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# Effect of Silicon Carbide on the Properties of Natural Rubber Blends with EPDM Rubber

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**Abstract:** Rubber composites are used in many applications such as the rubber O- ring in solid oxide fuel cell unit. O-ring is used to separate hydrogen and oxygen and it must withstand heat in the range of 600 – 1,000 °C. To improve thermal properties of O- ring rubber, silicon carbide (SiC) was applied to rubber owing to the high thermal stability and good oxidation and corrosion resistances. Blends of natural rubber/ ethylene propylene diene monomer (NR/EPDM) were prepared in an internal mixer. The semi-EV of Sulphur was used. The effect of the silicon carbide level (5, 10, 15, and 20 phr) on the cure characteristic, mechanical, thermal and morphology properties of silicon carbide filled 30:70 NR/EPDM were studied. The curing properties show that the $tc_{90}$ and $t_{S2}$ of NR/EPDM blends increased with the increasing SiC loading. The effect of SiC loading on the tensile strength of NR/EPDM blends showed that tensile of vulcanizates increased with the increasing SiC up until 10 phr, extra addition of SiC would deteriorate the tensile properties. The thermal oxidative property of SiC filled NR/EPDM were satisfactory at all SiC loadings.

**Keywords:** rubber blend, EPDM, Natural rubber, Silicon carbide, O-ring, solid oxide fuel cells

## 1. Introduction

One of the common rubber products used in industry is O-ring and its use is not limited only in industry but also in an environmentally friendly power generation unit such solid oxide fuel cells (SOFCs) [1]. O-ring is needed to ensure gas separation between oxygen and hydrogen in SOFCs which operate in temperature approximately 600 – 1,000 °C [2, 3]. The O-ring manufacturing for the high temperature application is crucial. For engineering applications, not only mechanical properties, but also dynamic mechanical properties at a sensible range of temperature, must be taken into account [4].

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In rubber products manufacturing, the blending of rubbers produces new materials by using attractive properties of the blend components and effectively avoids the technical uncertainties associated with synthesizing new polymeric materials [5]. However, rubbers are relatively low thermal stability; compared to metals or ceramics. Consequently, enhancing the thermal stability of rubbers is a major challenge for further extending their applications [6, 7]. Blending two or more rubbers is a versatile way of developing new materials with a desirable combination of properties [8, 9].

Natural rubber (NR) is easily deteriorated by ozone due to its highly unsaturated polymeric backbone. Improvement in the poor ozone resistance of NR can be achieved by blending it with low-unsaturated rubbers such as ethylene–propylene-diene rubber (EPDM). EPDM rubber is produced by co-polymerization of ethylene and propylene in the presence of non-conjugated diene, and it is highly saturated. The saturated backbone of EPDM has good mechanical, dynamic and electrical properties, good resistance to aging with high chemical and swelling resistances. These inherent properties make EPDM the preferred elastomer for high temperature application [10, 11].Different types of inorganic fillers had been blended through melt mixing using a twin-screw co-rotating extruder, solution mixing, or through two roller mill mixing (mastication). R. Bussaya and K. Wirunya [12] investigated the effect of light colored fillers ($CaCO_3$, clay, and silica) on the cure characteristics and mechanical properties of an NR/EPDM rubber blend. M.M. Abou Zeid [13] studied a blend of acrylonitrile butadiene rubber (NRB) and EPDM rubber (50:50) with different amounts of high abrasion furnace (HAF) carbon black. They found that the tensile strength, modulus, hardness, electrical conductivity, and thermal stability of the blend increased with increasing the amount of carbon.

Silicon carbide has wide applications in the fields of composite materials and semiconducting devices operated in high temperature, high frequency and high-power conditions. This is due to excellent properties of SiC such as high thermal conductivity, high thermal stability, high strength and hardness, and good resistance to oxidation and corrosion [5, 14].

A. Rattanapan *et al.* [15] used the waste silicon carbide (SiC) particles from abrasive industry as alternative filler in natural rubber compounds. The rubber was prepared by using natural rubber grade STR 5L and waste silicon carbide loading of 0, 10, 20, 30 and 40 phr. The results showed that tensile modulus and tensile strength increased with increasing waste silicon carbide. On the other hand, the elongation at break of the filled natural rubber decreased with increasing waste silicon carbide. Finally, they tested samples' hardness by using shore A, the hardness was directly proportional to SiC loading [15]. However, the cure characteristics and compound properties of silicon carbide filled NR/EPDM has not been reported in literature and this research attempted to fill this knowledge gap.

In this study, a varied amount of silicon carbide was incorporated in 30:70 of natural rubber/ethylene-propylene-diene monomer (NR/EPDM) blends. The aims of this work were to study the effect of the silicon carbide on the curing behavior, tensile properties, thermal oxidative and morphology of the SiC filled NR/EPDM blends which would be potential O-ring materials for SOFCs application.

## 2. Materials and Methodology

### 2.1 Materials

EPDM rubber (Keltan® 6950C DE) with ethylene content of 44 ± 2.1 wt%, ENB 9.0 ± 0.8 wt% was purchased from Lanxess Co., Ltd. (Bangkok, Thailand). Natural rubber (STR 5L) was purchased from Chana latex Co., Ltd. (Thailand). The activators consisting of stearic acid and zinc oxide (ZnO) were obtained from Imperial chemical Co., Ltd. (Thailand). N-cyclohexyl-benzothiazyl-sulphenamide (CBS) used as the accelerators was purchased from Henan Yuanye Industry Co., Ltd. (China). Elemental sulfur (S8) was purchased from the vessel Chemical Public Co., Ltd. (Bangkok, Thailand). The compatibilizer (Homogenisator 501) was obtained from Dog Deutsche Oelfabrik Co.,Ltd. (Germany). Silicon carbide were purchased from Sigma Aldrich.

### 2.2 Preparation of NR/EPDM Blends and Compound Testing

The formulations of all blends are shown in Table 1 and the physical characteristics of silicon carbide are shown in Table 2. The preparation of NR/EPDM blends was carried out in an internal mixer using conventional mixing procedures involving two stages. The first stage; the mixing was carried out in a laboratory-size internal mixer (MX500-D75L90 Charoentut Co., Ltd., Thailand) with a fill factor of 0.6, at a chamber temperature of 60 °C and a rotor speed of 40 rpm. NR was initially masticated in the mixer for 3 min. EPDM was then mixed and followed by addition of the activators (zinc oxide and stearic acid) and accelerators. After discharging, the compound was sheeted on a two-roll mill (YFCR 6; Yongfong machinery Co., Ltd., Thailand) for 1 min. Then, the curatives were added and mixed for 5 min. The second stage involved the 10 end-roll passes. Later, cure characteristics of all compounds were determined by using a moving die rheometer (MDR 2000; CNR engineering Co., Ltd, Thailand) at 160 $^{o}$C. Then, the compounds were vulcanized at 160 $^{o}$C in a compression mold according to their cure time ($tc_{90}$) to produce sheets and the test pieces which were stored at room temperature for at least 24 h before determination of properties. (Fig.1)

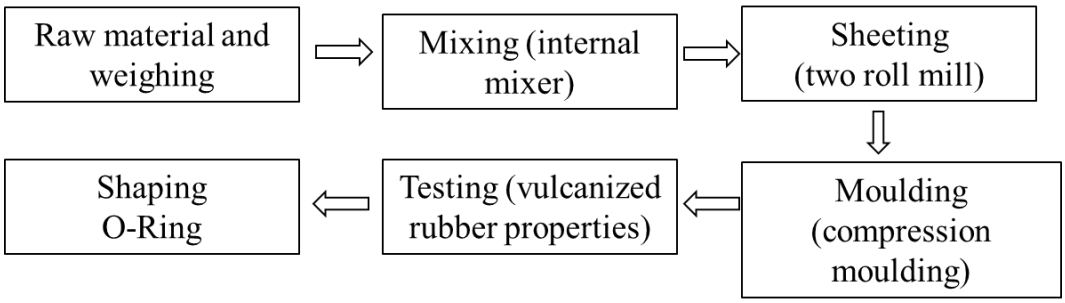


**Fig.1 - The flow chart of composite process.**

## 2.3 Mechanical Properties of NR/EPDM Blend Measurement

Hardness of the vulcanizates was measured using a Shore A durometer (model Shore S1; Instron, K. S. P. Co., Ltd., Thailand) based on ASTM: D2240-05(2010). Dumbbell-shaped samples were cut from the moulded sheets according to ASTM: D412-06ae2[16]. The gage thickness of the narrow was 4.5 mm. The gage length was 78.74 mm and tested by using a universal tester (model 10ST; Calserve Co., Ltd., Thailand). The specimens were tested by using a 1 kN load cell and a crosshead speed of 500 mm/min. The average values of tensile were taken from 5 specimens**.**

**Table 1 - Formulations of blend compound**

| **Ingredients** | **phr** [a] | | | | |
|---|---|---|---|---|---|
| | **SiC0** | **SiC5** | **SiC10** | **SiC15** | **SiC20** |
| NR(STR5L) | 30 | 30 | 30 | 30 | 30 |
| EPDM | 70 | 70 | 70 | 70 | 70 |
| CBS | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
| ZnO | 4 | 4 | 4 | 4 | 4 |
| Stearic acid | 1 | 1 | 1 | 1 | 1 |
| Silicon carbide | 0 | 5 | 10 | 15 | 20 |
| Sulfur | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 |
| Homogineser501 | 5 | 5 | 5 | 5 | 5 |

[a] phr = parts per hundred of rubber

**Table 2 Physical characteristics of silicon carbide**

| **Physical characteristics** | **Values** |
|---|---|
| Density (g/cm$^3$) | 3.21 |
| Mean diameter (μm) | 0.625 |
| Form | powder |

## 2.4 Thermo-oxidative Ageing Measurement

For the tensile tests, dumbbell shaped specimens were cut from a moulded sheet with a thickness of 2 mm. In order to evaluate property retention of silicon carbide filled NR/EPDM blend after ageing, 5 dumbbell shaped specimens were placed in an oven with an air-circulating system, at an operating temperature of 100 °C for 48 h (according to ISO 188). The tensile properties of both aged and unaged specimens were determined in the same manner, and then compared. Tensile testing was conducted according to ISO 37 using a universal tensile testing machine with a crosshead speed of 500 mm/min. Data for tensile strength, elongation at break, and tensile modulus (M100) was evaluated from stress-strain determinations and average values for each compound were recorded. The retained percentage values of tensile properties were calculated according to Equation (1):

$$Retention\ (\%) = \frac{Aged\ value}{Unaged\ value} \times 100 \qquad (1)$$

## 3. Results and Discussion

## 3.1 Cure Characteristics

Silicon carbide were incorporated with loading ranging from 0 to 20 phr in 30:70 NR/EPDM blends to study the effect of filler loading on the cure properties of the blends such as scorch time ($ts_2$, min), curing time (tc90, min), cure rate index (CRI), elastic minimum torque ($M_L$, dN.m), elastic maximum torque ($M_H$, dN.m), torque difference ($M_H - M_L$, dN.m). These values were reported in Table 3.

The cure characteristics of silicon carbide filled 30:70 NR/EPDM blend at various loading of SiC are presented in Table 3. The scorch and cure times of the NR/EPDM blend increased as the weight ratio moved towards higher loading of SiC. The SiC is a porous material so it is expected to adsorb curatives on its surface, the adsorption effectively decelerated the curing system, therefore, the scorch time and cure time were prolonged and increased with the added SiC. This phenomena is similar to results from P. Sae-oui *et al.* [17] who found that the addition of silica increased the scorch and cure times as well.

**Table 3 - Cure characteristics of 30:70 NR/EPDM blends**

| Name | $ts_2$ | $tc_{90}$ | $M_L$ | $M_H$ | $M_H - M_L$ | CRI |
|---|---|---|---|---|---|---|
| **SiC0** | 1.59 | 5.50 | 1.46 | 13.81 | 12.35 | 25.58 |
| **SiC5** | 2.12 | 6.01 | 1.58 | 14.33 | 12.75 | 25.71 |
| **SiC10** | 2.58 | 6.11 | 1.62 | 14.61 | 12.99 | 36.63 |
| **SiC15** | 2.25 | 6.13 | 1.60 | 14.21 | 12.61 | 23.36 |
| **SiC20** | 2.51 | 6.25 | 1.67 | 15.07 | 13.40 | 27.47 |

From Table 3, the torque of blends increased with the SiC content. The increment of torque values was caused by the increase in stiffness of the composite due to the restriction of the mobility of the rubber chains as fillers were incorporated [17]. The difference between the maximum and minimum torque values is a measure of the dynamic shear modulus, the difference between the maximum and minimum torque ($M_H - M_L$) of the NR/EPDM blend increased as the level of SiC increased. The enlarging torque difference indicated the increase in stiffness, which could be beneficial for a better interfacial interaction between the additive and the immobilized bound rubber.

## 3.2 Mechanical Properties of NR/EPDM Blend

Fig. 2 and Fig.3 show effects of silicon carbide on the tensile strength and the elongation at break (Eb) of 30:70 NR/EPDM blends. Both properties increased gradually with increasing silicon carbide loading. Our results agreed well with work from P. Pasbakhsh *et al.* [11]. The enhancement of the tensile properties depended on many factors such as the dispersion of the filler in the matrix, the interfacial interaction between the filler and matrix, and the interaction between the filler and other compounding ingredients such as accelerators and activators. The enhancement of the tensile strength by SiC was due to the interaction between SiC and metrix. Tensile strength of 30:70 NR/EPDM blends showed an increasing trend with increasing SiC loading up to a maximum value at 10 phr.

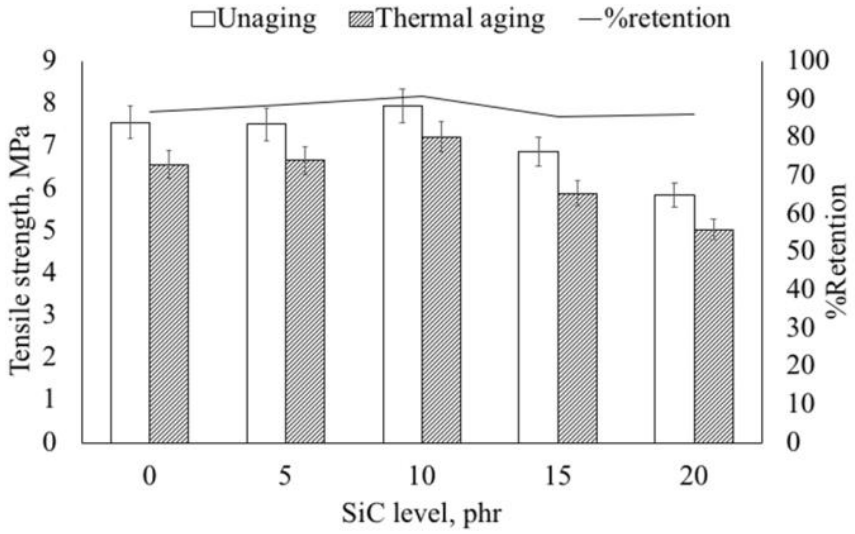


**Fig. 2 - The effect of silicon carbide loading on tensile strength of 30:70 NR/EPDM blends before and after heat ageing**

However, an excessive addition of SiC (more than 10 phr) reduced the tensile strength. The adverse effect of filler amount was explained by Arayapranee and Rempel (2008) [18] who found that excess filler caused voids in the matrix and reduced the mechanical strength of the composite.

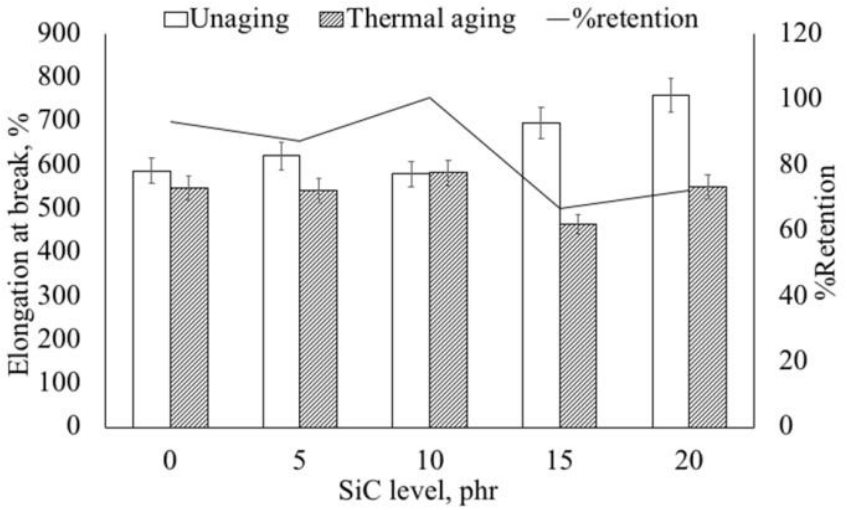


**Fig. 3 - The effect of silicon carbide loading on elongation at break values of 30:70 NR/EPDM blends before and after heat ageing**

The tensile strength and elongation at break of all aged samples reduced upon thermal ageing (Fig. 2 and 3). At a fixed blend ratio, reduction in tensile strength could be attributed to the oxidation of the polymer, which resulted in chain scissions. Scission of the larger molecular chains increased the number of shorter chains of the respective polymer, which led to fewer entanglements, and thereby decreased the tensile strength as well as elongation at break. The elongation at break is an indication of the elasticity or flexibility of the sample upon stretching till failure. Another crucial aspect of this study was to investigate the retained percentage of properties in the blends after ageing. The 10 phr of SiC filled NR/EPDM exhibited good retention in tensile strength and elongation at break. Addition of SiC more than 10 phr could not retain these properties after ageing. The retained tensile strength of both blends declined when SiC concentration was higher than 15 phr [19]. Tensile modulus or hardness directly related to the stiffness or rigidity of the blends. From Fig. 4 and 5, the modulus and hardness of unaged blends increased slightly with further increase in the concentration of SiC. It also found that the modulus and hardness of aged blends increased clearly with increasing SiC. This was probably due to the formation of additional crosslinks. Increase of the crosslink density after thermal ageing of the blends strongly related to the high rate of radical termination in the bulk of polymer; hence, the material was more cross-linked [19]

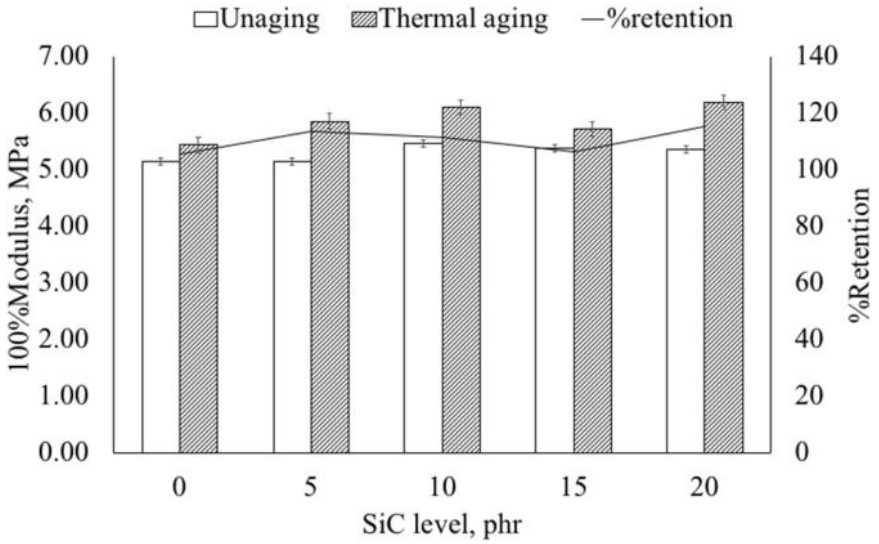


**Fig. 4 - The effect of silicon carbide loading on modulus values at 100% of 30:70 NR/EPDM blends before and after heat ageing**

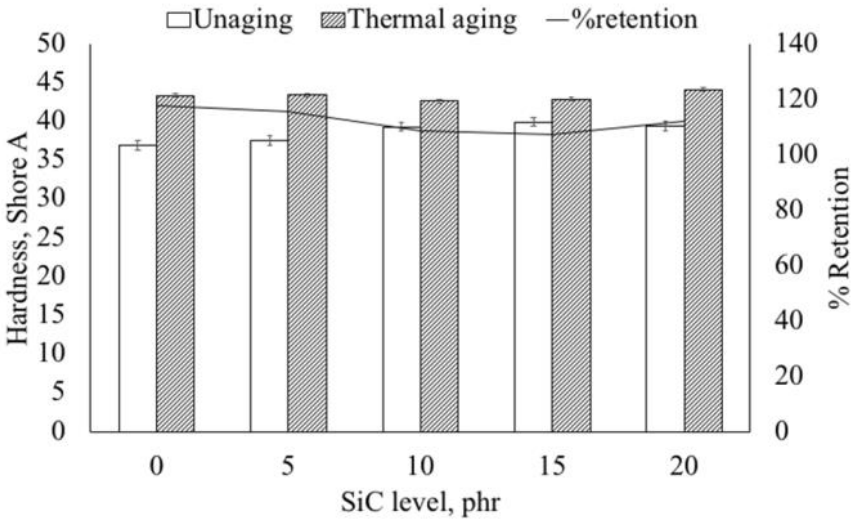


**Fig. 5 - The effect of silicon carbide loading on hardness properties of 30:70 NR/EPDM blends before and after heat ageing**

## 3.3 Morphology

The morphology of unfilled and silicon carbide filled 30:70 NR/EPDM blends are shown in Fig. 6. The surface of the unfilled 30:70 NR/EPDM blends was smooth (Fig. 6(a)) while the surface of the 10 phr silicon carbide filled 30:70 NR/EPDM blends (Fig. 6(b)) shows a homogenous phase dispersion. The dispersion of SiC (labeled in Fig. 6(b)) confirmed the successful integration of SiC in the 30:70 NR/EPDM blend

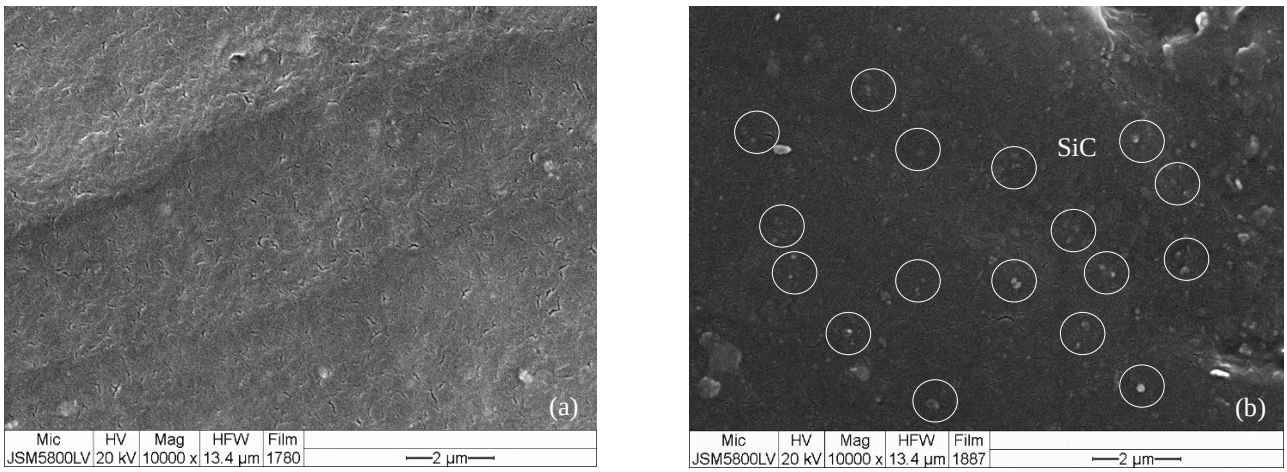


**Fig. 6 - SEM images of surface (a) Unfilled NR/EPDM blend; (b) 10 phr SiC filled NR/EPDM blend**

Arayapranee and Rempel [18] stated the SEM shows a homogenous phase dispersion, indicating the improvement of tensile strength. This finding agree with our results in Fig. 1 which 10 phr silicon carbide filled 30:70 NR/EPDM blends shows the highest tensile strength.

## 4. Summary

The cure time, the scorch time, minimum torque and maximum torque increased with increasing silicon carbide loading. The effect of silicon carbide loading on the tensile strength of NR/EPDM blends composite showed that tensile of vulcanizates increased with the increase of silicon carbide loadings. However, the effect was more significant at high silicon carbide content. The suitable SiC composite was determined to be 10 phr SiC loading composite. Its scorch time and cure time were 2.58 and 6.11 min, respectively. This values were longer than time required in the preparation of unfilled NR/EPDM blends. The minimum and maximum torque values were 1.62 and 14.61 dN.m, These values were higher than that of the unfilled NR/EPDM blends so the SiC composites was successfully prepared for O-ring application in solid oxide fuel cells unit.

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