Comprehensive Ablation Characteristics of Ceramic Fibers Impregnated Rubber Composites

Nadeem Iqbal, Sadia Sagar, and Mohammad Bilal Khan

***Abstract*—In this novel research, aluminum silicate fibers were incorporated into ethylene propylene diene monomer (EPDM) rubber to fabricate ablative composites, achieve better ablation performance, and thermal endurance for ultra-high temperature applications. Variant concentrations of ceramic fibers (CFs) were impregnated in the elastomeric matrix. Ablation testing of the composite specimens was carried out according to ASTM E285-08, in which oxy–acetylene torch was used as a high temperature source. The obtained results showed that anti-ablation performance of the polymer composites was remarkably augmented with increasing fiber concentration in the polymer matrix. Thermal decomposition of the fabricated composites was diminished with the progressive incorporation of CFs in the EPDM matrix. Ultimate tensile strength, elongation at break, and modulus of elasticity were reduced due to the weak fiber to matrix interaction while Shore A rubber hardness was augmented with increasing fiber to matrix ratio. Voids formation & polymer pyrolysis of the ablated specimens, char reinforcement interaction, CFs dispersion in the polymer matrix, elemental analysis and fiber diameter measurement of the CF, and the compositional analysis of ablative composite were analyzed using scanning electron microscopy coupled with energy dispersive spectroscopy.**

***Index Terms*—Ablative composites, ceramic fibers, mechanical properties, thermal degradation, thermal conductivity, temperature evolution.**

I. INTRODUCTION

A composite is commonly defined as a combination of two or more distinct materials, each of which retains its own distinctive properties, to create a new material with desirable properties that cannot be achieved by any of the components acting alone[1]. On the basis of continuous phase (Matrix), composites materials are classified into three main broad categories, i.e. Metal matrix composites (MMCs), Ceramic matrix composites (CMCs), and Polymer matrix composites (PMCs)[2].

PMCs are composed of a matrix (polymer) from thermoplastics materials (polycarbonates, polyvinyl chloride, nylon, polystyrene, etc) as continuous phase or thermoset (unsaturated polyesters, epoxies, phenolic resins, polydimethylsiloxane, etc) and embedded glass, carbon, silica clays, carbon nanotubes/fibers, synthetic chopped/continuous fibers, etc as dispersed phase in the composite.

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An ablative composite is a type of composites, which are used to protect certain structure or equipment from the intense heat environment. Mostly, such types of composites are used in aerospace industry. The basic definition of ablative composites is "These are highly endothermic sacrificial materials used to protect the hardware from ultra high temperatures and shear stresses in the propulsion system." Low backface temperature, high mechanical/thermal ablation resistance, and good interfacial adhesion between the ablative material and the aerodynamic surface are required for the composites used in Thermal Protection Systems (TPS)[3]. The main function of TPS materials is to protect the inner hardware of space vehicles and ballistic missiles from ultrahigh temperature/velocity flow of gases encountered during their missions. Crosslinked polymer composites have been used as TPS materials since long time due to their excellent thermal resistance, ablation resistance, low backface temperature evolution during ablation, and low density characteristics. Phenolic resin based polymer composites have high backface temperature elevation and low interfacial bonding with the metallic casings but high erosion resistance compared to the elastomeric crosslinked composites, i.e., ethylene propylene diene monomer rubber (EPDM), silicon rubber (SR), and acrylonitrile butadiene rubber (NBR) based composites. Silica/silicon carbide fibers impregnated polymer composites, carbon–carbon composites, phenolic composites and elastomeric composite tiles have been used to protect reentry vehicles and solid rocket motor from ultrahigh temperature environments[4]-[5].

Fig. 2 illustrates the ablation mechanism of the polymer composite in diminishing the backface temperature evolution with sufficient ablation resistance required in hyperthermal environments. The incoming heat flux is blocked, dissipated, and reradiated through the transpirational, vaporizational, charring, char–reinforcement, endothermic chemical reactions and reradiational cooling effects offered by the polymer composite. Only the conductive heat flux is transferred through the ablator and sensed at the backface of the composite. Diverse ablation mechanisms and zones developed during the ablation test of the composite specimen are depicted in the Fig. 1. Elastomeric composites have low thermal conductivity and high interfacial bond strength relative to other composites. Ethylene propylene diene monomer rubber (EPDM) and acrylonitrile butadiene rubber (NBR), etc are used as elastomeric matrixes to develop ablative composites as they have excellent thermal resistance properties, appropriate mechanical strength and easy processing.

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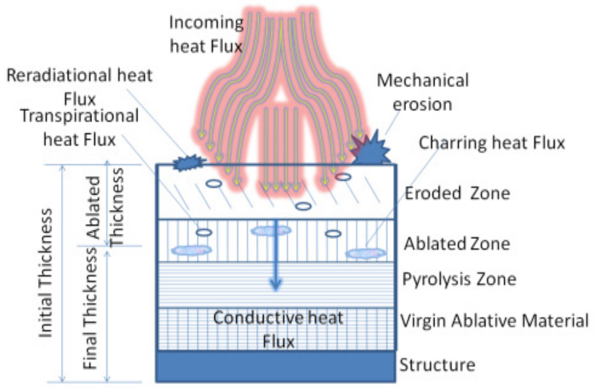

Fig. 1. Schematic illustration of the ablation mechanism of the rubber ablative composite

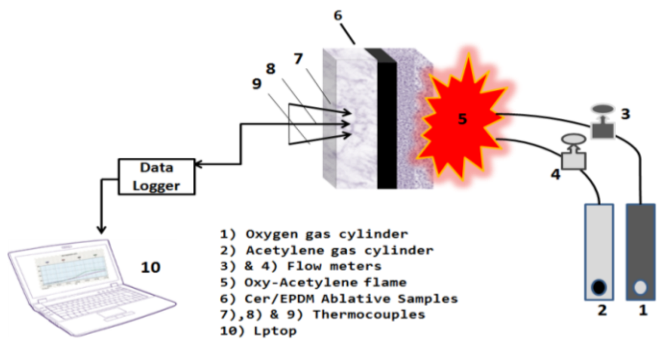

Fig. 2. Experimental setup of ablation testing of the elastomeric ablative composites

But these matrixes alone could not survive under the severe temperature and speed conditions. Therefore chopped/woven fibers (ceramic, Kevlar, carbon, glass, etc) and fillers (metal oxides, silica, carbon nanotubes, clays, etc) are used as reinforcements in the elastomeric polymers to enhance their thermal, mechanical and ablation properties. In the present investigation, novel EPDM/Ceramic fiber composites were fabricated using two roller mixing mill and hot isostatic press. The effect of variant concentration of ceramic fibers (CerFs) on the thermal decomposition/transport, ablation, backface temperature elevation, and mechanical properties of EPDM composites is scrutinized herein.

II. Experimental

A. Materials

Carbon black (N330) was supplied by Hebei Daguangming Juwuba, Co., Ltd. Sulphur, zinc oxide and stearic acid were supplied by Merck, Germany. MBTS (Mercaptobenzothiazole Disulphide) and HBS (Cyclohexyl Benzthiazyl Sulphenamide) were purchased from Dalian Richon Chemical Co. Ltd, China. Aromatic oil and wax were recieved from International petrochemicals Pvt., Ltd, Pakistan. EPDM (KELTAN 4331A) rubber was received from Technical Rubber Products, China. The contents of Ethylene (54wt %), Propylene (4wt %), and Diene third monomer (30-40wt %) are present in the EPDM rubber, used as matrix for the fabricated ablative composites. Ceramic fibers (Diameter ≈ 2-6μm) were supplied by Shandong alert soluble ceramic fiber and equipment Co. Ltd, China.

B. Formulation of Composite Materials

Ceramic fibers (CerFs) along with the carbon black (reinforcing filler), cross linker (Sulphur), accelerators (MBTS & HBS), activators (zinc oxide, stearic acid), and plasticizers (Aromatic oil & wax) were incorporated into the polymer matrix using internal dispersion kneader and two roller mixing mill according to the following formulation presented in Table I.

TABLE I: Formulation Scheme of CerF/EPDM Composites with Different Wt% Loadings of Ceramic Fibers in the Rubber Matrix

Sample ID/ Filler (wt%)	EC1	EC2	EC3	EC4
Ceramic Fiber	0	4	6	8

EPDM: Ethylene propylene diene monomer rubber (100 wt%)
Aromatic Oil (10 wt%), Wax (2.5 wt%), Zinc oxide (5 wt%)
Sulphur (2 wt%), Streaic Acid (2 wt%), Carbon black (40 wt%)
MBTS: Mercaptobenzothiazole disulphide (2 wt%)
HBS: Cyclohexyl Benzthiazyl Sulphenamide (2 wt%)

C. Fabrication of Ablative and Tensile Testing Specimens

Two roller mixing mill at speed, 40 rpm and temperature, 70°C for thirty minutes was used to uniformly dispersed the CerFs along with the processing aids in the EPDM matrix. The ablative composite specimens (CerF/EPDM ablators) having 0.01m^2 area and 0.01m thickness were fabricated on the hot isostatic press at 150°C and 1600 psi for 50 minutes. Four diverse concentrations of CerFs i.e. 0, 4, 6, and 8 wt% were incorporated in the rubber matrix and the fabricated composites were nominated as EC1, EC2, EC3, and EC4, respectively. Tensile testing composite specimens for all formulations were also fabricated according to the ASTM D412-98A.

D. Ablation Testing

1) Backface temperature elevation and insulation index

Ablation testing of the CerF/EPDM ablators was carried out according to the ASTM E285-08, in which Oxy-acetylene (O-A) torch was exposed on the surface of CerF/EPDM ablator as illustrated in Fig. 2. O–A torch was used as a high temperature source (Flame temperature ≈ 3000°C with heat flux of 8×10^6W/m^2 measured with pyrometer IRAH35 U, Japan) i.e. exposed on the central front facet of the CerF/EPDM ablator. The flow rate of both Oxygen and acetylene gases was 0.35m^3/h and their pressures were 50psi and 23psi, respectively during the ablation testing. The torch was kept at 10mm far from the testing specimen surface. Backface temperature profiles of the CerF/EPDM ablators during the ablation testing was monitored using three thermocouples at the backface of the ablator i.e. adhered with the aluminum tape. These temperature sensing devices were connected to the data logger, Tecpel 319 i.e. also linked with the laptop through RS-232 data cable. Time-temperature contours were developed meanwhile during the ablation testing of CerF/EPDM ablators on the laptop display. Insulation indexes of the ablative composites were measured according to the following formula.

$$\text{Insulation Index} = I_T = t_T/d \quad (1)$$

where t is the time required to reach at a specific backface temperature T of the ablator having thickness d.[6]

2) Ablation rates and % char yield

Linear/mass ablation rates and % char yields of CerF/EPDM ablated specimens were measured using the following mathematical equations i.e.

$$\text{Linear ablation rate} = v_L = (T_1\text{-}T_2)/t \quad (2)$$

$$\text{Linear mass ablation rate} = v_{Lm} = (m_1\text{-}m_2)/t \quad (3)$$

$$\%\ \text{char yield} = C_L = ((m_1\text{-}m_2) \times 100)/m_1 \quad (4)$$

Radial/mass ablation rates and % char yields of CerF/EPDM ablated specimens were measured using the following mathematical equations i.e.

$$\text{Radial ablation rate} = v_R = (T'_1\text{-}T'_2)/t \quad (5)$$

$$\text{Radial mass ablation rate} = v_{Rm} = (m'_1\text{-}m'_2)/t \quad (6)$$

$$\%\ \text{char yield} = C_R = ((m'_1\text{-}m'_2)\times 100)/m'_1 \quad (7)$$

where T_1, m_1 & T_2, m_2 are the thickness/mass of the linear CerF/EPDM ablator and T'_1, m'_1 & T'_2, m'_2 are the thickness/mass of the radial CerF/EPDM ablator before and after O-A flame exposure, respectively and t is the ablation testing duration[7]-[8].

E. Mechanical Properties

Ultimate tensile strength, elongation at break and modulus of elasticity were evaluated through universal testing machine (UTM, 20KNXD Plus, Shimadzu) of the tensile testing specimens according to the ASTM D418-98A. Shore A rubber hardness of the CerF/EPDM composite specimens were assessed using Torsee, Tokyo testing machine, Japan.

F. Thermal Degradation

Perkin Elmer Diamond Thermogravimetric/differential analyzer (TG/DTA), Japan were used to analyze thermal stability and endothermic/exothermic behavior of CerF/EPDM composites. Heating rate and temperature range during the TG/DTA of the polymer composite specimens was 10^oC/min and 25-1000^oC, respectively.

G. Morphological Characterization

Scanning electron microscopy (SEM, JSM 6940A, Jeol, Japan) along with the energy dispersive X-ray spectroscopy (EDS) were utilized for micro-spectroscopic and compositional analyses of the tensile fractured specimens, CerF/EPDM ablated composite samples and CerFs.

III. Results and Discussion

A. CFs Dispersion in the Rubber Matrix

Aluminum silicate fibers having average diameter 2.7µm are depicted in Fig. 3a along with the CerF's EDS analysis in Fig. 3c that elucidates the presence of three major elements Al, Si, and O. The even distribution of CerFs in the rubber matrix was acquired due to the longitudinal and transverse flow of the rubber material through the twin roll nip of heated two roller mixing mill. Well dispersed CerFs in the EPDM matrix are observed in Fig. 3b coupled with the elemental analysis that ensures the existence of N, C, O, Si, Al, Zn, and S in the EC4 ablator in Fig. 3d. The compositional analysis confirms the presence of additives incorporated into the rubber matrix (Table I).

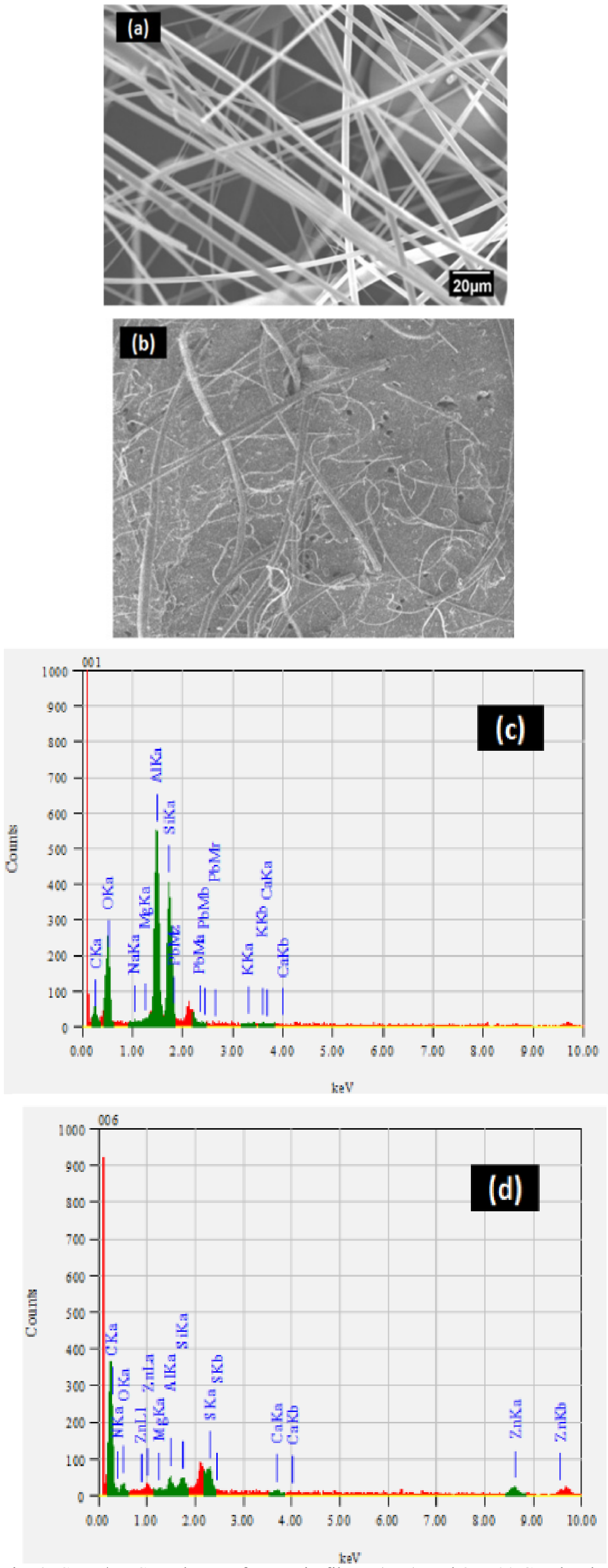

Fig. 3. SEM/EDS analyses of ceramic fibers (a, c) and 8 wt% CFs loaded composite specimen (b, d)

B. Backface Temperature Evolution and Insulation Index

Backface temperature evolution (BTE) of the CerF/EPDM ablators during the ablation testing is portrayed in Fig. 4a. Time–temperature contours of the ablative composites describes that BTE was diminished with increasing CerFs concentration in the rubber matrix. The maximum backface temperatures after 200s O–A flame exposure on the facets of CerF/EPDM ablators were observed 184.5, 112.4, 85.5, and 72.3°C for EC1, EC2, EC3, and EC4, respectively (Fig. 4b). It means that the incorporation of 8 wt% CerFs in the polymer matrix has reduced the peak backface temperature up to 112°C compared to EC1 ablator due to the low thermal conductivity/diffusivity and high thermal stability of the aluminum silicate fiber[9]. Peak backface temperature and backface temperature evolution rates (BTER) of the CerF/EPDM ablators are also displayed in Fig. 4b that shows the decline of BTER from 0.8 to 0.25°C/s with increasing fiber concentration from 0 to 8wt% in the rubber matrix. Insulation indexes of the composite specimens at backface temperatures 50, 60, and 70°C were measured according to the Equation 1 and displayed in Fig. 4c. A remarkable I_T enhancement at all selected temperatures is observed with increasing fiber concentration in the rubber matrix. Consequently, EC4 has higher capability to withstand against high temperature gases flow for a prolonged duration compared to the EC1 ablator, counterpart. SEM micrographs of the ablated EC4 composite specimen at diverse magnifications are depicted in Fig. 5(a, b). Well dispersed microfibers, porous char and char reinforcement interaction are observed in these micrographs. The porous structure of the ablated sample enhances the transpiration and vaporization heat fluxes, which reduce the backface temperature elevation during the ablation testing of the composite specimens.

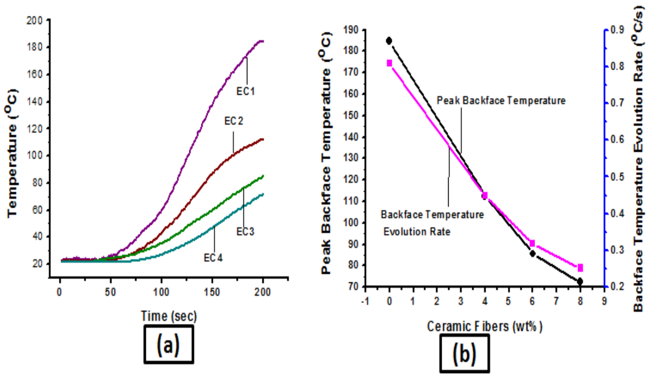

Fig. 4. Time-temperature profile (a) and peak backface temperature/backface temperature evolution rate (b) of CerF/EPDM composite

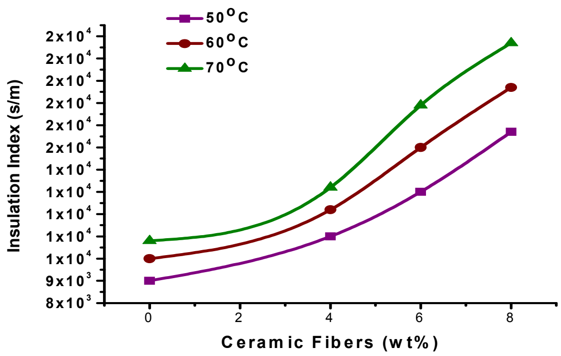

Fig. 4c. Insulation indexes at diverse ceramic fiber loadings in the rubber matrix

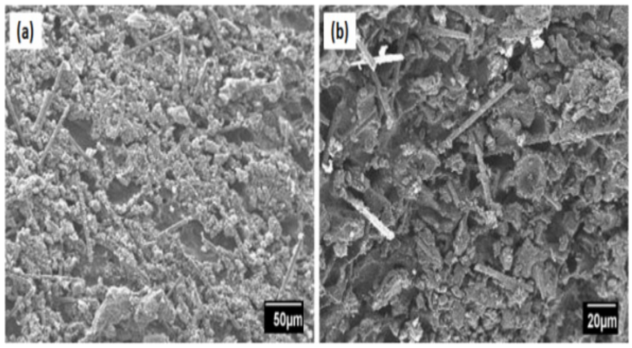

Fig. 5(a, b). Voids formation during ablation, polymer pyrolysis, char reinforcement interaction and distributed ceramic fibers in the EC4 ablated specimen

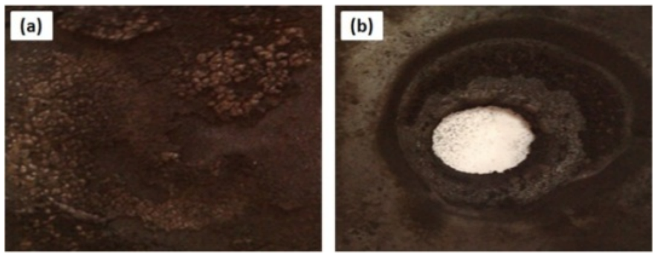

Fig. 6. Post burnt linear (a) radial (b) CerF/EPDM ablative composites

C. Ablation Resistance and % Char Yield

The photographs of the linear and radial ablated specimens are depicted in Fig. 6(a, b), respectively. An appropriate interaction between the ablated zone and virgin material zone is observed that eventually promotes the mechanical erosion resistance of the ablative composites i.e. a key parameter in hyperthermal and hypersonic environments encountered by an aerodynamic surface during its mission. Linear and mass ablation rates of the ablated composite specimens were measured using Equations 2 & 3 and displayed in Fig. 7. Linear/mass ablation resistance augmentation according to the descending order EC4<EC3<EC2<EC1 is observed in the ablation rates contours. The least linear and mass ablation rates were measured for EC4 ablator i.e. 0.015mm/s and 0.19g/s. It means that CerFs incorporation in the rubber matrix enhances the ablation resistance of the fabricated composite specimens. Percent char yields of the eroded ablators were measured using Equation 4 and the effect of CerFs concentration on the % char yield of the composite specimens (Fig. 7). Similar to ablation resistance, % char yield is also diminished with increasing fiber impregnation in the host polymer matrix due to the high thermal stability of CerFs. Radial/mass ablation rates and % char yield were measured according to the equations 5, 6, and 7 for CerF/EPDM ablators as shown in Fig. 8. Thermal transport through the EC4 was observed least due with increasing concentration of CerFs in the EPDM host matrix attributed owing to the high heat capacity, low thermal conductivity and high melting point of the incorporated fibers. Radial/mass ablation rates for CerF/EPDM ablators and % char yields were incredibly reduced with the progressive incorporation of CerFs into the EPDM rubber matrix due to the effective thermal endurance of the microfibers (Fig. 8).

D. Thermal Stability

Themogravimetric analysis in Fig. 9a elucidates the thermal stability enhancement with the progressive addition of CerFs in the rubber matrix due to their high thermal stability and low thermal conductivity of the impregnated fibers. The maximum mass loss in the heating air environment for all ablators was observed in the temperature range 500-650^{0}C.

Differential thermal analysis in Fig. 9b of the composite specimens also reveals the effective heat absorbance evolution with the 8 wt% increment of CerFs in the host polymer matrix and also EC4 absorbs maximum input heat[7]. The maximum heat variation regarding heat absorbance and exhaust was observed in the polymer composite pyrolysis temperature range.

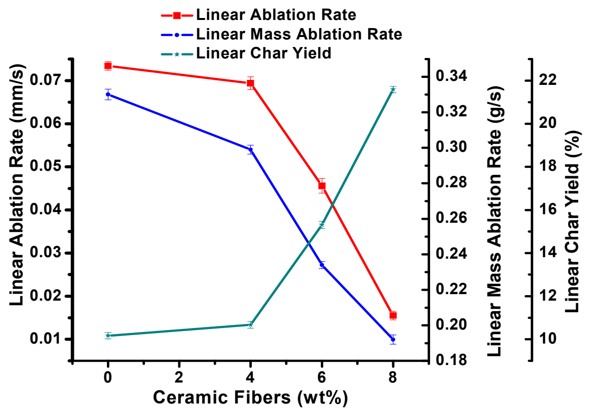

Fig. 7. Linear/mass ablation rates of the ablative composites at different CerFs concentrations in the polymer matrix

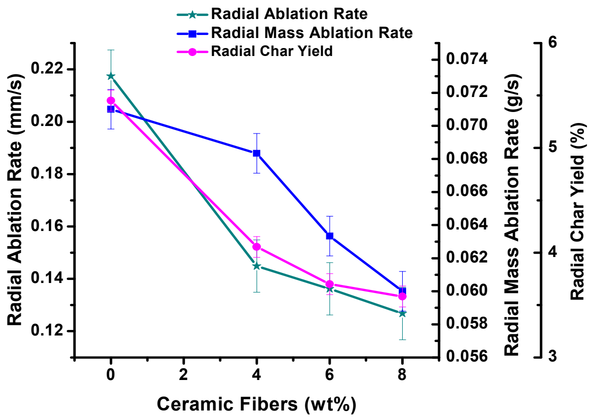

Fig. 8. Radial/mass ablation rates of the ablative composites at different CerFs concentrations in the polymer matrix

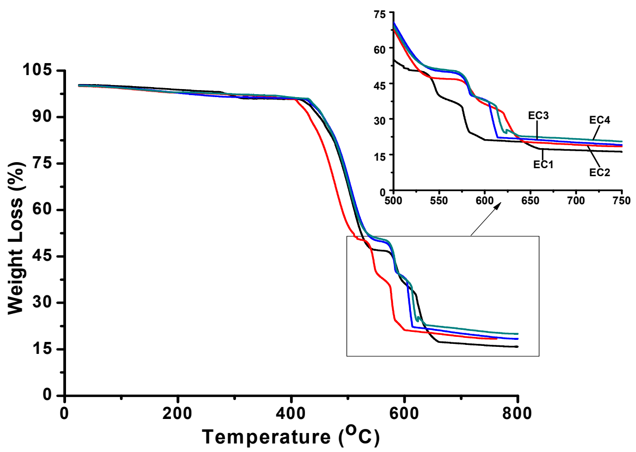

Fig. 9a. The effect of ceramic fibers concentration on the thermal decomposition of the CerF/EPDM composites

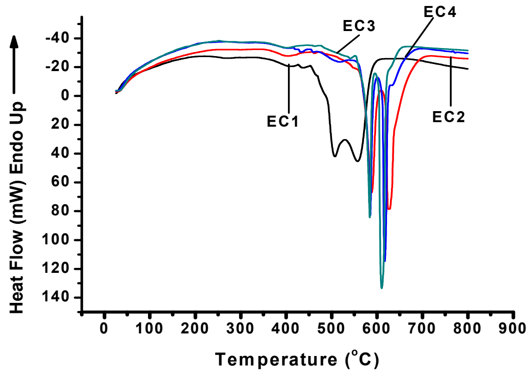

Fig. 9b. The effect of ceramic fibers concentration on the heat flow response of CerF/EPDM composites

E. Mechanical Properties

Stress-strain curves and Shore A hardness are depicted in Fig. 10 (a, b). The incorporation of CerFs into the NBR matrix has inversely affected the mechanical properties, while Shore A hardness of the NC ablators has been augmented up to 42%. These effects are attributed due to the low mechanical strength and high effective hardness of the incorporated aluminum silicate fibers[10].

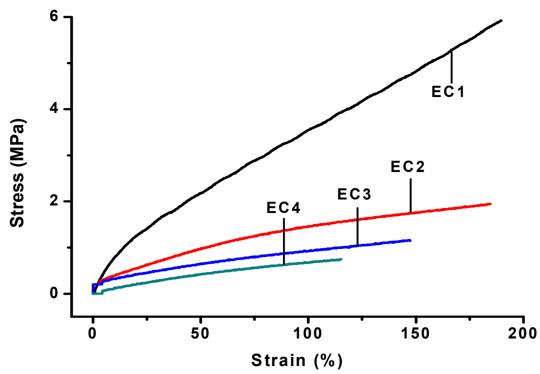

Fig. 10a.Stress-Strain contours of the fabricated CerF/EPDM composites

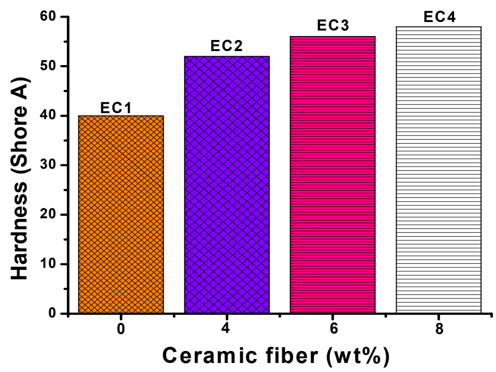

Fig. 10b. Variation in shore A hardness of the composite specimens at diverse loadings of ceramic fibers in the rubber matrix

IV. Conclusion

Ceramic micro-fibers have been uniformly dispersed within the EPDM matrix using conventional mixing techniques to fabricate ablative composites for hyperthermal environments. The obtained results showed that 8 wt% fiber' impregnation in the polymer matrix has enhanced the linear and radial ablation resistance up to 80 and 41%, respectively;

elevated linear and radial mass ablation resistance up to 44 and 16%, correspondingly; reduced the backface temperature elevation up to 61%; improved the thermal stability up to 5 % at 700^{o}C; rubber hardness up to 45%; and diminished the mechanical strength of the fabricated composite up to 700% as compared to base composite formulation, EC1.

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