fields where it is simplicity in industrialization and shaping as well as its distinctive qualities [1-6]. However, the RTVSR's molecular chains include a high concentration of flammable C and H atoms, so it combustible [7]. As a result, it has exceptional thermal stability and temperature tolerance, but because it may ignite at very low temperatures, its use in a variety of sectors constrained especially in aircraft, electrical and electronic appliances and sealing products. Many investigations have shown that rare earth compounds have specific functions in the production and use of rubber [8-10], thermal resistance [11], antifatigue [12], strengthening action [13-16], and antioxidation [17]. Metal oxides can be used as heat-resistant additions [18-20]. A notable rare earth chemical is CeO_2. It finds extensive usage in a variety of products, including glass, catalysts, polishing powder, phosphors, and UV absorption materials. A study on the utilization of CeO_2 in rubber has been released. SU Zhengtao et al. [21] claimed that adding CeO_2 to silicon rubber improved its thermal stability. According to Tengfei Gan et al. [22], the inclusion of modified CeO_2 considerably boosted silicone rubber's tear strength. On the other hand, metal oxides have a high surface energy and can easily agglomerate. Additionally, the poor dispersion of metal oxides in rubber is caused by the low compatibility of metal oxides with rubber. As a result, inadequate dispersion has a detrimental impact on the improving qualities of rubber. As a result, the main task is to develop a revolutionary way for improving metal oxide dispersion in rubber. Fortunately, this difficulty may be overcome by applying some unique procedures, Consider adding an ethoxy group surface modifying chemical, such as 3-(aminopropyl)triethoxysilane, to the surface[23]. The latter might undergo hydrolysis to create hydroxy, which could then interact with active groups on the surface of CeO_2. This prevents agglomeration, hence increases the compatibility between rubber and CeO_2, increasing rubber characteristics [24, 25]. Radiation techniques have found several useful uses in rubber composites. To compete with traditional crosslinking technologies, irradiation dosage must be reduced to reach the optimal crosslinking density. The purpose of this work is to explore the influence of varying concentrations of cerium oxide loaded on silicon rubber in order to improve its physical, thermal, electrical, and mechanical characters for industrial applications. The mechanical properties, volume resistivity, and thermal properties of silicon rubber before and after gamma irradiation were also investigated.

2. EXPERIMENTAL AND TECHNICAL METHODS

2.1. Materials

Two components of RTVSR were produced by Shanghai Rubber Product Institute (China), while Cerium oxide was sourced from Reda chem co., heptane and alcohol were obtained from El Gomhoria co., whereas 3-(aminopropyl) triethoxysilane obtained from Sigma co.

2.2. Cerium oxide surface modification

The **surface modification cerium oxide was carried out according to a reported method [26].** In this method, heptane and 3-(aminopropyl) triethoxysilane were mixed while being stirred, and CeO_2 was then added in the appropriate amount. The mixture was vigorously stirred and heated up to 70°C for 4 hours. Filtering the mixture and the resulted powder was washed with alcohol to remove any silane that could have remained on the surface of the CeO_2. The resulted powder was dried in a vacuum oven for 24 hours.

2.3. Preparation of RTV silicone rubber nanocomposites

The fillers utilized, modified CeO_2, was used in various ratios (0, 2, 5, and 10 phr). RTV silicone rubber was used in the rubber matrix. At room temperature, the 100 g of RTV silicon rubber were mixed vigorously with filler for three hours. After that, the 3g of the catalyst were added to the mixture and swirled for 60 seconds. After that, the mixture was shaped in a rectangular mould. After 24 hours of curing at room temperature (20^oC), the film was formed.

2.4. Gamma irradiation

Cobalt-60 gamma rays were used to irradiate samples. it dose rate around (1 kGy/h).

2.5. Mechanical test

Specimens were cut in the shape of dumbbells using a steel die. The mechanical characteristics were determined at 25°C. Hung-Ta Model HT-9112 (Taiwan) equipment was used to measure mechanical properties in accordance with ASTM D 412.

2.6. Morphology (SEM)

A Jeol 6060LV variable pressure scanning electron microscope was used for SEM (Jeol UK Ltd).

2.7. Thermogravimetric analysis (TGA)

According to ASTM E1641-07, TGA was studied using a Shimadzu (Japan) TG-50 at a heating rate of 10°C/min and up to 700°C. The samples were contained in platinum pans and had weights ranging from 3 to 5 mg. The flow rate of nitrogen gas through the tests was 20 ml/min.

2.8. Volume resistivity

For the measuring the volume resistivity, a Keithley electrometer model 6517 was employed (Ohio, USA). An external connection between the electrometer and a Resistance Fixture of type 8009 exists. The volume resistivity was measured using a circular type probe with a diameter of 63.5mm at room temperature.

3. RESULT AND DISCUSSION

3.1. Mechanical Characters

The change in tensile strength (TS) is one of the most obvious impacts of irradiated elastomeric materials owing to cross-linking and degradation. **Fig.1**. were displays the relation between TS and irradiation dose for the nanocomposites'. When the irradiation dose was increased, the TS values for all nanocomposites rose until they reached their maximum levels at around 100 kGy, after that they gradually decreased. Depending on the overall irradiation dosage, dose rate, and irradiation setting, irradiation triggers, production of cross-links and macromolecular chain scission are two contrasting processes that take place in the rubber matrix. Chain scission, which is more frequent at higher irradiation doses and results in polymer breakdown, might be to reason for the decline in tensile value. Also as seen in Fig.1, the tensile strength increases with increasing the content of modified cerium oxide, reaching its maximum at 5 phr modified cerium oxide. This might be due to the aggregation CeO_2 at high concentrations (10 phr). **Figure 2** shows the **effect of gamma irradiation dose on the elongation at beak of silicon rubber nanocomposites filled with different concentrations of Cerium (CeO_2).** As the crosslinking density increases, the E% values for all nanocomposites will decrease at varied rates based on each formulation's sensitivity to irradiation dose needed to create free radicals. As a result, cross-linking density increases, and therefore the impediment to molecular chain mobility increased, resulting in a fall in E%. Furthermore, the elongation at break point decreased as the nano CeO_2 concentration raised (2–5 phr), yet at the same radiation dosages, raising the CeO_2content to 10 phr causes a relative increase in E% compare to the values obtained at 5 phr this may be due to the agglomeration of filler at high content has a plasticizing effect.

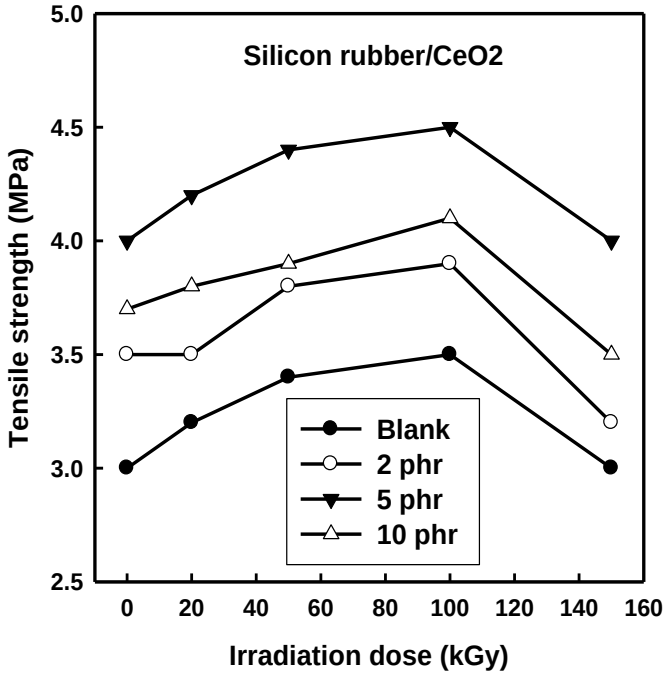


Fig. (1): Effect of gamma irradiation dose on the tensile strength of silicon rubber nanocomposites filled with different concentrations of cerium (CeO_2).

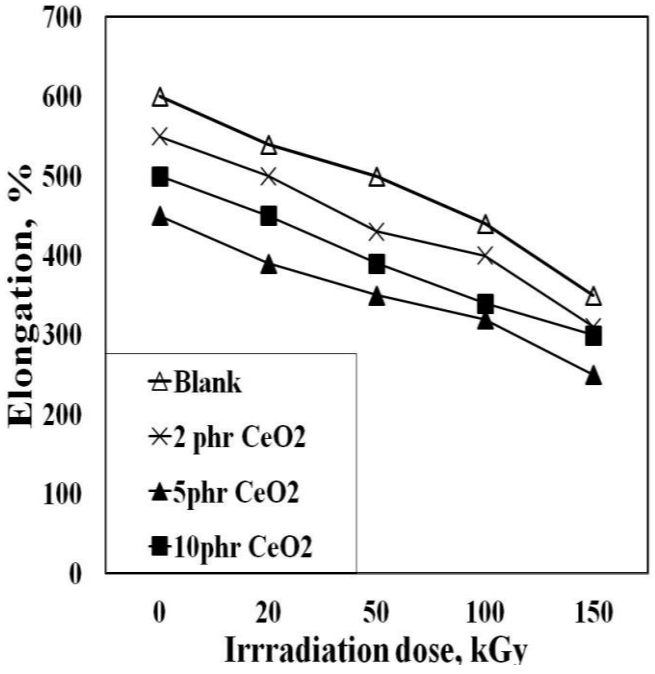


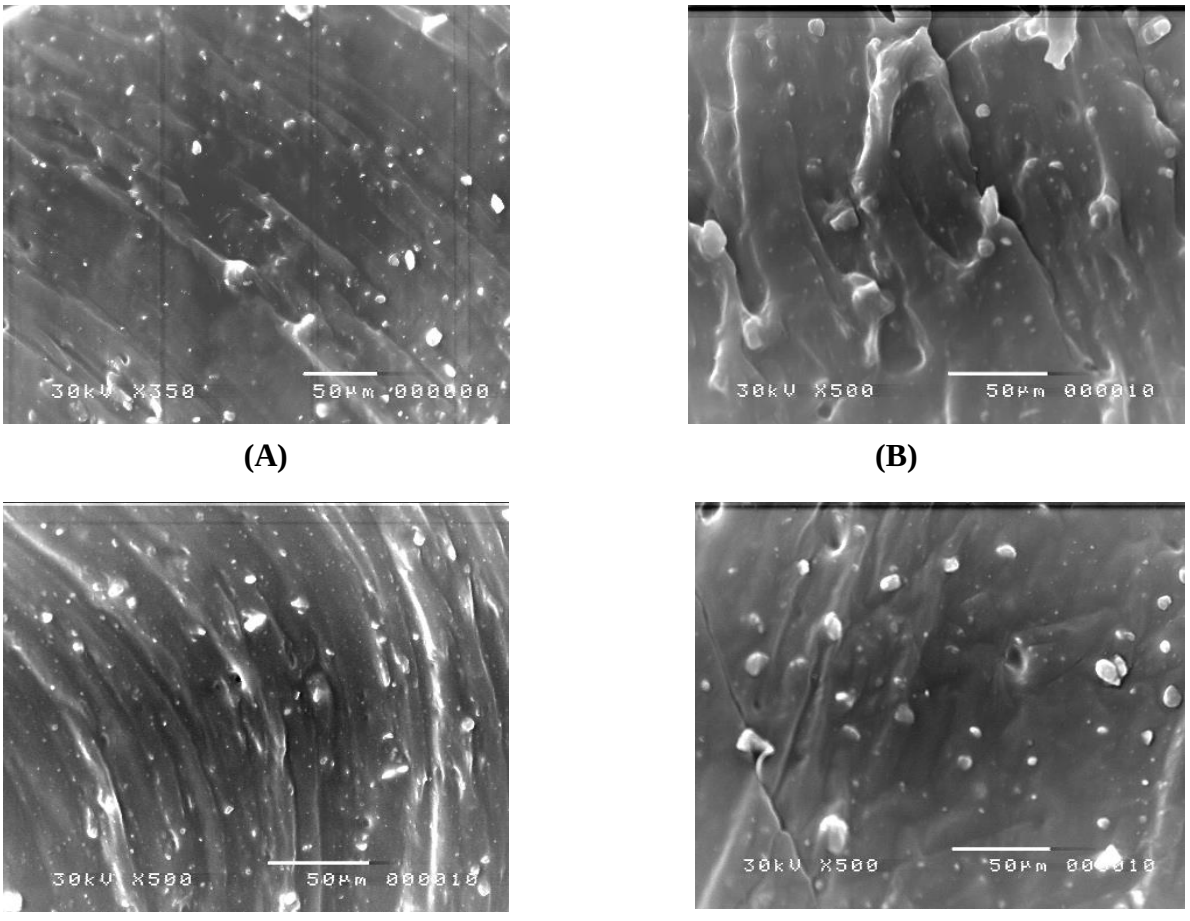
Fig. (2): Effect of gamma irradiation dose on the elongation at beak of silicon rubber nanocomposites filled with different concentrations of cerium (CeO_2).

3.2. Morphology

The morphology of silicon rubber nanocomposites with varied ratios of modified CeO_2 and irradiated to 100 kGy was examined using SEM. **Fig.3** (a-d) represents the SEM micrographs of these samples. As can be seen, the filler CeO_2 was appeared on the whole fracture surface of the modified silicon rubber (**Fig 3 b-d**), indicating that these reinforcement fillers were evenly distributed in the rubber matrix. In low concentrations of CeO_2, the nanoparticles are dispersed throughout the matrix with few or no clusters, although some clusters may be seen in higher concentrations (**Fig. 3d**). The effects of the radiation are clear since the surface is uniform and smooth and shows no signs of phase separation because of cross-linking.

3.3. Thermal characteristics

The thermal characteristics of the nanocomposites subjected to 100 kGy have been studied since they have the superior mechanical performance. TGA was commonly employed to assess the thermal stability of various rubber nanocomposites [27]. Figure 4 depicts the TG and DTG curves for various nanocomposites. **Table 1** also includes data from the TG-DTG curves of all samples. It was shown that silicone rubber with CeO_2 has higher initial weight loss temperature than silicon rubber without CeO_2, suggesting that CeO_2 can boost silicon rubber's heat resistance. The silicon nanocomposites' T 30% and T_{max} values increased with the addition of cerium oxide. i.e., this sample's T 30% and T_{max} values are 22 and 11 degrees Celsius higher than the blank's, respectively. The fact that $CeO_2$is an inorganic substance with excellent thermal stability and excellent barrier qualities, which might block heat from transferring fast and so restrict the ongoing disintegration of the nanocomposites, could be one cause for the increase in the onset temperature.



(A) **(B)**

(C) **(D)**

Fig. (3): SEM micrographs of silicon rubber, before and after had been modified by loading with different contents cerium oxide (CeO_2): (A) Blank, (B) 2 phr, (C) 5 phr and (D) 10 phr. All the modified rubbers exposed to gamma irradiation to a dose of 100 kGy.

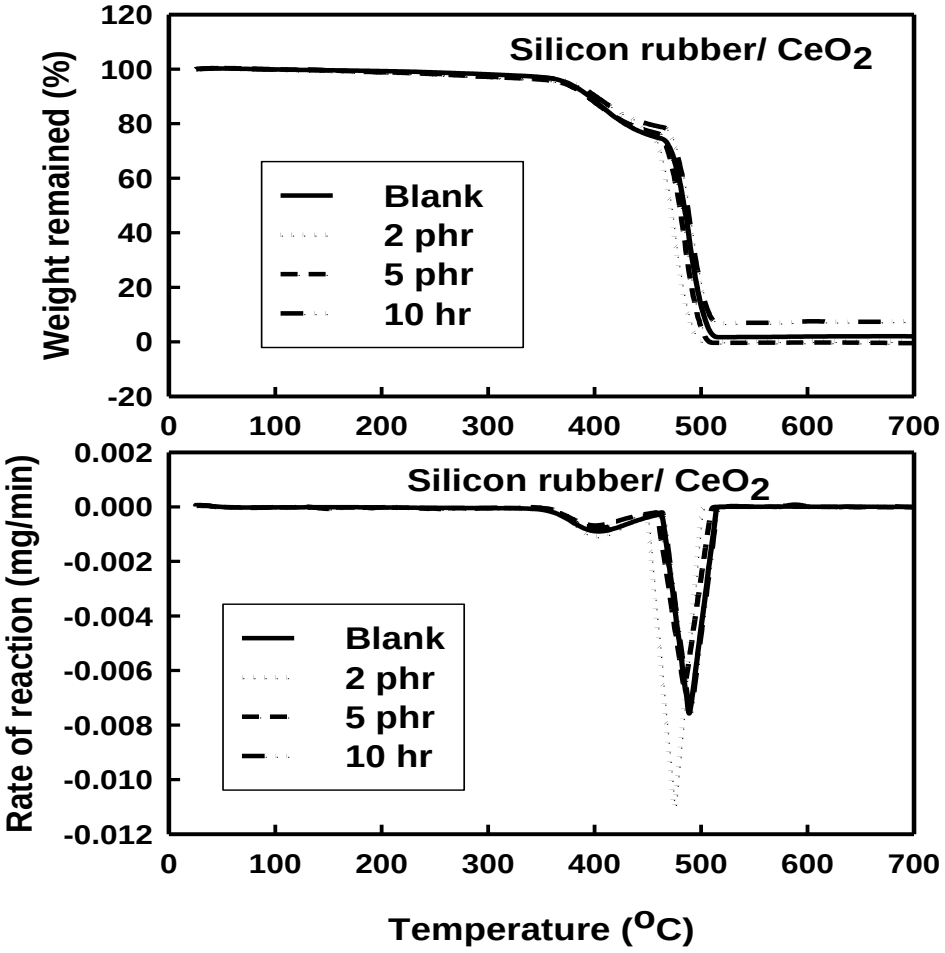


Fig. (4): TGA thermograms and the corresponding rate of thermal decomposition reaction curves of silicon rubber loaded with different concentrations of cerium oxide and gamma irradiated to a dose of 100 kGy.

Table (1): Weight loss temperatures for rubber nanocomposites

Cerium oxide	$T_{mid\text{-}point}$ (ºC)	O_{nset} (ºC)	$T_{end\ set}$ (ºC)	Wt. loss (%)	$T_{30\%}$ (ºC)	T_{max} (ºC)
Blank	396	375	421	18	461	477
	488	479	502	73		
2phr CeO_2	410	380	448	22	469	472
	479	467	493	10		
5 phr CeO_2	415	384	449	22	477	484
	490	480	500	11		
10 phr CeO_2	420	390^0	462	26	483	486
	495	482	510	10		

T_{onset} describes the temperature at which the sample begins to break down.
"$T_{Midpoint}$" describes the temperature at which materials are losing weight at a moderate rate.
"T_{endset} " describes the temperature at which weight loss stops occurring.
"Tmax" describes the temperature at which the rate of weight loss is at its highest level.
T30% describes the temperature at which a 30% weight loss rate occurs.

3.4. Volume resistivity

Table 2 shows the volume resistivity of rubber nanocomposites at room temperature (300K) after being gamma irradiated to 100 kGy. The direct radiation of polymers increases their electrical conductivity. Radiation induces conductivity by generating mobile charge carriers such as electrons, holes, and ions. The kind of filler, particle size, content, degree of dispersion, and interfacial adhesion between the filler and the polymer are all factors that would be predicted to affect the number of charge carriers in addition to the polymer structure, irradiation dosage, and any incorporated fillers. The volume resistivity of the nanocomposites rose as the cerium oxide content increased.

Table (2): Volume resistivity of silicon rubber nanocomposites loaded with different concentrations of Cerium oxide.

Cerium oxide	Volume resistivity (Ω cm)
Blank	$2*10^{12}$
2 phr CeO_2	$2.3*10^{12}$
5phr CeO_2	$2.5*10^{12}$
10phr CeO_2	$3.5*10^{12}$

4. CONCLUSION

For all compositions, the influence of γ irradiation on the values of TS raised with raising irradiation dose, peaking at around 100 kGy, and subsequently decreased with increasing irradiation dose up to 150 kGy. In contrast, the E% values decreased as the irradiation dose increased. Over all irradiation doses evaluated, the composite with the highest TS and the lowest E% was the one containing 5 phr cerium oxides. The morphological, thermal, and electrical, properties of the composites have been studied. The addition of cerium oxide increased the thermal properties were the curves of TG-DTA of the composites shafted to higher temperatures. T30% and T_{max} values of silicon nanocomposites rose, meaning that they are 22 ^{0}C and 11 ^{0}C higher in this sample than in the control, respectively. As a result of their excellent thermo mechanical, and volume resistivity properties, silicon rubber composites containing 5 phr cerium oxide and exposed to 100 kGy radiation dose have a wide range of industrial uses as effective thermal and electrical insulating materials.

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