Microstructure and Mechanical Properties of Carbon Fiber Phenolic MatrixComposites containing Carbon Nanotubes and Silicon Carbide

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Received: 14 February 2024 | Revised: 25 February 2024 | Accepted: 27 February 2024

 DOI: https://doi.org/10.48084/etasr.7070

ABSTRACT

A novel class of hybrid composites was prepared containing carbon fibers along with carbon nanotubes and silicon carbide particles in phenolic resin for improved mechanical performance. The loading of carbon fibers was ~60 wt% while carbon nanotubes and silicon carbide particles were reinforced in the fractions of 0.1 wt% and 5 wt%, respectively. Individually reinforced composites containing 0.1 wt% carbon nanotubes and 5 wt% silicon carbide particles were also manufactured for comparison with hybrid composites. Microstructural and mechanical property characterization was performed using electron microscopy and mechanical testing, respectively. Uniform dispersion of nanometer-scale carbon nanotubes and micrometer-scale silicon carbide particles was observed under microscopy. The pooled effect of carbon nanotubes and silicon carbide particles significantly increased the tensile, compressive, and flexural performance of composites while carbon nanotubes offered greater weight fraction value improvement than silicon carbide particles.

Keywords-carbon fibers; phenolic resin; carbon nanotubes; silicon carbide; composite; mechanical properties

I. INTRODUCTION

The combination of carbon fibers with phenolic resin (Cf-Ph) makes a unique composite material ideally suitable for aerospace structural and functional applications [1]. This is due to the outstanding mechanical and thermal properties of this distinctive composite material stemming from its constituents. Carbon not only has a high heat capacity and vaporization energy, but also high strength and stiffness while maintaining a low density value. On the other hand, phenolic resin produces char in large quantities and releases low amounts of evolved gases during applications at high temperatures [2]. In order to further improve the properties of traditional carbon-based composite systems, the scheme of hybrid reinforcements has been investigated [3, 4]. As such, a secondary reinforcement, made of carbon fibers and carbon nanotubes, is incorporated along with the primary carbon-based one. Nanotechnology made possible the use of nanocomposites where the reinforcement at nanometer scale is incorporated in the matrix material [5]. Furthermore, it allowed for the combination of multiscale composites with reinforcements at different scales, i.e. micrometer and nanometer [6]. Carbon based nanomaterials, typically carbon nanotubes [7, 8], nanodiamonds [9, 10] and graphene nanoplatelets [11], have been extensively used in multiscale composites in polymeric [12], ceramic [13] and metallic [14, 15] matrices.

In the present investigation, multiwalled carbon nanotubes (MWCNTs) and silicon carbide (SiC) particles have been incorporated in carbon fiber phenolic resin composites, both individually and combined, to prepare novel hybrid composites. The underlying aim is to investigate the synergistic effect of carbonaceous and ceramic materials, at nanometer and micrometer scales, with particulate or nanotube morphologies, upon the mechanical properties of carbon fiber phenolic resin composites. The effect of the combination of MWCNTs and SiC particles has previously been investigated in a ceramic matrix, i.e. alumina [16].

II. EXPERIMENT

A. Materials

MWCNTs had an average diameter of 35±5 nm and length of 20±2 μm. SiC particles had an irregular shape with an average diameter of 22±4 μm. Carbon fibers were used in discontinuous form with an average length of 10 cm and a diameter of 8 μm. Barium phenolic resin was used as the matrix material having a 70% phenolic content.

B. Manufacturing

Both MWCNT and SiC particles were stirred together in a mixer (Cole-Parmer Model RZ0414905) for 2 h at a speed of 100 rpm. Then, they were placed in the oven at 100 ^{o}C for 30 min. Subsequently, the carbon fibers, MWCNT and SiC

particles were combined appropriately with the phenolic resin. The composite constituents were mixed together for 30 min, in a special laboratory mixer (UTAS-0095, UTest, Turkey). Prepregs were, then, prepared by heat-treating the composite mixture at ~75 ^{o}C for 1 h. Next, the prepregs were compression-molded using a steel die of appropriate shape, and heat-treated at 180 ^{o}C for 2 h. Finally, the resulting composites were cut into parts with the desired dimensions to be tested. Four types of composites were prepared: (a) reference carbon fiber phenolic resin (Cf-Ph), (b) carbon fiber phenolic resin composites containing 0.1 wt% MWCNTs (MWCNT-Cf-Ph), (c) carbon fiber phenolic resin composites containing 5 wt% SiC particles (SiC-Cf-Ph), and (d) carbon fiber phenolic resin composites containing both 0.1 wt% MWCNTs and 5 wt% SiC particles (MWCNT-SiC-Cf-Ph). All types of composites had 60 wt% carbon fibers.

C. Characterization

The densities of the composite specimens were determined using a densimeter (GF-300, A&D Japan) and verified employing the Archimedes principle. The relative densities were calculated by dividing the actual with the theoretical densities. The latter were determined making use of the rule of mixtures. Microstructural observation on fracture specimens was performed on a scanning electron microscope MIRA3 TESCON at an accelerating voltage of 5 kV. Tensile, compression and flexural tests were performed against ASTM standards D3039, D0695 and D0790 on a universal testing machine (WDW-30, JINAN) at strain rates of 2mm/min, 1mm/min and 1mm/min, respectively.

III. RESULTS AND DISCUSSION

A. Microstructure

Figure 1 shows the SEM images of fractured composites at two different magnifications with and without secondary reinforcements of MWCNT and SiC particles. Figures 1(a) and 1(b) show the carbon fibers in the reference Cf-Ph composite. It can be seen that the carbon fibers inside the composite are randomly oriented. However, locally, they may attain a certain direction, as observed. The phenolic resin is adhered to the surface of the fibers. Being brittle in nature, the fragmented parts of the phenolic resin are, also, visible. Figures 1(c) and 1(d) show composites comprising of MWCNT and carbon fibers. The random orientation of the latter is clearly visible. The presence of MWCNTs has also been indicated, though it is difficult to identify the MWCNTs at the chosen magnification. Figure 2(a) shows the image of MWCNT-Cf-Ph at a higher magnification. Now, they can clearly be observed without an indication of agglomeration. Figures 1(e) and 1(f) show the images of composites containing SiC particles along with carbon fibers. Figures 1(g) and 1(h) show the images of hybrid composites containing both MWCNT and SiC particles along with carbon fibers. A high magnification image of an MWCNT-SiC-Cf-Ph composite is shown in Figure 2(b) where the presence of MWCNTs is indicated.

B. Density

The theoretical, actual, and relative densities of composites are given in Table I. The relative densities of composites are shown in Figure 3(a). The Cf-Ph reference composite had a relative density of 99.6±0.2%. The addition of 0.1 wt% MWCNTs reduced the density to 98.9±0.3%. Similarly, adding 5 wt% SiC particles to the Cf-Ph composite also reduced the density to 99.1±0.3%. Cavities and pores are produced by micrometer sized particles during packing, if not properly wetted by the resin. They further reduce the density of the composite materials. Generally, composites have relatively lower densities than the reference materials due to the presence of reinforcements which hinder the polymeric matrix flow. It is to be noted that a small fraction of MWCNTs (0.1 wt%) lowered the density more than a large fraction of SiC particles (5 wt%). This may be due to the large aspect ratio and diameters in the range of nanometers for MWCNTs, providing a large surface area with a flexible nature, thus hindering the densification. Moreover, the tendency of nanoparticles to cluster while dispersing in resins, results in porosity in composites. The combined addition of 0.1wt% MWCNTs and 5wt% SiC particles further lowered the density of composites to 98.5±0.4%. Nevertheless, the density values are still in an acceptable range allowing for an estimation of the mechanical performance of composites.

TABLE I. THEORETICAL, ACTUAL AND RELATIVE DENSITY OF COMPOSITES

Composite	Theoretical density (g/cm^3)	Actual density (g/cm^3)		Relative density (%)
		Geometric method	Archimedes method	
CF-Ph	1.50	1.49±0.01	1.49±0.02	99.6±0.2
SiC-CF-Ph	1.49	1.47±0.02	1.48±0.03	99.1±0.3
MWCNTs-CF-Ph	1.49	1.47±0.03	1.48±0.04	98.9±0.3
MWCNTs-SiC-CF-Ph	1.48	1.46±0.02	1.47±0.03	98.5±0.4

TABLE II. TENSILE, COMPRESSIVE AND FLEXURAL STRENGTH OF COMPOSITES

Composite	Tensile strength (MPa)	Compressive strength (MPa)	Flexural strength (MPa)
CF-Ph	58±1	62±2	68±2
SiC-CF-Ph	64±3	64±3	72±3
MWCNTs-CF-Ph	74±2	78±2	86±2
MWCNTs-SiC-CF-Ph	80±3	80±4	94±3

C. Tensile Strength

Figure 3(b) shows the effect the addition of MWCNT and SiC particles has on the tensile strength of the composites. The addition of 0.1 wt% MWCNTs increased the tensile strength by 10 % to 64±3 MPa from 58±1 MPa in the reference composite. On the other hand, a rise in tensile strength of 27% was observed when 5 wt% SiC particles were added, reaching a value of 74±2 MPa. Furthermore, when both secondary reinforcements were introduced, the tensile strength rose by 38 % to 80±3MPa (Table II). At the nanometer scale, the presence of MWCNTs in phenolic resin may impede the progress of cracks by facilitating a bridging effect and crack deflection [6]. The bridging effect between carbon fibers and phenolic resin may be another possible reason, as discussed elsewhere [12]. Conversely, the inherent brittle nature of SiC particles and their

stiff character may produce localized stress regions around the particles thus deflecting the cracks. To be sure, crack pinning may be another possibility. In hybrid composites, however, the combined effect the presence of both reinforcements has, further improves the mechanical performance.

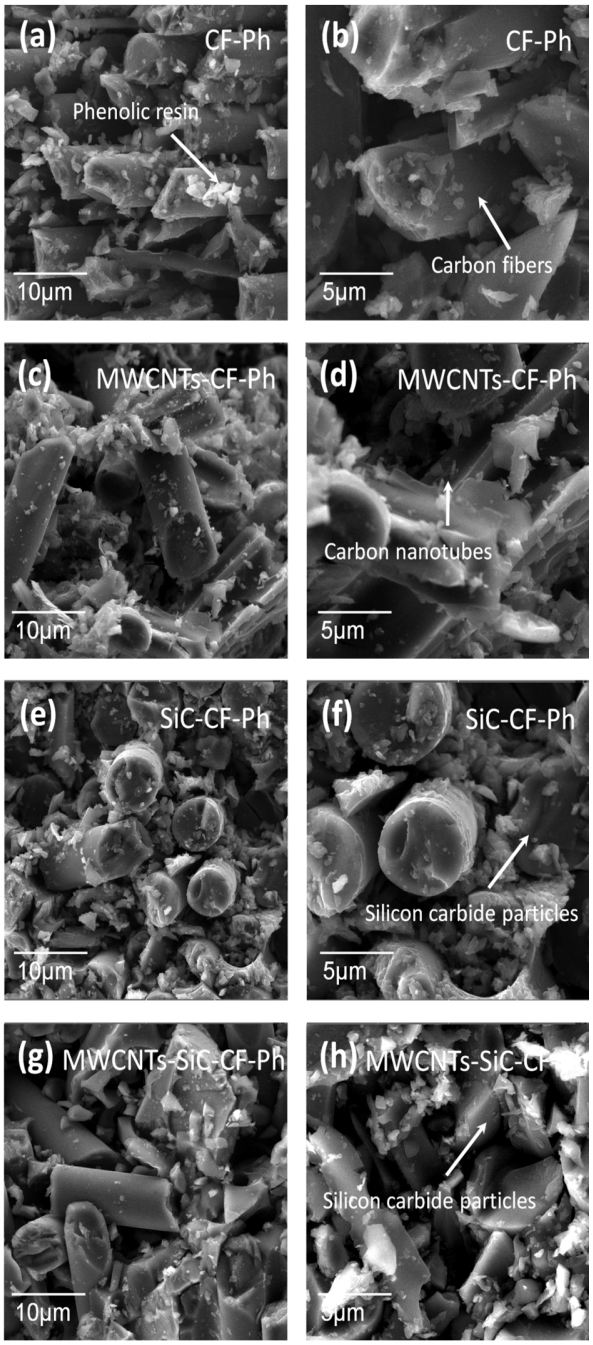

Fig. 1. SEM images of (a-b) reference Cf-Ph, (c-d) MWCNT-Cf-Ph, (e-f) SiC-Cf-Ph, and (g-h) MWCNT-SiC-Cf-Ph composites.

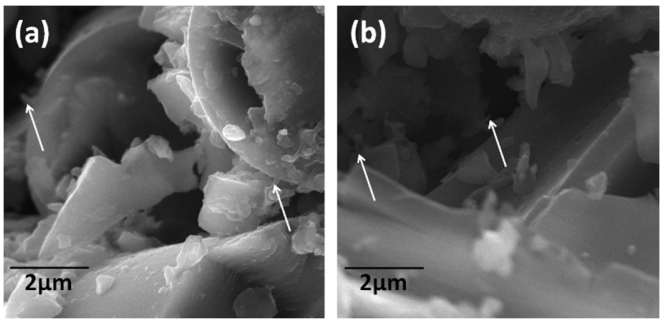

Fig. 2. High magnification SEM images of (a) MWCNTs-Cf-Ph and (b) MWCNT-SiC-Cf-Ph composites.

D. Compressive Strength

Figure 3(c) shows the compressive strength values of composites with and without the addition of secondary reinforcements. Indeed, the behavior of composites under compressive load has been investigated since they can also be used when compressive strength becomes more important than tensile strength. The reference composite shows a compressive strength of 62±2 MPa, which increased by 3% to 64±3 MPa, by adding 0.1 wt% MWCNTs. In comparison, a rise in compressive strength of 26% was observed when 5 wt% SiC particles were added, reaching a value of 78±2 MPa. Furthermore, in hybrid composites, the compressive strength rose by 29 % to 80±4 MPa (Table II). The fact that the tensile strength, when just MWCNTs are added, raised more than the compressive strength will be further discussed below.

E. Flexural Strength

Flexural strength values of the composites are shown in Figure 3(d). A similar trend as before is observed. The reference composite showed the lowest value of 68±2 MPa, which improved to 72±3 MPa by adding 0.1 wt% MWCNTs showing a rise of 6%. On the other hand, the addition of 5 wt% SiC particles improved the value to 86±2 MPa showing a rise of 26%. The combined effect of secondary reinforcements improved the flexural strength to 94±3 MPa resulting in the maximum rise of 38% (Table II). It has been observed [17, 18] that a 66% increase in flexural strength is achieved by adding 1.0 wt% MWCNTs in carbon fiber phenolic matrix composites while a further rise in MWCNT content defects composite centers. In another study, the addition of 1.5 wt% MWCNTs in carbon fiber composites improved the flexural strength up to 12.3% while further increasing the MWCNT contents did not lead to any additional improvement [6].

The presence of MWCNTs plays a vital role in strengthening the composite and changing the nature of fractures. The uniform dispersion of SiC particles and their good interface adhesion improves the strength of composites. The literature indicates a mixed trend in the mechanical properties of polymeric matrix composites containing MWCNTs. Furthermore, the degree of improvement also differs among different studies depending upon the fraction of MWCNTs added and their uniform dispersion [5].

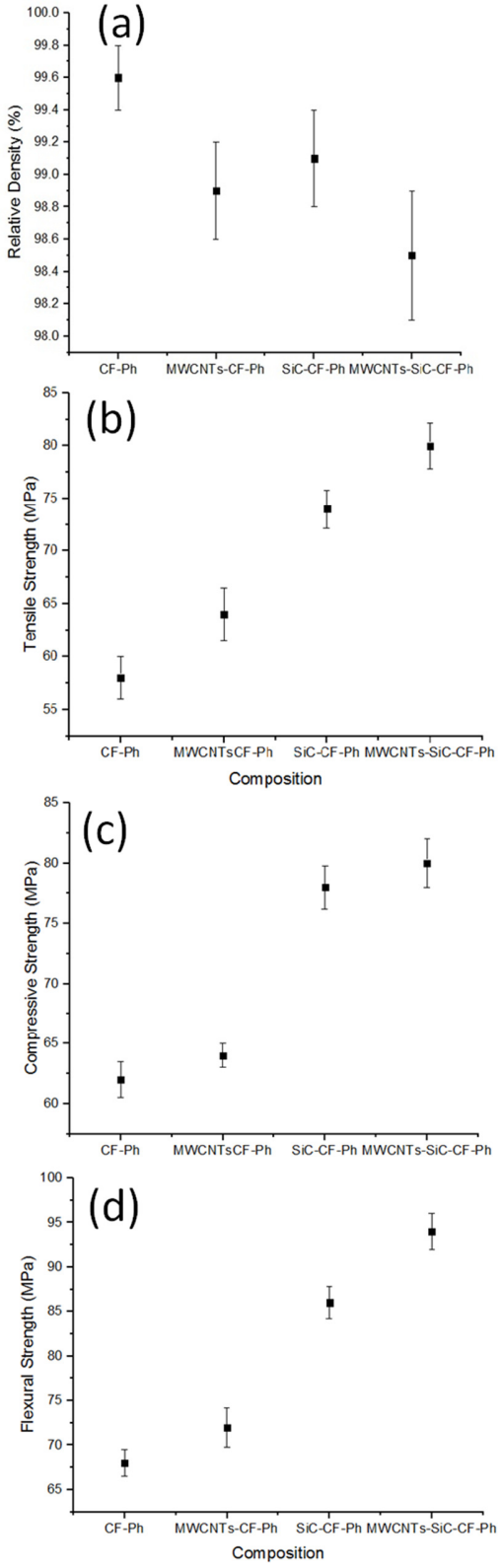

Fig. 3. Graphs showing (a) density, (b) tensile, (c) compressive and (d) flexural strength values of composites.

For example, in [6], 25%, 31% and 40% improvements were observed by adding 0.5 wt%, 1.0 wt% and 1.5 wt% MWCNTs respectively. However, the rising trend reversed after adding 2.0 wt% MWCNTs. It has been thought that the presence of MWCNTs increases the strength as long as they are uniformly dispersed. Upon the development of agglomerates the strength of composites decreases. Due to the flexible nature and curviness of MWCNTs, mechanical keying and interlocking are believed to be some of the key mechanisms by which the mechanical properties of the composites are improved. Further, the MWCNT pull-out is another energy absorbing phenomenon, which increases the strength of composites [6].

Along with strength, the toughness of the composites is also expected to rise. As discussed in a separate study, the presence of secondary reinforcements in the form of particulates and nanotubes, introduces toughening mechanisms such as reinforcement/matrix debonding, pullout of reinforcements, crack deflection and bridging [5].

F. Relative Improvement in the Mechanical Properties

Figure 4(a) shows the percentage relative improvement in tensile, compressive, and flexural strength values of composites containing MWCNTs, SiC particles and both MWCNTs and SiC particles. MWCNTs improved the tensile strength of composites more than the compressive and flexural strengths; Furthermore, the flexural strength improvement was greater than that in compressive strength. This indicates that the addition of MWCNTs has a greater impact on composite properties while under tension than compression. A possible reason may be that CNTs bend or buckle under compression, while under tensile loading CNTs stretch and demand a high load for fracture. Therefore, the addition of MWCNTs offers better tensile than compressive strength. The addition of SiC particles has an almost similar behavior in the three loading modes. Ceramic materials are always strong under compression loading. However, they fracture under tensile loading. The presence, however, of SiC particles, which are strong enough to bear the load coming from the matrix in both tension and compression, hinder the breakage under tension. In flexural testing, both tension and compression loadings are applied, and the presence of SiC in composites improves the strength. In hybrid composites containing both MWCNTs and SiC particles, the compressive values are lower than the tensile and flexural strength ones. This indicates that in hybrid composites, the presence of MWCNTs with their high tensile strength, improves the tensile properties of the composite. Furthermore, the MWCNTs also play a positive role in flexural testing of hybrid composites.

G. Loading Fraction of Secondary Reinforcement and Improvement in Mechanical Properties

Figure 4(b) shows the effect of loading fractions of the secondary reinforcements, to tensile, compressive and flexural strengths. As shown, the addition of only 0.1 wt% of MWCNTs increased tensile, compressive, and flexural strengths by 10%, 3%, and 6% respectively while the addition of 5 wt% SiC particles, improved the tensile, compressive, and flexural strengths by 27%, 26% and 26%, respectively. This indicates that increasing the loading fraction of MWCNTs

should increase the relative improvement in the mechanical properties provided their uniform dispersion and efficient load transfer. This agrees with the results of [19-21]. Moreover, a significant improvement is expected to be observed in tensile strength of composites, as discussed above. Therefore, components in real applications demanding high tensile strength should be manufactured with composites containing CNTs.

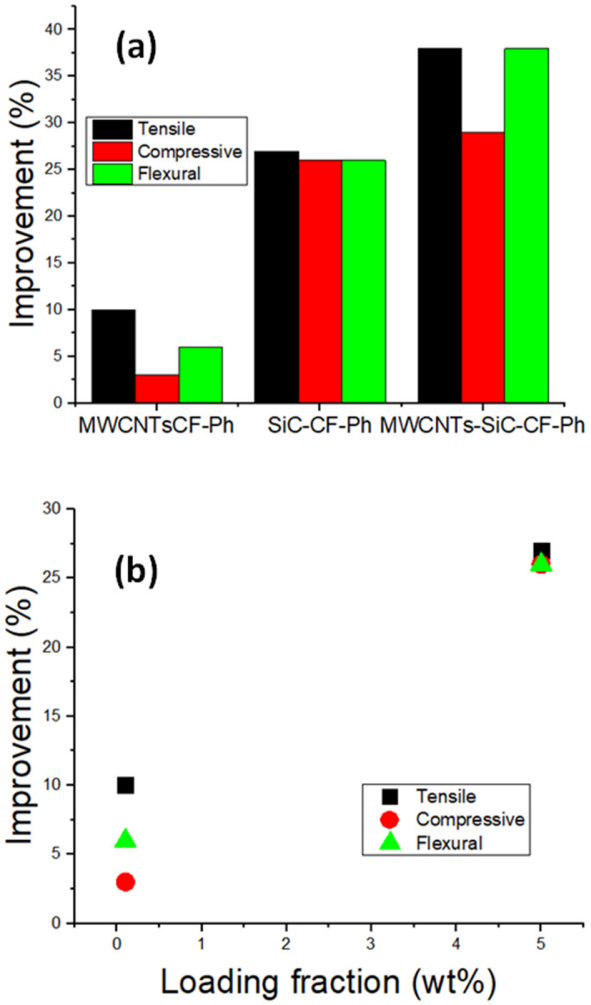

Fig. 4. Graphs showing (a) the percentage improvements in tensile, compressive and flexural strength values of composites containing MWCNTs, SiC particles and both MWCNTs and SiC particles and (b) percentage improvement against loading fractions.

IV. CONCLUSION

Carbon fiber phenolic matrix composites were manufactured with nanometer and micrometer sized particulate reinforcements, i.e. carbon nanotubes and silicon carbide particles, so as to investigate the individual and combined effect of the reinforcements on the microstructural evolution and mechanical performance of the composites. The loadings of carbon nanotubes and silicon carbide particles were kept at 0.1 wt% and 5 wt%, respectively, while the content of carbon fibers was 60 wt%. Microstructural observation revealed the uniform dispersion of both reinforcements without an indication of agglomeration. Individual rises in tensile, compressive and flexural strengths due to the addition of nanotubes and carbide particles were found to be 10%, 3%, 6% and 27%, 26% and 26%, while their combined presence resulted in a rise of 38%, 29% and 38%, respectively.

The present investigation revealed that the high aspect ratio of carbon nanotubes together with their high tensile strength improved the tensile properties of composites both in individually reinforced and hybrid composites. For improved compressive properties, SiC particles are the preferred choice. For combined results, the hybrid approach of manufacturing composites overcomes the limitations of individual incorporation of reinforcements.

Finally, the pooled effect of carbon nanotubes and silicon carbide particles significantly increased the mechanical performance of composites while the addition of carbon nanotubes offered greater value improvement in terms of their weight fractions than silicon carbide particles.

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