Materials Sciences and Applications, 2018, 9, 740-750
http://www.scirp.org/journal/msa
ISSN Online: 2153-1188
ISSN Print: 2153-117X

Role of Metallic Nanofillers on Mechanical and Tribological Behaviour of Carbon Fabric Reinforced Epoxy Composites

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How to cite this paper: Divya, G.S. and Suresha, B. (2018) Role of Metallic Nanofillers on Mechanical and Tribological Behaviour of Carbon Fabric Reinforced Epoxy Composites. *Materials Sciences and Applications*, **9**, 740-750.
https://doi.org/10.4236/msa.2018.99054

Received: July 9, 2018
Accepted: August 14, 2018
Published: August 17, 2018

Abstract

In this study, hybrid composites based on carbon fabric and epoxy (C/Ep) were fabricated by hand lay-up method followed by compression moulding. The C/Ep with optimum carbon fiber (60 wt%) was chosen as a reference material, and to it, the metallic nanoparticles like aluminum (Al) and zinc (Zn) of different wt% (0.5 and 1.0) were included as secondary fillers. To understand the synergism effect of these hybrid reinforcements, mechanical properties and tribological behavior of composites were studied. From the test results, it was proved that hybridization improved the mechanical and tribological properties. The C/Ep consisting of 0.5 wt% Zn and Al showed higher tensile properties in comparison with all other fabricated composites. Increase in flexural strength and flexural modulus also observed as the filler content increased in C/Ep composite. Higher impact strength is noted at 1 wt% Zn filled C/Ep composite. Wear test data revealed that 0.5 wt% Zn in C/Ep has got superior wear resistance. Wear mechanisms were discussed using scanning electron micrographs of selected worn surfaces of the composites.

Keywords

Carbon-Epoxy, Metallic Nanofillers, Mechanical Properties, Wear, Wear Mechanisms

1. Introduction

Carbon fiber composites cover the vast part among the extensively used advanced materials for various industrial applications due to their better strength/modulus to weight ratio, good electrical properties, excellent wear and corrosion resistance [1]. Polymer composite with carbon fiber reinforcements can be made from different carbon fiber patterns such as uni-directional, biaxial, chopped and woven mats in various thermoset matrices such as epoxy, polyester or phenolic [2].

Thermosetting epoxy resins are the widely used matrix system for the development of fiber reinforced composites in numerous engineering applications due to their good adhesion, excellent dimensional stability, and superior chemical as well as thermal resistance. Some of applications are limited due to inherent brittleness with crack resistance based on their extremely cross linked network which poses difficult in absorbing the energy on impact load. Therefore, many researches [3] [4] [5] [6] have been carried out for improvisation of epoxy resins mechanical properties. The efficient design can be done by utilizing high strength fiber as reinforcement in the epoxy resin [7] [8] [9]. Few researchers concentrated on carbon fiber surface treatment in a way to enhance the mechanical properties by improving adhesion along with interlocking between the fiber and matrix of the composites. Wazzan, *et al.* have studied the influence of potassium hydroxide solution on tensile strength of uni-directional carbon fabrics reinforced epoxy composites and they inferred that higher vol% of carbon fabrics increased the tensile properties and chemical stability whereas the higher temperature and treatment duration caused drastic degradation in tensile modulus and strength in composites fabricated [10]. Gao, *et al.* investigated influence of the carbon fiber surface modification on mechanical properties. Modification of carbon fibers by polyhedral oligomeric silsesquioxane (POSS) in presence of poly (amidoamine) (PAMAM) enhanced of surface energy, wettability also the roughness of fibers leading to improved mechanical property and thermal stability due to augmented interfacial bond strength of fiber-matrix [11]. Jinshui, *et al.* found significant improvement in mechanical strength along with modulus of carbon/epoxy with silane coupling agent [12].

Though carbon fiber reinforced polymer composites are showing better mechanical properties, fall back in the wear resistance as well as impact strength. This made the carbon fiber reinforced composite applications scope limited and restricted in the crucial engineering application wherein high strength, modulus, impact resistance, better chemical and wear resistance are the key factors for the material selection. Several researchers also focused on improving the required properties by hybridizing the two-phase composite system by introducing fiber/filler to enhance mechanical as well as wear resistance. Chensong, *et al.* developed carbon-epoxy, glass-epoxy further glass-carbon-epoxy hybrid composites and investigated their flexural properties. Higher flexural strength was observed in hybrid composites [13]. Manwae, *et al.* analyzed the effect of incorporation of fixed vol% micro and nano-sized Al_2O_3 ceramic particles in unidirectional carbon fabrics reinforced epoxy composites separately with varying vol% of carbon fabric. Young's modulus and bending strength of carbon/epoxy composite with nanoparticles were higher compared to micron sized particles filled composites due to small size of the particles, better interfacial adhesion and mechanical interlocking between the constituents of composites [14]. Suresha, *et al.* and coworkers found significant increase in mechanical properties and enhanced wear resistance carbon-epoxy/epoxy composites [15] [16].

Hybrid polymer composites emerged as a solution to combat wear situation. Suresha, *et al.* studied two-body abrasive wear characteristics of glass-carbon fabric reinforced in vinyl ester composite and found highest specific wear rate in glass fabric reinforced vinyl ester similarly lowest rate of wear in carbon fabric reinforced vinyl ester composites [17]. Suresha, *et al.* also focused on investigating three-body abrasive characteristics of glass/epoxy also the carbon-epoxy composite then concluded that carbon/epoxy composite give excellent resistance to wear property in comparison with glass/epoxy composites because of the presence of strong bonding between the carbon and epoxy [18]. There has been increasing effort for improving the wear resistant property of carbon fiber composites by the incorporation of fillers. Incorporation of micron and nanoparticles in two phase materials showed higher wear resistance property in several researches. Various types of fillers such as ceramics, metals and elastomers are being used extensively used as fillers for improving the tribological properties [16]. Feng, *et al.* studied the mechanical as well as wear characteristics of unfilled together with nanoparticles filled carbon fabric reinforced phenolic resin composite. Nanosized TiO_2, SiO_2 and $CaCO_3$ are taken as fillers for the research work and found lowest coefficient of friction and the best wear resistance in SiO_2 and $CaCO_3$ filled composites respectively [19].

Based on the literature survey, it is understood that carbon fabric is widely used in automotive and aerospace applications pertaining to the reason that higher ratio of strength to weight, better anti-corrosion with wear resistance characteristics. It is also observed from the literature survey that, many researchers have used organic and ceramic fillers in their work. Importantly, not much research works have been done on metallic filler filled carbon/epoxy composites. In this study an attempt is made by fabricating hybrid composite system by using nanofillers such as zinc and aluminum. The wear behavior and mechanical effect of these fillers are found by considering low wt% (0.5 and 1.0). The main purpose of this investigation is to determine the combined effects of carbon fibers and nanofillers (Nano-Al and nano-Zn) on the mechanical properties and tribological behaviour of epoxy composites.

2. Composites Fabrication

2.1. Materials

Bidirectional 2/2 twill 200 gsm carbon fabric procured from Carbon Light Manufacturers, North Street Cooling Towers (P) Ltd., Ghaziabad, UP is used as the primary reinforcement in Epoxy LY556 resin of density 1.15 g/cm^3, supplied by M/s. Huntsman Advanced Material, Mumbai. Matrix and Hardener HY951 are mixed in the weight ratio 10:1 for fabricating the composites. Metallic nanoparticles namely, aluminum (Al) and zinc (Zn) with density 2.7 g/cm^3 and 7.14 g/cm^3 respectively are used as secondary fillers. Nano fillers used are irregular shaped with size 30 - 50 nm and supplied by Intelligent Materials Pvt. Ltd., NANOSHEL, Punjab, India. **Figure 1** shows scanning electron micrographs of Al and Zn nanoparticles.

2.2. Fabrication

Carbon fabrics are impregnated in epoxy solution for 12 h later dried in oven at 100˚C for 2 h. Further, 55, 60 and 65 wt% resin impregnated carbon fabrics are used for fabricating the mono-C/Ep composites. Impregnated fabrics are laid one above the other by Hand lay-up process and then laminates are prepared using compression moulding technique at 90˚C and 7.35 MPa pressure. From the physico-mechanical test results best combination of C/Ep is selected and nano-Al and nano-Zn particles are introduced into the composite separately with different wt% as listed in **Table 1**. Mixing of nanoparticles in the epoxy resin is accomplished using ultrasonicator for 30 min at room temperature to avoid agglomeration of nanoparticles in the composites.

3. Results and Discussion

Fabricated composites are tested to determine the mechanical properties and dry sliding wear behavior as per ASTM standards. Hardness, tensile and flexural properties are investigated using J.J. Lloyd Universal Testing Machineat 10 mm/min and 5 mm/min respectively. Wear behavior of the prepared composites are found by pin on disc apparatus under a constant sliding distance, sliding velocity and normal load of 3000 m, 1.5 m/s and 25 N respectively. Five samples from each fabricated composites are tested and the average results are considered for discussion.

3.1. Hardness

The hardness (Shore D) values of the seven types of C/Ep based composite samples are presented in **Table 2**, three of which are mono-composites (C/Ep) reinforced with 55, 60 and 65 wt% and for 60 wt% C/Ep type, there are two levels (0.5 and 1.0 wt%) of nano-aluminium (Al)/nano-zinc (Zn). Among three C/Ep mono-composites, 60 wt% carbon fabric reinforced epoxy (C60/40Ep) had higher hardness compared to other mono-composites. The hardness results of nanofiller filled C/Ep composites indicated that compared to mono-composites, the hardness values of all nanocomposites were marginally higher and a little increase with increase in filler loading. The type of nanofiller (Al or Zn) did not have considerable influence on the hardness of C/EP mono-composite. Among the nanofillers used in this work 1 wt% Zn in C/Ep exhibited maximum hardness of 55.

In hardness test, a compressive load is in action and consequently the epoxy matrix, carbon fiber and nanofiller phase would be hard-pressed together and

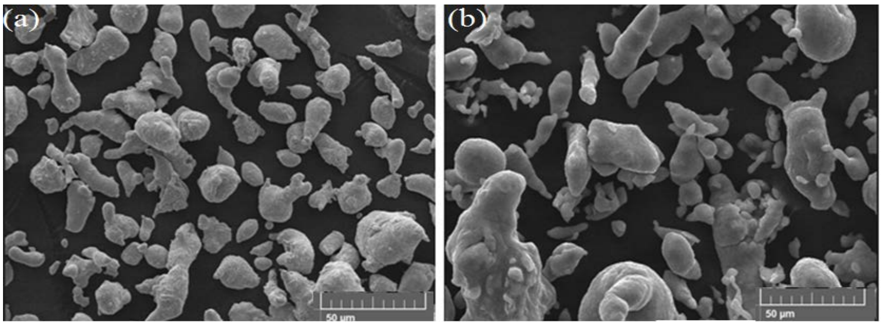

Figure 1. SEM images of (a) Aluminum; (b) Zinc nanoparticles.

Table 1. Composition of fiber, matrix and filler in hybrid composites.

Sample Code	Constituents			
	Fiber wt%	Matrix wt%	Al wt%	Zn wt%
C55/E45	55	45	-	-
C60/E40	60	40	-	-
C65/E35	65	35	-	-
C60/E39.5/Al0.5	60	39.5	0.5	-
C60/E39/Al1	60	39	1	-
C60/E39.5/Zn0.5	60	39.5	-	0.5
C60/E39/Zn1	60	39	-	1

Table 2. Tensile properties of C/Ep and their hybrid composites.

Composite Code	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation (mm)	Hardness (Shore-D)
C55/E45	491 ± 4	15.26 ± 1.25	3.70	47 ± 1
C60/E40	528 ± 6	20.87 ± 1.45	2.90	51 ± 2
C65/E35	312 ± 7	13.07 ± 1.15	2.75	48 ± 1
C60/E39.5/Al0.5	642 ± 5	25.82 ± 1.05	2.89	52 ± 2
C60/E39/Al1	625 ± 4	24.80 ± 1.75	2.77	54 ± 1
C60/E39.5/Zn0.5	644 ± 3	26.55 ± 1.35	2.78	53 ± 1
C60/E39/Zn1	610 ± 4	22.27 ± 1.95	2.73	55 ± 1

they are bound to each other more tightly. Thus, the interface can transfer load more effectively, although the interfacial bond may be poor. In the present work compared with mono-composites (C/Ep) the hardness of 0.5 and 1.0 wt% Zn filled C/Ep increases by 4% and 8%, respectively. This increased hardness is associated to the high rigidity and hardness of the dispersed-phase particles which allows strengthening due to its load-carrying capacity.

3.2. Tensile Properties

Experimental results from tensile tests conducted on C/Ep and their hybrid composites are shown in Table 2. Failures of test coupons in the tabs are successfully avoided in almost all coupons. The average tensile strength of unfilled C/EP composites showed increasing trend till 60 wt% fibers loading and later showed decreasing trend due to improper wetting of the fibers and poor adhesion between the fiber and matrix. C60/E40 composite showed healthier tensile properties compared to other unfilled composites due to optimum combination of carbon fiber in the epoxy matrix.

Referring Table 2, it is clear that in the case of nano-Al/nano-Zn filled C/Ep composites, the tensile strength is increasing up to 0.5 wt% filler loading. This increase is about 21.6% and 22% for nano-Al and nano-Zn filled 60C/40Ep composites, respectively. However, in case of mono-composites 60 wt% carbon fiber reinforced epoxy (60C/40Ep) exhibited the highest tensile strength and Young's modulus. Highest tensile strength as well as Young's modulus is obtained in C60/E39/Zn0.5 hybrid composites followed by C60/E39.5/Al0.5 hybrid composite. Beyond 0.5 wt% fillers loading, there is some drop in the strength as well as the modulus of hybrid composites. This could be due to agglomeration of nanoparticles and poor bonding between the constituents of the hybrid composite. As the incorporation of filler content increased, not much difference in elongation is found (Table 2). Higher percentage of elongation is found in C55/E45 composite due to higher epoxy content. Lower percentage of elongation is found in C60/E39/Zn1 composites due brittle nature and excess of Zn nanoparticles.

Young's modulus for mono and hybrid C/Ep composites is listed in Table 2. Considering the Young's modulus of mono-composites; 60 wt% carbon fiber revealed thebest modulus. In general, higher fiber loading in the epoxy matrix possess higher modulus. However, in the present work, 65 wt% carbon fabric reinforced epoxy (C65C/E35) showed lower modulus and this could be attributed to poor interfacial bonding at the fiber-matrix interface. The increase in Young's modulus is found for nanofiller filled C/Ep composites. Significant improvement in the Young's modulus of 0.5 wt% nano-Al/nano-Zn filled C/Ep can be attributed to enhancing the cross linking density caused by limited number of nanoparticles.

3.3. Flexural Properties

Similar trend as that of tensile properties is found in flexural properties for two-phase composite samples. As the fiber reinforcement increased above 60 wt%, the flexural properties deteriorated due to lack of bonding. From the results, it is observed that 60 wt% carbon and 40 wt% of epoxy is the optimum combination. Table 3 shows the flexural properties of C/Ep and their hybrid composites. Incorporation of Al and Zn nanoparticles enhanced the flexural properties. As the filler addition increased positive trend is observed. Higher flexural strength and flexural modulus are noted in C60/E39/Al1 composite followed by C60/E39/Zn1, C60/E39.5/Al0.5 and C60/E39.5/Zn0.5 among hybrid composites. Highest and lowest deflections are found in unfilled composites with lower and higher carbon fiber loading respectively in unfilled C/Ep composites. Deflection of hybrid composites reduced with the addition of nanofillers. However, as the filler content increased from 0.5 wt% to 1 wt%, slight increase in the deflection is observed due to higher bending strength.

According to data presented in **Table 3**, the incorporation of both Zn and Al nanofillers improved the flexural strength and modulus. The incorporation of Al in C60/E40 improved the flexural strength and modulus by 13% and 14% respectively. However, in case of Zn filled C60/E40, the improvement is 11% and 12.4% respectively. It is interesting to note that both metallic nanofillers in C/Ep modified the fiber-matrix interface which leads to significant synergy in the tensile as well as flexural properties. The synergistic effect of fiber and matrix modification on improving these properties can be attributed to 1) superior fiber/matrix interfacial adhesion in which nanofillers (Al and Zn) with their high aspect ratio act as an interface for load-transfer. 2) better fiber wetting in modified resin mix and uniform dispersion of nanoparticles within the matrix and 3) the increase in the force needed for crack initiation and propagation due to the Al/Zn particles pull-out phenomena and the nanoparticles bridging effect retarding crack initiation and propagation via energy absorbing and dissipation mechanisms [20].

3.4. Impact Strength

Impact strength of the composites are found using Charpy impact test. **Table 4** presents the impact energy of C/Ep and their hybrid composites.

To complement the earlier studies of increasing the carbon fiber loading in epoxy (**Table 4** first three series) on the impact behavior, the effect of small quantities (0.5 and 1.0 wt%) of metallic fillers of nanosized (Al and Zn) is examined. Due to the presence of metallic nanoparticles, the impact energy increased effectively. Higher impact strength is noted in 1 wt% Zn particles filled C/Ep composites due to higher weight percentage of Zn nanoparticles, followed by 1 wt% of Al, 0.5 wt% of Zn and Al. Due to poor wetting of fibers and excess fiber incorporation on C65/E35, delamination of carbon layers observed and the lowest impact energy is observed.

Improvement in the impact energy obtained in this study may be attributed to interfacial adhesion properties of fiber/matrix. Zhang, *et al.* reported that inclusion of nanoparticles did not significantly affect fiber-matrix interfacial bonding strength in carbon fiber-nanosilica enhanced epoxy composites [21]. In the present work, however, the inclusion of both Zn and Al nanoparticles showed increase in the impact strength as compared to unfilled C/Ep composites.

3.5. Wear Volume and Specific Wear Rate

Dry sliding wear test is conducted using pin-on-disc to C/Ep and their hybrid composites under a sliding distance of 3000 m, sliding velocity as 1.5 m/s at 25 N applied load. The variations in wear volume are summarized in **Table 5**.

Table 3. Flexural properties of C/Ep and their hybrid composites.

Composite Code	Flexural Strength (MPa)	Flexural Modulus (GPa)	Deflection (mm)
C55/E45	452 ± 3	26.47 ± 0.50	9.1
C60/E40	502 ± 5	27.11 ± 0.55	9.2
C65/E35	459 ± 6	26.15 ± 0.75	7.5
C60/E39.5/Al0.5	534 ± 2	28.25 ± 0.98	8.4
C60/E39/Al1	566 ± 3	30.13 ± 0.15	8.7
C60/E39.5/Zn0.5	512 ± 4	27.49 ± 1.15	8.5
C60/E39/Zn1	558 ± 5	29.75 ± 0.95	8.8

Table 4. Impact property of C/Ep and their hybrid composites.

Composite Code	Impact Energy (J)
C55/E45	8 ± 1
C60/E40	9 ± 2
C65/E35	7 ± 1
C60/E39.5/Al0.5	10 ± 1
C60/E39/Al1	12 ± 2
C60/E39.5/Zn0.5	12 ± 1
C60/E39/Zn1	14 ± 1

Table 5. Wear volume C/Ep and their hybrid composites.

Composite Code	Wear volume (m^3) × 10^{-9}
C60/E40	1.8377
C60/E39.5/Al0.5	0.9100
C60/E39/Al1	1.0425
C60/E39.5/Zn0.5	0.3743
C60/E39/Zn1	0.5546

Dry sliding wear test data, are similar to research work of Suresha, *et al.* [22], where incorporation of filler enhanced the wear resistance. Sliding wear test revealed that C60/E39.5/Zn0.5 hybrid composite is exhibiting lower wear volume as well as lower specific wear rate followed by 1 wt% Zn, 0.5 wt% Al and 1 wt% Al filled C/Ep composites and unfilled C/Ep composite. Particulate filled C/Ep composites excelled in wear resistance because of better interlocking and void filling nature of the nanoparticles. As the wt% of Al and Zn increased from 0.5 to 1, the wear volume and specific wear rates are increased. It may be due to excess filler incorporation, which caused poor quality of bonding and improper distribution of the filler. Specific wear rate of fabricated composites are illustrated in **Figure 2**.

3.6. Worn Surface Morphology

Worn surface morphology of samples having better wear resistance and poor wear resistance are studied using scanning electron microscope and are as shown in **Figure 3**. Few fiber breakage (Marked as FF), exposure of fibers, good bonding between fiber and matrix, more matrix cracks (Marked as MC)and less material removal during the wear test are observed on worn surface shown in **Figure 3(a)** for 0.5 wt% Zn filled C/Ep hybrid composite. The superior wear resistance could be due to higher fiber and particle-matrix interaction and higher hardness of the metallic nanoparticles compared to the mono-C/Ep composites. However, in mono-C/Ep composite worn surface under the similar test conditions showed severe fiber fracture, network of microcracks in the matrix, fiber thinning and also debonding of fibers from the matrix and the features are as shown in **Figure 3(b)**.

4. Conclusion

In this work, we reported on epoxy hybrid composites developed using compression moulding technique with carbon fibers and nanofillers like Al and Zn as reinforcements. The mechanical properties of the fabricated composites were determined in terms of hardness, tensile and flexural properties, impact strength

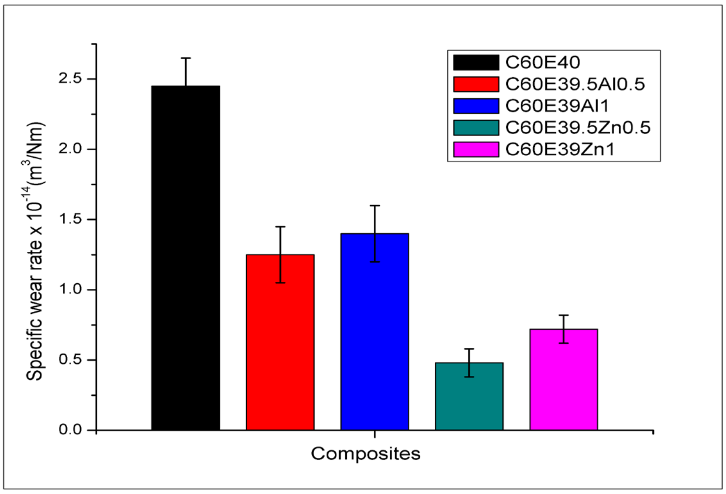

Figure 2. Specific wear rates of C/Ep and their hybrid composites.

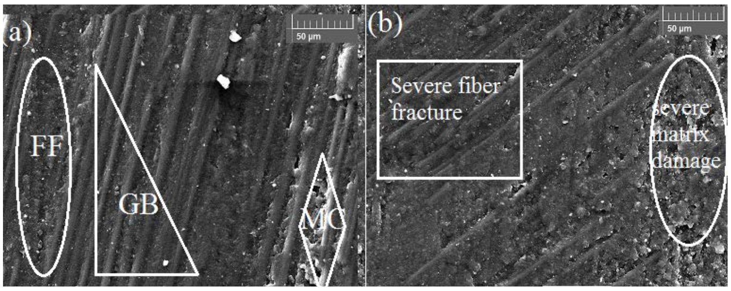

Figure 3. Worn surface micrographs of (a) C60/E39.5/Zn0.5; and (b) C60/E40 composites.

as well as tribological behaviour. For mono-C/Ep composites, the superior mechanical properties were obtained for epoxy with 60 wt% carbon fiber reinforcement. The incorporation of metallic nanoparticles also improved the mechanical properties of the composites. The flexural strength increased to 566 MPa, 558 MPa with 1 wt% of Zn/Al as compared to 502 MPa for mono-C60/E40 composites. The impact strength was increased by 55.5% from 9 J to 14 J at 1 wt% Zn loading. The addition of metallic nanofillers reduced the specific wear rate till 0.5 wt% Al/Zn filler loading. Also, the experimental wear test data are validated with worn surface morphology using SEM photomicrographs. Finally, mono-C/Ep with 0.5 wt% of metallic nanofillers Al/Zn) can be used as secondary reinforcement in different applications due to favorable mechanical properties and superior wear resistance.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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