Effect of Incorporation of Carbon Fiber and Silicon Carbide Powder into Silicone Rubber on the Ablation and Mechanical Properties of the Silicone Rubber-Based Ablation Material

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ABSTRACT: This study examined the effects of the incorporation of carbon fiber (CF) and silicon carbide powder (SCP) into a high temperature vulcanized (HTV) silicone rubber, poly(dimethylsiloxane) (PDMS) containing vinyl groups on the ablation properties using an oxy-acetylene torch test. The ablation test results showed that CF enhanced the hardness of the char formed on the composite surface during the oxy-acetylene torch test and was an important factor determining the ablation properties. SCP was also beneficial in enhancing the surface char hardness of the HTV/CF composite. A new method was devised to evaluate the ablation properties more objectively by measuring the time elapsed for a rectangular-shaped silicone rubber composite with specimens loaded with a constant weight to burn and fail off during the oxy-acetylene torch test. The mechanical properties of the silicone rubber composites were also examined as a function of the additive content using a universal test machine (UTM). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 831–838, 2011

Key words: silicones; fibers; thermal properties

INTRODUCTION

The temperature of the combustion gas in a rocket motor chamber normally increases to well over 2600–3500 K.[1] Therefore, an appropriate thermal protection system should be used to protect the rocket motor case. In general, an insulation layer is placed on the inner wall of the motor chamber for this purpose. During propellant burning, the combustion chamber is under severe conditions because of the high shear produced by the fast flowing combustion gas as well as the excessively high temperatures. Therefore, the insulation layer should have good ablation properties to protect the motor case efficiently.[2,3] Char formation on the insulator may slow down the penetration of combustion heat through the insulator and provide an effective thermal protection system for the motor chamber. Therefore, the mechanical strength of a char layer is a critical factor for the ablation resistant properties of these insulation composites.[4–6] Particle-filled and fiber-reinforced ethylene-propylene-diene rubber (EPDM) has been used as an insulation material owing to its advantages in easy processing, low density, and low thermal conductivity. However, this elastomer does not form a strong enough char layer and is unsuitable for insulation in long range rocket motor cases.

Polydimethylsiloxane (PDMS) is a widely used polymer that has attracted considerable attention owing to its unique properties, such as high thermal stability, low glass transition temperature, outstanding dielectric properties, and physiological inertness.[6–9] Therefore, silicone rubber is a strong candidate as an insulation material. Some countries with advanced technologies have already attempted to use silicone rubber composites for thermal insulation of the ram jet combustion chamber.[10] However, silicone rubber does not form a strong enough char at severely high temperatures. Consequently, inorganic materials and organic fibers have attracted considerable interest over the past decade[11–15] to increase the ablation properties of silicone rubber. Polyacrylonitrile (PAN)-based carbon fiber (CF) is expected to be a good material to improve the mechanical and ablative properties of silicone rubber-based insulation composites because of its high carbon residue (>45% at 1000°C) in nitrogen.[16]

This study examined the ablation properties of silicone rubber and silicone rubber composites containing silicon carbide powder (SCP) and CF[17] using oxy-

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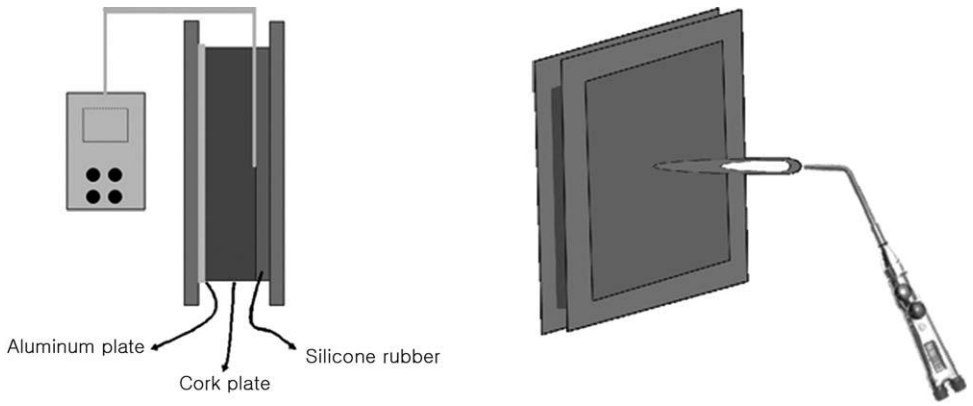


Scheme 1 The oxy-acetylene torch apparatus for the measurement of the back face temperature.

acetylene torch tests. The temperature at the back face of the specimen was measured to assess the ablation performance of the silicone rubber composites. A new method for an integrated evaluation of the ablation properties was proposed, taking into consideration the rate of thermal degradation as well as the mechanical strength of the charred composite formed under the oxy-acetylene torch test.[10,18,19] The mechanical properties of silicone rubber composites were also examined as a function of the additive content.

EXPERIMENTAL

Materials

LT-50® is a PDMS (Dow-Corning, Midland, MI) end-blocked with vinyl groups containing vinyl-methylsiloxane units in the main chain. LT-50® consists of trimethylated silica (30–60 wt %), dimethylcyclosiloxanes (1–5 wt %), phenylmethyl siloxane (15–40 wt %), and methylvinyl siloxane (7–13 wt %). The silicone rubber was cured with 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane (model number : LS-5; DMBPH peroxide; Dow Corning Co.) as a curing agent. The chopped CF was obtained from Wooshin Chemtech (Korea). The PAN-based CF was chopped into staples, 5–6 mm in length. A chopped CF is normally coated with a certain organic compound to prevent the CF scattering problem by bundling the chopped CF together. The organic compound used for the coating was removed by burning CF in air at 400°C for 2 h to obtain naked CF. SCP (Aldrich, St. Louis, MO) ranged from 200–450 mesh in size.

Preparation of silicone rubber/CF composites

The silicone rubber sheet was prepared from high temperature vulcanized (HTV), which is vinyl-terminated PDMS, LT-50®. CF and SCP compounded HTV mixtures were prepared using the solution cast method. HTV was dissolved completely in toluene with 1 wt % DMBPH peroxide. The resulting solution was dried in a vacuum oven at 60°C for 48 h. For the HTV/CF composites, CF was introduced into the HTV-toluene solution. The resulting solution was stirred until a solution containing well dispersed CF was obtained and then dried in a vacuum oven at 60°C for 48 h. The HTV and HTV/CF/SCP composites were cured in a hot press at 175°C for 10 min under a pressure of 19.4 atm.

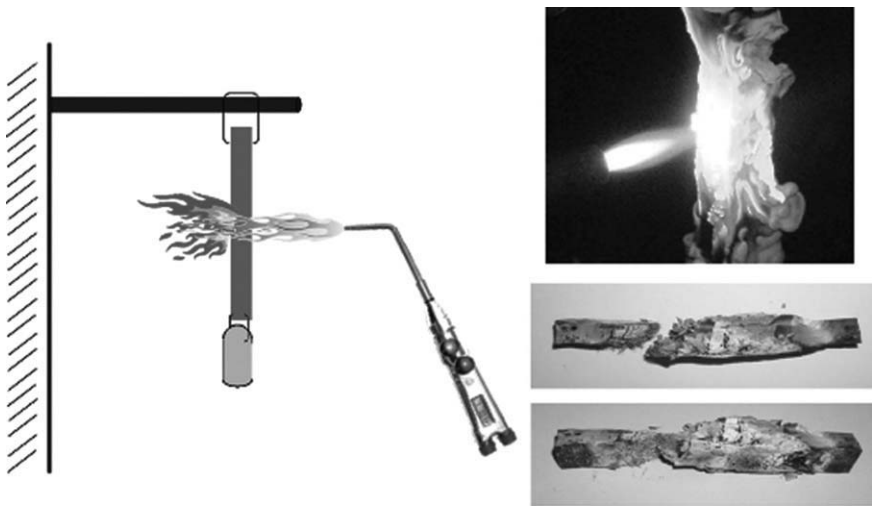
Measurements

The cross section of the silicone rubber/CF composites was observed by scanning electron microscopy (SEM, Hitachi, *S*-4300, Japan) The tensile properties of the composites were measured using a universal testing machine (UTM) (Hounsfield H 10KS-0061, UK). The specimens were prepared according to the KSM 6518, and the cross-head speed was set to 500 mm/min. The results of the five specimens were averaged. The tear strength of the specimens was measured using the same UTM with a cross-head speed of 100 mm/min. The specimens were prepared in a trouser shaped mold according to the KSM 6783, and the results of at least five specimens were averaged. The tear strength was calculated from eq. (1).

$$\mathrm{TR} = \frac{F}{t} \tag{1}$$

where TR, F, and t are the tear strength (N/mm), tearing force (N), and specimen thickness (mm), respectively.

In the ablation properties measurements, the temperature at the back face of the specimen was measured as a function of the flame exposure time. Flow meters for acetylene and oxygen were installed to supply an accurate amount of gases. The oxygen to acetylene volume ratio was set to 1.20, which corresponds to a neutral atmosphere. The test method was followed according to the ASTM E 285-80. The back-face temperature record was measured using a thermocouple, which was shielded with a mass of silicone rubber to allow accurate measurements of the temperature, as shown in Scheme 1. The dimensions



Scheme 2 An apparatus to measure the time elapsed for the silicone rubber composite specimens to burn and fail off.

of the insulation index specimens were 70 mm × 70 mm × 6 mm. The distance between the specimen face and oxy-acetylene torch tip was 2 cm.

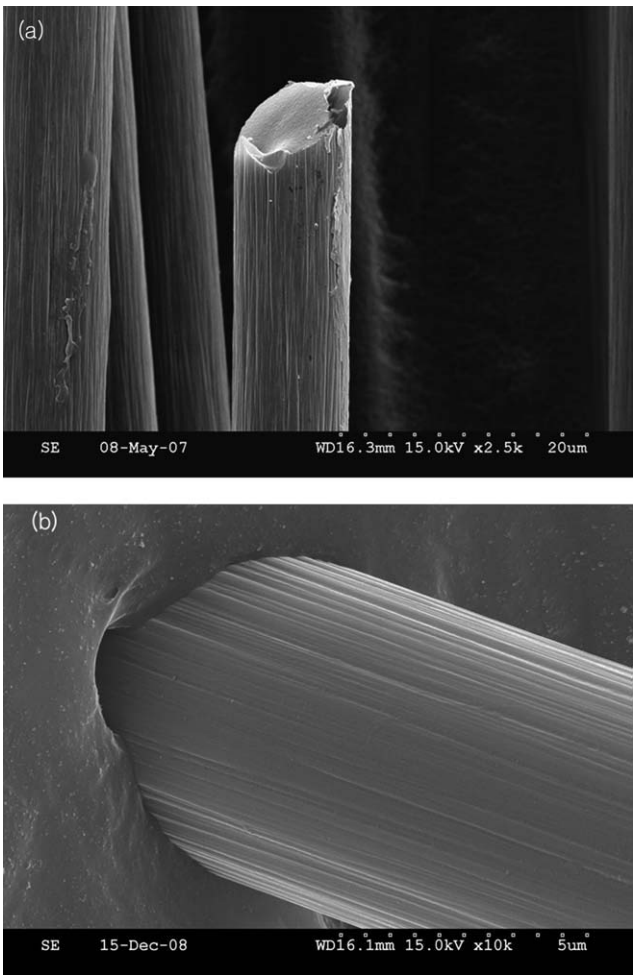


Figure 1 SEM image of the (a) naked CF and (b) fractured surface of PDMS/CF.

A new method was devised to evaluate the ablation properties more objectively. A specimen with dimensions of 10 mm × 70 mm × 6 mm was clamped and hung with a 400 g load. As shown in Scheme 2, an oxy-acetylene flame was burst on the center of the specimen and the time elapsed for the specimen to burn and fail off was measured. The oxy-acetylene torch tip was also placed 2 cm away from the middle of the rectangular-shaped specimen. The volumetric flow rate of oxygen and acetylene was also adjusted to a ratio of 1 : 1.2 (v/v).

RESULTS AND DISCUSSION

The mechanical properties and ablation performance of PDMS/CF was examined as a function of the CF content in the range of 0–3.5 wt %. Figure 1 shows the morphology of the organic compound removed CF and PDMS/CF. The naked CF surface contained many scratches but was clean. The CF in the PDMS/CF composite also exhibited a clean and smooth surface, indicating that PDMS adhered poorly to the CF surface.

Table I shows the tensile strength and elongation at break of the PDMS/CF composites. The tensile strength decreased slightly with increasing CF content to 3.5 wt %, whereas the elongation at break decreased significantly. In general, the incorporated fibers tended to resist the unidirectional tension to

TABLE I
Tensile Properties of the PDMS and the PDMS/CF Composites

	Max stress (MPa)	Elongation at break (%)
PDMS	8.2	1100
CF0.5	8.1	995
CF 1.5	7.9	872
CF 3.5	7.3	547

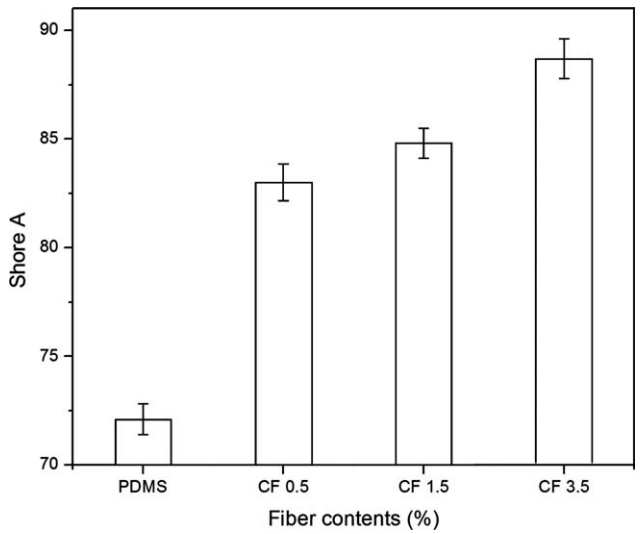


Figure 2 Shore A hardness of PDMS/CF composites as a function of CF content.

reduce the elongation at break, as shown in Table I. CF cannot be classified as an effective filler because the tensile strength of the PDMS/CF composites was not enhanced but reduced compared to that of PDMS. The weak interaction between CF and PDMS should be responsible for the facile mechanical failure of the composite. However, the Shore A hardness increased considerably with increasing CF content, as shown in Figure 2, due to the hardness of CF.

The back-face temperature of the PDMS composite sheet was measured after the oxy-acetylene flame was burst onto the specimen surface using the apparatus shown in Scheme 1. The back-face temperature after 150 s of the burning decreased with increasing CF content.

As the temperature of the oxy-acetylene flame is well over 3000°C, the PDMS matrix and CF cannot endure the severe burning. Therefore, the reduced temperature rise, as a result of CF incorporation, is attributed to the formation of char shielding the thermocouple from intimate contact with the flame.

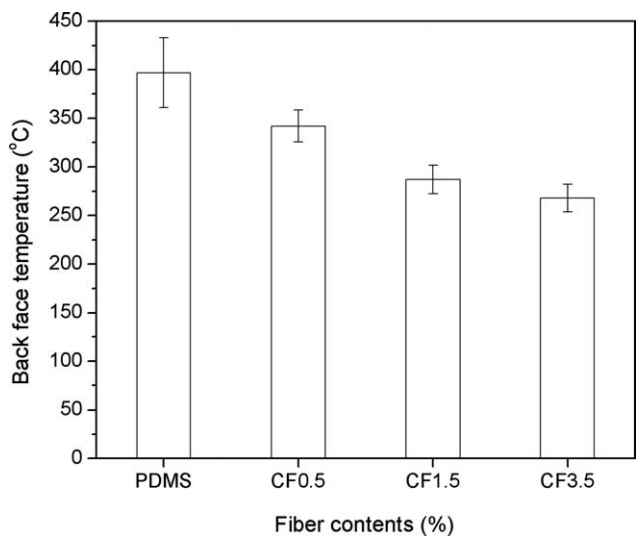


Figure 3 Back face temperature of PDMS/CF composites as a function of CF content.

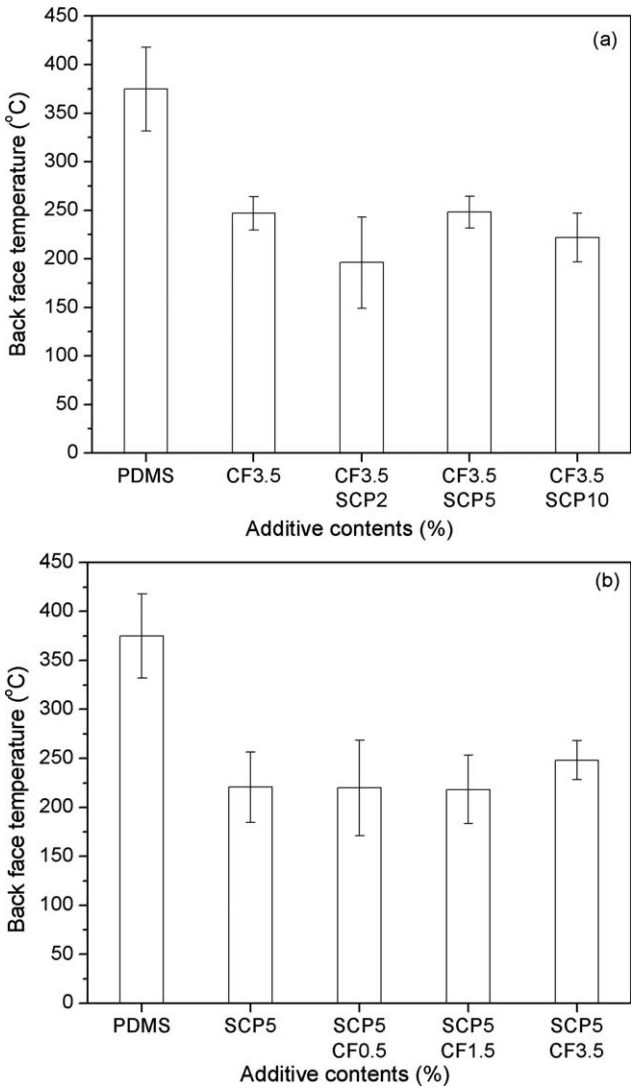


Figure 4 Back face temperature of PDMS/CF/SCP composites as a function of (a) SCP and (b) CF content.

Char formation is one of the most important properties of an insulation material to protect the rocket motor case efficiently against the severe conditions in the combustion chamber. In addition, the char layer should have sufficient mechanical strength to withstand the shear induced by the fast flowing combustion gas. Because of the increase of CF contents made more thick char layers, the back face temperature was decreased with the CF contents (Fig. 3).

Since the char formed is mechanically too fragile, the char strength cannot be evaluated quantitatively. An attempt was made to measure the char hardness instead of the char strength but a precise measurement of the char hardness was not possible because

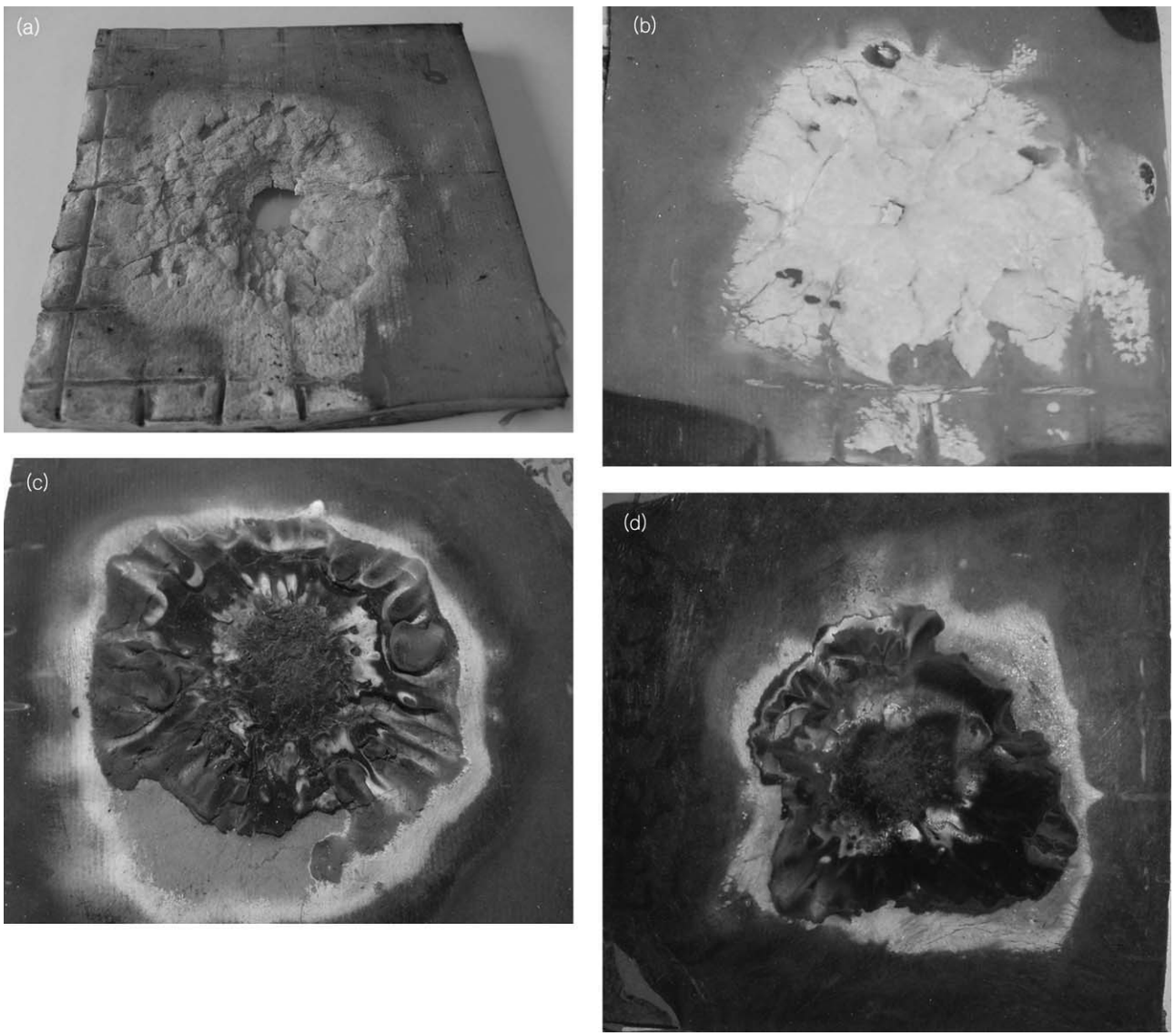


Figure 5 Image of sample after the oxy-acetylene torch test (a) PDMS, (b) PDMS/SCP, (c) PDMS/CF, and (d) PDMS/CF/SCP.

the char layer surface was rough and uneven. Therefore, the char hardness was measured manually. The results suggested that the char hardness increased with increasing CF content.

Since silicon carbide (SCP) has been reported to be beneficial for improving the ablation properties,[17-18,20] the effects of SCP incorporation into the composites on the physical and ablation properties were explored as shown in Figures 3 and 4. At a CF content of 3.5 wt %, the SCP content was varied from 0 to 10%. At a SCP content of 5 wt %, the CF content was changed from 0 to 3.5%. The ablation performance of the composites was assessed by measuring the back-face temperature. The back-face temperature decreased because of the addition of CF or SCP. In contrast to expectation, the addition of both CF and SCP did not decrease the back-face temperature significantly.

Figure 5 shows the morphology of the char formed after the oxy-acetylene torch tests. CF (3.5%) and SCP (5%) were incorporated into the silicone rubber composites. During the tests, neat PDMS and PDMS/SCP were burnt through and a very weak powdered char had formed on the surface, as shown in Figure 5(a,b). In contrast, the silicone rubber composites incorporated with CF or CF/SCP were not burnt through and formed a char layer with good strength on the surface, as shown in Figure 5(c,d).

Figure 6 presents SEM images at low and high magnification of the char layer formed after the oxy-acetylene tests. The morphology of the char formed from neat PDMS appeared to be different from that formed of the other composites. The SEM image at low magnification of the burnt PDMS surface exhibited a sharp and acute morphology, whereas that of the burnt PDMS/CF displayed a lumpy surface. The

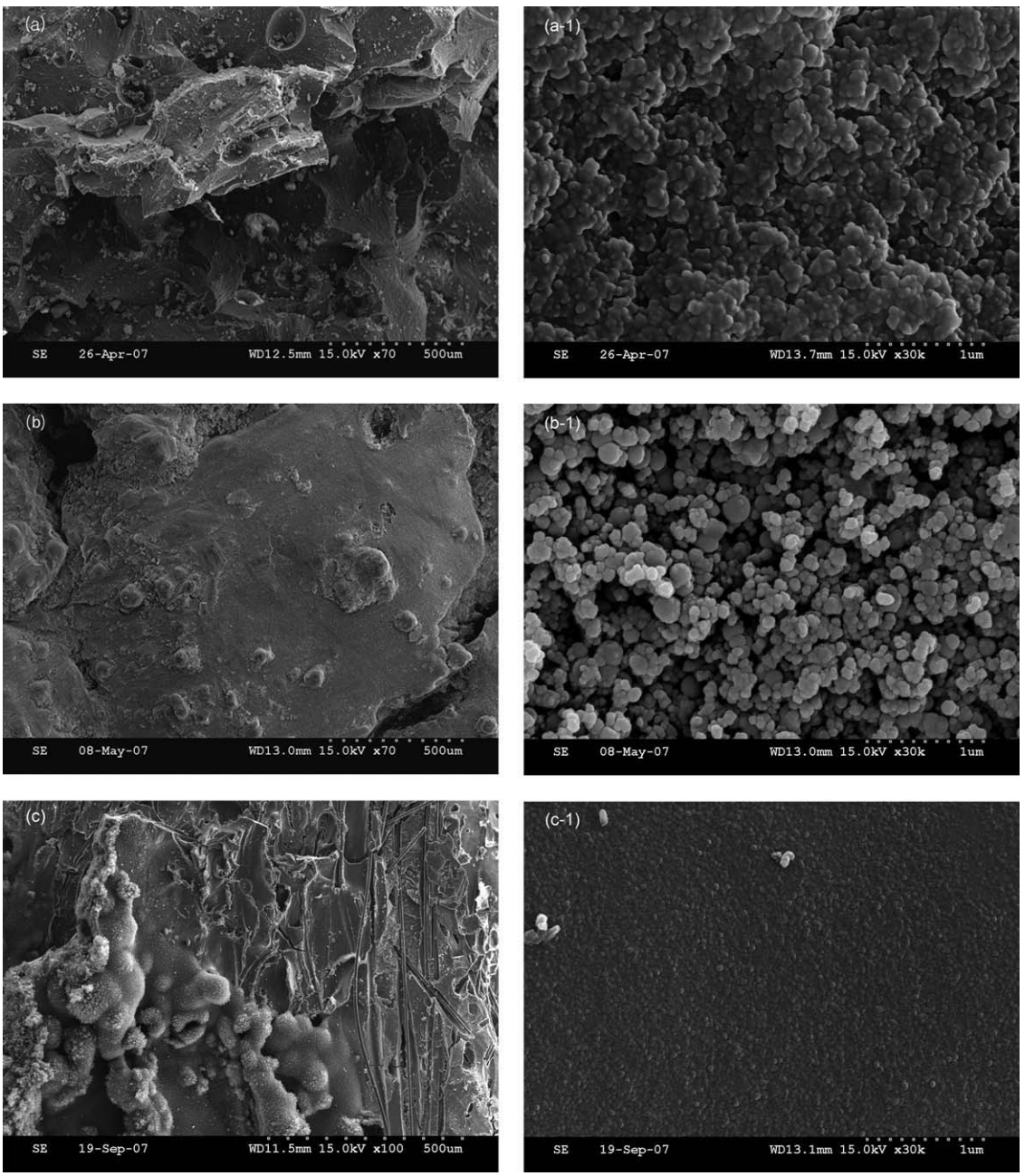


Figure 6 SEM image of the char formed during the oxy-acetylene torch tests at low and high magnification: (a), (a-1) PDMS; (b), (b-1) PDMS/CF; (c), (c-1) PDMS/CF/SCP.

PDMS/CF/SCP exhibited some traces indicating that a fluid had melted and rolled down during the tests, as shown in Figure 6(c). The dust-like char formed on the neat PDMS flew away from the surface, whereas CF in PDMS/CF still contained a tightly held lumpy char. The highly magnified SEM image of the char formed from PDMS/CF in Figure 6(b-1) shows an acinous morphology, indicating that the char had been eroded during burning. In contrast, the SEM image at high magnification of the char formed from PDMS/CF/SCP exhibited a flat surface and an acinous morphology was not observed. This is because the SCP incorporated was comingled with the other constituents during burning. Hence, the addition of SCP into PDMS/CF made the char denser and harder, which should be beneficial for efficient shielding of the motor case against the scorching combustion heat.

The combustion heat is absorbed by the decomposing insulation material. Hence, a material with greater susceptibility to decomposition is more effective in decreasing the increase in back-face temperature. At the same time, the rapid burning might result in intimate contact between the back-face-temperature-measuring thermocouple and an oxy-acetylene flame to increase the rate of the temperature

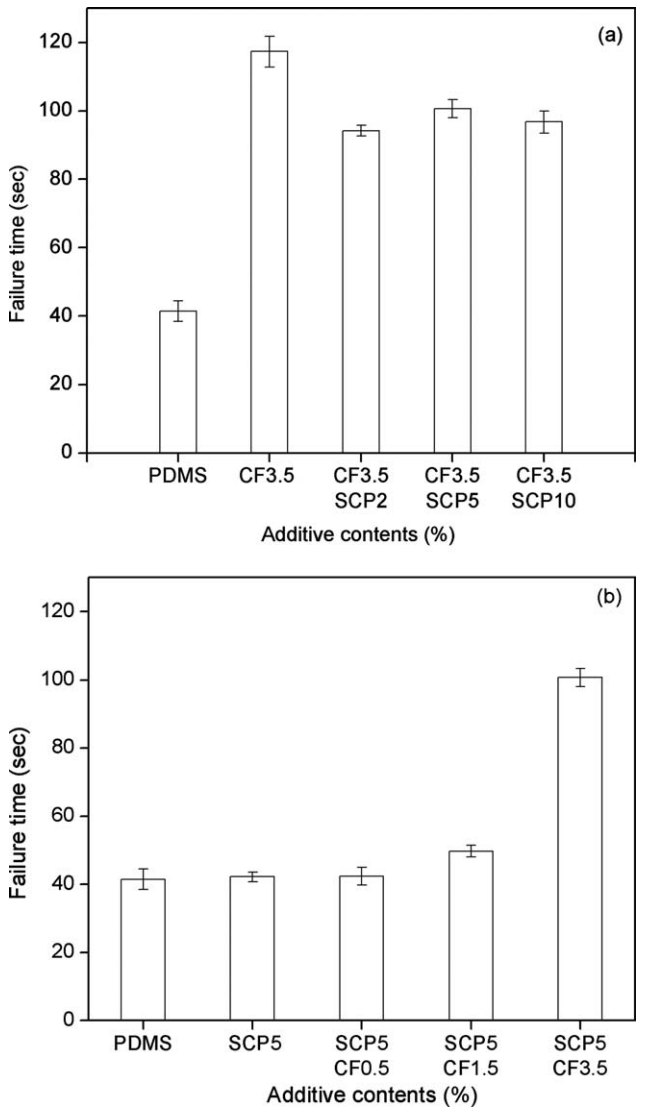


Figure 7 Failure time of PDMS/CF/SCP composites as a function of (a) SCP and (b) CF content.

rise. Therefore, the ablation performance cannot be assessed by the rate of the back-face temperature rise alone. In this regard, a new scheme was devised to obtain supplementary data for an evaluation of the ablation properties, as shown in Scheme 2.

The time elapsed for a specimen to burn and fail off could be a measure of both the char strength and endurance of the specimen against burning. Hence, it could be an integrated measure of the ablation properties.

Figure 7(a) shows that the addition of CF prolonged the failure time. However, the incorporation of SCP in PDMS/CF did not increase the failure time. In contrast, the failure time increased with increasing CF content in PDMS/SCP, indicating that CF was more effective in extending the failure time than SCP, as shown in Figure 7(b). This was attributed to the fibrous CF holding the char together and the specimen not failing until the CF had burnt off. In contrast, the powdery SCP comingled and could not link the char lumps together and was less effective in extending the failure time than CF despite the fact that SCP incorporation formed a denser char layer. Therefore, the failure time cannot be a universal measure of the ablation properties and should be used as a complementary gauge together with the back-face temperature rise.

The physical properties of the silicone rubber composites were measured as a function of the composite composition. According to Table II, the Shore A hardness increased because of the incorporation of CF and SCP, and that CF was more effective in enhancing the Shore A hardness.

Table II list the tensile properties of the PDMS/CF/SCP composites. The tensile strength of the PDMS/CF composites decreased slightly, but the elongation at break increased with increasing SCP content in PDMS/CF/SCP from 0 to 10 wt %. In contrast, the addition of CF to PDMS/SCP reduced the tensile strength and the elongation at break.

The results in Table II indicate the tear strength of the silicone rubber composites. SCP did not contribute to the tear strength. In contrast, CF was beneficial in enhancing the tear strength because CF may block the path of tear crack propagation. However, the enhancement effect was not significant.

CONCLUSION

The ablation performance of PDMS composites with CF and SCP was examined as a function of the composite composition. The ablation performance of the composites was assessed by measuring the back-face temperature, which decreased as a result of the addition of CF or SCP. However, the addition of both CF and SCP did not decrease the back-face temperature significantly. Neat PDMS and PDMS/SCP were burnt through and a very weak powdered char was formed on the surface. On the other hand, PDMS/CF/SCP was not burnt through and formed a char layer with a good strength. The addition of

TABLE II
Mechanical Properties of the PDMS/CF/SCP Composites as a Function of the SCP and CF Content

Samples	Max stress (MPa)	Elongation at break (%)	Tear strength (N/mm)	Shore A
PDMS	8.2	1100	13.65	72.1
PDMS/CF3.5	7.9	608	18.89	86.5
PDMS/CF3.5/SCP2	7.8	597	19.56	90.5
PDMS/CF3.5/SCP5	7.7	610	16.38	92.5
PDMS/CF3.5/SCP10	7.4	787	13.67	89.0
PDMS/SCP5	6.9	906	12.52	79.8
PDMS/SCP5/CF0.5	7.5	800	13.94	81.2
PDMS/SCP5/CF1.5	7.5	704	16.18	86.8
PDMS/SCP5/CF3.5	7.7	610	16.38	92.5

SCP to PDMS/CF made the char denser and harder, which should be beneficial for efficient shielding of the motor case against the scorching combustion heat. The time elapsed for a specimen to burn and fail off was measured to obtain complementary data on the ablation properties. The addition of CF prolonged the failure time. However, the incorporation of SCP in PDMS/CF did not extend the failure time despite the fact that SCP incorporation resulted in the formation of a denser char layer.

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