

**Mechanical and Tribological behaviour of Tungsten carbide
nanoparticles filled Carbon-Epoxy polymer hybrid Nanocomposites**

**A thesis submitted in partial fulfilment of
the requirements for the degree of**

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in

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by

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Abstract

The increased demand for high-performance materials have opened a new era in the use of composites. Composites or composite materials are the outcome of a combination of two or more materials to achieve optimized properties. This optimization is done by a keen observation of individual material properties in the composite.

Among the vast varieties of composites available, carbon fiber epoxy composites have a major role in meeting the requirements in various applications in automotive industry, construction, marine industry, aircraft industry, etc. Carbon fiber composites possess high strength, are lightweight, have resistance to corrosion, are hydrophobic, resistant to chemical reaction and easy to fabricate, etc; However, carbon fiber composites have their own disadvantages too. Carbon fiber epoxy composites are more susceptible to anisotropic loads and show less resistance towards erosion. The properties of composites can be further enhanced by adding nano fillers to the composites, which has caught the attention of most of the researchers nowadays. Researchers have proposed other inexpensive ways to improve the properties of carbon epoxy composites by incorporating nanoparticles into composites, which makes them hybrid composites.

At present, adding Nanofillers to the composites is one of the promising methods among several other methods in improving overall properties of a hybrid composite, a method which has caught the attention of researchers. However, the literature available on the role of nanofillers in hybrid composites is limited. In the present work Tungsten carbide nanofillers have been used due to their excellent properties in wear, thermal, corrosion, hardness and strength.

This thesis reports research dealing with the processing, characterization as well as experimental study on the mechanical and tribological behaviour of Tungsten carbide nano filler reinforced epoxy nanocomposite and also mechanical and tribological behaviour of Tungsten carbide nano filler reinforced with carbon-epoxy hybrid nanocomposites. The objective is to introduce Tungsten carbide nano filler in carbon fiber epoxy composites in a balanced way to achieve high-performance characteristics to carbon fiber composites to meet various demands. The first part provides a detailed discussion of the effect of filler in enhancing the properties of

polymer composites while also creating interest in the researcher about their various advantages. The second part presents comprehensive discussion of literature about carbon fibers and filler and hybrid composites. Besides, it provides some experimental results based on research by other researchers in various fields. The third part of the research presents a detailed discussion of mechanical and tribological properties of Tungsten carbide reinforced with epoxy composites. The last part emphasises preparation of Tungsten carbide reinforced carbon/epoxy hybrid composites and the mechanical and tribological properties of composites.

From the test results it was observed that, compared to neat epoxy, tensile strength of nanocomposite is increased from 24 MPa to 33 MPa. i.e it increases by 37.5%, which is at 2 wt% of Tungsten carbide filled epoxy nanocomposite. Compared to neat carbon-epoxy, the strength of the hybrid composite increases from 322 MPa to 402 MPa. i.e it increases by 24.4%, It was observed at 2.5wt% of Tungsten carbide filled carbon-epoxy hybrid nanocomposite. Compared to neat epoxy, hardness value increases from 17.4 to 25.4 vicker's hardness value. i.e it increases by 43%, which is observed at 2 wt% of Tungsten carbide filled epoxy nanocomposite. Independent of impact angle, erosion rate decreases with an increase in filler volume up to 2 wt% of Tungsten carbide filled epoxy nanocomposite. Compared to neat epoxy friction wear for nanocomposite reduces from 0.87 to 0.3 gm, which is observed at 2 wt% of Tungsten carbide filled epoxy Nanocomposite. Irrespective of impact angle erosion rate increases with increase of fiber volume, as the fiber orientation increases, the erosion rate also increases. But it has very little significance on fiber orientation.

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Chapter 1

Introduction

1.1 Background

Composite materials have performed a great role in many industrial applications because of their light weight, strength, resistance to corrosion and other properties [1]. Epoxy has been used as a matrix widely due to its excellent properties such as strength to weight ratio, stiffness, hardness, corrosion resistance, hydrophobic nature, etc.

Composites reinforced with carbon fiber have been used for decades as structural members extensively in automobile, aircraft, marine, electrical and electronic applications etc, due to their excellent properties.

The increased demand for materials with superior mechanical characteristics relative to existing materials leads to a search for new and advanced materials. This search for advanced materials with superior mechanical properties has significantly contributed to the advent of new materials in the field of polymer composites. The advent of mechanically superior materials will facilitate engineers to work with a great degree of freedom by minimizing material constraints, which allows extensive improvements for designs in industrial applications [2].

Polymeric composites are highly susceptible to mechanical loads, such as tensile and flexural load. Anisotropic property (having different properties in a different orientation) of the composite is the primary reason behind mechanical failure [3,4]. Hence, it is essential to design composites with high damage tolerance. Also, solid particle erosion has been a worrying problem in the field of engineering due to the reason that it is considered responsible for several failures. Polymer composites have tremendous applications where solid particle erosion is predominant.

There are a number of ways to enhance the performance of polymer composites using various methods. However, these methods involve additional manufacturing elements and expensive labour, which leads to increase in cost of the finished composites [5-7]. Some researchers have found inexpensive ways to improve inter laminar shear strength of the composites by incorporating nanoparticles into fibre reinforced composites [8-13]. Many attempts have been made in enhancing the mechanical properties of composites using fillers [14-16].

Adding fillers to the epoxy matrix makes the composites have better mechanical properties and reduces the overall cost due to lower consumption of other materials in the matrix [17].

Fillers play a significant role in influencing the mechanical properties such as tensile strength and flexural strength when incorporated with epoxy composites [18-20].

1.2 Polymeric composite

Polymeric materials have been used in the field of engineering for centuries because of their low density, low cost and other beneficial features compared to metals and ceramics. A polymer is a large molecule which contains tens and thousands of small molecules called monomers (repeating molecular units linked together). This lengthy structure of polymers can provide versatile properties to the composites. Additional properties can be acquired with reinforcements to the polymer. The polymer with reinforcement is called “polymer matrix composite” or PMCs.

1.3 Definition and Classification of Polymers

In composite making, both thermosetting and thermo plastic polymeric materials have been used due to their attractive features as matrix materials. Some of them are shown in table 1.1 below.

The polymeric matrix materials are chosen depending on their properties like resistance to fatigue load, resistance to heat, resistance to chemicals, resistance to moisture, etc.

Table 1.1. Advantages and disadvantages of polymers as matrix

| Advantages | disadvantages |
|---------------------------------|-----------------------|
| Low density | Low flexural strength |
| Anti-corrosion | Low thermal stability |
| Thermal conductivity is less | |
| Electrical conductivity is less | |

The strengths of resin and reinforcement should be appropriate and the reinforcement should possess the property of ease of fabrication. The resin should easily wet the fiber in order to avoid any defect in fabrication and to give proper strength to the composite.

Internal molecular forces in large macromolecules are formed as polymers. Polymers can be classified as amorphous, crystalline and semi-crystalline based on the orientation of polymer chains. In an amorphous polymer, polymer chains are randomly oriented and irregularly packed. Conversely, polymer chains in highly crystalline polymers are regularly oriented and packed with respect to each other. In semi-crystalline type, the polymer has both amorphous and crystalline regions. In the crystalline region, how much is extended will decide the amount by which the polymer is crystalline. The crystallinity [21-25] degree of the polymer is the quality which decides the mechanical, thermal and physio-chemical properties of polymers. Based upon the structure polymer can be sub-categorized as follows, which is shown in the Fig 1.1.

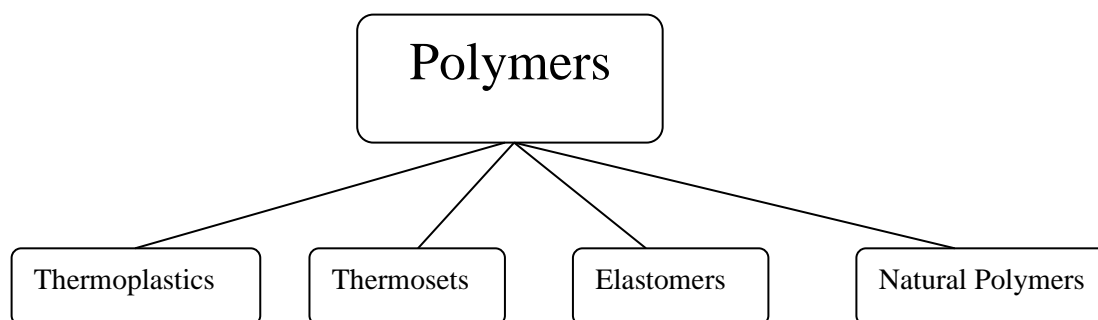


Figure 1.1 Classification of polymer types [21]

1.3.1 Introduction to Epoxy Polymers

There are so many thermoset polymers, among these, epoxy resins are widely used in composite applications. These resins are identified based on epoxide end groups in monomer. Epoxides contain three-membered ring of cyclic ether group, which has one oxygen and two carbons, as shown in Fig 1.2. The cyclic ether group of epoxides is highly reactive when compared with other ethers [26], because of its triangular configuration, which creates strains within the ring.

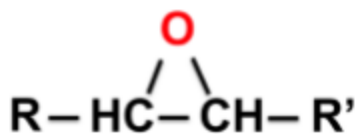


Figure 1.2. Example of an epoxide functional group, where R and R' may refer to a hydrogen atom or other functional groups [26]

In general, anhydrides, amines and aldehydes are used as cross-linkers. Nitrogen atoms in amines react with monomers of epoxy. Epoxy polymers use aliphatic amines widely, when compared to other amines. Aldehyde group aldehydes react with epoxy monomers via their oxygen atoms. Carboxylic group will be formed when alcohol reacts to anhydrides, this carboxylic group then reacts with epoxy monomers.

The cross-linking agents are mixed with epoxy monomers in pre-determined ratio. The type of monomer and the type of cross-linking agent will decide the ratio of mixing. After mixing properly, it is cured under a curing temperature. This curing temperature depends on mixing pair and typically it will be above the T_g value of the material [27]. During the curing process, nitrogen atom of cross-linker reacts with the carbon present in methylene and oxygen of epoxide reacts with hydrogen of amine group. After the curing time period, the sample is taken out from the chamber and then cooled under room temperature [28]. Fig 1.3, shows the cross linking between hardener and epoxy.

High performance composites require an autoclave to produce it [29-30]. Hardener and epoxy monomer react at different rates at different temperatures, which further will affect the chemical and physical properties of the polymer matrix. Therefore, in the process of polymer curing, the curing temperature plays a major role. Cross-links are successfully formed at high temperatures. The collision between the molecules increases with increase of temperature, which further enhances the cross-link formation. The reaction kinetic studies of polymer will determine the optimum temperature at which faster cross-linking reaction takes place [31,32]. Once the reaction starts, it continues and ends only when all the reactive molecules react successfully. In practice, this is rarely possible. The degree of cross linking (DOC) is the expression which can express the extent of cross link reaction. Theoretically, for epoxy polymer, DOC can be expressed as the ratio of number of reacted carbons in epoxy to the total number of carbons available in the entire epoxy. However, in an experimental system it cannot be measured. In

curing reaction, as DOC increases, the polymer chains become more restricted. i.e the mobility of chains decreases [33,34].

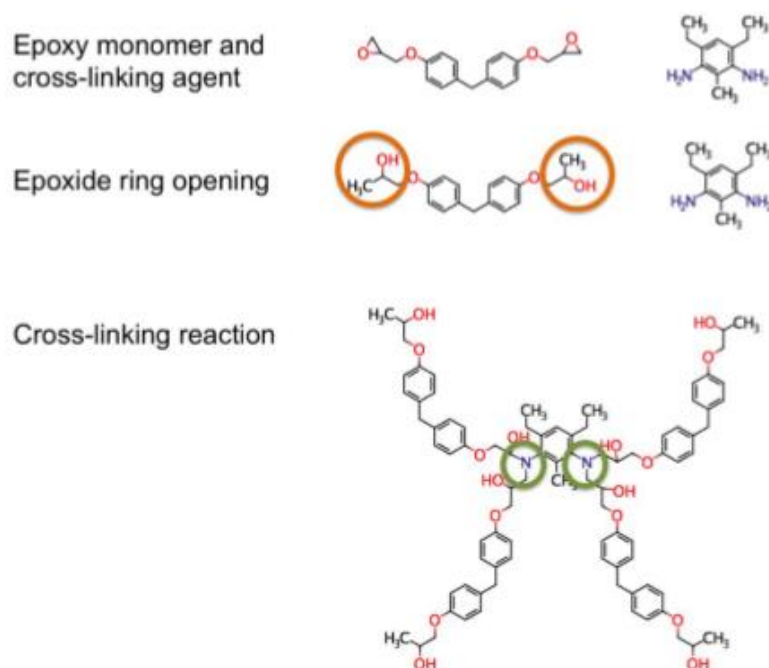


Figure 1.3. Illustration of epoxy monomer and cross-linking agent, ring-opened monomer and the product of the cross-linking reaction [28]

The mechanical and thermal properties of epoxy polymer will be influenced by the cross-linking structure of polymer [35]. Another important factor which influences the properties of resultant matrix is the curing time [36]. The availability of more reactive atoms at the beginning of curing process makes the cross-linking formation at a faster rate. As the time progresses this rate decreases and polymer sample solidifies. The rigidity of sample impedes the dispersion of unreacted atom; hence it needs more time for new link formation. Epoxy samples require more curing time as we get these samples at lower curing temperatures. Fast curing of matrix may cause defects in polymer matrix. These defects, such as voids may cause inferior thermo-mechanical properties [37]. For example, Liu et al. [38] observed decrease in the tensile strength of carbon/epoxy composite as a function of void content. Also, Sun et al. [39] noted higher Tg value of epoxy polymer matrix because of higher heating rate.

1.3.2 Properties of Epoxy Polymers

Several factors, like curing time, curing temperature, pair of cross-linker and epoxy etc. decide the properties of epoxy polymer matrix. Moreover, by changing monomer and cross-linker with one another one can produce different properties of polymer matrix [40].

The term “epoxy resin” is applied to both prepolymer and cured resin; the former contains reactive epoxy groups (see Fig. 1.4), hence the name.

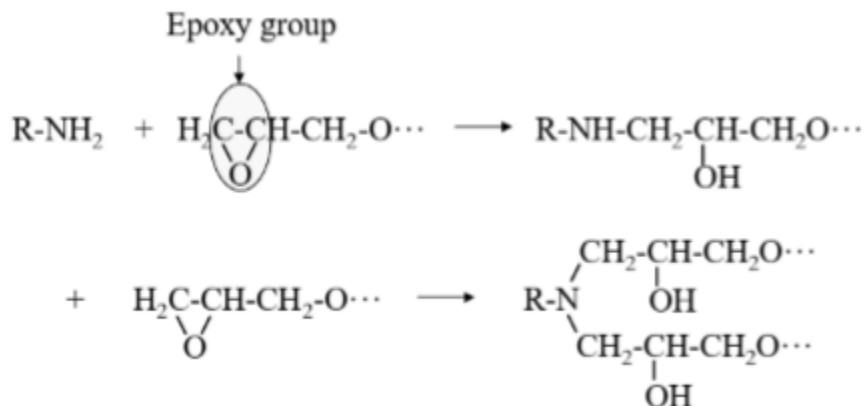


Figure 1.4. Mechanism of cure of epoxy with primary amines. $-\text{CH}_2\text{O}\dots$ indicates that only the reactive epoxy group is shown [41]

Curing agents are required to convert epoxy into infusible and hard thermoset networks. Since diamines have good reactive properties with epoxy groups, these are the widely used as curing agents for epoxy. Fig 1.4 shows the addition of primary amine active hydrogen atom to the epoxy group, then followed by the addition of secondary amine to another epoxy group. Epoxy ring-opening will be formed by hydroxyl groups, which accelerate the reaction.

1.4 Carbon fibres

Carbon fibers have excellent properties such as low thermal expansion, high stiffness, high chemical resistance, high tensile strength, high temperature resistance and low weight. Hence, carbon fibers are extensively used in military, aerospace, civil structures and sports, especially in motorsports. These are more expensive when compared with other fibers such as glass fibers and plastic fibers. Carbon fibers are mainly composed of carbon atoms, with a fiber diameter about 5-10 micrometres.

Based on precursor and fiber materials, carbon fibers are classified into:

- PAN-based carbon fibers
- Rayon-based carbon fibers
- Mesophase pitch-based carbon fibers
- Pitch-based carbon fibers
- Gas-phase-grown carbon fibers
- Isotropic pitch-based carbon fibers

1.4.1 Manufacturing Process:

The raw material of carbon fiber, which is used to make carbon fibers is called the precursor. Polyacrylonitrile is used as a precursor for about 90% of carbon fibers; petroleum pitch or rayon is used for about 10% of carbon fibers. These precursors are the long strings of bounded carbon atoms, so these are organic polymers. The trade secret of composition of precursor may vary from one company to another. Different types of liquids and gases are used during the manufacturing of carbon fiber. These materials add distinct and specific properties to carbon fiber. Some of these are used to prevent certain reactions with fiber.

The Manufacturing Process of PAN based carbon fibers

Spinning

Polyacrylonitrile plastic is formed by mixing of acrylonitrile powder with methyl methacrylate or methyl acrylate and by reacting these under catalyst in sol-polymerization process or convention suspension process. The Polyacrylonitrile plastic is then rolled into fibers by using any one of the different methods. some methods mix the plastic with some chemicals and drive them through small jets into a quench chamber where it solidifies into fibers. In other methods heated plastic mixture pumped through small jets into a chamber where solid carbon fiber is obtained after evaporation of solvents. This spinning process is the process where desired diameter of the fiber is formed after stretching. Molecules are aligned properly due to stretching and form tight bonded carbon crystals after carburization.

Stabilizing

The fibers are heated in air for 30-120 minutes at a temperature of 200-300⁰C to alter the fibers chemically. This is to be done before carbonization, as it is needed to change their linear atomic bonding to ladder bonding, which is thermally stable. In the process, oxygen molecules present in the air are picked up by the carbon fibers and form new atomic bonding pattern by rearranging themselves. These chemical reactions are complex in nature and comprise numerous steps, few of which may happen at a time. This process is done using different techniques and equipment. Few may use hot rollers over which fibers are passed and others may use series of hot chambers through which fibers are drawn. In some cases, stabilization is done by passing the gas heated air over the fibers.

Carbonizing

After stabilization process, the fibers are heated in a furnace for some time to a temperature of 1000-3000⁰C. This furnace contains gas mixture without oxygen, which prevents burning of fibers at high temperatures. The pressure inside the furnace is higher than the outside pressure and sealing is done at the entry and exit of carbon fibres into furnace, which will stop oxygen from entering the furnace. Because of high temperature heating, fibers lose some of their carbon and all non-carbon atoms, in various forms such as hydrogen, water vapour, CO₂, CO, nitrogen, ammonia and others. The remaining carbon atoms which are available after expelling non carbon atoms form a tightly bonded carbon crystals and align nearly parallel to the fiber length or along the axis. In a few cases, two furnaces are used to control the rate of de heating, where furnaces are maintained at different temperatures.

Treating the surface

Oxidation of carbon fiber surfaces would be done after carbonization of fibers. It is required because after carbonization process the fiber surface is such that it is able to bond to epoxies properly, this can be overcome by oxidation. Not only epoxies, other matrix materials also not able to form proper bonds with carbon fiber after carbonization. So, it requires oxidation to form proper bonds. Oxidation of fibers involves the addition of oxygen atoms to the fiber surface, which make the surface better to chemical reactions and improve surface roughness. The higher the surface roughness, the better the mechanical bonding with matrix materials. The oxidation process can be done by dipping the carbon fibers in several gases (ozone, CO₂ or air) or various liquids such as nitric acid or sodium hypochlorite. The positive terminal is created in

fibers by coating them electrolytically and this can be achieved by immersing the fibers in a bath containing different materials which are electrically conductive. To avoid formation of small surface defects like pits, this process should be controlled carefully, failing which there is failure of the fiber.

Sizing

After oxidation, the surface of the fiber is coated to protect the fibers from damage which may happen during weaving or winding. The process of coating is called as sizing. Distinctive coating materials used include polyester, urethane, epoxy, nylon and others. These coating materials are chosen based on adhesives which are used to form composites and these should be compatible to adhesives. These coated fibers are coiled on cylinders, which are called bobbins. The fibers are warped into various sizes of yarn by loading, these bobbins in a spinning machine.

1.4.2 Properties of Carbon Fiber

The specific strength of carbon fiber is high, i.e. strength of material at failure is higher when compared to its density. Materials have good strength/weight ratio, when they are light weight and have high strength. Materials like glass fiber, magnesium, high strength alloys, aluminium and carbon fibers have better strength to weight ratios. Including high specific strength, the carbon fiber has the following properties:

- Fire resistance/non flammable
- Non-poisonous, biologically Inert, X-ray permeable
- Good tensile strength
- Electrically conductive
- Good Fatigue resistance
- Low coefficient of thermal expansion
- Very Rigid
- good thermal conductivity
- Resistance to corrosion and chemically stable

1.4.3 Limitation of Carbon fiber

Carbon Fiber is relatively expensive

Although carbon fibers have good specific strength and rigidity, the cost of these fibers is very high compared to other fibers. In aeronautics and in racing, the weight of the product plays a major role and that makes the carbon fibers enjoy advantage in these applications even though they are expensive. The maintenance of carbon fiber is not much required which makes it an added advantage. Carbon fiber makes an impression which makes traders enthusiastic to pay more for the privilege of having it.

Carbon Fibers are brittle

The strong covalent bonds in a carbon fibre layer make the sheets allowing the propagation of cracks, when they bend. They fail at low strain.

1.5 Fiber-reinforced polymer composites (FRPC)

In any composite, fibers are the main constituent and matrix is the secondary constituent. Fibres are main, because they bear the entire load acting on the polymer composite, but matrix is only a binding agent to keep and hold the fibers in position and protect polymer composite from damage. The fibers have high modulus and specific strength, the load will be transformed uniformly to the fibres through matrix. Any single constituent cannot have these properties, so both are needed. The use of Fiber-reinforced polymer composites (FRPC) started many thousand years back [42]. In recent times i.e. in 1960s, we can observe that these were used in aeronautical engineering applications. In olden days, these applications were restricted due to high production cost, but nowadays, with the development of computer aided manufacturing, the cost has reduced greatly [43]. The most promising fields, where FRPC have applications are wind energy, automotive, naval and civil construction applications.

1.5.1 Role of fiber reinforcement in FRP

The properties of polymer composites will depend mainly on the properties of fibers. These enhanced properties are called fiber dominant properties, as fibers will influence these properties. With increase of fiber volume, the fiber dominant properties improve up to certain

optimum level of fiber volume, beyond which the properties decrease. If the fiber volume increases in a fixed volume of composite, the matrix volume is not sufficient to wet all the fibers and to hold all the fibers together, which causes non uniform load distribution and finally failure of the composite and decrease in mechanical properties. Fiber orientation, fiber length etc., also influences the mechanical properties of the final composite [44].

1.6 Nanocomposite Concept

The composites formed by mixing of nanoparticles in the polymer matrix are called as polymer nanocomposites. It was observed that, the addition of nanoparticles into the matrix, resulted in good improvement in mechanical properties of nanocomposites. Due to high surface area of nanoparticles when compared to microparticles, only low quantities of nanoparticles can be added to the matrix. One of the dimensions of the nanoparticles should be of nano meter size. Based upon the dimensions of nanoparticles, these are classified as (i) only one dimension is of nano size, e.g., layered silicates (mica, clay, etc.) (ii) two dimensions are of nano size, e.g., whiskers, nanotubes (iii) all three dimensions are of nano size, e.g., spherical alumina, silica. A composite consisting of one reinforcement as a nanoparticle in a polymer matrix is called as polymer nanocomposite. Similarly, a composite comprising of two reinforcements such as fiber and nanoparticles in a polymer matrix is called as polymer hybrid nanocomposite. It is a tough technical and scientific challenge to prepare polymer nanocomposites. The distribution of particles, particle shape and surface morphology of particles have an impact on the properties of polymer composites.

1.6.1 Polymer Nanocomposites

The polymer composites, where the primary constituents in the polymer matrix have at least one dimension as nano size are called as polymer nanocomposites [45]. Generally, these composites have light weight and low filler loading. These composites provide excellent property improvements and are easy to fabricate.

1.6.2 Filler

Fillers play a major role in enhancement of various properties of a final composite. There are huge number of fillers, both organic and inorganic which are available in nature. These fillers

improve tribological properties of composite and the fillers also reduce the shrinkage effect of the composite. Creation of various composites which are superior to metal in thermal, mechanical and tribological properties depends on a combination of filler and matrix.

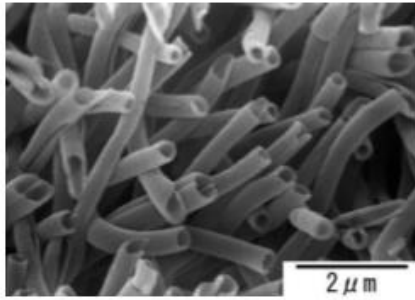
Conventional Fillers

Commercial type of polymers can be developed by using different particulate fillers. Primarily these fillers are classified as synthetic fillers and natural fillers. Silica, Calcium carbonate, calcium sulphate etc., are the most commonly used natural fillers. Carbon black is one of the synthetic fillers which is most commonly used and using some chemical process, these synthetic fillers are prepared. In rubber, carbon black is used as a reinforcement. In silicone elastomers, synthetic silica is used as reinforcement [46].

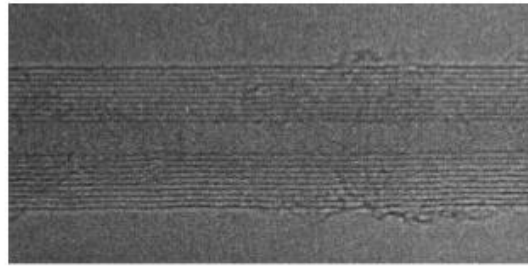
Basically, these fillers are cheap, though the benefits of modifying the properties of polymers are prominent, hence these fillers are gaining much attention. Addition of fillers will improve flame retardancy, thermal conductivity, mechanical properties and controlled thermal expansion at reduced cost. Obviously, all these benefits are not able to get through a single filler only. The enhancement of property mainly influenced by not only the filler loading but also filler shape, ability to bond with matrix and the size of a filler and so on.

Nano Fillers

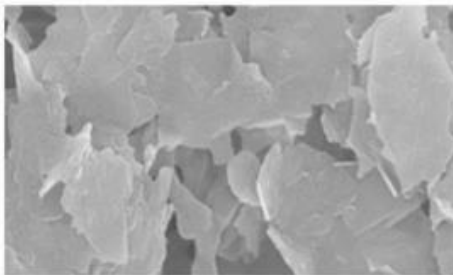
Fillers are considered nano fillers if at least one dimension of the filler is in nano meter range. Silica, POSS, carbon black, SiC, TiO₂ etc., are a few examples of fillers in which all the three dimensions are may be of nano meter scale. Nanotubes and nanofibers are examples of fillers which are having two dimensions in nano meter scale and third one in microns. Nano clay and mica and graphite flakes are an example of fillers which have only one dimension in nano meter scale and the remaining are in microns; in these the particles are in the form of sheets. Fig. 1.5 illustrates various types of nanofillers. The addition of nanoparticles will enhance strength and stiffness of the composite, with the decrease in size of the filler from microns to nano meters, various composite materials with enhanced mechanical properties have been developed [47].



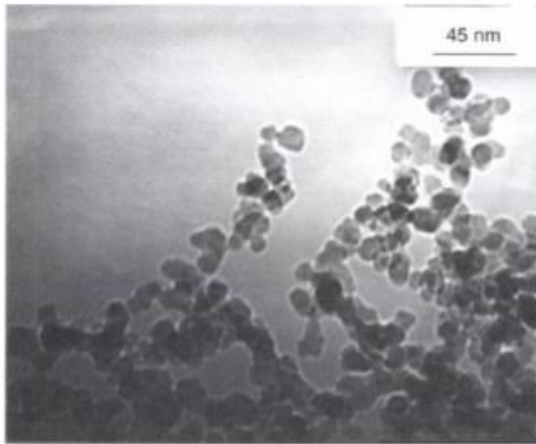
(a) Single wall carbon nanotubes



(b) Multiwall carbon nanotubes



(c) Graphite flakes



(d) Silica nanoparticles

Figure 1.5 Different types of fillers (a) Single-wall carbon nanotubes (b) Multiwall carbon nanotubes (c) Graphite flakes (d) Silica nanoparticles [47]

With the reduction of particle size from microns to nano meters, the area of contact between matrix and fillers increases, hence bonding strength also improves. Due to the high surface energy of nanoparticles, these particles tend to agglomerate, which reduce the area of contact with matrix, thereby decreasing strength. So, composite properties have a great effect on how well nanoparticles are distributed inside a composite. Fig 1.6. shows the comparison of various particle sizes.

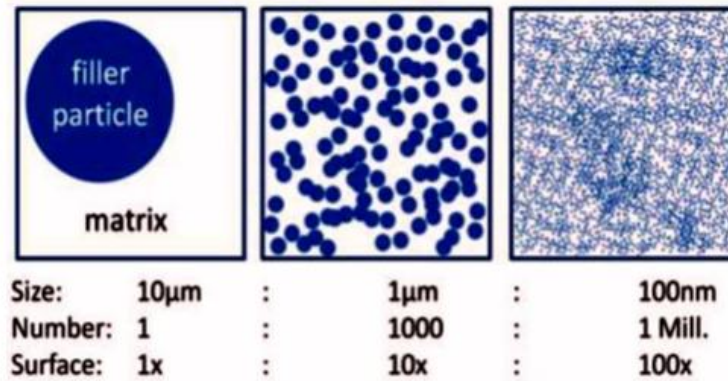


Figure 1.6. Filler particles of same weight and sizes (a) 10 μ m (b) 1 μ m (c) 100 nm [48].

1.7 Thesis organization

The entire thesis is organized into six chapters

- The first chapter presents an introduction to polymer composites, carbon- epoxy composites, properties of carbon fiber, epoxy and Tungsten carbide filler.
- The second chapter provides a comprehensive review of the literature on carbon epoxy nanocomposites and hybrid nanocomposites. This chapter briefly outlines the research work carried out by various researchers; it identifies gaps in the literature and formulates problem(s) based on the lacunae identified.
- In the third chapter, mechanical and tribological properties of Tungsten carbide-epoxy polymer nanocomposites are studied.
- In the fourth chapter, mechanical and tribological properties of carbon fiber reinforced epoxy polymer composites are discussed.
- In the fifth chapter, mechanical and tribological properties of carbon fiber reinforced Tungsten carbide-epoxy polymer hybrid nanocomposites are detailed.
- In the sixth chapter, conclusions drawn from the above studies are mentioned as also the scope for future work.

Chapter 2

Literature Survey

2.1 Introduction

The purpose of this thesis is to communicate the importance of Tungsten carbide in modifying the mechanical and tribological properties of carbon fiber reinforced epoxy composites. Composite materials perform a vital role in industrial applications because of their superior weight to strength ratio, resistance to corrosion and other desirable properties. Epoxy has been used as a matrix material widely due to its excellent mechanical, tribological and thermal properties.

Composites reinforced with fiber have been used for decades as structural members extensively in automobile, aircraft and marine industries and electrical and electronic industry. The increased demand for materials with superior mechanical characteristics relative to existing materials has led to the search for newer and more advanced materials. There are several ways to enhance the performance of polymer composites. One of the effective ways of enhancing the mechanical properties of polymer composites is to reinforce the matrix with fillers and fibers.

Other properties that make composites special are specific strength, specific stiffness well-controlled anisotropy, fatigue strength, corrosion resistance and flexibility in varying the properties.

Composite properties are controlled by two very basic constituents i.e. matrix and its reinforcement; by tailoring the proportion of reinforcement, we get a unique matrix far different from the parent composite. The orientation of the fiber in the composite also plays a major role in the behaviour of the properties of the composite. The fibre can have different orientation and each orientation will result in different properties of composites.

Fiber-reinforced plastic composites are composed of distinct chemical constituent which can be two or more. The unique combination is obtained by permutation and combination of reinforcement and the resulting fiber results in a unique composite. The reinforcement which is discontinuous in nature is embedded in the continuous phase in the composite. The outcome obtained is a composite with very attractive properties which are dictated by careful selection of basic constituents i.e., reinforcement and fibers.

The major function of fiber in the composite is to distribute stress uniformly within the material to increase the load-bearing properties when compared with bare material.

Polymer composites are used in many sectors such as aircraft industry, automobile industry, sports industry, etc. There is an increased demand for polymer composites in recent decades due to the improvement attained in the field of nanomaterials. This can be possible only with radical combinations of two or more than two materials which in turn gives superior strength compared to individual materials.

2.2 Material Selection

Materials in fiber form have good properties only in combination with a suitable matrix. The matrix should hold the fibers together to prevent failure. The matrix must elongate sufficiently upon the action of weight to transfer the load evenly without stress concentration. In making polymer composites, two types of resins are used. These are thermosets and thermoplastics.

2.2.1 Thermosets

Most of the matrix materials used in making the composites belong to thermosetting resins. Enough adhesion is required between the fiber and resin in the composite.

Epoxy resins belong to the group of thermosetting resins. In the production of composites, epoxy has been used as a matrix material extensively due to its wettability and adhesion to the carbon fiber. Resins like epoxy form good covalent crosslinks. Epoxy and phenolic resins cure at room temperature and the epoxy resin does not produce any type of volatile elements while curing. This in turn produces voids in the composite.

Epoxy resins are costlier than polyester but have the potential in making high strength composites for value-added components.

Fiber impregnation is done at high pressure and temperature. Resins enhance the processability but reduce thermal resistance. The curing time of epoxy is a little higher and this is said to be a disadvantage of epoxy resin. The mould release property of epoxy is yet another disadvantage

2.2.2 Reinforcement

Reinforcement provides strength, stiffness, and other required properties to the composite. Reinforcement reduces the density of the composite without affecting strength.

The following characteristics are to be observed in selecting proper reinforcement.

1. Shape
2. Surface (either smooth or rough)
3. Surface defects
3. Structural defects
4. Properties like strength and density

2.3 Literature Survey

Carbon fiber Epoxy composites find various industrial applications in aircraft, automobile, marine, etc. due to their outstanding properties like strength, stiffness, lightweight, corrosion resistance, etc [49].

Epoxy possesses good adhesion, moderate viscosity, low shrinkage and low creep. However, carbon epoxy composites are more susceptible to mechanical loads, such as tensile load and flexural load.

Anisotropic property (having different properties at different orientations) of the composite is the primary reason behind mechanical failure [3]. Also, the wear resistance of pure epoxy composites is very poor. Hence, it is essential to design composites that can withstand high damage tolerance.

There are several ways to enhance the performance of polymer composites using micro or nano fillers into the matrix [50]. However, these methods involve additional manufacturing elements and expensive labour, which leads to increase in cost of finished composites.

Some researchers have found inexpensive ways to improve interlaminar shear strength of composites by incorporating nanoparticles into fiber reinforced composites [51-58].

Adding suitable fillers to pure epoxy composites can enhance the tribological properties of composites [17]. Due to high surface contact area with the matrix, nanoparticles have proved to be efficient in varying the physical characteristics of the composite [59-62].

According to Zhou et al. [51], the addition of 2 wt.% nanofibers of carbon into glass fiber reinforced epoxy composites, resulted in the growth of ILSS by 22%.

According to Siddiqui et al. [54] fracture toughness and crack growth resistance in carbon fiber reinforced composites can be improved by adding organoclay nanoparticles.

Khun et al., [63] studied the mechanical and tribological properties of epoxy composites reinforced with graphene. With the increase in graphene content, the tensile strength and hardness of the composites increased.

Soon et al., [64] conducted an experimental study on the composite correlation between two different sized particles and their mechanical properties. The composites were made from spherical silica particle having diameter 0.24 and 15.6 μm and the composition varying from 0.1 to 1.0 with a constant volume fraction of 0.30. The mechanical properties like fracture toughness and bending strength are strongly dependent upon the composition of the particle.

Iskender et al. [65] studied how micro and nano filler in the composite vary mechanical properties. The composites matrix was epoxy which was made up of micro filler Al_2O_3 10%, fly ash 30%, TiO_2 10% added in by weight ratio. The nanofillers used were clay, Al_2O_3 , TiO_2 in the range 2.5-10% by weight ratio

Yasmin and Daniel [66] fabricated anhydride-cured diglycidyl ether of bisphenol A (DGEBA) reinforced with 2.5–5% by weight graphite platelets. The study provides thermal, structural, viscoelastic and mechanical properties. From the XRD study, it was confirmed that the d spacing of graphene will not change if the composite is processed. AS the concentration of graphene platelets increases, mechanical properties show improved results.

Kharat and Sindhu [67] investigated the mechanical properties of epoxy-based composite by varying the amounts of fillers such as Boron carbide (B_4C) & Tungsten disulphide (WS_2) in weight %. The mechanical properties such as hardness, flexural strength, tensile strength, impact

strength and density were tested. The results were encouraging with the increase in filler content the hardness and tensile strength was increased up to 2.5 wt% of B₄C and 4 wt% of WS₂. All the specimens were tested as per ASTM standards.

Fouad et al., [68] carried out experiments on glass fiber reinforced plastic (GFRP) to observe the wear mechanism and solid particle erosion behavior of commercially available epoxy. Irregular silica sand (SiC) particles were used as erodent having a size of $(150 \pm 15 \mu\text{m})$ for erosion experiment. The composite was impinged by SiC particles at 30°, 60° and 90° and erosion loss were computed by changing erosion time. The result obtains shows maximum erosion occurs at 60°. i.e., composite behaviour changes from ductile to brittle at 60°.

Tewari et al., [69] studied the erosion behaviour of carbon cum glass fiber (laid in a different orientation) epoxy composites at different sand impact angles (0°, 45°, and 90°). The composites with unidirectional glass and carbon fiber showed a semi ductile nature. The orientation of fiber can influence erosion resistance.

Barkoula and Karger [70] studied the erosive behaviour of polypropylene composites reinforced with glass fiber at different sand impact angles (30°, 60°, 90°). Based on their results, the erosion wear of the composites depends on fiber orientation at low impingement angles 30° to 45° and at higher impact angles 60° to 90° observed very low dependence.

Suresha et al., [17] studied the mechanical and tribological properties of composites reinforced with glass fiber and graphite filler. Their observations showed an increase of tensile strength and tensile modulus of up to 7.5wt% of filler addition.

Basappa et al., [71] reported the tensile and flexural properties of glass fiber epoxy composites reinforced with different fillers (silicon, graphite). Plain woven glass fiber epoxy composites showed an increase in tensile and flexural properties with an increase in filler loading.

Osman Asi., [72] had investigated the mechanical properties of glass fiber epoxy composites reinforced with Al₂O₃ in different ratios. From the results, the tensile strength and shear strength of the composites were found to decrease with filler percentage. The flexural

strength of the composites increased with an increase of Al_2O_3 up to 10% and after 10% filler, flexural strength decreased.

Arpitha et al., [73] made an analysis of tensile strength, flexural strength and impact strength of glass fiber epoxy composites reinforced with Sic. The percentage of silicon carbide filler in the glass fiber composites was 3wt%, 6wt% and 9wt %. Their results showed that the composites without filler proved to be better in strength.

Devendra and Rangaswamy [74] made an analysis of the mechanical properties of glass fiber composites reinforced with different types of fillers. Their results showed composites with 10% hematite powder had maximum ultimate tensile strength and hardness.

Muralidhara B et al., [91] explored thermal, mechanical and tribological behaviour of carbon fiber/epoxy composites reinforced with micro boron nitride (BN) filler. BN filler reinforced carbon fiber/epoxy composites show noticeable enhancement in ILSS, flexural, hardness and tensile except impact resistance. Further, it was observed that 1 wt% reinforced BN filler prompts better mechanical properties with predominant wear resistance, thermal and damping behaviour.

Hanumantharaya Rangaswamy et al., [92] Investigated mechanical behaviour of MWCNTs filler reinforced Glass/Kevlar/epoxy composites. Effect of mould temperature, duration of compressive load and magnitude of compressive load on mechanical properties also observed. Magnitude of Compressive load had maximum influence on mechanical strength followed by temperature of mould and duration of compressive load applied. Optimized mould conditions give a tensile strength, flexural strength and hardness value of 181.2 MPa, 143.3 MPa and 22.8 HV respectively.

Anurag Namdev et al., [93] Conducted experiments to understand wear and mechanical behaviour of Graphene nanoplatelets (GNP) reinforced carbon fiber/epoxy hybrid composites. From the results it was observed that at 0.5 wt% GNP reinforced carbon fiber/epoxy shows reduced wear loss and higher bending and tensile strength than any other composite.

Çağrı Uzay [94] Studied thermal and mechanical behaviour of cubic boron nitride (c-BN) nanoparticle reinforced carbon fiber/epoxy composites. The findings show that 20% and 42%

enhancement in tensile and impact strength respectively. Also, better thermal stability can be observed as T_g values enhanced from 16.09% to 21.14%.

Beibei Wang et al., [152] Conducted experiments to know the tribological and mechanical characteristics of Carbon fiber/phenolic resin composites reinforced with graphite nanoplatelets (GNPs). From the results, a significant improvement of tensile strength by 47.5% was observed for Carbon fiber/phenolic resin composites modified by GNPs compared to unmodified composites. Also, there is a substantial improvement in wear resistance of GNPs modified Carbon fiber/phenolic resin composites.

Santosh Kumar et al., [153] Studied influence of graphene nanoplatelets (GNPs) reinforcement at different loading on tribological and mechanical performance of glass fiber/epoxy composites. The study reveals that the addition of GNPs by 1 wt% give clear enhancement in hardness, tribological performance and ILSS of the glass fiber/epoxy composites. However, there is negligible enhance of tensile strength of the glass fiber/epoxy composites at 1 wt% addition of GNPs.

Ahmed Fouly et al., [154] Developed agriculture waste corn cob natural material into powder and added in different weight ratios to the epoxy polymer. The Corn cob/epoxy composites are tested for mechanical and tribological properties. The results show that at 8 wt% of corn cob there is significant improvement of 21.26% and 22.22% in young's modulus and compressive yield strength respectively. Also, at 8 wt% reinforcement of corn cob in epoxy there is increase of wear resistance by 4.8% and decrease in the coefficient of friction by 35%.

Sangamesh Shivaputrappa Pasare and Bheemappa Suresha [155] examined tribological and mechanical behaviour of carbon fiber/epoxy composites reinforced with micro boron nitride (BN) filler and nano BN filler. It was observed that tensile and flexural strength increases at 1.5 wt% nano BN filled carbon fiber/epoxy compared to micro BN filled carbon fiber/epoxy. Also, nano BN filled carbon fiber/epoxy shows enormous improvement in wear resistance of epoxy, despite with small increment of coefficient of friction value.

Akeem Yusuf Adesina et al., [156] fabricated micro waste tire rubber (WTR) reinforced epoxy coatings and tested for mechanical and tribological behaviour. Hardness was enhanced by

22% at a loading of 5 wt% WTR. The wear resistance shows enormous improvement by 70% for loading of 10 wt%. similarly, friction coefficient value reduced significantly for all WTR loadings.

Adding to the above literature review, an additional literature review in a short tabulated form figures in Table 2.1.

Table 2.1 Additional literature review

| | | | | |
|-------------------|------|--|--|------|
| Suresha et al. | 2007 | Glass epoxy hybrid composites with graphite | Mechanical and tribological properties | [17] |
| Suresha et al. | 2007 | Glass epoxy hybrid composites with sic filler | Mechanical and tribological properties | [75] |
| Single and chawla | 2010 | Epoxy resin with fly ash filler | Mechanical properties | [76] |
| Veena et al. | 2011 | Epoxy with nano sized silica fillers | Tribological and electrical | [77] |
| Pravuram | 2012 | Glass epoxy hybrid composites with aluminium nitride | Erosion wear | [78] |
| R. Baptista et.al | 2016 | Epoxy with graphite filler | Mechanical properties | [79] |
| Wang et al. | 2013 | Epoxy with nano silica | Mechanical and tribological | [80] |
| Ramesh et al. | 2014 | Glass epoxy hybrid composites with $Al_2O_3/SiO_2/TiO_2$ fillers | Mechanical properties | [81] |

| | | | | |
|-----------------|------|---|--|------|
| Antunes et al. | 2014 | Polyester with sic | Mechanical and tribological | [82] |
| Sandesh et al. | 2014 | Epoxy with red granite powder | Mechanical properties | [83] |
| Chensong et al. | 2014 | Bidirectional hybrid epoxy composites reinforced by E glass | Flexural strength | [84] |
| Sidhu et al. | 2014 | Epoxy resin with Tungsten disulphide Particles | Mechanical properties | [85] |
| Sudheer et al. | 2014 | Glass epoxy hybrid composites with graphite fillers | Mechanical and tribological properties | [86] |
| Win et al. | 2015 | Graphene modified epoxy Composites | Mechanical and Tribological Properties | [63] |
| Wang et al. | 2016 | Basalt FRP and hybrid FRP laminates | Interlaminar shear behavior | [87] |
| Swapnil et al. | 2017 | Glass fibre/epoxy composites | mechanical properties | [88] |
| Song et al. | 2018 | Carbon fiber | Interfacial strength | [89] |
| Song et al. | 2019 | Carbon fiber/epoxy composites | Interfacial shear strength | [90] |

2.4 Summary

After a comprehensive study of existing literature, several gaps have been identified in carbon/epoxy composites used for high-performance applications. The polymeric composites are more susceptible to mechanical loads, such as tensile and flexural load. Anisotropic property (having different properties in a different orientation) of the composite is the primary reason behind mechanical failure. Solid particle erosion has been a stern problem in the field of

engineering due to the reason that it is considered responsible for several failures. The available literature on conventional fillers and their role in modifying the composite properties are limited to either mechanical or tribological properties. Limited work has been made to enhance the combined mechanical and tribological properties of carbon epoxy composites using Tungsten carbide nano filler. No systematic attempt has been reported on the effect of Tungsten Carbide filler reinforcement to enhance mechanical and tribological properties of epoxy polymer.

2.5 Objectives framed for the proposed work

- Preparation of Tungsten carbide-epoxy polymer nano composites and investigation of their tensile strength, flexural strength, void content and micro hardness.
- Preparation of carbon fiber reinforced Tungsten carbide-epoxy polymer hybrid nano composites and investigation of their tensile strength, flexural strength, void content and micro hardness.
- Preparation of Tungsten carbide-epoxy polymer nano composites and investigation of their erosion resistance and wear resistance.
- Preparation of carbon fiber reinforced Tungsten carbide-epoxy polymer hybrid nano composites and investigation of their erosion resistance and wear resistance.

Chapter 3

Mechanical and Tribological properties of Tungsten carbide-epoxy polymer Nanocomposites

3.1 Introduction

Polymeric materials are well known for their exceptional adhesion to various types of substrates, excellent electrical resistance, high chemical resistance, better toughness, durability at all temperatures, flexibility, and low void shrinkage [95-97]. Plenty of polymers and particles reinforced polymer matrix composites have so many industrial applications [98]. Composites that have high thermal durability are used in high temperature applications [99]. The main aim of addition of particulate fillers in to the polymers is to reduce the cost and to improve stiffness; these composites are used for commercial applications. Under hard working conditions, the use of these high-performance polymer composites has been increasing in demand.

Epoxy resin is one polymer which is most widely used thermosetting polymer called matrix; in composite industry and other structural materials such as adhesive joints, automobile industry and in the manufacturing of paints and coating of surfaces epoxy is used [100, 101]. It has the following advantages of high hardness, excellent resistance to humidity, better thermal and mechanical properties, excellent insulating properties for electricity, and better adhesive property to be used in reinforcements [102, 103]. Like other thermosets, epoxy resins form a network after curing with several curing agents like anhydrides, amines, etc. [104].

The performance of epoxy resin can be further improved by the addition of different types of fillers. Recently short fibers, particulates and whiskers type of reinforcements have gained attention and have addressed key issues in polymer industry. The composite properties depend on the reinforcement, matrix and the interaction between matrix and reinforcement. Reinforcement size, surface modification, volume, and shape can change several properties such as wear resistance, strength, stability, hardness, etc. Several researchers have added different types of filler reinforcements to epoxy, and found improvement in the properties of epoxy. Hard ceramics like silicon carbide, boron carbide, alumina type of filler were found to improve in wear and mechanical properties of epoxy [105-107].

Solid particle erosion is one of the wear types of a complex nature, in which erosion occurs by a combination of surface degradation and continuous loss of target substance due to continual impact of solid particles [115]. This type of erosion can cause loss of shine and transparency, increase in surface roughness and also pre-mature failure of structures and engineering components. Erosion leads to unnecessary costs and allied shutdowns in many

industries. The surfaces of high-speed moving objects like windmill blades, vehicles, surfing boats, aircrafts, etc. always undergo solid particle erosion due to solid particles present in the environment. In addition, steam turbine blades and inner surfaces of pipes in oil and gas production industries may erode due to the impingement of particles present in the slurry. Hence, Solid particle erosion is of main concern for these types of applications and materials with low erosion rate are essential.

For the past two decades, polymer utilization in a wide variety of industrial applications has increased significantly where body parts are exposed to fast moving solid particles [114]. Polymer coating is regularly used as a foregoing layer to take care of body components from erosion, corrosion and abrasion [114]. However, when compared to metals, the erosion wear resistance of polymers is two to three times lower in scale [122]. This can be overcome by the addition of small particles, platelets, carbon nanotubes, chopped fibers and hollow spheres in the polymers.

The key factors that influence erosion wear of a filled polymer composites are: filler or fiber type [118, 124], filler content [129, 132], orientation of fibre [131, 120] filler and matrix interface [109], fiber volume and composition of a polymer [110, 121]. On the other hand, testing conditions also influence erosion wear behaviour, which includes impingement velocity of a particle [126, 109], angle of impact of particle [124, 125], erodent type [114], mass flow of erodent [131, 129], erodent size [128] and test temperature [117, 114]. In the literature, only some studies have concentrated on the particle filled polymer composites, particularly for nanoparticle reinforced polymers, and many works have been on the fiber reinforced polymer composites.

There are so many applications where polymer composites are used in which resistance to wear is very important. Polymers, due to their seizure, corrosion resistance, low friction coefficient and tolerance to small misalignments are considered ideal material for low load bearing applications. The acceptability for wear conditions depends largely on its wear rate and mechanical load carrying capacity. There are many reports in the literature that polymer composites are used in dry sliding wear application. However, only a few publications are available on dry sliding wear characterization of polymer composites and as per my knowledge, no report was available on friction and wear characterization of WC particle reinforced epoxy polymer nano composites.

The current section deals with the preparation of tungsten carbide nanoparticles incorporated epoxy polymer, and analysing the erosion wear behaviour of these composites at different test conditions such as particle impingement angles and particle impingement velocities. Also, mechanical properties and dry sliding wear and friction behaviour of tungsten carbide filled epoxy polymer composites were analysed. Finally worn surfaces were examined using SEM.

3.2 Materials and Methods

3.2.1 Materials

Epoxy (LY556), which can be cured at room temperature was used as a resin. This resin belongs to family of diglycidyl ether of bisphenol A (DGEBA). Along with resin, an amino group family-based hardener (HY951) was used as matrix. These two materials were supplied by SISCO Research Laboratories Pvt., Ltd., Hyderabad, India. Tungsten Carbide nano particles were used as filler reinforcements. Tungsten Carbide (WC) nano particles were used as filler reinforcements, which has a density of 15.63g/cc and of particle size 55nm. Nano particles were supplied by US Research Nanomaterials, Inc., Houston, USA. The properties of epoxy and hardener were mentioned below in Table 3.1 and Table 3.2 respectively.

Table 3.1 Properties of epoxy resin

| Characteristic | Specification |
|-------------------|---------------|
| Viscosity at 25°C | 10,500 mPa.s |
| Epoxy Content | 185 g/eq |
| Density at 25°C | 1.15 g/cc |
| Flash Point | > 200°C |

Table 3.2 Properties of Hardener

| Characteristic | Specification |
|-------------------|---------------|
| Viscosity at 25°C | ~20 mPa.s |
| Density at 25°C | 0.97 g/cc |
| Flash Point | 115°C |

3.2.2 Preparation of composites

Tungsten Carbide nano fillers of known amount were mixed with epoxy resin using mechanical stirrer for 20 minutes for getting uniform dispersion. After that, the required amount of hardener (epoxy to hardener by weight 100:12) according to stoichiometry was mixed thoroughly in resin for 10 minutes, using mechanical stirrer. A wooden mould of size 200mm x100mm x 4mm was prepared. Releasing agent was sprayed on the wooden mould surface, so that samples could be removed easily from the wooden mould. Then the matrix with nano particles was poured into the wooden mould and kept at room temperature for 48 hours. After that composite were removed from the mould, and finally the required samples for tensile, flexural test and to the sand Erosion test as per ASTM standards were cut using a diamond cutter. Cylindrical mould is used to make samples for dry friction wear test. Erosion test samples are shown in Fig. 3.1, Tensile and flexural Samples are shown in Fig. 3.2. and Fig. 3.3 respectively and friction wear test samples are shown in Fig. 3.4. Samples that are prepared for different filler loading are shown in Table 3.3.

Table 3.3 Different types of composite samples prepared

| Sample Code | Matrix (epoxy + hardener) Wt. % | Filler (WC) Wt. % |
|-------------|------------------------------------|----------------------|
| W0 | 100 | 0 |
| W1 | 99 | 1 |
| W2 | 98 | 2 |
| W3 | 97 | 3 |
| W4 | 96 | 4 |

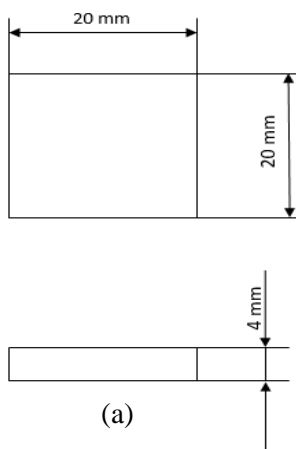


Figure 3.1 Nanocomposite samples for erosion test (a) line diagram with dimensions (b) sample prepared

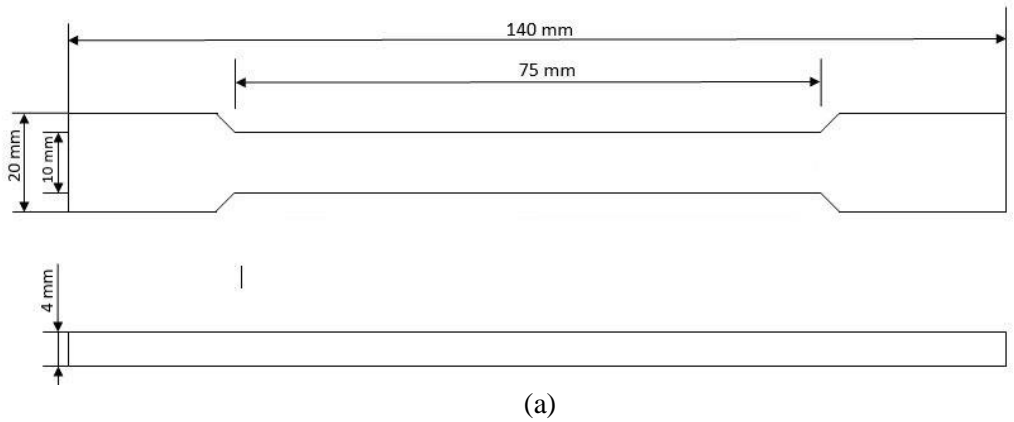


Figure 3.2 Nanocomposite sample for tensile test (a) line diagram with dimensions (b) sample prepared

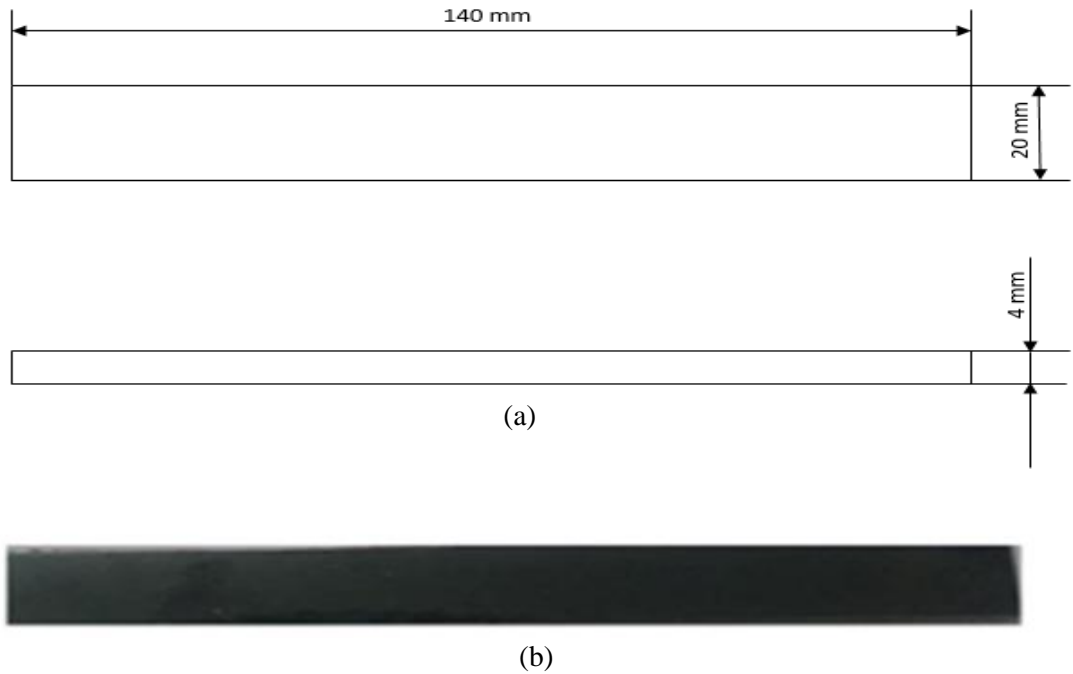


Figure 3.3 Nanocomposite sample for Flexural test (a) line diagram with dimensions (b) sample prepared

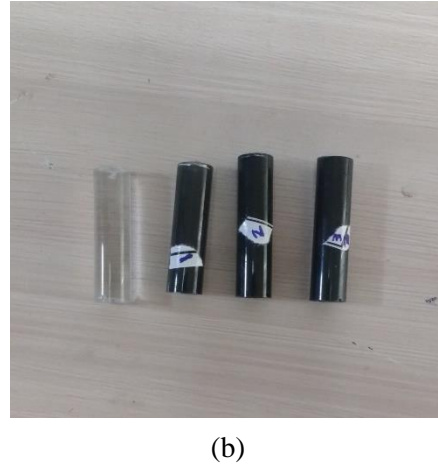
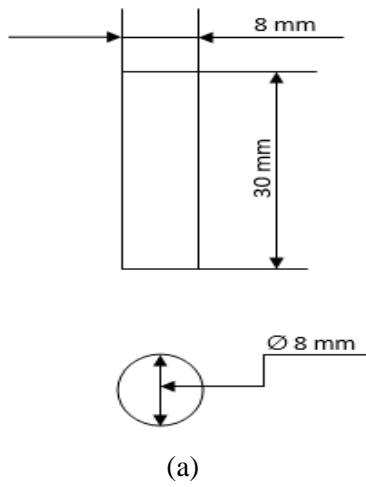


Figure 3.4 Nanocomposite samples for dry sliding friction test (a) line diagram with dimensions (b) sample prepared

3.3 Characterization of the Composites

3.3.1 Density and void content

The actual density of the composites was determined by using the equations 3.1 and 3.2 given below.

$$S_c = \frac{W_o}{W_o + (W_a + W_b)} \quad (3.1)$$

Where S_c = specific gravity of the composite,

W_o = weight of the sample,

W_a = weight of the bottle + kerosene,

W_b = weight of the bottle + kerosene + sample.

$$\rho_{ca} = S_c \times \rho_k \quad (3.2)$$

Where ρ_{ca} = actual density of composite

ρ_k = density of kerosene.

From the following equation 3.3, the theoretical density of the composite is determined in terms

of weight fraction;

$$\rho_{ct} = \frac{1}{\frac{w_f}{\rho_f} + \frac{w_m}{\rho_m}} \quad (3.3)$$

In the above equation ‘w’ is the weight fraction, ‘ρ’ represents density, suffix ‘f’, ‘m’ and ‘ct’ represent filler, matrix, and composite materials respectively.

The void percentage of composite is calculated as per ASTM D-2734-70 standards. The volume fraction of voids (V_v) in the composites was calculated by using equation 3.4

$$V_v = \frac{\rho_{ct} - \rho_{ca}}{\rho_{ct}} \quad (3.4)$$

Where, “ ρ_{ct} ”= theoretical density “ ρ_{ca} ”=actual density of composite.

3.3.2 Tensile testing

The tensile test for the specimens was conducted according to ASTM D 3039-76 standards. The gauge length, gauge width, and thickness of the specimen are 75mm × 10mm × 4 mm. The strain rate for all the specimens for tensile loading is 2mm min⁻¹. The tensile strength value is considered from the average of Five specimen values and the tensile strength is calculated using equation 3.5.

$$\text{Tensile strength} = \frac{P}{bh} \text{ MPa} \quad (3.5)$$

Where

P =Maximum load (N), b= width of the specimen (m), h= Thickness of the specimen (m).

Testing of the specimen was carried out on a hydraulic universal test machine with a load cell capacity of 100 kN. The instrument was made by M/S Jin Ahn Testing company, China and the model number is WDW-100S. which is shown Fig. 3.5.



Figure 3.5 Universal Testing Machine

3.3.3 Three-point bend test

A 3-point bending test for the composites is done according to ASTM D 790 standard method using Universal testing machine (UTM). All the specimens are tested at room temperature at a constant moving rate of 2 mm min^{-1} . The size of the specimen used for the test is $140\text{mm} \times 20\text{mm} \times 4\text{mm}$. Flexural strength is calculated using the following equation 3.6:

$$\text{Flexural strength} = \frac{3FL}{2bd^2} \quad (3.6)$$

Where F = Ultimate failure load (N), L = Span of supports for the specimen on the machine (m), b = Specimen width (m), d = specimen thickness (m)

3.3.4 Microhardness

Vickers hardness test method was used to measure micro-hardness of the composites. By the penetration of right pyramid form of diamond indenter, hardness value was measured for the sample.

Vickers hardness value is measured using the following relation:

$$\text{Vickers hardness number (HV)} \approx \frac{1.854P}{d^2} \text{ (kg/mm}^2\text{)}$$

where P is load applied in kgf and d is the mean of two diagonals of indentation in mm.

Microhardness was measured using Leitz microhardness tester according to ASTM E384 standard. The instrument is made by Shimadzu Corp., Japan and the model is HMV-G20ST, which is shown in Fig. 3.6.



Figure 3.6 Photograph of Microhardness tester

3.3.5 Erosive wear test

Solid particle erosive wear test experiments on composites were conducted as per standard ASTM G76 method on the erosion test rig. This erosion test rig is drawn schematically in Fig. 3.7. The equipment consists of a compressor for accelerating sand particles by supplying compressed air into flow stream of sand particles, a conveyor belt for feeding particles and also controls sand particle flow moment, a mixing chamber for mixing sand particle and air, an adjustable sample holder and a swivel head for adjusting the angle of impact of sand particles on specimen and for maintaining the specimen at nozzle distance. An electronic weighing balance was used to determine the weight of the sample before erosion and after erosion. The accuracy of the weighing balance was $\pm 0.01\text{mg}$. Eroded samples before weighing were cleaned with a flash of compressed air, so that any loosely adhering debris would be removed. The erosion rate of samples was measured in terms of the weight of composite specimen removed per unit weight of the erodent impacted during the experiment.

The rate of erosion wear is expressed in terms of $\frac{\Delta w_1}{\Delta w_2}$

where represents Δw_1 composite weight loss and represents Δw_2 erodent weight used for testing a sample.

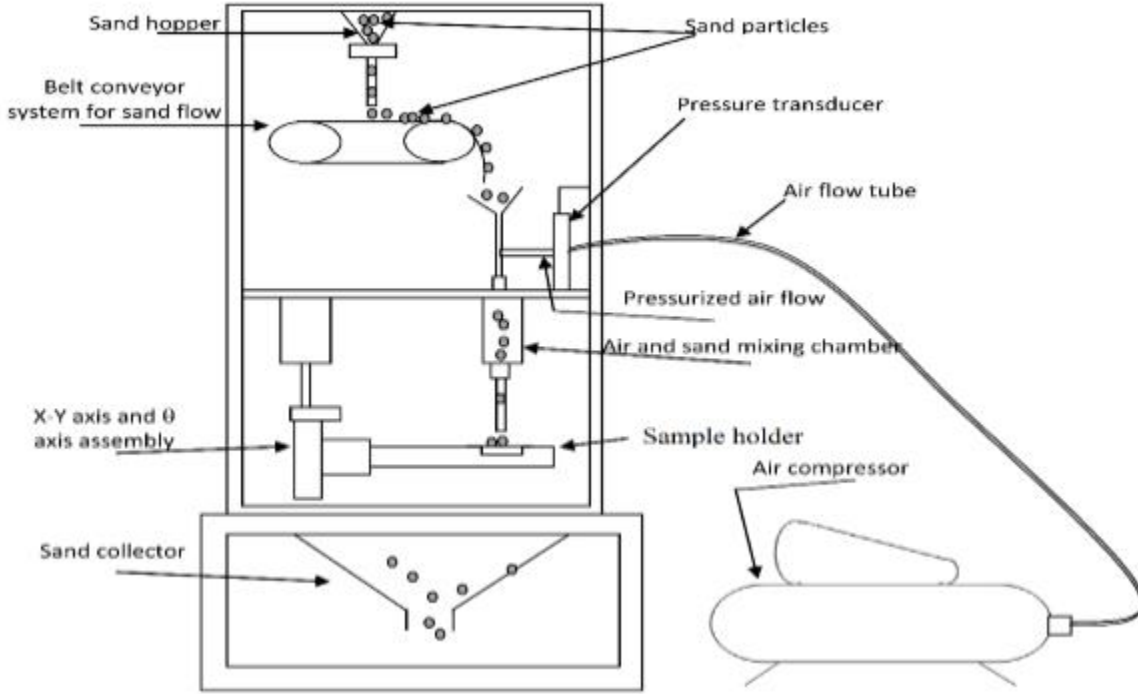


Figure 3.7 Schematic representation of solid particle erosion experimental setup

3.3.6 Pin on disc wear test

Wear properties of the composites were measured by conducting dry sliding wear tests on pin on disc at room temperature as per ASTM standards. Schematic diagram of pin on disc wear test is shown in Fig. 3.8 [136]. Samples that are to be tested were glued to the pin of dimensions 5mm square cross section and 24 mm length. These samples come in contact with the surface of the rotating carbon steel disc and treated as counter surface to the test samples. After testing, samples are cleaned to remove any debris present. Four samples are taken for every trial. Before and after testing, the weight of the samples with pin is measured using electronic measuring machine, which is having an accuracy of 0.01mg. The difference in weight of the sample before and after testing was taken as wear loss due to sliding. Loss in volume of the specimen can be measured using density of the specimen. Finally wear rate can be measured as follows:

$$W_s = \frac{\Delta V}{(P \times d)} \quad (3.7)$$

Where ΔV is loss in volume in mm^3 , P is load in Newton and d is sliding distance in mm.

Frictional force was measured from system monitor directly. Coefficient of friction can be measured as follows:

$$COF = \frac{\text{Frictional Force}}{\text{Normal Load}} \quad (3.8)$$

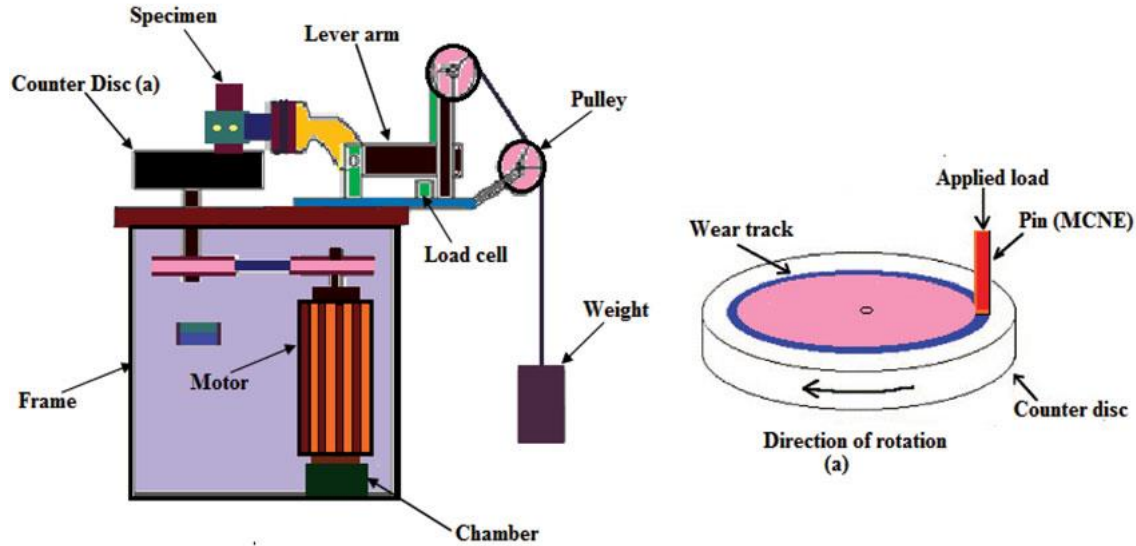


Figure 3.8 schematic diagram of pin-on-disc apparatus [136]

3.3.7 Scanning Electron Microscope

Worn surface morphology of selected composites was observed by using a “scanning electron microscope (SEM)”. Before microscopic examination, the worn surfaces of the samples were coated with gold Particles. SEM was made by Tescon and the model is VEGA 3 LMU, which is shown in Fig. 3.9



Figure 3.9 Scanning Electron Microscope

3.4 Results and Discussion

3.4.1 Void fraction of composite samples

The amount of void content present in the composite samples was determined as per ASTM D-2734-70 standard method. The void fraction present in the sample is given by the equation below:

$$V_v = \left(\frac{\rho_t - \rho_a}{\rho_t} \right) \times 100 \quad (3.9)$$

Where ρ_t is theoretical density of a composite, ρ_a is actual density of a composite.

The procedure for measuring theoretical and actual density was given by Shanti Kiran Zade et al.,[108] Theoretically calculated density, experimentally measured actual density and void content of nano composites is given in Table.3.4. From the results, at higher percentage of addition of particles has more amount of void content. The main reason for the formation of void is due to the formation of bubbles during the stirring process, to mix particles in to the epoxy resin. At higher percentages, due to the agglomeration of particles, the void content is further increasing. The results show at 2 wt% the void content less.

Table 3.4 Theoretical density, actual density and void contents of the composites prepared

| Sl.No | Composite sample | Theoretical density (g/cc) | Actual density (g/cc) | Void content (vol%) |
|-------|------------------|-------------------------------|--------------------------|---------------------|
| 1 | W1 | 1.16 | 1.123 | 3.189 |
| 2 | W2 | 1.17 | 1.136 | 2.905 |
| 3 | W3 | 1.18 | 1.139 | 3.474 |
| 4 | W4 | 1.19 | 1.144 | 3.865 |

3.4.2 Tensile properties of Epoxy-WC nano composites

The tensile test for the composites was carried out for epoxy without addition of filler and WC filled epoxy as per standard ASTM D638 method. The results are plotted as WC particle wt% versus Tensile strength (MPa) shown in Fig.3.10. Tensile strength gradually increases up to 2 wt% of filler and then it decreases due to the agglomeration of nanoparticles. The same phenomenon was observed in void content also.

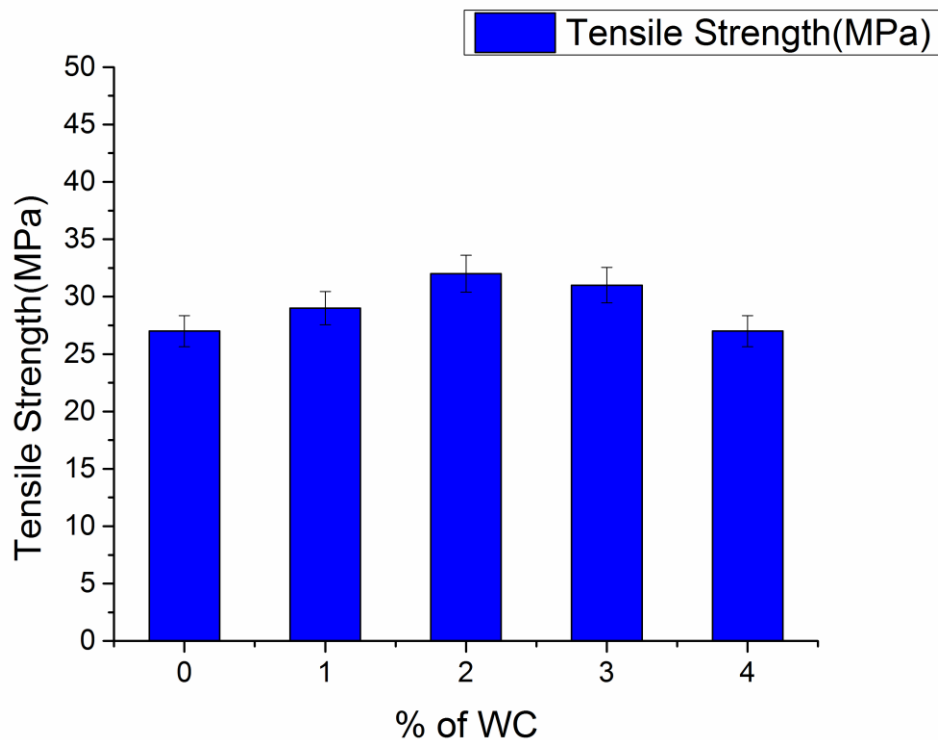


Figure 3.10 Effect of Tungsten carbide particles wt% on tensile strength of epoxy nano composites

3.4.3 Flexural Properties of the Epoxy-WC nano composites

The flexural test for the composites was carried out for epoxy without addition of filler and WC filled epoxy as per standard ASTM D790 method. The results are plotted as WC particle wt% versus flexural strength (MPa) and shown in Fig. 3.11. Bending strength of epoxy nanocomposites is increased up to 2 wt% and then it decreases. The reason for decrease in bending strength would be formation of voids in the composites and also due to agglomeration of particles.

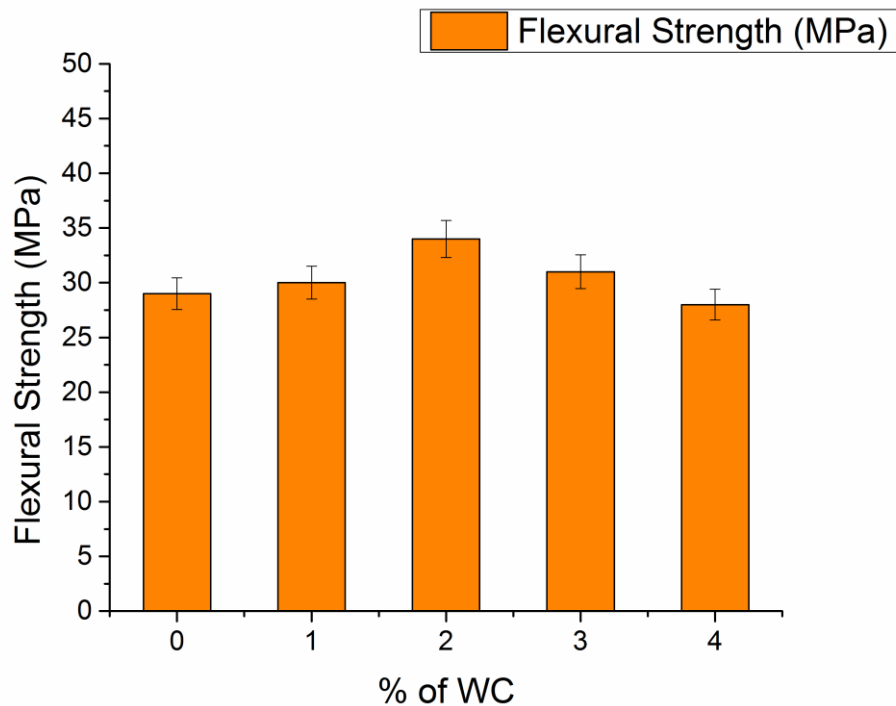


Figure 3.11 Effect of Tungsten carbide particles wt% on flexural strength of epoxy nano composites

3.4.4 Hardness of epoxy/WC nanocomposites

In the current section, hardness of WC nanoparticles filled epoxy matrix nanocomposites have been discussed. A load of 10kgf was used to conduct Vickers Hardness test on the samples. With the variation of filler content in the epoxy, the variation of hardness is shown in Fig. 3.12. It was observed that incorporation of 2 wt% WC nanofiller achieved higher hardness, while at 3 wt% and 4 wt% WC filler, there was reduction in hardness. By the addition of particles from 1 wt% WC to 2 wt% WC, trend shows an increase in hardness, this corresponds to uniform dispersion of nanofiller. While at 3 wt% and 4 wt% of WC particles, the reduction of hardness is due to weak adhesion between WC nanofillers and epoxy matrix and also agglomeration of particles due to increase of particle weight percentage.

Table 3.5 Hardness of Epoxy nanocomposites with addition of different wt% of WC nanoparticles

| Sample name | Vickers Hardness number (HV) |
|--------------|------------------------------|
| Neat epoxy | 17.4 |
| Epoxy+1% Wc | 23.1 |
| Epoxy+2% Wc | 25.4 |
| Epoxy +3% Wc | 21.3 |
| Epoxy +4% Wc | 20.2 |

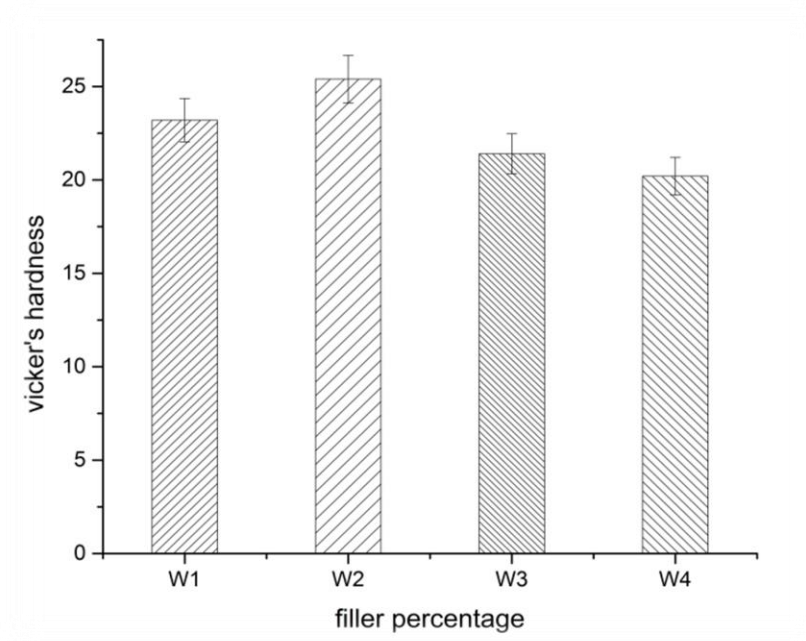


Figure 3.12 Hardness of epoxy nanocomposites with addition of different wt% of WC nanoparticles

3.4.5 Sand Erosion Wear Test

In this section, tribological characterization of nanocomposites has been reported. The influence of nanoparaticles, which change the erosive wear properties of epoxy, has been studied. Nowadays, when compared to other conventional coatings, nanofiller reinforced polymer composite coatings are found to have uniform protection of coating surfaces for abrasive resistance and enhanced wear properties [119, 127]. For studying the effect of filler weight percentage on erosive wear of nanocomposite, the composite specimens of varying filler weight percentage were subjected to erosion test for different impact angles and at a constant

impact velocity of 86m/s. Fig. 3.13 plots the change in the rate of erosion of epoxy resin reinforced with a range of weight fractions of WC for definite impact angles ranging from 30^0 to 90^0 . Except for neat epoxy of all other nanocomposites, the rate of erosion at impact angles (45^0 and 60^0) were in excess of those at impact angles (30^0 and 90^0) and utmost erosion rate was at an impact angle of 45^0 . However, for neat epoxy, erosion rate was maximum at 30^0 impact angle. In general, based on previous research, for any material, if the maximum rate of erosion occurs at low impact angles (i.e. 15^0 - 30^0) then the erosion failure mode of a material is ductile in nature, On the contrary, if the maximum rate of erosion occurs at higher impact angles (i.e. 70^0 - 90^0) then the erosion failure mode of a material is brittle in nature [111-113]. From the results, irrespective of filler weight percentage, maximum erosion rate for all the specimens was observed at an impact angle of 45^0 . So, erosive wear behaviour for these composites is semi ductile in nature, but for neat epoxy, the behaviour is ductile in nature. The change in nature from ductile to semi-ductile by the addition of particles is due to the brittle nature of tungsten carbide particles. This type of change in erosion wear behaviour by the addition of carbon fiber to the neat epoxy was observed by [113]. From the test it was evident that the erosion resistance can be enhanced with the addition of WC nano filler into epoxy resin which is shown in Fig. 3.13. It was still observed that 2 wt% filled epoxy resin samples showed maximum erosion resistance compared to 1 wt% and 3 wt% WC filled epoxy nanocomposites. Higher erosion rate at 3 wt% of filler is due to reduction in hardness.

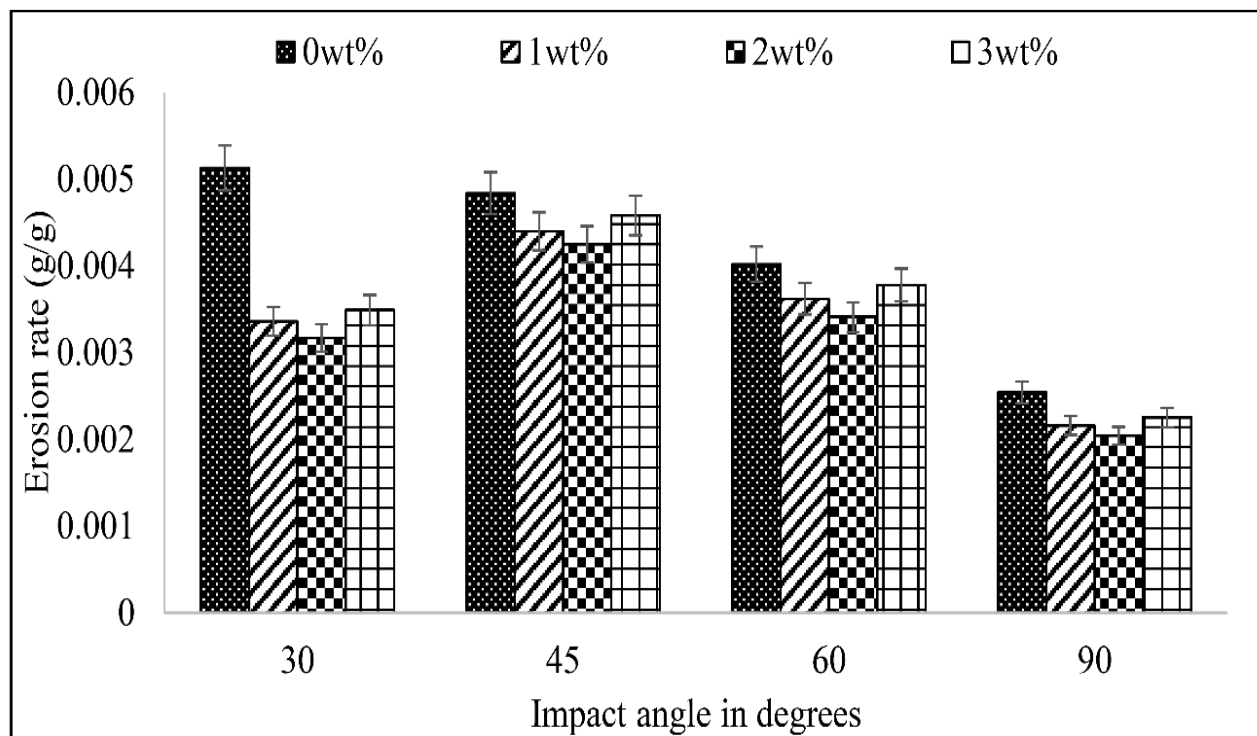


Figure 3.13 Erosion rate of epoxy resin filled with various WC weight fractions, for different impact angles and at an impact velocity of 86m/s

Material removal at high impact speed of solid particles present in the surrounding environment of equipment is one of the major causes of failure occurring in materials. Fig. 3.14, Fig. 3.15 and Fig. 3.16 represent the loss of material due to erosion of composites, incorporated with various WC contents for two levels of impact velocity. Erosive particle impact velocity has a strong impact on wear process. From the results it was concluded that erosive rate was higher at higher impact velocity caused by high kinetic energy of the impending particles [130]. The same type phenomena i.e., increase of erosion rate with increase of velocity was observed by [123]. However, irrespective of the particles impact velocity, erosion behaviour of composites at various weight percentages of Tungsten carbide particles is the same.

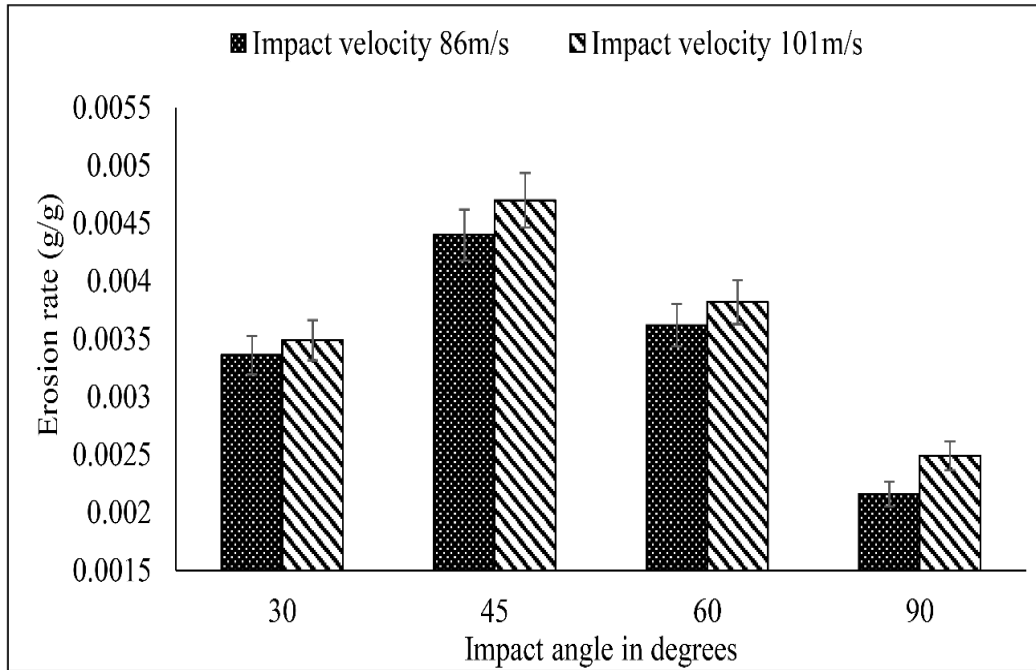


Figure 3.14 shows Erosion rate of nano-composites at an impact velocity of 86m/s and 101m/s for 1 wt%

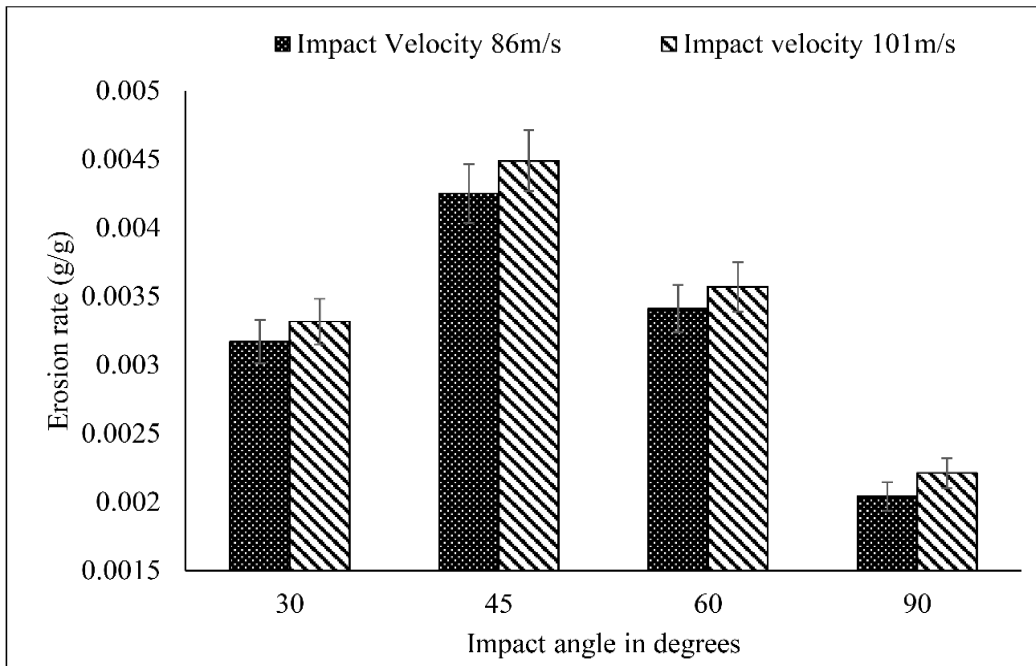


Figure 3.15 shows Erosion rate of nano-composites at an impact velocity of 86m/s and 101m/s for 2 wt%

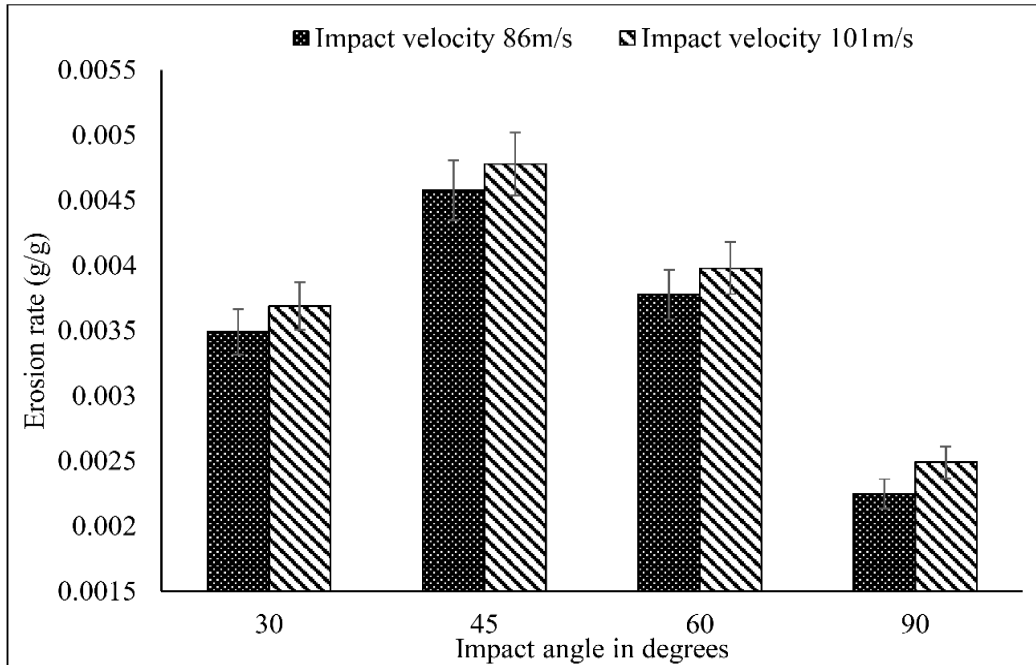


Figure 3.16 shows Erosion rate of nano-composites at an impact velocity of 86m/s and 101m/s for 3 wt%

3.4.6 Effect of filler loading on friction wear

Wear rate of WC nanoparticles reinforced epoxy is shown in Fig. 3.17. It was observed that, with the incorporation of WC nanoparticles, epoxy matrix nanocomposites wear rate decreased significantly. However, for 3 wt% WC wear rate increases slightly when compared to the other, 1 wt% and 2 wt% WC nanofiller, this is due to the agglomeration of nanoparticles for incorporation of higher percentage of particles. At 2 wt% WC nanofiller, better wear resistance has been achieved because of uniform dispersion. Bond strength between filler and matrix plays a main role in enhancing wear resistance. Also, the presence of WC particles on the counter surface, which act as a transfer layer and effective barriers, prevents large-scale fragmentation of epoxy.

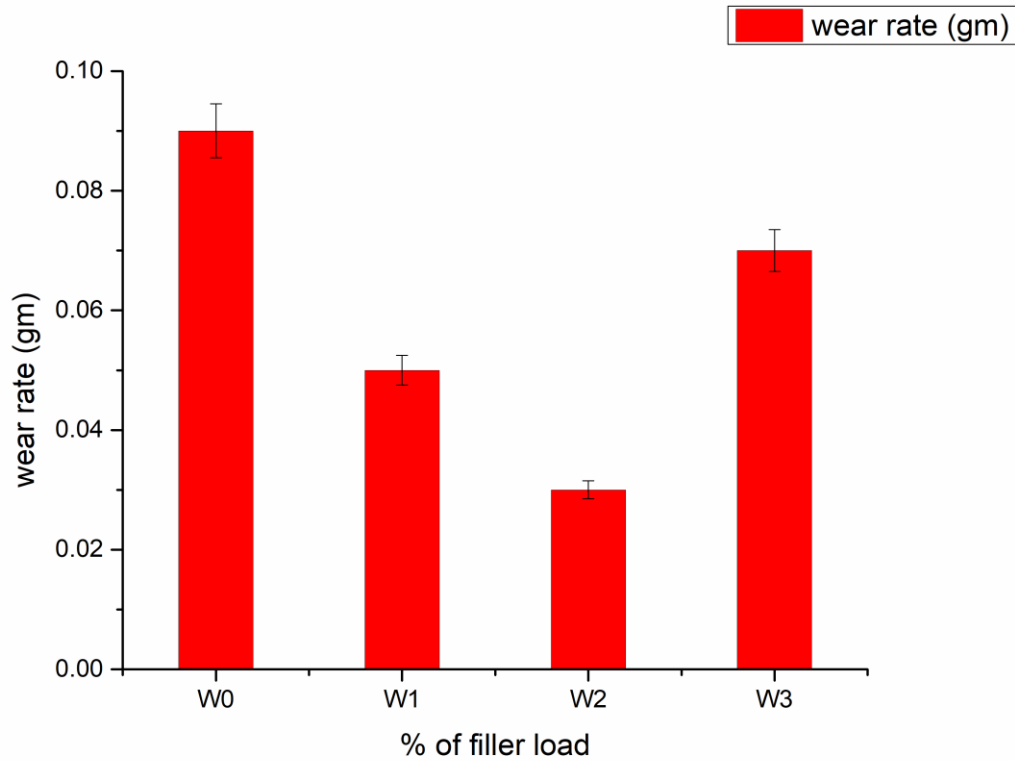


Figure 3.17 Wear rate of nano-composites for different filler loading at a constant speed of 1m/s and at a normal load 10N

3.4.7 Variation of wear rate with changing in sliding speed

To find the effect of change in sliding speed on the wear rate, wear test was conducted for different sliding speeds of 1m/s, 2m/s and 3m/s. It was observed that with an increase of speed, wear rate increases, which is shown in Fig. 3.18. With an increase in sliding velocity and/or normal force, ample frictional heat energy accumulates around the contact area, making the polymer composite samples softer at elevated temperatures and enabling easier deformation during wear.

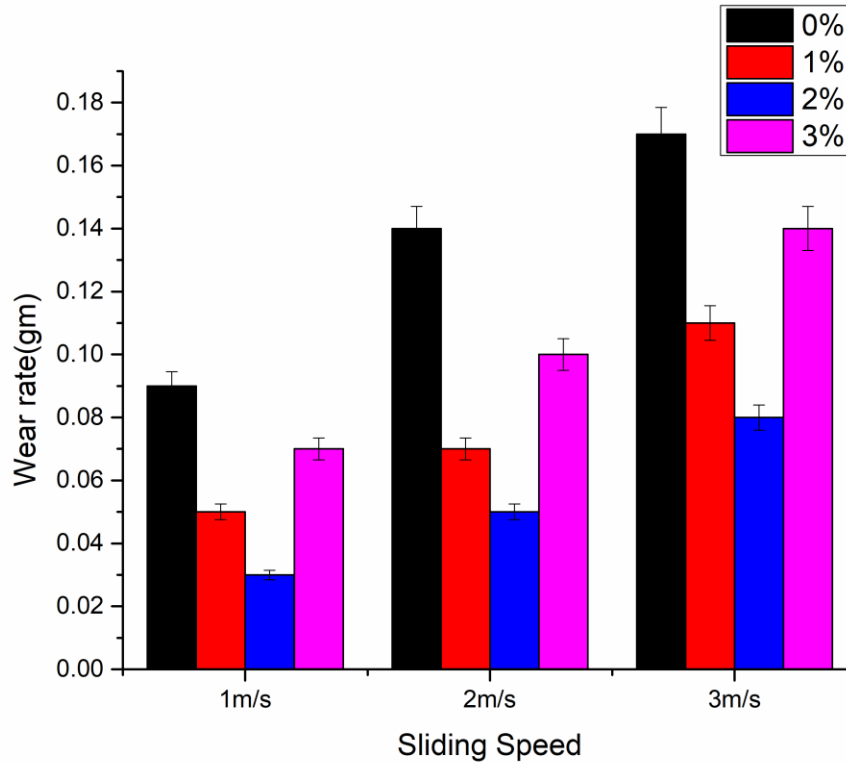


Figure 3.18 shows Variation of wear rate with changing in sliding speed at a constant normal load of 10N

3.4.8 Variation of wear rate with changing in Normal load

To find the effect of change in applied normal load on the wear rate, wear test was conducted for different normal loads of 10N, 15N and 20N. It was observed that with an increase of load, wear rate increases as shown in Fig. 3.19. The increase in normal load will in turn increase the contact stresses, which cause brittle failure of carbon fibers on the surface of the specimen and severe material removal due to faster removal of epoxy from the surface of the specimen, leaving the top layer of fibers/filler particles exposed to the environment. As the load increases, the plastic zones are enlarged leading to an increase in frictional forces. These frictional forces would in turn cause a temperature rise, a decrease in the hardness of the matrix surface because of which wear rate increases.

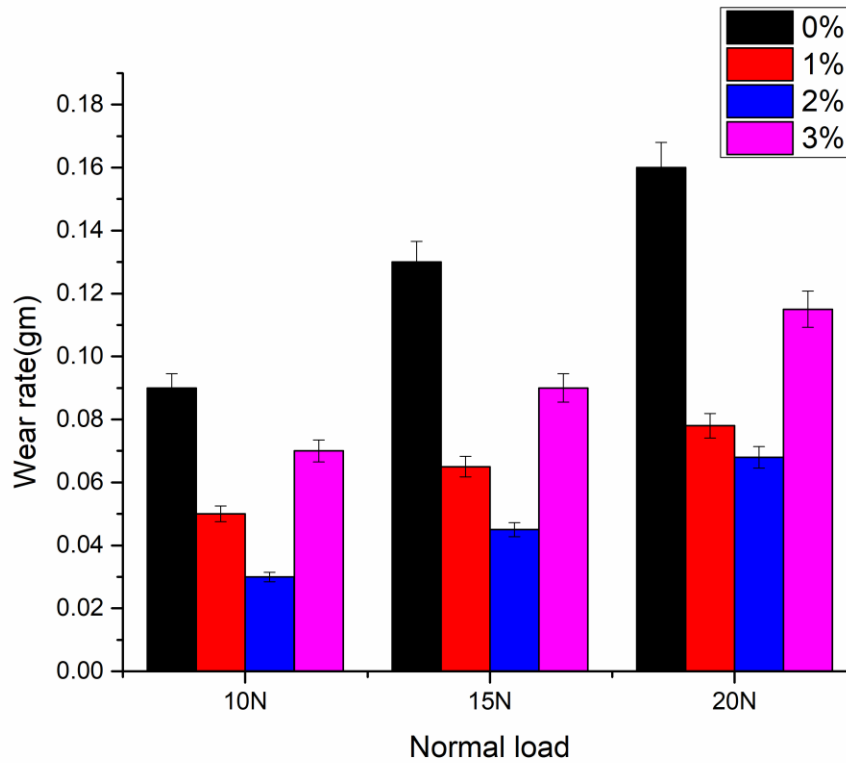


Figure 3.19 Variation of wear rate with changing in normal load at a constant sliding speed of 1m/s

3.4.9 Effect of filler loading on Coefficient of Friction (COF)

Coefficient of friction on addition of varying weight percentage of WC nanoparticles reinforced epoxy is shown in Fig. 3.20. It was observed that, with the incorporation of WC nanoparticles, epoxy matrix nanocomposites COF increased. However, for 3 wt% WC, COF decreases slightly due to poor dispersion of particles in epoxy at higher volume.

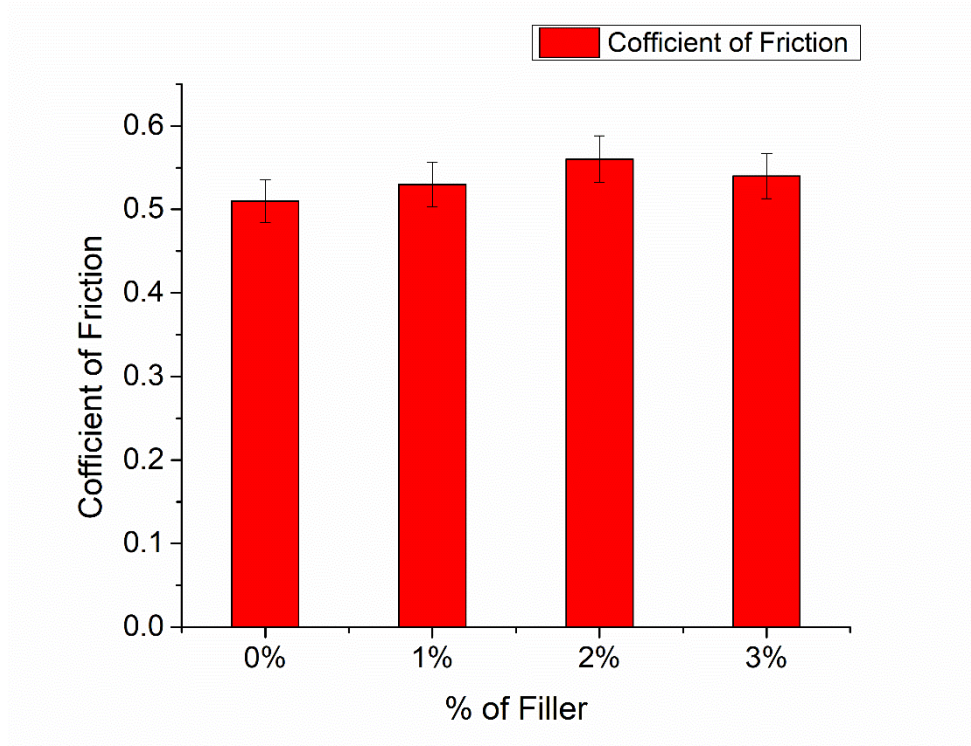


Figure 3.20 Coefficient of friction of nano-composites for different filler loading at a constant speed of 1m/s and at a normal load of 10N

3.4.10 Variation of COF with changing in sliding speed

To find the effect of change in sliding speed on the COF, wear test was conducted for different sliding speeds of 1m/s, 2m/s and 3m/s. It was observed that with an increase of speed, COF decreases, which is shown in Fig. 3.21. With an increase in sliding speed, more heat is generated at the contact surface resulting in softer and makes easy to deform. Hence friction decreases with sliding speed.

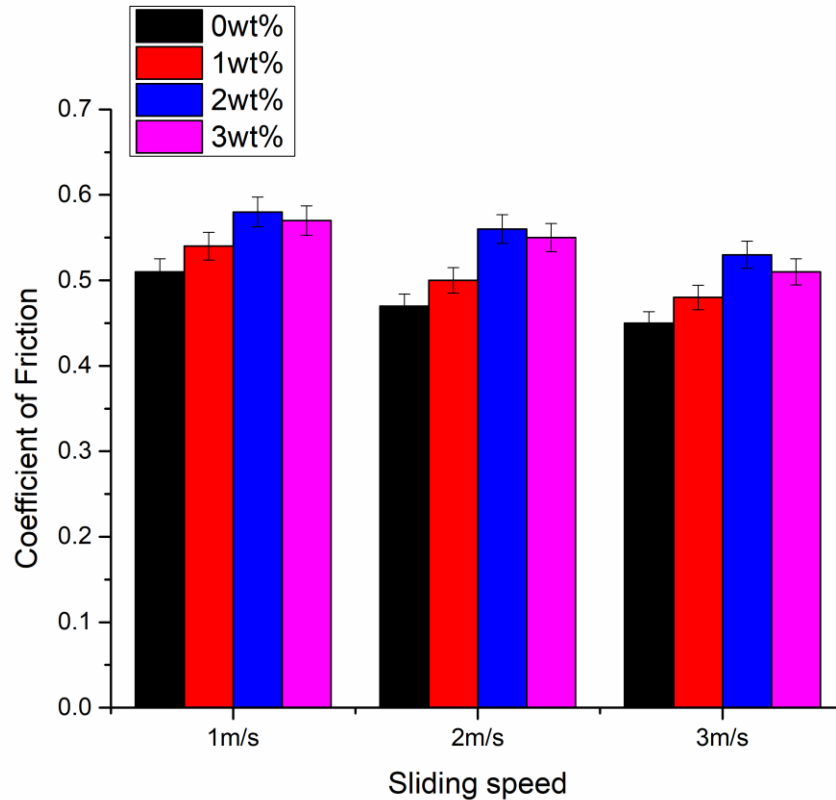


Figure 3.21 Variation of coefficient of friction with changing in sliding speed at a constant normal load of 10N

3.4.11 Variation of COF with changing in Normal load

To find the effect of change in applied normal load on the COF, wear test was conducted for different normal loads of 10N, 15N and 20N. It was observed that with an increase of load, COF increases, as shown in Fig. 3.22. This may be because during sliding under high applied normal loads, high friction is generated on the composite pin and the disc contact surface, which in turn may increase the actual contact area and contact temperature with increased applied normal load. Due to this friction, heating is generated, that results in an increase in frictional coefficient.

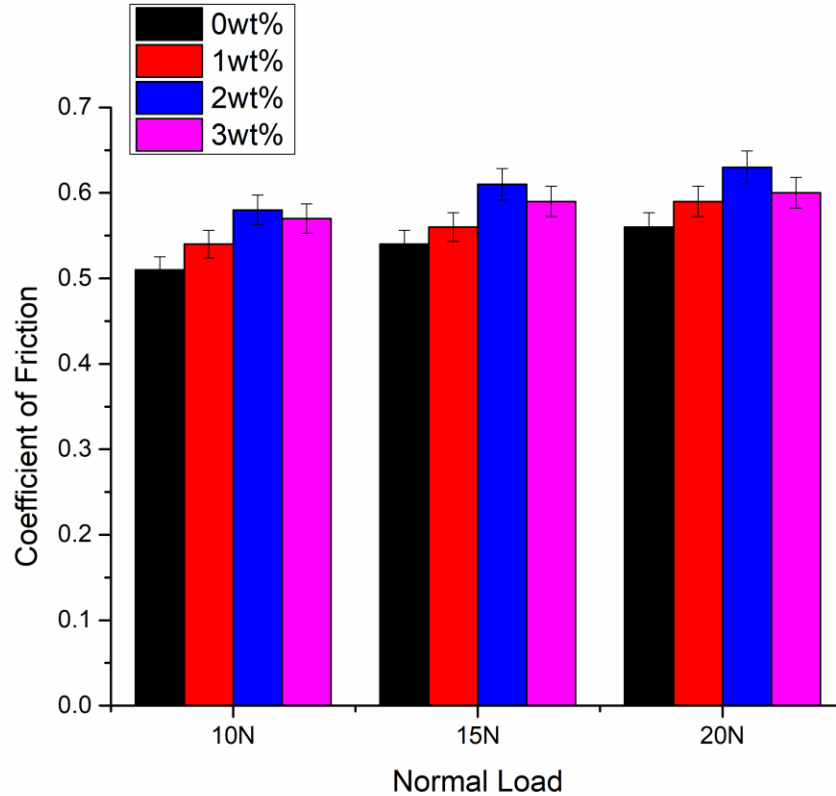


Figure 3.22 Variation of coefficient of friction with changing in normal load at a constant sliding speed of 1m/s

3.4.12 Morphological Studies of Eroded Samples

Eroded surface was observed using SEM, which is shown in Fig.3.23. In general, Basic erosion wear, a mechanism of polymer composites, is as follows: there is micro crack on matrix surface to start with, followed by de-bonding of matrix and finally removal of material. SEM image in Fig. 3.24 shows how the impact of solid particles on composite causes matrix breakage micro cracks on the composite. Crater and flake type Debris of matrix on the sample surface were also observed. Zhou et al. [135] also observed similar type of wear mechanisms.

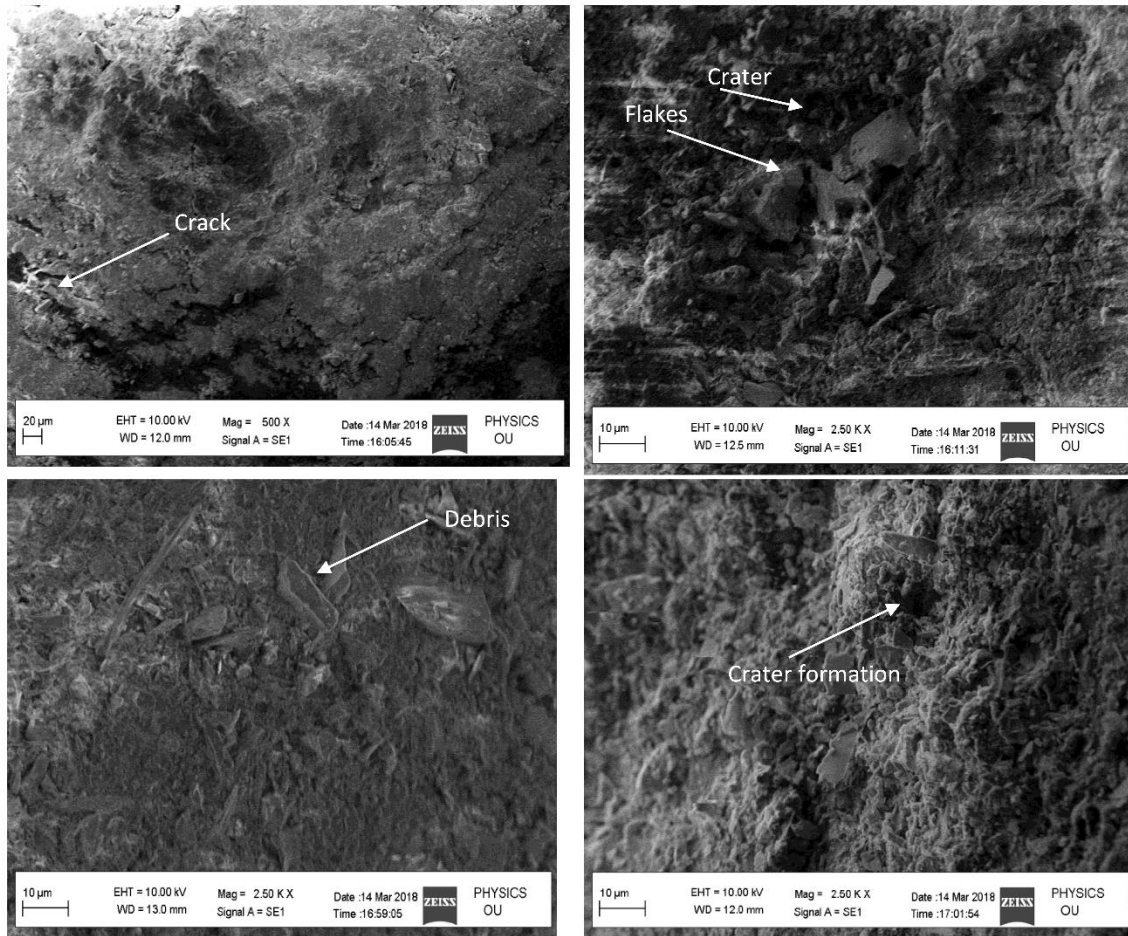


Figure 3.23 SEM images of worn surfaces at particle impact angle of 60° and at particle impact velocity of 86m/s

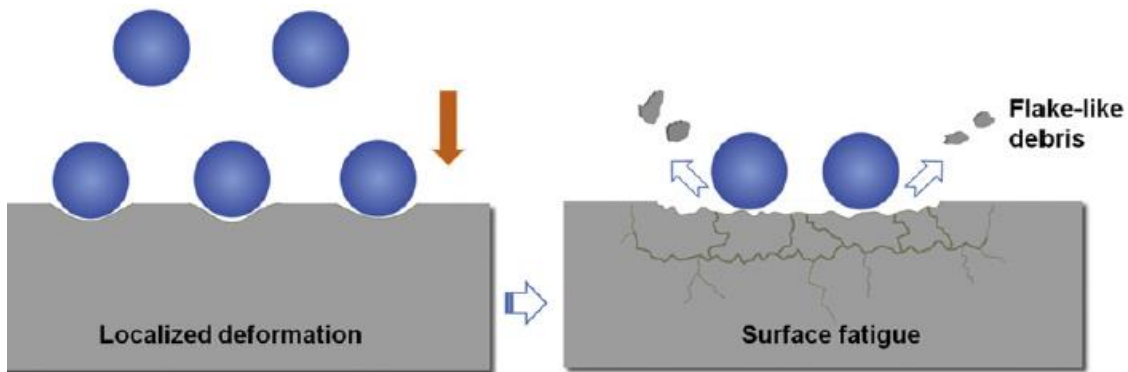


Figure 3.24 Schematic illustration of the erosion mechanism [135]

3.4.13 Surface Morphology of friction wear surfaces

The main evidence for the wear operation can be obtained from SEM images of worn-out surfaces of the specimens after sliding. Fig. 3.25 shows SEM images of specimen worn surfaces,

which underwent sliding. From the Fig. 3.24(a), it was observed that bulky wear debris was left on the surface of specimen, is mainly due to the fragmentation of epoxy matrix. Small cracks were also observed on the surface of the specimens which underwent sliding. Deep grooves were formed due to high normal load, which can be observed in Fig 3.24(c). From Fig 3.24(b) it is observed that excess wear rate occurred at 3.5 wt% of filler.

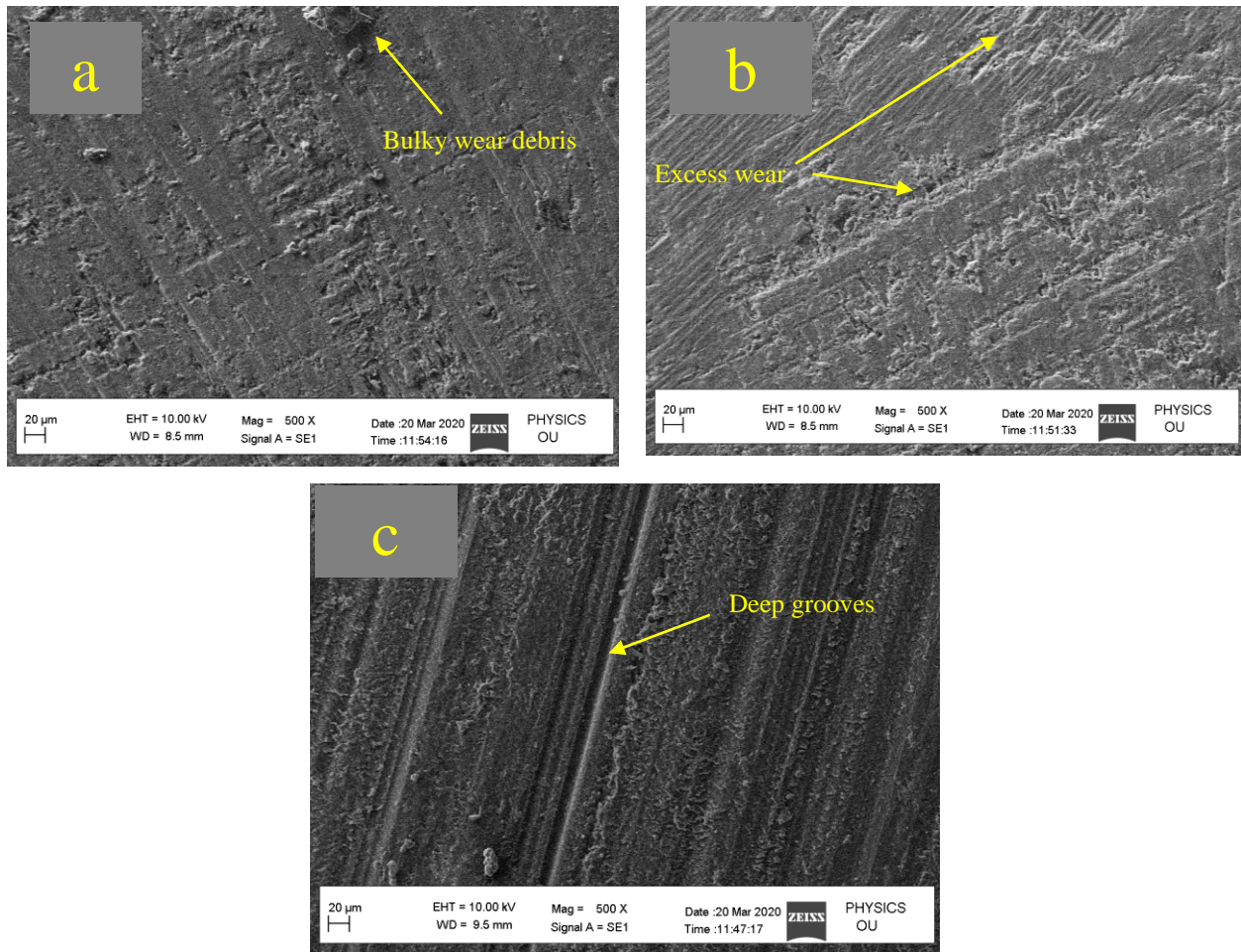


Figure 3.25 SEM images of worn surface a) 1 wt% at a speed 1m/s and load 10N b) 3 wt% at speed 1m/s and load 10N c) 2 wt% at a speed 1m/s and load 20N

3.5 Conclusions

- At 2 wt% addition of WC particles showed better tensile strength when compared to neat epoxy and other wt% of particles. Compared to neat epoxy it increased from 24 MPa to 33 Mpa.
- Flexural strength also has maximum value at 2 wt% of WC filler.

- At higher weight percentage, on the addition of particles, i.e. more than 2 wt%, due to agglomeration of particles, both tensile and flexural strength decreased.
- Density and void content at addition of different weight percentages of particles to neat epoxy are also discussed.
- Compared to neat epoxy, the addition of filler hardness value increases from 17.4 to 25.4 in Vicker's hardness value.
- With increase in filler volume in neat epoxy up to 2 wt%, erosion rate decreases, irrespective of impact angle.
- It was observed that erosion is lower at 90⁰ impact angle for any given epoxy/WC composite.
- Erosion rate increases with increase of impact velocity, irrespective of filler loading and impact angle.
- Friction wear decreases with increase of filler loading up to 2 wt% in neat epoxy.
- Compared to neat epoxy, with the addition of filler to epoxy, friction wear reduces from 0.87 to 0.3 gm.
- Wear rate increases with increase of sliding speed and also with increase of normal load.
- Coefficient of friction increases with an increase in filler loading up to 2 wt% in neat epoxy.
- Compared to neat epoxy, with the addition of filler to epoxy, coefficient of friction increases from 0.51 to 0.58.

Chapter 4

Mechanical and Tribological properties of Carbon fiber reinforced epoxy polymer composites

4.1 Introduction

Since 1940s, fiber reinforced plastics (FRP) have been widely used in industry due to their high corrosion resistance and also for the superior specific strength. Initially glass fiber reinforced (GFRP) composites were deployed; however, later on, new fiber reinforcements such as graphite, aramid and carbon fibers have amplified their significance. Growth of these fibers helps in the use of FRP in industrial applications. For example, bridges, transportation, load bearing parts such as tanks and buildings use them extensively [137,138]. It is necessary to check the longevity of industrially used FRPs by observing its degradation mechanism and behavior under different conditions such as erosion, corrosion and stress etc. There are many equipments and machine parts in the automotive and machine tool industry, which are vulnerable to erosive environment conditions. for example, hydraulic pipes, pipes for pneumatic transportation [139, 140], impeller and nozzles for sand blasting facility [141], high velocity vehicle nose, vessels for catalysis and fluidized bed vessels internal surfaces, helicopter blades and plane propellers [142], etc. Several of them are made of fiber composites. This study focuses on fibrous composites that are likely to be damaged due to sand erosion under environmental conditions. There are several literature reports which discuss fiber composite's erosive behavior as a function of impact velocity [143-145], fiber orientation [146-149], fiber volume [146, 150, 151]. Although various types of fiber reinforced plastics are used, only few papers have been published in, on the effect of fiber orientation and fiber volume on the damage caused by sand erosion.

The current section deals with the preparation of carbon-epoxy polymer composites, and analysis of its tensile strength and Erosion wear behaviour of the composites at different test conditions, such as particle impingement angles and particle impingement velocities. Finally, worn surfaces were examined using SEM; also, erosion wear mechanisms were discussed.

4.2 Materials and Methods

4.2.1 Materials

The properties of epoxy and hardener are mentioned in section 3.1.2.1. The carbon fabric of T-300 PAN based is used in the polymer matrix composites is shown in Fig. 4.1. In the present investigation, 8H satin weave carbon fabric supplied by Ram Composite Products Hyderabad,

was used. The fibers were cut to sizes 200mm × 100mm from the long sheet. The properties/specifications of carbon fabric are given in Table 4.1.



Figure 4.1 Photograph of Carbon fiber mat

Table 4.1 Properties of PAN based Carbon Fabric

| Characteristic | Specification |
|------------------|----------------------------|
| Aerial Density | $380 \pm 40 \text{ g/m}^2$ |
| Thickness | $0.45 \pm 0.05 \text{ mm}$ |
| Tensile Strength | 3.75 GPa |

4.2.2 Preparation of composites

LY 556 and HY951 were mixed properly in the weight ratio of 10:1. A mechanical stirrer was used for mixing epoxy and hardener. A wooden mold of size 100mm x 100mm x 4mm was used for making composite sheets. Mold release spray was used for easy removal of the sheet. Hand lay-up method was used for making composite sheets. Polymer (mixture of epoxy and hardener) was used for stacking fibre mats together until the required thickness was achieved. After stacking all fibers, ample weight was put on the mold and it was allowed 48 hrs to cure at room temperature. After that the composite sheet were removed from the mold and samples cut for the required dimensions of tensile and erosion testing from the sheets.

4.3 Results and Discussion

4.3.1 Tensile strength of carbon-Epoxy composites for different no. of layers (varying fiber volume)

Tensile strength of carbon-Epoxy composites for different no of layers (varying fiber volume) is given in Table 4.2. It was observed that increase in fiber volume, increases the strength of the composite. But at higher fiber volume, due to the deficiency of resin to wet all the fibers, the strength of the composite is reduced. Maximum Ultimate Tensile strength was observed when the number of layers of fibers in the composite is 5.

Table 4.2 Tensile strength of carbon-Epoxy composites for different no of layers

| Sample specifications | Ultimate tensile strength (MPa) |
|-----------------------|---------------------------------|
| 3 Layers | 260 |
| 4 Layers | 275 |
| 5 Layers | 312 |
| 6 Layers | 286 |

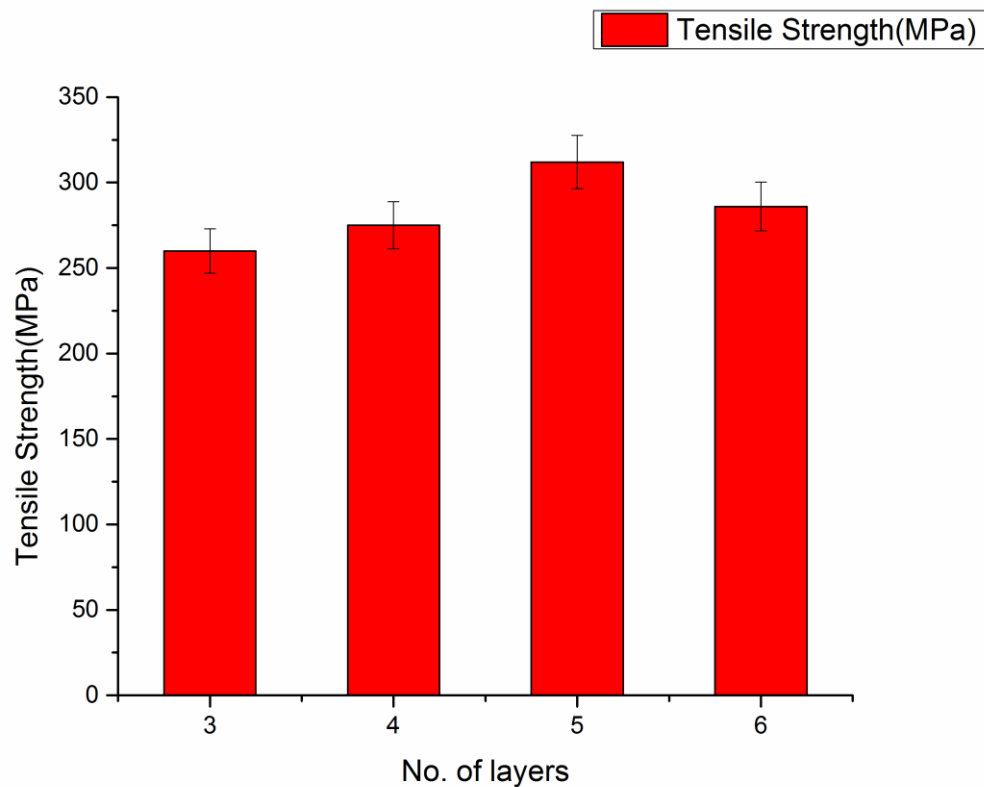


Figure 4.2 Tensile strength of carbon-epoxy composites for different no of layers

4.3.2 Effect of fiber volume on erosion wear of Carbon/epoxy polymer composite

For studying the effect of fiber volume on erosive wear of composite, specimens of 4 mm thickness were made by changing fiber volume to 20%, 25% and 30% and subjected to erosion test at a constant impact velocity of 48m/s and for different impact angles. Angle of impact is the angle between the erodent particle trajectory immediately before impact and eroded surface. In general, based on the previous research, for any material, if the maximum rate of erosion occurs at low impact angles (i.e. 15° - 30°) then the erosion failure mode of a material is ductile in nature.

On the contrary, if maximum rate of erosion occurs at higher impact angles (i.e. 70° - 90°), the erosion failure mode of a material is brittle in nature. The effect of fiber volume on the rate of erosion of carbon-epoxy material is studied, and the results are shown in Fig. 4.3. From the test it is evident that the fiber volume has a major influence on the rate of erosion and with increase of fiber volume, the rate of erosion increases. Irrespective of fiber volume maximum erosion rate for all specimens occurs at an impact angle of 60° - 75° . So, erosive wear is semi ductile in nature.

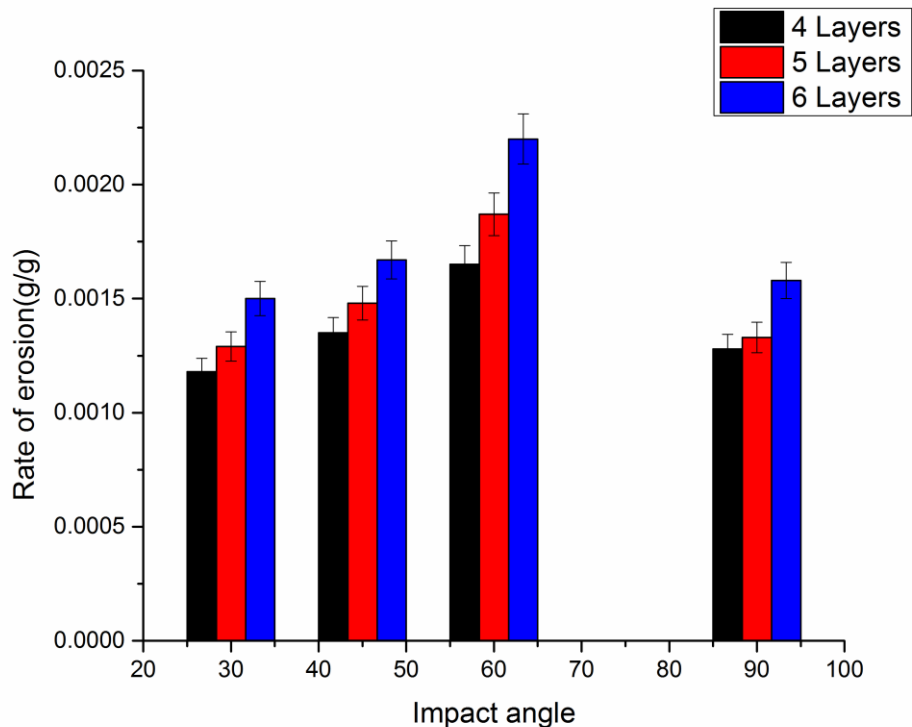


Figure 4.3. Erosion behaviour of carbon-epoxy composites for increase in number of layer of fibres with zero -degree orientation for different impact angles (in degrees).

4.3.3 Effect of fiber orientation on erosion wear of Carbon/epoxy polymer composite

For studying the effect of fiber orientation on erosion rate of composites, composite samples were prepared by changing fiber orientation to 30° , 60° and 90° respectively of 25% fiber volume. Samples of 4mm thickness underwent erosion test at a constant impact velocity of 48m/s and at different impact angles. The results are shown in Fig. 4.4. From the results it is evident that fiber orientation has very low impact on erosion rate. Even though it has low significance, the rate of erosion increases with increase of fiber angle. Whenever fibers are kept at some angle, the horizontal component of impact velocity is divided into two components, hence the rate of erosion is more in samples which have maximum fiber orientation. Irrespective of fiber angle, the maximum rate of erosion occurs at 60° - 75° impact angle.

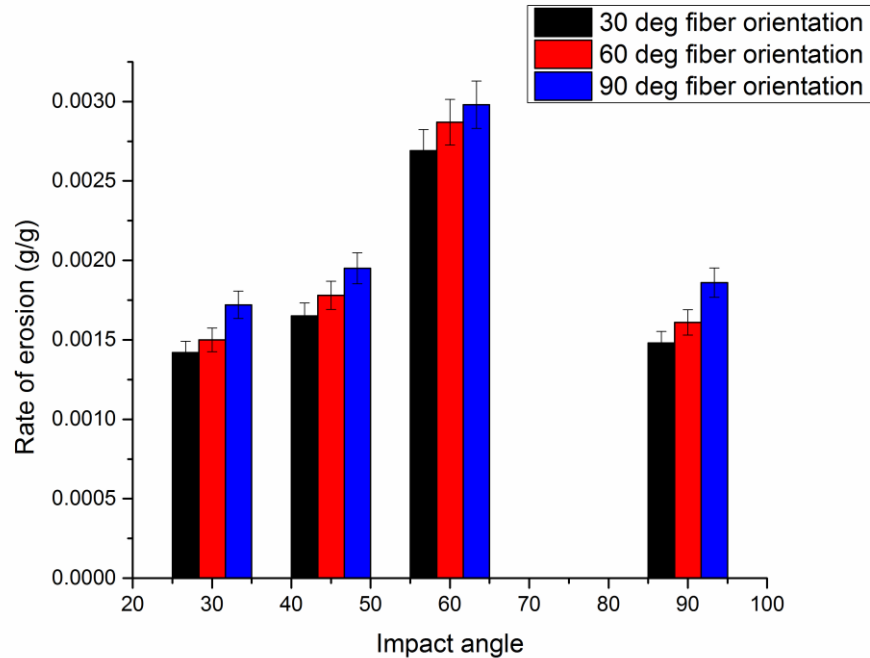


Figure 4.4 Erosion behaviour of carbon-epoxy composites with fibres having various degrees of orientations for different impact angles (in degrees).

4.3.4 Surface morphology of Eroded surface

Eroded surface was observed using SEM. Basic erosion wear mechanism of polymer composites is as follows: there is micro crack on the matrix surface to start with, followed by de-bonding of matrix and fiber; then there is fiber breakage, and finally material removal takes place. SEM image of Fig. 4.5 shows how the impact of solid particles on fibre causes fiber breakage and

hence the bulk of fibers underwent cutting. Detachment of some fibers was also observed. Debris of matrix and fiber on the sample surface was observed. Grooves were formed after the fiber was removed due to cutting.

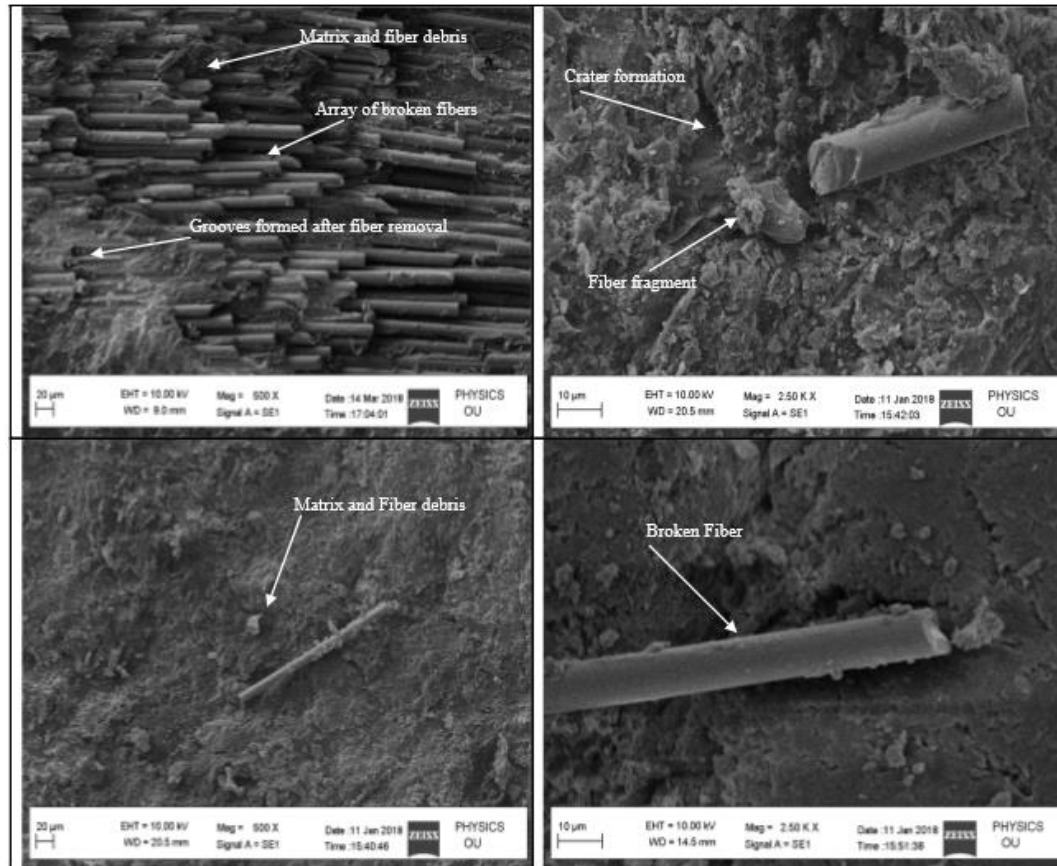


Figure 4.5 SEM images of eroded sample (25% fiber volume, 0° fiber orientation) at 90° impact angle and 48m/s impact velocity

4.4 Conclusions

- Increase in fiber volume in neat epoxy, increases the strength of the composite. But at higher volume due to the deficiency of resin to wet all the fibers reduces the strength of the composite.
- Irrespective of impact angle, with an increase of fiber volume in neat epoxy, the erosion rate increases.
- As the fiber orientation angle in carbon/epoxy increases, the erosion rate also increases. But it has very little significance.
- It was observed that erosion was maximum at 60° impact angle for any given carbon/epoxy composite.

Chapter 5

*Mechanical and tribological properties
of carbon fiber reinforced Tungsten
carbide-epoxy polymer hybrid
nanocomposites*

5.1 Introduction

In the current decade, it is looks promising to prepare epoxy polymer hybrid composites with excellent mechanical and tribological properties by reinforcing them with suitable reinforcements such as fillers or fibers or both in proper quantity. Excellent mechanical characteristics can be obtained by incorporating fibrous reinforcements like graphite, glass, aramid and carbon fibers. Now a days, these fibers are used extensively. Due to the combined properties, FRPCS are effectively used in fabricating so many mechanical products like bearings, brakes, seals, gears, wheels, clutches and cams[157]. Most of the products are subject to tribological loadings such as wear and erosion.

In bearings, carbon fiber reinforced composites are used extensively, without any lubrication. In many cases, two kinds of polymer matrices are used in fabrication of carbon fiber reinforced composite bearings; one is thermosetting matrices like phenol or epoxy, while another is thermoplastic matrices like polyethylene or polytetrafluoroethylene. Even though the composites prepared with thermoplastics show better tribological properties compared to composites that are prepared with thermosetting matrix, the mechanical properties of thermoplastic composites are inferior to that of thermosetting composites. Also, the surface energy, which is important for adhesion to other structure materials is low for thermoplastics. So, thermosetting matrix with carbon reinforcement is prepared for components in which tribological loading is high.

5.2 Materials and Methods

5.2.1 Materials

Epoxy resin, carbon fiber and Tungsten carbide particles are used to fabricate carbon fiber reinforced Tungsten carbide-epoxy polymer hybrid nanocomposites. The specifications of epoxy, hardener and Tungsten carbide are mentioned in section 3.1.2.1. The specifications of carbon fabric are mentioned in 4.2.1.

5.2.2 Preparation of composites

WC nano fillers of known amount were mixed to epoxy resin using mechanical stirrer for 20 minutes for getting uniform dispersion. After that the required amount of hardener (epoxy to hardener by weight 100:12) according to stoichiometry was mixed to resin and it was mixed thoroughly for 10 minutes, using mechanical stirrer. A wooden mould of size 200mm x100mm x 4mm was prepared. Releasing agent was sprayed on the wooden mould surface, so that samples can be removed easily from the wooden mould. Hand lay-up method was used for making composite sheets. Polymer (mixer of epoxy and Tungsten carbide particles) was used for stacking carbon fibre mats together until the required thickness was achieved. After stacking all the fibers, ample weight was put on the mould and it was allowed for 48 hrs to cure at room temperature. After that the composite sheet was removed from the mould and samples cut as per required dimensions from the composite sheets.

5.3 Results and Discussion

5.3.1 Tensile strength of carbon fiber reinforced Tungsten carbide – epoxy hybrid nanocomposites by varying filler volume

Tensile strength of fiber reinforced Tungsten carbide–Epoxy Hybrid Nanocomposites by varying filler volume is shown in Fig. 5.1. The results were plotted between WC filler % versus Tensile strength. It was observed that the addition of filler up to 2.5 wt% increases the strength of the composite. This is due to the good bonding between matrix and fiber, which can be observed in SEM image. SEM image is shown in Fig. 5.10. Compared to neat carbon-epoxy the strength increases from 312 MPa to 402 MPa.

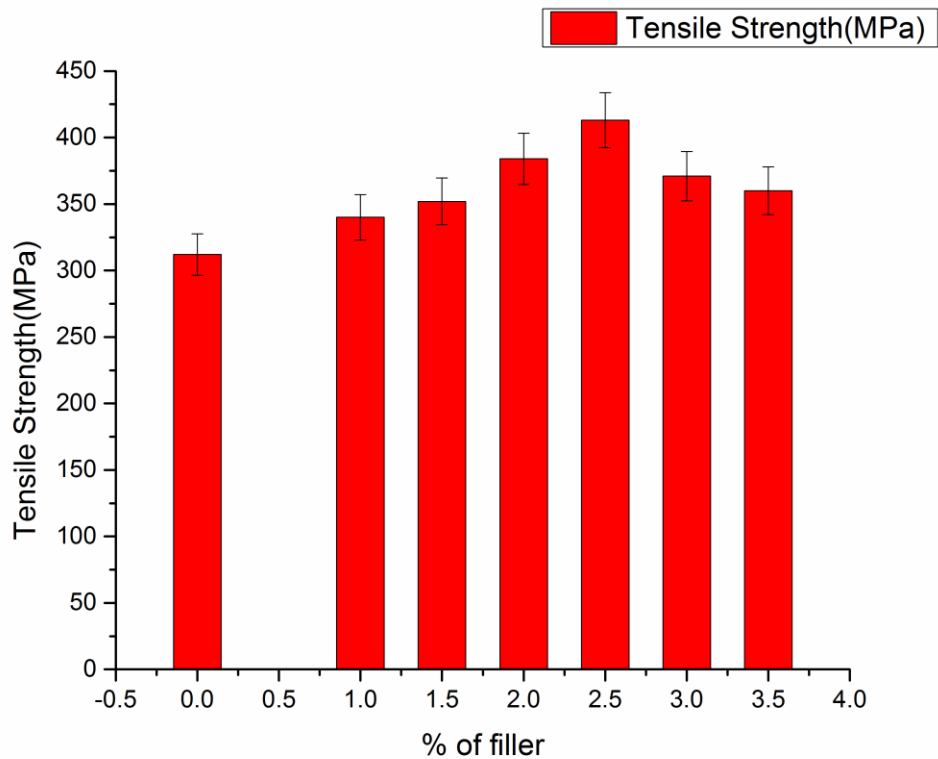


Figure 5.1 Tensile strength of fiber reinforced Tungsten carbide – epoxy hybrid nanocomposites by varying filler volume

5.3.2 Flexural strength of fiber reinforced Tungsten carbide – epoxy hybrid nanocomposites by varying filler volume

Flexural strength of fiber reinforced Tungsten carbide –epoxy hybrid nanocomposites by varying filler volume is shown in Fig. 5.2. The results were plotted between WC filler % versus Flexural strength. It was observed that the addition of filler up to 2.5 wt% increases the strength of the composite. This is due to the good bonding between matrix and fiber, which can be observed in SEM image. SEM image is shown in Fig. 5.11.

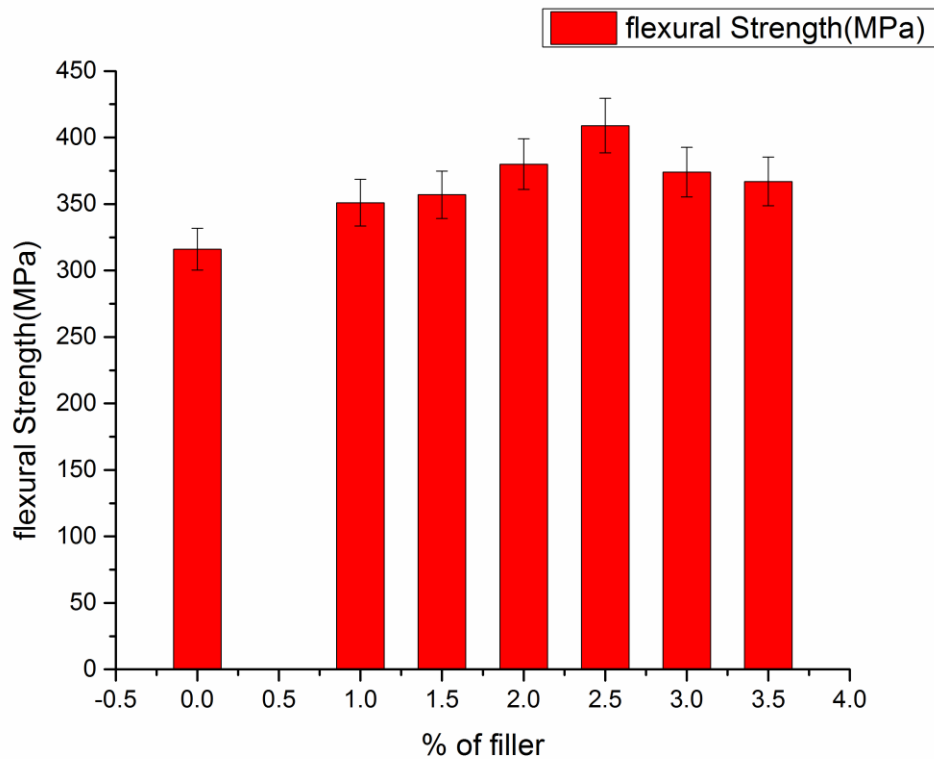


Figure 5.2 Flexural strength of fiber reinforced Tungsten carbide – epoxy hybrid nanocomposites by varying filler volume.

5.3.3 Effect of addition of tungsten carbide (WC) filler on erosion wear of Carbon/epoxy hybrid nanocomposite.

For studying the effect of filler weight percentage on erosion rate of composites, composite samples were prepared by varying weight percentages of filler at 25% fiber volume and samples of 4mm thickness underwent erosion test at a constant impact velocity of 48m/s and for different impact angles. The results are shown in Fig. 5.3. From the results, it is evident that by the addition of filler, the erosion rate decreases. This is mainly due to the increase of hardness of hybrid nano composite with the addition of nano filler. Irrespective of filler volume, the maximum rate of erosion occurs at 60⁰- 75⁰ impact angle.

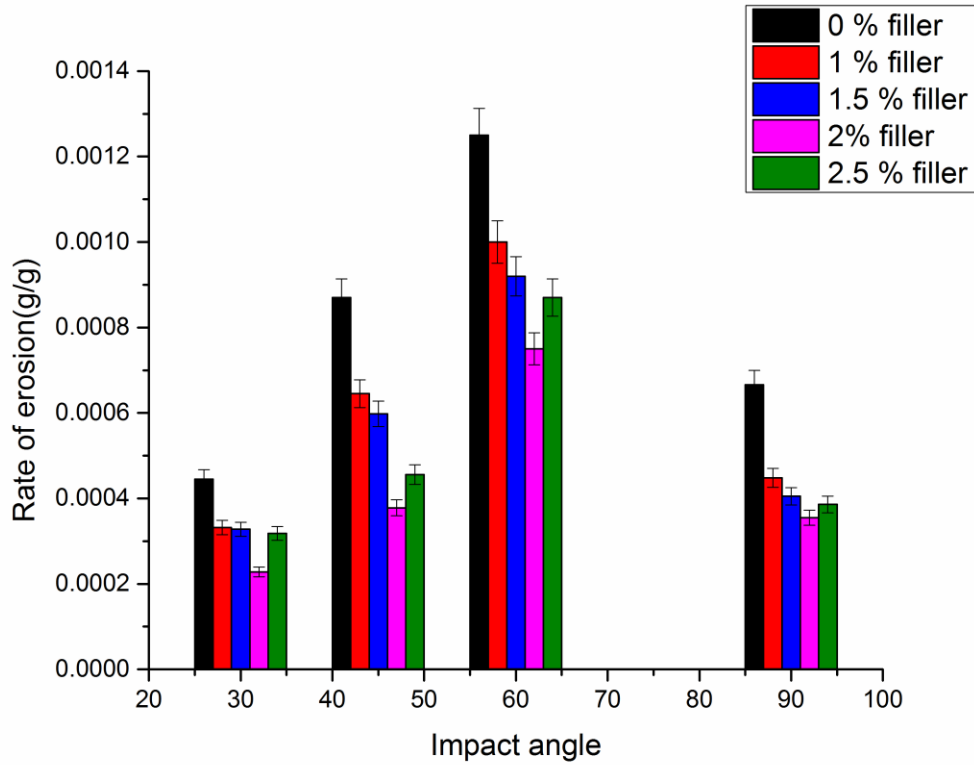


Figure 5.3 erosion behaviour of carbon fiber reinforced tungsten carbide-epoxy hybrid nano composites by varying filler loading for different impact angles (in degrees).

5.3.4 Effect of addition tungsten carbide (WC) filler on friction wear of carbon/epoxy hybrid nanocomposite

To know the effect of filler loading on friction wear of carbon/epoxy hybrid nanocomposite, hybrid nanocomposites of different filler loadings were prepared. These samples were tested at a constant speed of 1m/s and at a normal load of 10N. From the results it was observed that wear rate decreases with an increase of filler loading up to 2 wt% of filler. With further addition of filler, it increases. The results are shown in Fig. 5.4.

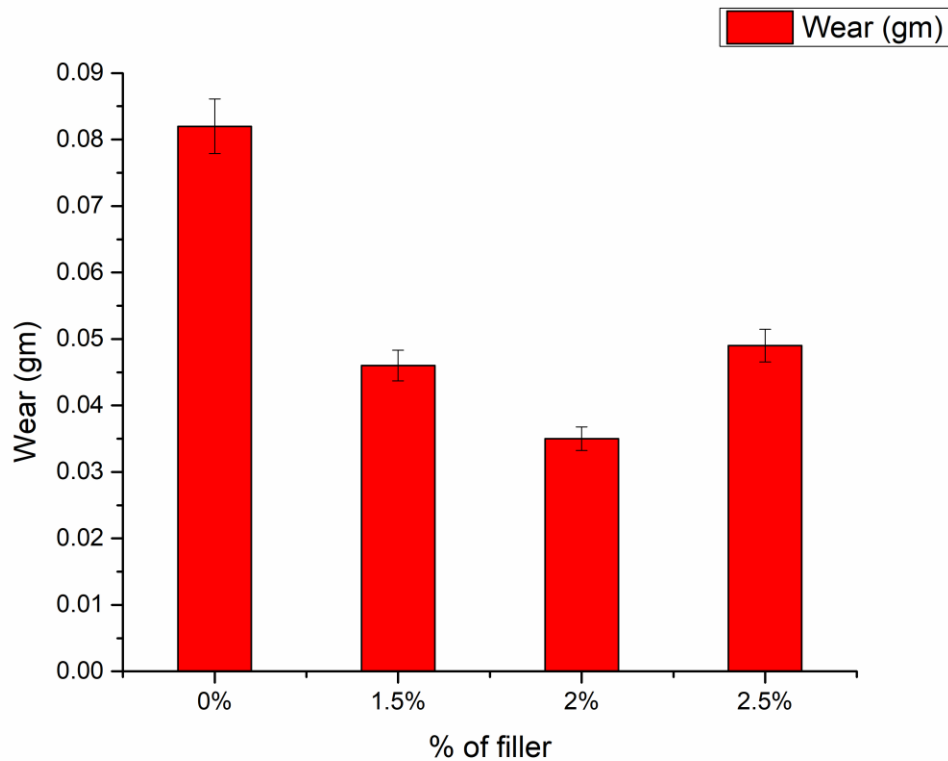


Figure 5.4 Wear Rate of carbon fiber reinforced tungsten carbide-epoxy hybrid nano composites for different filler loading at a constant speed of 1m/s and at a normal load of 10N

5.3.5 Variation of wear rate with changing in sliding speed

To find the effect of change in sliding speed on the wear rate, wear test was conducted for different sliding speeds of 1m/s, 2m/s and 3m/s. It was observed that with an increase of sliding speed, wear rate increases which is shown in Fig. 5.5. With an increase in sliding velocity and/or normal force, ample frictional heat energy accumulates around the contact area, making the polymer composite samples softer at elevated temperatures and easier deformation during wear.

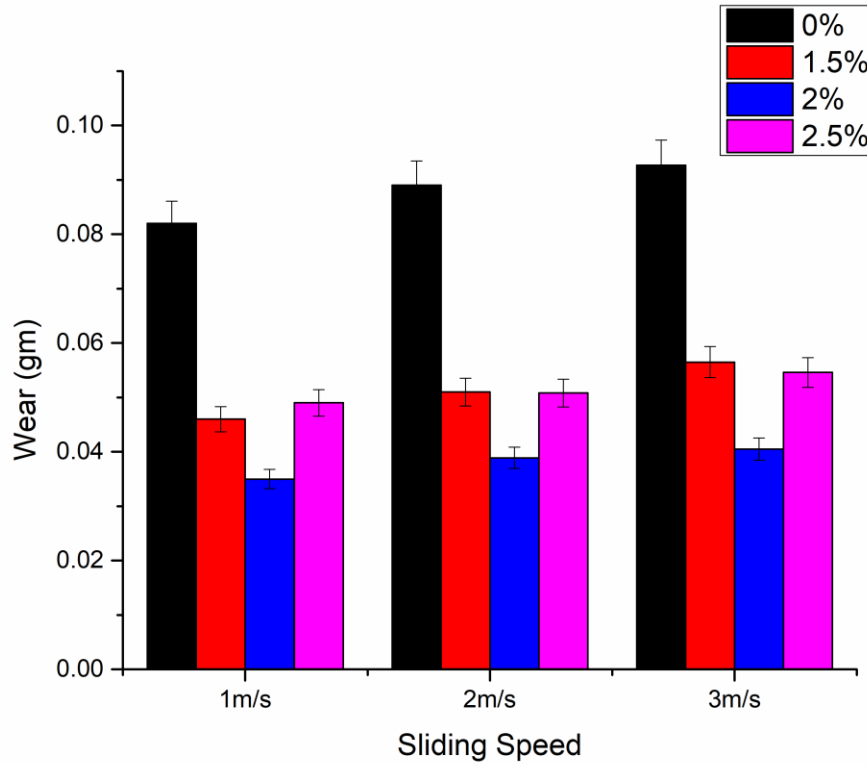


Figure 5.5. Variation of wear with changing in sliding speed (m/s) at a constant normal load of 10N

5.3.6 Variation of wear rate with changing in Normal load

To find the effect of change in applied normal load on the wear rate, wear test was conducted for different normal loads of 10N, 15N and 20N. It was observed that with an increase of load, the rate of wear increases as shown in Fig. 5.6. The increase in normal load will in turn increase the contact stresses, which causes brittle failure of carbon fibers on the surface of the specimen and severe material removal due to faster removal of epoxy from the surface of the specimen, leaving the top layer of fibers/filler particles exposed to the environment. As the load increases, the plastic zones are enlarged leading to an increase in frictional forces. These frictional forces would in turn cause a temperature rise, a decrease in the hardness of the matrix surface, and hence the increase in wear.

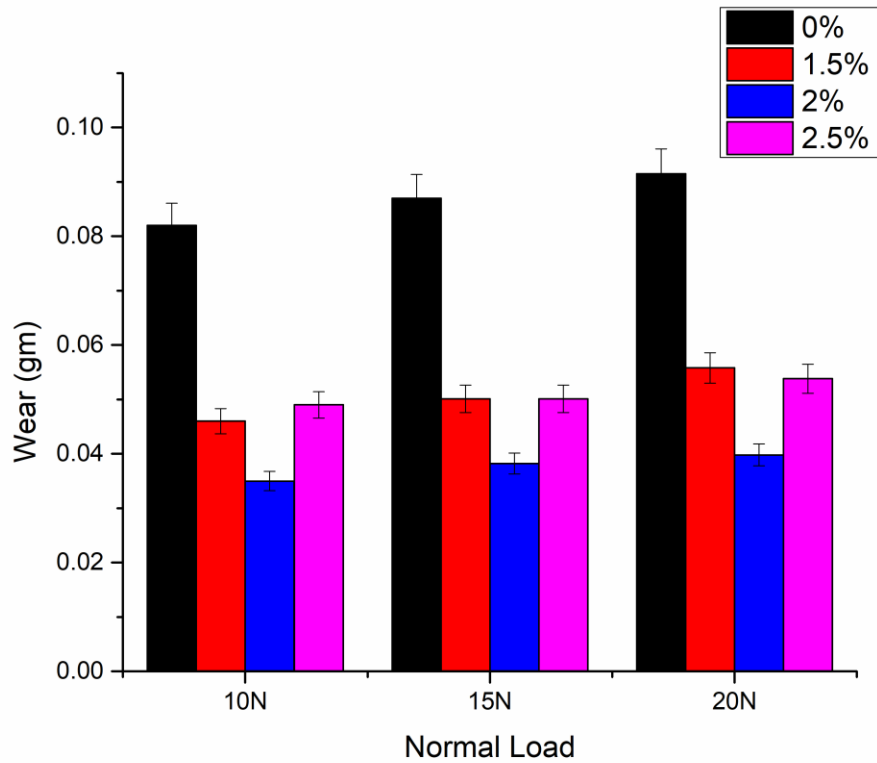


Figure 5.6 Variation of wear with changing in normal load at a constant sliding speed of 1m/s

5.3.7 Effect of addition tungsten carbide (WC) filler on COF of carbon/epoxy hybrid nanocomposite

To get the effect of filler loading on COF of carbon/epoxy hybrid nanocomposite, hybrid nanocomposites of different filler loadings were prepared. These samples are tested at a constant speed of 1m/s and at a normal load of 10N. From the results it is observed that COF increases with increase of filler loading. This is due to the increase in hardness of the composite at higher filler volume. The results are shown in Fig. 5.7.

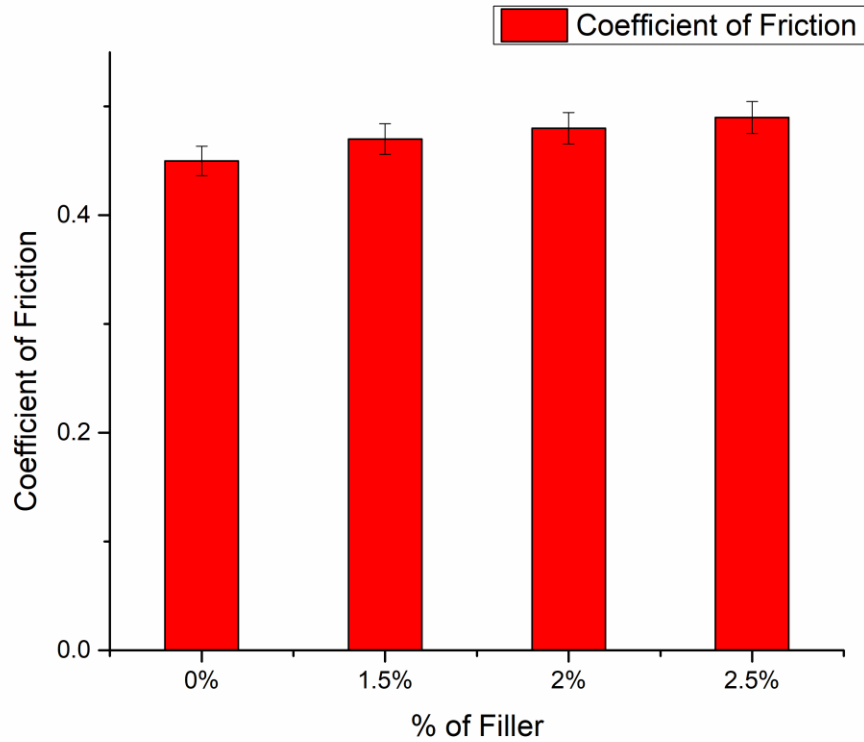


Figure 5.7 COF for carbon fiber reinforced tungsten carbide-epoxy hybrid nano composites for different filler loading at a constant speed of 1m/s and at a normal load of 10N

5.3.8 Variation of COF with changing in sliding speed

To know the effect of change in sliding speed on COF, wear test was conducted for different sliding speeds of 1m/s, 2m/s and 3m/s. It was observed that with an increase of speed, COF decreases, which is shown in Fig 5.8. With an increase in sliding speed, more heat is generated at the contact surface resulting in softer and makes easy to deform. Hence friction decreases with sliding speed.

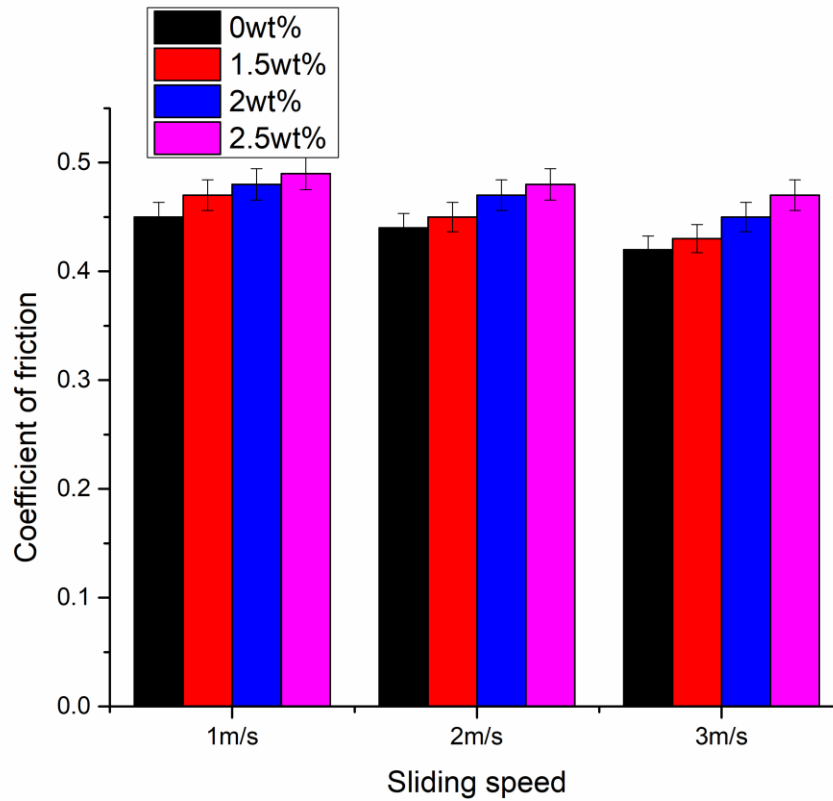


Figure 5.8 Variation of COF with changing in sliding speed (m/s) at a constant normal load of 10N

5.3.9 Variation of COF with changing in Normal load

To find the effect of change in applied normal load on the COF, wear test was conducted for different normal loads of 10N, 15N and 20N. It was observed that with increase of load COF increases which is shown in Fig. 5.9. This may be due to the reason that during sliding under high applied normal loads, the high friction is generated on the composite pin and the disc contact surface, which in turn may increase the actual contact area and contact temperature with the increased applied normal load. Due to this friction heating generates which results an increase in the frictional coefficient.

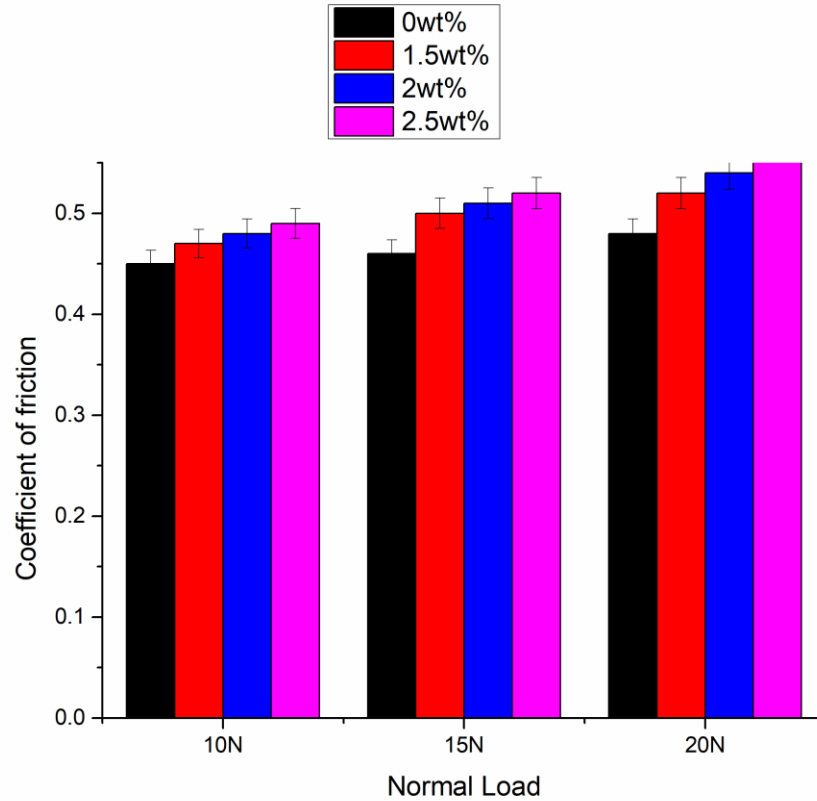


Figure 5.9 Variation of COF with changing normal load at a constant sliding speed of 1m/s

5.3.10 Surface morphology of tensile and flexural tested samples

Failure surfaces of tensile tested specimens and three point bending tested specimens are shown in Fig. 5.10 and Fig. 5.11 respectively. Good bonding between fiber and matrix is observed when 2.5 wt% of filler is added to the matrix, as is shown Fig 5.10(a). Fig 5.10(b) shows how the fibres are stretched when tensile load is applied to the specimen. Bending of fibers due to flexural load can be observed in Fig 5.11(a). Fig 5.10(c) and 5.11(c) shows poor bonding between fibre and matrix and the reason may be due to the agglomeration of particles at higher filler loading into the matrix.

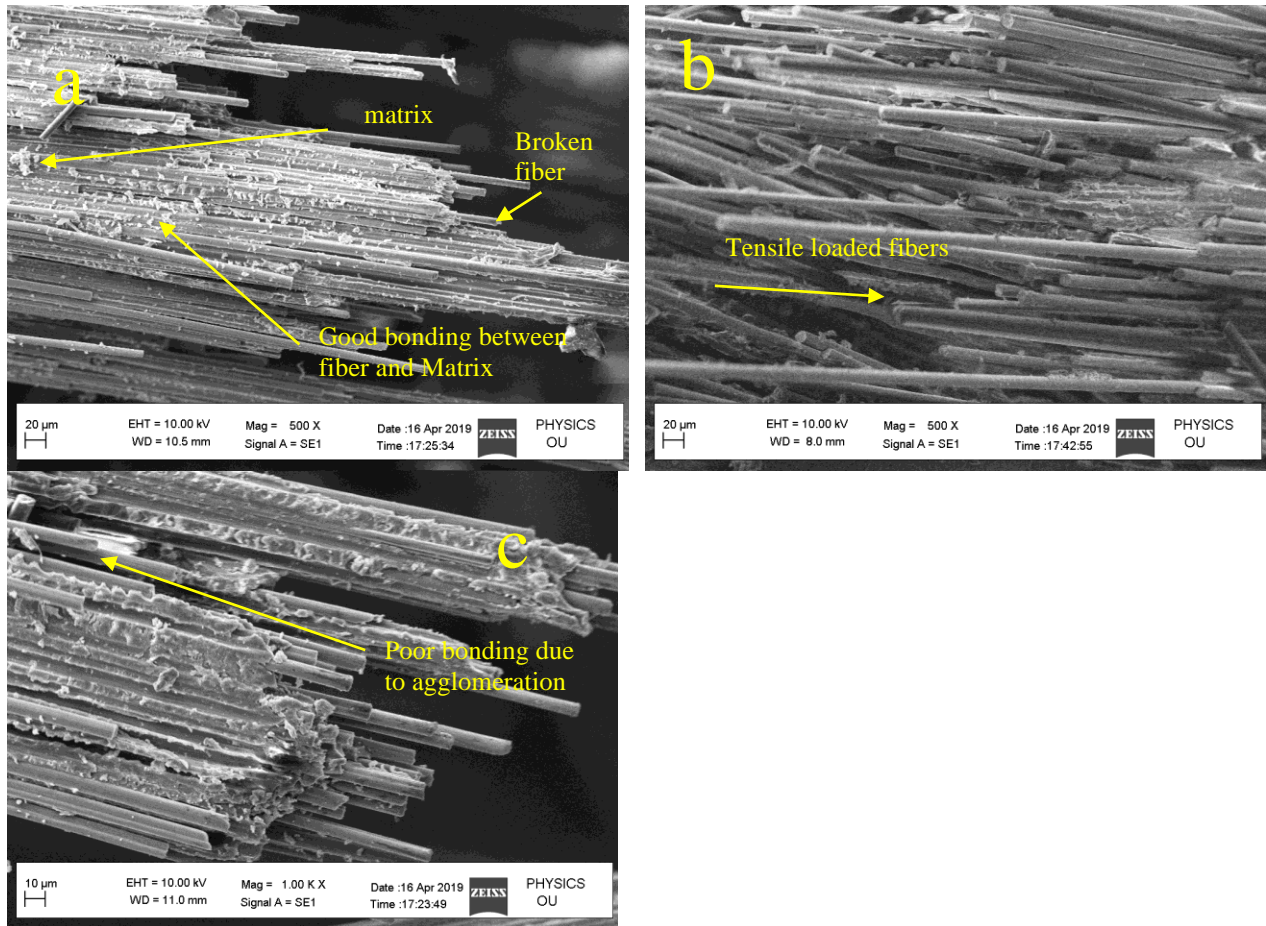


Figure 5.10 shows SEM images of Specimens failed due to Tensile loading a) 2.5 wt% b) 1 wt% c) 3.5 wt%

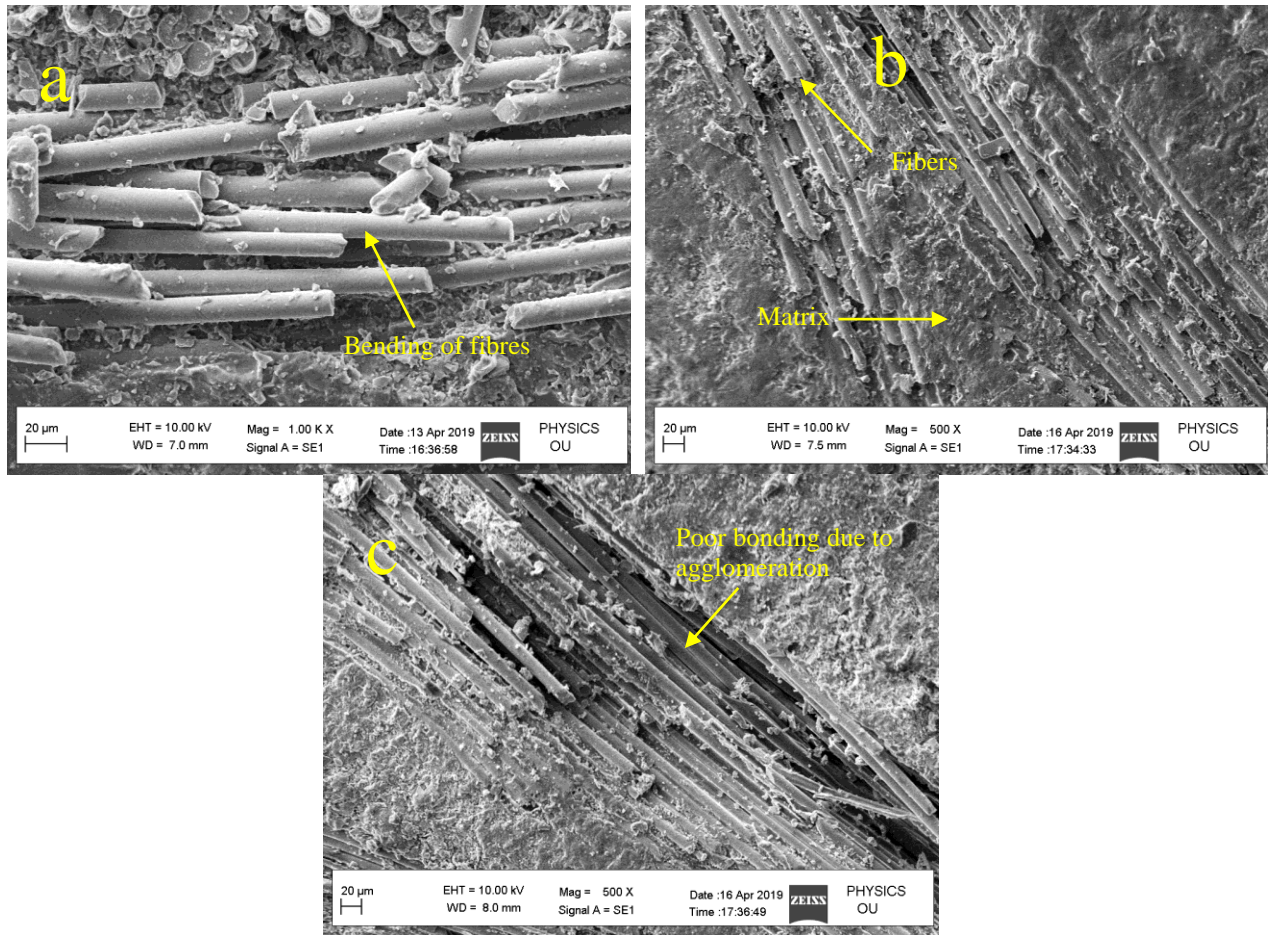


Figure 5.11 shows SEM images of Specimens failed due to Flexural bending a) 2.5 wt%
b) 2.5 wt% c) 3.5 wt%

5.3.11 Surface morphology of wear tested samples

SEM images of friction wear samples for two different fillers loading at a speed of 1m/s under 10N load is shown in Fig. 5.12. The wear process of fiber reinforced polymer composites contains four steps: matrix wear, fiber matrix interfacial debonding, fiber wear and fiber fracture. This can be observed in Fig. 5.12. Fig. 5.12(c) shows fiber pulling out, indicating that the matrix which covers the fibres has completely washed out. This suggests high wear at this filler loading.

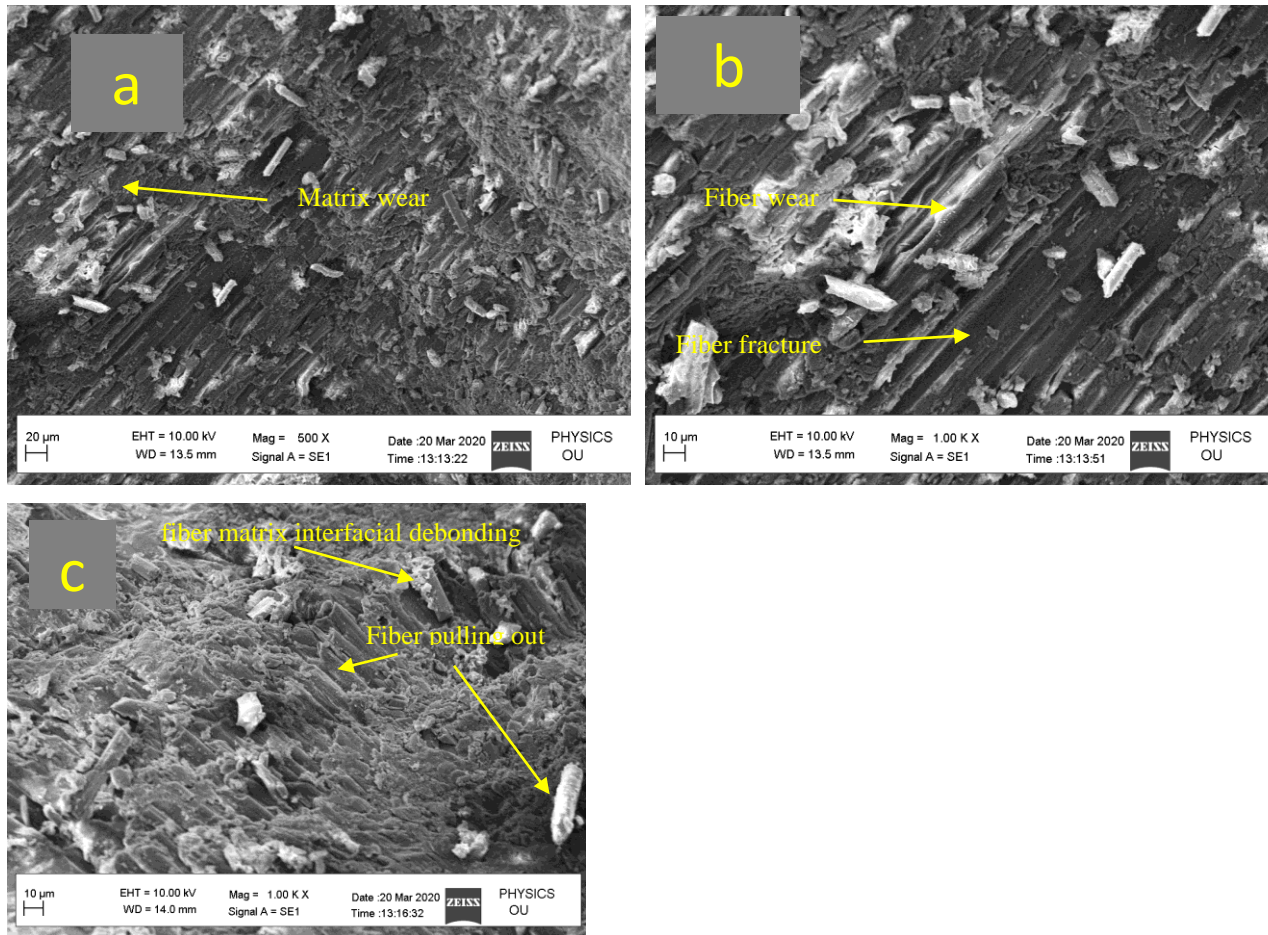


Figure 5.12 SEM images of worn surfaces a) and b) are 2 wt% at 1m/s speed and 10N load
c) 2.5 wt% at 1m/s speed and 10N load

5.4 Conclusions

- Addition of WC filler up to 2.5 wt% in carbon/epoxy composite, increases the strength of the composite.
- Compared to neat carbon/epoxy, the strength of the hybrid nano composite (i.e., addition of filler to carbon/epoxy composite) increases from **322 MPa to 402 MPa**.
- Independent of impact angle, erosion rate decreases with increase in filler volume up to 2.5wt% in carbon/epoxy composite.
- It was observed that erosion is more at 60° impact angle for any given carbon/epoxy hybrid nano composite.
- Friction wear decreases with increase of filler loading up to 2 wt% in carbon/epoxy composite.

- Compared to neat carbon/epoxy, friction wear reduces from 0.81 to 0.35 gm due to the addition of WC nano particles to carbon/epoxy composites.
- Wear rate increases with an increase of sliding speed and also with increase of normal load for carbon/epoxy hybrid nano composite.
- Coefficient of friction increases with increase of filler loading in carbon/epoxy composite.
- Compared to neat carbon/epoxy coefficient of friction increases from 0.45 to 0.49 due to the addition of WC nano particles to the carbon/epoxy composites.

Chapter 6

Conclusions and scope for future work

6.1 Conclusions

In the present work, a detailed discussion of mechanical and tribological properties of WC reinforced with epoxy composites by adding the filler to neat epoxy in the range of 0 wt% to 4 wt% is reported. Also, the mechanical and tribological properties of carbon/epoxy by varying the fiber volume in a range of 3-6 layers of fiber in neat epoxy are studied. Finally, the composites of Tungsten carbide reinforced carbon/epoxy hybrid composites are made for different filler volume in the range of 0-2.5 wt% in carbon/epoxy composites and the mechanical and tribological properties are studied. Surface morphology was observed for all fractured samples. Based on the results obtained from these three different types of composites, the following conclusions have been drawn.

1. Compared to neat epoxy, tensile strength of nano composite is increased from 24MPa to 33Mpa. i.e it increases by 37.5%. It was observed at 2 wt% of WC filler in nano-composite.
2. Compared to neat carbon-epoxy, the strength of the hybrid composite increases from 322 MPa to 402 MPa. i.e it increases by 24.4%. It was observed at 2.5 wt% of WC filler in hybrid nano-composite.
3. Compared to neat epoxy, hardness value increases from 17.4 to 25.4 HV. i.e it increases by 43%. It was observed at 2 wt% of nanocomposite.
4. Independent of impact angle, erosion rate decreases with increase in filler volume up to 2 wt% of the nanocomposite.
5. Compared to neat epoxy friction wear for nano-composite reduces from 0.87 to 0.3 gm. It was observed at 2 wt% of nanocomposite.
6. Compared to neat epoxy, Coefficient of friction increases from 0.51 to 0.58. This was observed at 2 wt% of the nanocomposite.
7. Irrespective of impact angle, an increase of fiber volume increases rate of erosion.
8. As the fiber orientation increases, the erosion rate also increases. But it has very little significance.
9. Independent of impact angle, erosion rate decreases with an increase in filler volume up to 2.5 wt% of the hybrid nano-composite.

10. Compared to neat epoxy, friction wear reduces from 0.81 to 0.35 gm. It was observed at 2 wt% of hybrid nano-composite.
11. Compared to neat epoxy, Coefficient of friction for the hybrid nano-composite increases from 0.45 to 0.49.

6.2 Recommendations for Potential Application

The proposed tungsten carbide reinforced carbon-epoxy hybrid nanocomposite possesses unique tribological and mechanical properties, making it suitable for various real-life applications, especially in stationary (non-rotating) components. Below are three specific applications:

1. In the aerospace industry, interior panels are utilized to create lightweight and durable cabin structures. The tungsten carbide carbon-epoxy polymer composites are well-suited for aerospace interior panels due to their exceptional tribological properties, such as good wear resistance. These composites can withstand the constant rubbing and contact with passenger luggage and accessories, ensuring prolonged durability and reduced maintenance costs. Additionally, their lightweight nature contributes to overall weight reduction in aircraft, leading to improved fuel efficiency and reduced environmental impact.



Figure 6.1 image of Aircraft interior panels [158]

2. The brake pedal assembly in automotive vehicles is subject to constant friction and wear due to the repetitive action of braking. The tungsten carbide carbon-epoxy nanocomposite's exceptional tribological properties, having good wear resistance, make it

an ideal material for the brake pedal. Its ability to withstand frequent and intense contact with the driver's foot ensures consistent performance and extended service life, reducing the need for frequent replacements and maintenance.



Figure 6.2 image of Automotive Brake pedal [159]

3. Pump casings are stationary components used in various industrial applications to enclose and protect the pump mechanism. The proposed tungsten carbide carbon-epoxy nanocomposite offers excellent tribological properties, making it a suitable choice for pump casings that experience sliding and abrasion due to the flow of fluids. The material's high wear resistance ensures reduced wear and extended service life, while its mechanical strength allows it to withstand the pressures and mechanical stresses present in industrial pumping systems.



Figure 6.3 image of Pump Casing [160]

6.3 Future scope for the present work

This work can be further extended by changing epoxy to other polymers which can withstand high temperatures. The performance under higher temperatures can be verified. By adding rubber particles along with WC particles, the performance of the composites under damping conditions can also be verified. There are many fabrication techniques available such as injection molding, compression molding, and VARTM method, where the volume fraction of reinforcement can be increased. There is good scope for the study to examine the effect of Tungsten carbide particles in natural fiber reinforced epoxy composites, which can become a new area of research. This work can be further extended to the techniques stated above. The results reported here would become a reference for industrial designers and researchers to design and develop PMC components using Tungsten carbide filler as reinforcement.

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