Post-Ablation Micro-structural Analysis of Nanoparticle Reinforced Carbon Fiber Epoxy Matrix Composites

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***Abstract*-- A comparative study has been performed on macro- and micro-structural changes and weight-loss of carbon fiber epoxy composites with two types of nanofillers, i.e. carbon nanotubes (CNTs) and nanodiamonds (NDs) under hyper-thermal conditions. Vacuum assisted resin transfer molding (VARTM) technique has been employed to prepare the composites. CNTs and NDs were introduced in carbon fiber epoxy matrix composite and ablated through the thickness to examine the erosion rate and response of material. Oxy-acetylene torch apparatus was used to simulate hyper-thermal environment. Scanning electron microscopy (SEM) was performed to studythe composites from different ablated locationsin order to investigate the behavior of nanofillerreinforced composites. Ablative behavior of carbon fiberepoxy matrix composite and nano fillers reinforced composites was dominated by thermo-chemical ablation and mechanical erosion. Ablative properties improvedconsiderablyat low loadings of the CNTs and NDs but decreased with further increase in weight percent, nevertheless, still higher than reference carbon fiber epoxy matrix composite.**

Key words: CNTs; NDs; oxidation; ablation.

I. INTRODUCTION

Nanoscale materials are becoming prominent in the scientific community due to their excellent properties and outstanding behavior under different environments**[1-3]**. Nanoscale materials such as carbon nanotubes (CNTs) were successfully employed in different kind of composites for high temperature applications. The behavior of these nanomaterials is being studied to develop advanced thermal protection systems (TPS). In chemical combustion systems, flame temperatures approach 1500^{o}C or even higher. Almost twice of the gas temperatures have to be faced by space vehicle structural members during atmospheric re-entry**[4]**. These extreme conditions encountered in reentry of space craft and rocket motor nozzles may cause thermal destruction of an exposed component unless suitable protection is ensured.Scientific community is now investigating different thermal protection systems, i.e. radiative systems, heat sink systems, transpiration and film cooling systems and the ablative systems**[4]**. Ablative systems comprise sacrificial materials, which evaporate on exposure to hyper thermal environmentsmaking the system cool and thus provide thermal protection. Ablative systems or ablative materials are unique in a sense that they can accommodate extreme kind of heat and flux conditions.Sublimating type thermosetting resins were used successfully in missile dome parts as ablators and they prove to be very effective due to their low weight, homogeneityin microstructure and higher oxidation temperatures. In principle, sublimating type ablators absorb heat and convert into gases.This change of phase reduces the heat flux effectively. However, a general problem with thesetypes of ablators is their higher erosion rate. Different types of fibers including Kevlar andNomex® are under investigation to improve the erosion rate of such ablators**[5]**.

In the present study, carbon fibers were embedded with aerospace grade thermosetting epoxy resin after being impregnated with CNTs and evaluated microscopically after their ablation tests. The effect of CNTs and nanodiamonds (NDs) on the ablation mechanism of carbon fiber epoxy matrix composites was thoroughly investigated under scanning electron microscope (SEM) in order to understand the behaviour of these composites under hyper-thermal conditions.

II. EXPERIMENTAL SETUP

The composite specimens were provided by the Experimental Physics Labs, NCP, Quaid-i-Azam

University, Islamabad, Pakistan. The specimens were: (1) carbon fiberepoxy matrix composites, (2) carbon fiberepoxy matrix composites containing0.2wt% CNTs, (3) carbon fiber epoxy matrix composites containing 0.4wt% CNTs, (4) carbon fiberepoxy matrix compositescontaining 0.2wt% NDs, and (5) carbon fiber epoxy matrix composites containing 0.4wt% NDs. The loading fraction of carbon fibers in each of the composites was 50wt% in the form of 2D woven fabric. Araldite® 5052 epoxy was used as a matrix material in the composites.Vacuum assisted resin transfer molding (VARTM) technique was used to manufacture the composite materials.Densimeter(model GF-300) was used to measure densities of composites. At least fivemeasurements were acquired for each type of composite specimens.Oxy-acetylene torch apparatus,as shown in **Figure 1**, was used for the ablation tests following ASTM standard E 285-80 **[6]**.

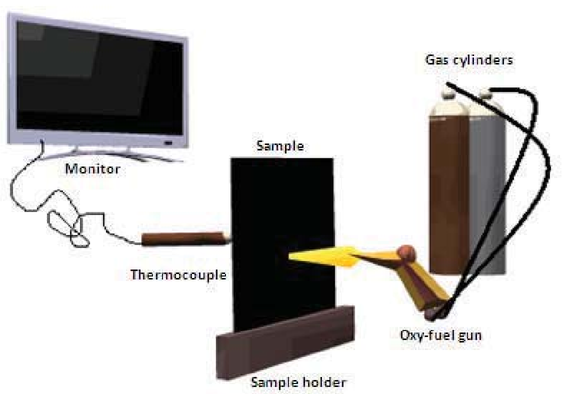


Figure 1: Oxy-acetylene torch apparatus used for the ablation test of the composites.

Specimens of 25x25x1mm were cut and held firmly in a specimen holder for ablation testing. K-type (chromal-alumal) thermocouple was used to measure the temperature of the rear side of the specimens. Oxy-acetylene flame was directed perpendicularly to the specimens from a Victor type tapered torch until burn-through of the specimens was achieved. The nozzle diameter of the torch was 1.1mm. The pressure levels of O_2 and C_2H_2 were set at 35bar and 7bar, respectively. A neutral flame was achieved by adjusting the flow of both the gases using manual controls of the torch. Neutral flame has a characteristic velocity of 200m/s, heat flux of approximately 830W/cm^2 and a temperature of about 3000^{o}C.

SEM was performed to thoroughly investigate the micro-structural changes and ablation morphologies in the composite specimens after ablation tests. For comparison, SEM of as-received composites was also performed. Specimens were gold-coated to avoid charging during SEM, as epoxy is a non-conducting material. MIRA3 TESCON scanning electron microscope was used with an accelerating voltage of 20KV.After ablation test, composite specimens were analyzed as follows:

- Mechanism of ablation was studied microscopically using SEM.
- Mass of the sample was measured with a digital balance(model GF-300) and compared with the initial mass before ablation tests.
- Time of complete flame penetration of composite specimens was measured.

III. Results and discussion

The densities of as-received composites were measured using Archimedes' method and given in **Table 1**. The densities of the five type of composites ranges between 1.31g/cm^3 to 1.40g/cm^3.

Table 1: Densities of as-received composites.

Sample ID	Composition	Density (g/cm^3)
A	CF/Epoxy	1.40 ±4
B	0.2wt%CNTs/CF/Epoxy	1.37 ±5
C	0.4wt%CNTs/CF/Epoxy	1.36 ±7
D	0.2wt%NDs/CF/Epoxy	1.37 ±3
E	0.4wt%NDs/CF/Epoxy	1.31 ±6

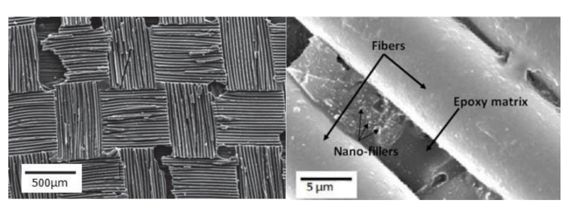


Figure 2: SEM micrographsof composite specimens (a) showing 2D woven structure of carbon fabric completely impregnated with epoxy matrix and (b) homogenous dispersion of nanofillers in the epoxy matrix.

Figure 2(a) shows an SEM image of as-manufactured carbon fiber epoxy matrix composite containing CNTs and NDs. 2D woven structure of carbon fibers is evident. However CNTs and NDs are not visible due to low magnification. **Figure 2(b)** reveals uniform distribution of nanofillers, i.e. CNTs and NDs in the epoxy matrix, as achieved by chemical treatment and functionalization of nanofillers. Carbon fibers can also be seen in the same figure, which are completely embedded in the nanofiller reinforced epoxy.

Table 2summarizes the results obtained from ablation tests.The erosion rate was measured by dividing the burn-through time with thickness of the specimens. The erosion rate of carbon fiberepoxy matrix compositeswas foundhigher than the compositescontaining nano fillers. With the addition of 0.2wt% CNTs in composites, erosion rate decreased by 9.0%. However, a further increase in CNTs, i.e. 0.4wt%, considerably increased the erosion rate, i.e. 4.3%.Nevertheless, the erosion rate of composites containing 0.4wt% CNTs is still lower than the erosion rate of reference carbonfiber epoxy matrix composites.With the addition of 0.2wt% NDs in carbon fiberepoxy matrix composites, the erosion rate decreasedby 13.3%. However, similar to the composite containing 0.4wt% CNTs, the erosion rate of the composite containing 0.4wt% NDs also increased but still less (11.8%)than the erosion rate of the reference carbon fiberepoxy matrix composite without nanofillers.Photographic images of the five types of composite specimens after ablation tests are shown in **Figure 3**.Burn-through of the composites is clearly evident. It was observed that the burn-through holes were not circular in any type of composite specimens. As carbon fabric used in the presentinvestigation was 2D woven andcarbon fiber towswere placed at 90^{o} to each other, therefore, they were erodedafter the preferential burning of the epoxy matrix. The edges found in the burn-through holes are the ablated tows of carbon fibers, as also evident in **Figure 5**.

The weights of the specimens before and after ablation testsare given in **Table 3** and shown graphically in **Figure 4.**The weight-loss of carbon fiberepoxy matrix composites is less compared to carbon fiberepoxy matrix composites containing nanofillers. By adding CNTs in the composites, the weight-loss increases and it enhances with an increase in the loading of CNTs. High thermal conductivity of CNTs maybe the possible reason of increased weight-loss and associated erosion rate when compared to the composites without CNTs. PAN based carbon fibers have a thermal conductivity of 20W/m.K**[7]** while thermal conductivity of individual multiwall CNTs is reported to be 3000W/m.K**[8]**. This value is greater than that of diamond and the basal plane of graphite, i.e., 2000K/m.K**[9]**. The increased thermal conductivity of composites containing 0.2wt% CNTsincreasedthe affected volume of the ablated composite material. However,the penetration time was more compared to reference composite. It can be attributed to the alignment of CNTs along the plane of carbon fabric thus producing anisotropy in the thermal conductivity of the composites. A further increase in the loading of CNTs, i.e. 0.4wt%, may have increased the thermal conductivity of the composite not only along the carbon fabric direction but also along the thickness of the composites. As a result, the time for through-thickness penetration in composites containing 0.4wt% CNTs decreased. In short, higher degradation temperature of epoxy after the addition of CNTs **[10]** and the increased thermal conductivity of composites along the carbon fabric direction tend to improve the ablative properties of 0.2wt% CNT-reinforced carbon fiberepoxy matrix composites. However,an increase in CNTs (0.4wt%)might have resulted in randomly oriented CNTs. As a result, the time for through-penetration decreased and thus the ablative properties decreased.

NDs also demonstrated the similar effect on composites after ablation tests, as shown by CNTs in composites. However, composites containing 0.4wt% NDs have shown less weight-loss after ablation tests than composite specimens containing 0.2wt% NDs. Increased porosity maybe the possible explanation to this behavior observed in composite specimens containing 0.4wt% NDs. Diamond is a very good conductor of heat and is used in heat dissipaters **[11]**. However, due to its low aspect ratio NDs are unable to transfer heat effectively in the current investigation as compared to CNTs. With the increasein the content of NDs in composite, the porosity increases and thus the thermal conductivity decreases. It is observed that the through-thickness penetration is more in composites containing 0.4wt% NDs compared to composites containing 0.2wt%NDs. An increase in the amount of NDs lowers the density of composites (**Table 1**), which is due to the increased porosity. The porosity acts as active sites for ablation, as ablation starts from interfaces and defects and causes the flame to penetrate easily **[12]**.

Table 2: Erosion rate of composite specimens after ablation testing.

Sample ID	Composition	Thickness (mm)	Burn through time (s)	Erosion rate (mm/s)
A	CF/Epoxy	1	10.6	0.094± 4
B	0.2wt%CNTs/CF/Epoxy	1	11.6	0.086±3
C	0.4wt%CNTs/CF/Epoxy	1	11.1	0.090±5
D	0.2wt%NDs/CF/Epoxy	1	12.2	0.082±6
E	0.4wt%NDs/CF/Epoxy	1	12	0.083±4

Figure 3: Photographic images of composite specimens after ablation testing.

Table 3. The weight of composite specimens before and after ablation testing.

Composite specimens	Weight before ablation (g)	Weight after ablation (g)	Weight-loss (%)
A	1.06±2	0.6±3	41.9 ±3
B	1.12±4	0.6±5	45.9 ±4
C	1.21±3	0.66±3	47.7 ±3
D	1.18±2	0.62±3	47 ±5
E	1.15±3	0.63±4	45.5 ±2

Ablation behavior is generally characterized by two mechanisms (1) chemical oxidation and (2) mechanical erosion. Carbon fibers consist of graphitic layers and these layers are bonded together by weak Vander Waals forces. As a result, these layers can be easily peeled off. Moreover, fiber thinning occurs due to severe mechanical erosion. This mechanical shearing of graphitic layers actually weakens the fiber.The effect of insulating epoxy matrix and later the conductive epoxy matrix after the addition of nanofillers on the fiber thinning was examined using SEM. Three different locations in the ablated composite specimens were identified for the observation, as indicated in **Figure 5**.

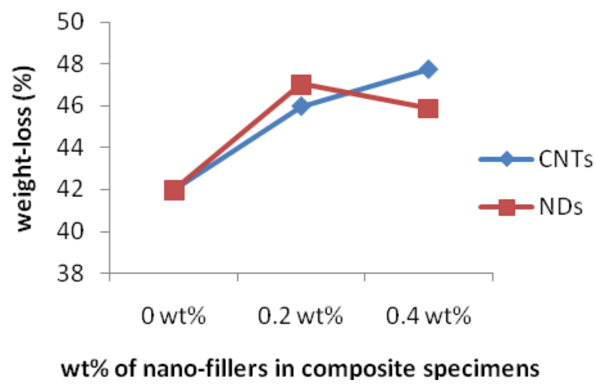


Figure 4: Graphical representation of the weight-loss of composite specimens after ablation testing.

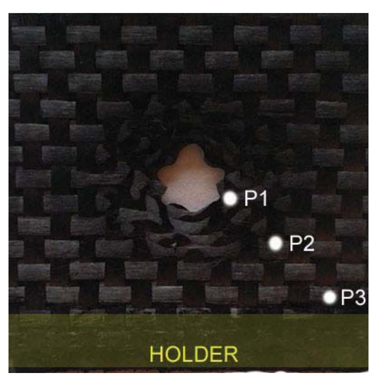


Figure 5: The locations of the composite specimens examined under SEM after ablation tests.

P1 is the position close to the place where oxy-acetylene flame actually hit, i.e. burn-through hole.

P2 is midway from the flame and the edge of the specimen and P3 is near the place where the specimens were clamped during testing.

SEM images of specimens from P1 positionsare shown in **Figure 6**. As can be seen from **Figure 6(a)**, carbon fibers were severely damaged and even broken in the reference carbon fiberepoxy matrix composite due to mechanical shearingeffect of oxy-acetylene flame. Fiber breakup in other composite specimens is also visiblein images (**Figures6 (b), (c), (d) and (e)**) but the extent of fiber breakup is less and the oxidation behavior is uniform compared to reference carbon fiberepoxy matrix composite. This uniform oxidation leads to less fiber breakage.However, the oxidation products can be seen in all composite specimens.

Figure 7 is showing SEM images of the specimens from P2 positions of the composite specimens. Oxidation products are evident and are not fully eroded as compared to that at P1 locations, where the quantity of the oxidation products was very less**(Figure 6)**. Fiber thinning was also not observed at these positions. Carbon fiberepoxy matrix composite with nano fillers have yielded increased oxidation products on the ablated surfaces of the specimens compared to reference carbon fiberepoxy matrix composite. Such a behavior increases the overall ablation properties of the composites and supports our hypothesis of increasedaffected area due higher thermal conductivity caused by the introduction of nano fillers in epoxy matrix.

P3 locations of the composite specimens were also examined and same behavior was observed as found at P2 positions (Figures not provided here). The part of the specimenclamped in the holder was also examined and it was found that the nanofillers were not present there. However, a reasonable amount of epoxy was observed, which was firmly bonded with the carbon fibers.

The location P1 in the composite specimens was further examined at a higher magnification (**Figure 8)** to verify the above hypothesis. The edges of the fibers in carbon fiberepoxy matrix composites are blunt (**Figure 8(a)**). In contrast, the fiber edges in the composite containing nanofillers are sharp and assumed a needle-like shape (**Figures8(b), (c), (d) and (e)**),a characteristic oxidation behavior of carbon fiber under hyper-thermal environment due to uniform heat transfer in thermally conductive matrix**[12]**.Fiber thinning was also observed along the length of the fibers.

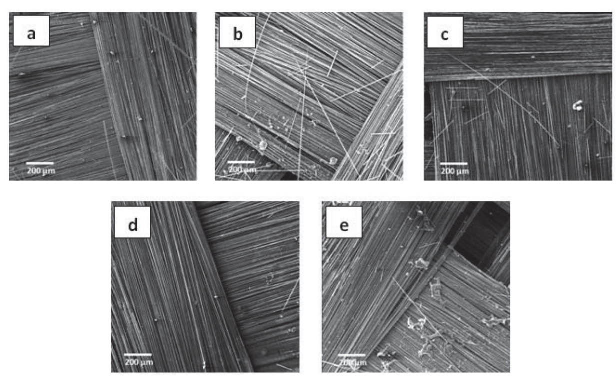
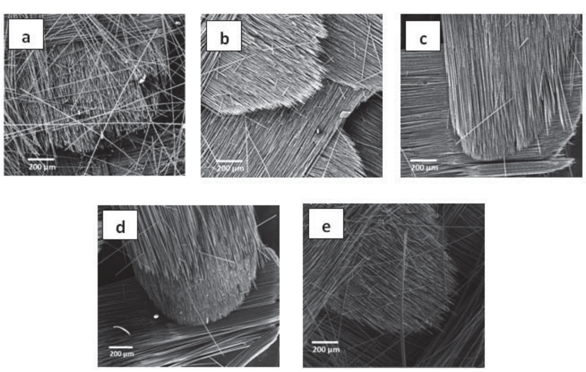


Fig 7



:ation of P1 (a) Carbon fiberepoxy matrix composite (b) Carbon Carbon fiberepoxy matrix composite containing 0.4wt% CNTs (d) Carbon fiberepoxy matrix composite containing 0.2wt% NDs, and (e) Carbon fiberepoxy matrix composite containing 0.4wt% NDs.

Figure 7: SEM images of composite specimens at the location of P2 (a) Carbon fiber epoxy matrix composite (b) Carbon fiber epoxy matrix composite containing 0.2wt% CNTs (c) Carbon fiber epoxy matrix composite containing 0.4wt% CNTs (d) Carbon fiber epoxy matrix composite containing 0.2wt% NDs, and (e) Carbon fiber epoxy matrix composite containing 0.4wt% NDs.

Carbon fiberepoxy matrix composites having 0.2wt% NDs show almost the same behavior of fiber thinning as observed in CNT-reinforced composites. However, the difference appeared in the form of the presence of pits in ND-reinforced composites **(Figure 8(d)),** which maybe due to the localized heating as a result of the presence of spherical shaped NDs. This localized heating causes excessive oxidation around the place wherethese rest and weakens the fiber, which ultimately leads to an easy heat penetration through the thickness. Excessive pitting in F**igure 8 (e)** is due to an increasedcontentsof NDs in composites containing 0.4wt% NDs. This pitting weakens the fiber and causes low heat conduction along the fiber direction. The weight-loss of carbon fiberepoxy matrix composite containing 0.4wt% NDs is lower compared to composite containing 0.2wt% NDs **(see Figure 4)** due to the overall small affected area after ablation testing.

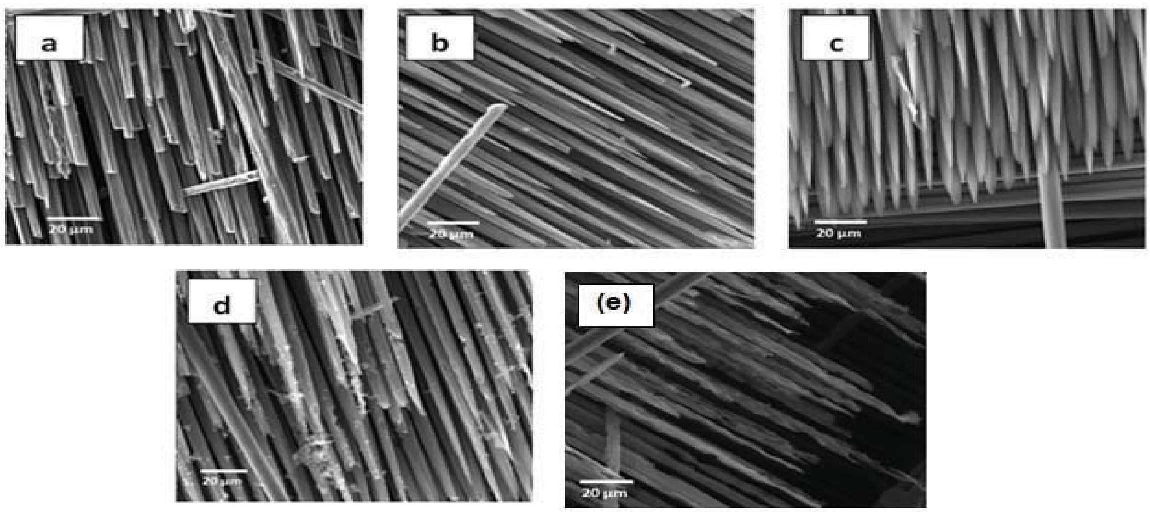


Figure 8: SEM images of composite specimens at a location of P1 (a) Carbon fiberepoxy matrix composite (b) Carbon fiberepoxy matrix composite containing 0.2wt% CNTs (c) Carbon fiberepoxy matrix composite containing 0.4wt% CNTs (d) Carbon fiberepoxy matrix composite containing 0.2wt% NDs, and (e) Carbon fiberepoxy matrix composite containing 0.4wt% NDs.

IV. Conclusion

A comparative macro- and micro-structural study was carried out to investigate the effect of CNTs and NDs on the ablative behavior of carbon fiber epoxy matrix composite. The study ofmicro-structural changes was co-related with the weight-loss obtained after the ablation tests of composite specimens and following conclusions were drawn:

Fibers oxidized in their characteristic needle like morphology when epoxy matrix was made conductive by the addition of nano fillers.

Ablated area under the oxy-acetylene flame increasedby converting an insulating epoxy to a conducting one, i.e.by the addition of nano fillers.

Composite specimens containing 0.2wt% CNTs and 0.2wt% of NDs individually show 9% and 13.3% decrease in erosion rate respectively, but erosion rate increases with increasing amounts of CNTs and NDs in carbon fiber epoxy matrix composite.

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