The Effect of Different Surface Treatments of Carbon Fibers and Their Impact on Composites

Mohammed Khashman Almutairi[1], Reham Abdulkhaleq Felemban[2], Shahad Esmail Pasha[2], Nuha Talal Abo khashaba[2], Heba Ibrahim Mubaraki[3], Rawan Ahmed Yankesa[4], Alaa Yahya Algamdi[4], Afnan Mohammed Bakkar[4], Amal Abdulkarim Aldouweghri[4], Mohammed Fareed Sannan[4], Danah Saeed Basaad[4],Mohamed Fawzi Almaghmsi[5], Majid awad Alonazi[5], Mohammed Musayyab Alruwaili[7],Hawra Mohammed Alhamad[8]

1-Alkharj Armed Forces Hospital, 2-Alfarabi College for Dentistry and Nursing, 3 -Batterjee Medical College for Sciences and Technology,4 -Ibn Sina National College for Medical Studies, 5-Future University, Egypt, 6-October 6 University,7-Imam Abdurrahman Bin Faisal University.

Corresponding author: Mohammed Khashman Almutairi, E-mail: drkhashman90@gmail.com, mobile: +966561675948

ABSTRACT

Background: The performance of composites profoundly depends on the quality of the fiber-matrix interface. Good interfacial adhesion provides composites with structural integrity and efficient load transfer between fiber and matrix. Nevertheless, untreated carbon fibers are extremely inert and hence have low adhesion to resin matrices. In the meantime, the relatively weak transverse and interlaminar properties significantly limit the composite performance and service life. To overcome these barriers, a fiber-based reinforcement which has strong interfacial adhesion to the matrix is highly desired to improve the overall composite properties.

Aim of the study: was to assess the Effect of different surface Treatments of Carbon fibers and their influence on the interfacial properties of carbon fiber/epoxy composites.

Methods: A review of the scientific literature (from 1970 to 2017).

Pubmed, Embase and CENTRAL were searched to identify studies that investigated the different types of surface treatment of carbon fibers and how this can affect the quality of carbon fiber composite. Identification of papers and data extraction were performed by different independent researchers.

Conclusion: Various combinations of surface treatment of carbon fibers are crucial to improve its adhesion with various matrices. Treatment significantly influences fiber characteristics. Nevertheless, optimization is required to select appropriate treatment method per application and desired properties.

Keywords: Carbon fibers, surface treatment, composites.

INTRODUCTION

Carbon fibers are defined as a fiber materials containing at least 92 wt % carbon in composition, however the fiber containing at least 99 wt % carbon is usually called a graphite fiber (1). Carbon fibers generally have superior tensile properties, low densities, high thermal and chemical stabilities in the absence of oxidizing agents, good thermal and electrical conductivities, and excellent creep resistance (1). CFs have been extensively used for manufacturing of thermoplastic composites, such as carbon-reinforced polyetherimide (CF/PEI). This high-performance material has found multiple applications in aerospace, marine and automobile industry due to its favorable engineering properties, such as lower density, enhanced toughness, excellent fire resistance and easy recyclability. Furthermore, they have been extensively used in composites in the form of woven textiles, prepregs, continuous fibers/rovings, and chopped fibers. The composite parts can be produced through filament winding, tape winding, pultrusion, compression molding, vacuum bagging, liquid molding, and injection molding (2).

Thus, CF composites are suited to applications where strength, stiffness, lower weight, and outstanding fatigue characteristics are critical requirements. They are also finding applications where high temperature, chemical inertness and high damping are important criteria. CFs also have good electrical conductivity, thermal conductivity and low linear coefficient of thermal expansion(3).

One problem that can seriously compromise the performance of this material (when no previous surface treatment of CFs is applied) is to obtain composites with low interlaminar shear strength (2). Polyacrylonitrile (PAN) and mesophase pitch (MP) are the two most important carbon fiber precursors. Optimizing the carbon fiber microstructure can improve carbon fiber strength through decreasing its flaw sensitivity. The carbon fiber microstructure is dependent on the precursor morphology and processing conditions. Research in these two areas will aid in the development of carbon fibers with improved performance (4).

When CFs are used without surface treatment , they result in composites with low interlaminar shear strength (ILSS). This has been attributed to weak adhesion and poor bonding between the fiber

Received: 20/12/2017
Accepted: 30/12/2017
DOI: 10.12816/0044635

and matrix [5]. Treatments increase the surface area and surface acidic functional groups and thus improve bonding between the fiber and the resin matrix [6]. This tends to increase the wettability of the CFs and enhances the ILSS. Surface treatments may be classified into oxidative and non-oxidative treatments. Oxidation treatments involve gas-phase oxidation, liquid-phase oxidation carried out chemically or electrochemically [7] and catalytic oxidation. The non-oxidative treatments involve deposition of more active forms of carbon, such as the highly effective whiskerization, the deposition of pyrolytic carbon [8]. CFs can also be plasma treated to improve bonding between the fiber and matrix. Liquid phase oxidation treatments are milder, very effective and are preferred.

In the present study, we aim to assess the different Surface Treatments of Carbon Fibers and their impact on Composites.

MATERIALS AND METHODS

Data Sources

We searched the scientific database from 1960 10 2017.

Data Sources: Literature searches of MEDLINE, EMBASE, SCOPUS, Current Contents, Cochrane Library, Google Scholar, and individual Dentistry journals such as International Journal of Prosthodontics, International Journal of Periodontics and Restorative Dentistry and Clinicaltrials.gov between 1960.

The search terms included “Composite”, ” Carbon fibers”, “surface treatment” “Plasma,” “oxidative treatment” and “Gama treatment”.

EFFECT OF SURFACE TREATMENT OF CFs

Despite the high cost of CFs, they are still mostly favored for tailoring high performance composites and tribo-composites. Yet their surface is chemically inert and leading to the most potential problem of inadequate adhesion and hence weaker composite than the expected one [9]. It is essential to treat them with proper treatment so as to explore their full potential in composites. Several types of reported surface treatments of CFs are classified in two categories. First, improves the adhesion by physical means thereby enhancing the roughness resulting in more surface area and plenty of contact points, micro-pores or surface pits on already porous CFs surface. The second on the other hand, involves chemical reactions leading to inclusion of reactive functional groups that promote good chemical bonding with the polymer matrix. Most of the methods bring both the changes simultaneously. Interestingly any surface treatment method especially which etches fiber’s surface also leads to affect the strength of the fiber adversely[9]. First effect called as positive effect leads to the enhancement in fibermatrix adhesion and hence improvement in the strength of composite since matrix supports the fibers more firmly. Simultaneously, other effect which is in negative direction reduces the strength of fibers due to etching contributing to deteriorate the strength of composite. The final strength of the composite depends on the net contribution of these two opposing effects. It is hence imperative to optimize the extent of treatment to get the maximum possible enhancement in the performance properties of composite. Various surface treatment methods viz. electrochemical, chemical, thermal, discharge plasma etc. have been practiced to improve the adhesion between fiber and matrix which can be improved by the following means [10]:

- Matrix molecules physical expansion with the molecular network of polymer coating applied on the fibers.
- Successive chemical bonding with the unreacted species in the matrix resin through Increasing the number of active sites on the fiber surface
- Mechanical interlocking endorsement between the fiber and the matrix. This can be achieved by creating surface porosity, into which resin molecules can penetrate.
- Wettability increase of the fiber surface by the matrix resin.
- Weak boundary layer elimination such as contaminant species or gas molecules physically adsorbed on the fiber surface. This would provide a more intimate contact between the fiber and the polymer to ensure a significant level of van der Waals force which being a short-range force would otherwise be relatively weak.
- Applying a thin layer of 'coupling agent' that will chemically bond to both; fiber and matrix.

TYPES OF SURFACE TREATMENT OF CFs

1. **Oxidative surface treatments**

There are various methods of oxidative treatments, including dry oxidation in the presence of gases, plasma etching and wet oxidation [11].

a. Oxidation treatment

Dry oxidative treatments are normally performed with air, oxygen and CO2 at low or elevated temperatures with:

1- Gases (by air, oxygen, ozone etc.) or
2- Liquids (by nitric acid, hydrochloric acid etc).

Sellitti *et al.* [12] performed oxidation of Rayon-based graphitized CF for 5, 15 and 25 hrs and observed the presence of carboxylic acid, ester, lactone, enol, and quinone structure moieties in Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR) spectra.

The tensile strengths of the fiber decreased with an increase in oxidation time and revealed that the surfaces of fibers were pitted and fragmented.

The surface area of CFs after oxidation was much larger than that of the virgin fibers. Tran *et al.* [13] modified CFs by boiling for 5h in HNO3 and observed that with increasing severity of oxidation, the surface oxygen and nitrogen content increased and led to a rise in overall surface energy of the fibers. However, refluxing CFS with 68% fuming nitric acid for periods of 9, 12, 25 and 50 hr and observed increment in the external surface area of the fibers by a factor of 3.7 after 50 hr treatment in the form of edge, or active sites. In another study [14], CFs was refluxed in 60% nitric acid for 40, 60, 80 min at 100 0 C and found that the (Brunauer-Emmett-Teller) BET surface area of 60 min treated CF is 10 times as large as that of untreated CF.

In a recent study conducted by Zhang and colleagues [15] oxidation of PAN was performed based CFs with strong HNO3 by heating (90°C) for 1.5 h and observed that after treatment fiber surface became rougher and the oxygen concentration increased greatly after surface treatment, which improved the adhesion between the fiber and the PI matrix.

Following HNO3 oxidation, more active groups (–O–C–, –C=O, –O–C=O) appeared on the surfaces of fibers, which increased the total surface energy and polarity which is helpful in enhancing the wettability of the CFs with the matrix. Another study[16] performed oxidization of CFs by nitric acid treatments to improve the interfacial adhesion with polyimide matrix. XPS analysis showed oxidation not only affects the oxygen concentration but also produces an appreciable change the chemical functions, by the conversion of hydroxyl-type oxygen into carboxyl functions.

Dai *et al.* [17] has attempted to study the influence of heat treatment on carbon fiber surface properties and fibers/epoxy interfacial adhesion. The sizing agent on T300B and T700SC fiber surface was negative for the interfacial bonding. This is contrary to the general principles. Desizing reduced the acid parameter of carbon fibers surface which promoted bonding strength at the fiber/epoxy interface. The IFSS of T300B/epoxy increased from 63.72 MPa to 87.77 MPa after desizing, with an improvement of 38%. This was attributed to the increment of work of adhesion. The IFSS of desized T700SC/epoxy (89.39 MPa) was 9% greater than that of T700SC/epoxy (81.74 MPa). The thicker sizing might result in weak layer in the interface region. They concluded that IFSS for carbon fiber/epoxy systems depended not only on the chemical bonding but also on the physical and adhesive interactions.

Tiwari *et al.* [18] oxidized CFs by boiling in nitric acid (HNO3, 65-68%) at 110 °C. The duration of the acid treatment varied from 15 to 180 minutes and observed that with increasing treatment time, roughness of fiber surface increased and for treated fibers, ether, carboxyl and carbonyl groups were observed on spectra corresponding to wave number range of 950-1200 cm-1 and 1650-1710 cm-1 respectively.

ensile force by fabric tow had an inverse proportional relationship with treatment time and load bearing capacity of fibers reduced by almost 40% after 3 hrs of oxidation.

b. Plasma Treatment

Plasma treatments are known to enhance significantly the adhesion of polymer fibers to epoxy resins [19].

By definition, Plasma is an electrically conducting medium of basically negatively charged electrons, positively charged ions, and neutral atoms or molecules or both. The main objective of using surface treatment of fibers or whiskers used as reinforcements in composite materials is to modify the chemical and physical structures of their surface layer, tailoring fiber-matrix bonding strength, but without influencing their bulk mechanical properties. The control of interfacial bonding is vital to strengthen or toughen fiber-reinforced composites [20].

Several adhesion mechanisms can be endorsed by plasma treatments such as[20]:

1. Mechanical keying between the fiber and the matrix because of the increased fiber surface roughness
2. Promotion of surface energy which would promote wetting of the fiber by the matrix
3. Removal of surface contaminants to provide better fiber/resin contact
4. Functional groups deposition for potential chemical interactions between the fiber and the matrix resin.

Cold Plasma treatment

The application of cold plasma in the treatment of carbon fibers has been approved to be effective, In the cold plasma state, ionization, excitation, dissociation, recombination, and other reactions can occur because of the collision of electrons and other species in the plasma medium[20]. Consequently, when the plasma contacts a solid material, a highly efficient energy exchange can occur. If properly controlled, plasma can be used to modify the physical and chemical state of the carbon fiber surface without significantly altering the bulking properties. Moreover, Phenolphthalein polyaryletherketone (PEK-C) is a kind of amorphous thermoplastic polymer, which has the excellent mechanical properties and remarkable thermal and chemical resistance. It is expected that the carbon fiber/PEK-C composites have the huge potential of application in aerospace, automobile, and construction industries [21].

Oxygen Plasma treatment

Jang and Yang [22] investigated the effect of oxygen plasma treatment on surface morphology of CF for varying time from 1 min to 5 min.

They observed that the BET surface area on the CF surface increased due to results from micropittings with increasing treatment time and showed the maximum value at 3 min. which allowed more interpenetration between CF and PBZ matrix, so that the maximum mechanical interlocking was achieved at 3 min plasma treatment. The surface roughness was proportional to the surface area and this was the major contributor to the adhesion enhancement through improving wettability and mechanical interlocking. It was proposed that active species in the plasma gas aggressively attack the defect-rich or the edge-carbon site, resulting in the increase of CF surface area. On the contrary, severe plasma treatment of CF reduced the specific surface area due to overall smoothing of the CF surface. By XPS analysis also observed that the ratio of O1s to C1s atom of CF increased slightly with plasma treatment time. Plasma treatment produced the oxygen containing functional groups such as hydroxyl, carbonyl and carboxylic groups.

Though, the weak boundary layer of CF is removed by oxygen plasma treatment so that the increment of O1s to C1s ratio was relatively small. Further studies [23] were carried out to evaluate the effect of plasma treatment from 2-30 min on the mechanical properties of T300 CFs and found that the tensile breaking load of CFs is lowered by 8% due to plasma treatment. Increased amount of oxygen content on CFs and presence of polar components, increased etching and deeper crevices were observed on fiber with increase in treatment time from 2-30 min.

Approximately, 20-50% improvement in all mechanical properties was observed due to the treatment. This improvement was due to the introduction of new polar oxygenated functional groups on CF surface during CRNOP treatment as indicated by FTIR-ATR and XPS analysis. These groups on fiber surface altered the original inertness of CFs and led to the enhanced interaction with matrix resulting in stronger composites.

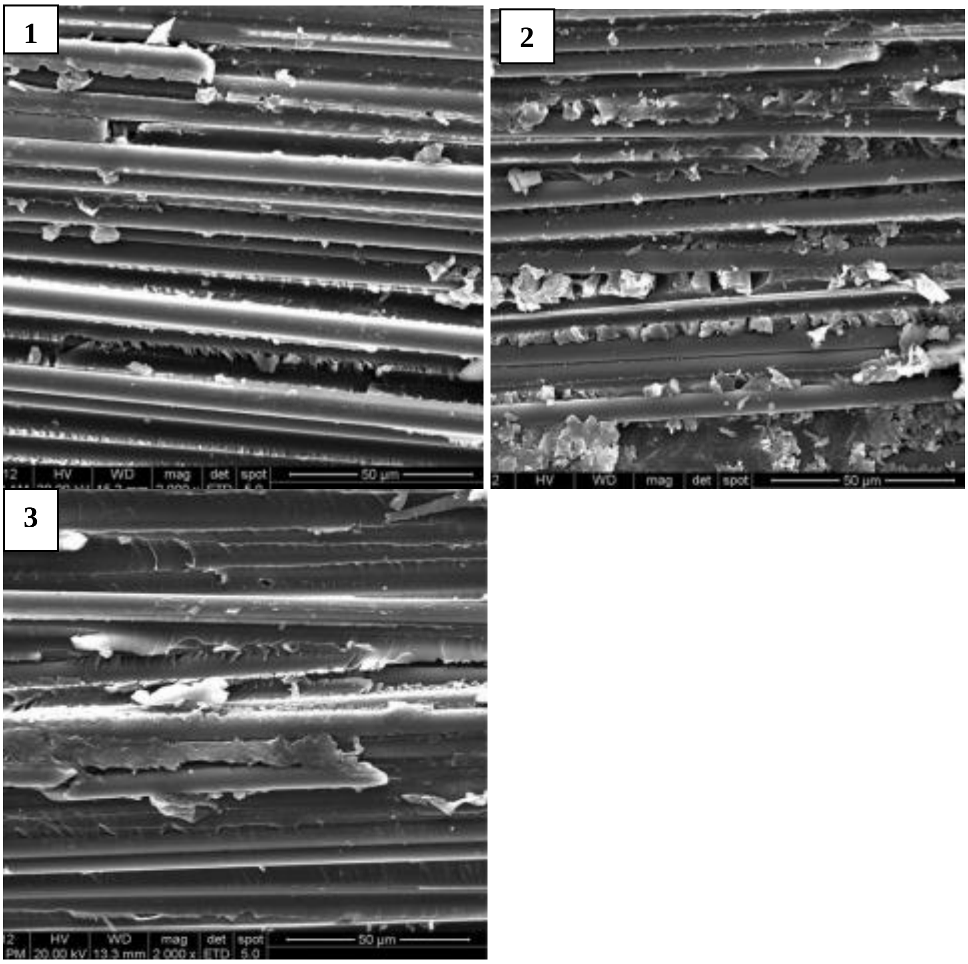

Figure 1: photographs of fracture morphologies of composites Scanning electron microscope: (1) untreated ; (2) plasma treated at 200 (3) plasma treated at 500 W[24]

2. Non-Oxidative surface treatments

Non-oxidative methods, including the deposition of an active form of carbon, plasma polymerization and grafting of polymers onto the fiber surface have been used for the carbon fiber surface treatments. Whiskerization involves the growth of thin and high strength single crystals, such as silicon carbide (SiC), silicon nitride (Si3N4) and titanium dioxide (TiO2) at right angles to the fiber surface(25). Many polymerizable organic vapors are used for plasma polymerization process, such as polyamide, polyimide, organosilanes, propylene, and styrene monomers. Plasma polymerization is demonstrated to increase the polar component of surface free energy of carbon fibers(24) .

3. Gamma Treatment

In Gamma treatment, fibers are typically exposed to high-energy gamma-irradiation or laser irradiation resulting in surface roughening in addition to chemical groups such carbonyl. If the composites are exposed to irradiation, resin hardening takes place leading to enhanced strength and wear behavior. Performance of the fiber-reinforced composites considerably improved when fibers exposed to radiation because of surface roughening and improved fiber-matrix adhesion etc. (9)

Gamma-ray radiation was used to surface treat PAN carbon fibers. The efficiency of gamma-ray radiation was compared with air oxidation in terms of variations in the surface structure of carbon fibers and the mechanical performance of their composites. It was observed that the composites reinforced with the gamma-radiated carbon fibers showed higher interfacial adhesion strength and thus better flexural and shear properties than the composites reinforced with air-treated fibers. The observed higher content of carboxyl group on the surface of the gamma-radiated carbon fibers is likely to be responsible for the stronger fiber-matrix bonding. It is concluded that gamma-ray radiation is an effective approach of tailoring surface properties of carbon fibers (27).

In another study (28) the mixture of CFs and 0.5 wt% water solution of praseodymium nitrate was irradiated by gamma-ray for the dose of 3×105 Gy and found that oxygen functional group amount increased by inducing free radical reaction between CFs surface and oxygen dissolved in solution. They argued that the increasing amounts of oxygen-containing functional groups on the fibers played an important role in improving the degree of adhesion at interfaces and proved that gamma ray irradiation was beneficial to strengthen the chemical bonding between CFs and rare earth and increase the oxygen groups of fiber surface.

Furthermore, Li and colleagues (29) used Co60 gamma ray irradiation for CFs surface amendment. It was indicated that the oxygen/carbon ratio increased rapidly by XPS analysis. Moreover, two new photopeaks were emerged as C=O and plasmon, respectively. AFM study confirmed that the degree of surface roughness was increased by lower absorbed dose (30 kGy), yet excessive irradiation (>250 kGy) was not of value for mechanical interlocking between CF and epoxy resin.

Adding to that, high density of surface carbon oxygen functional groups was observed by gamma-ray irradiation process. As increasing the absorbed dose the gamma photons etched the surface of CFs continuously, however roughness reduced after treated by higher absorbed dose. It was indicated that irradiate CF at proper absorbed dose benefitted only.

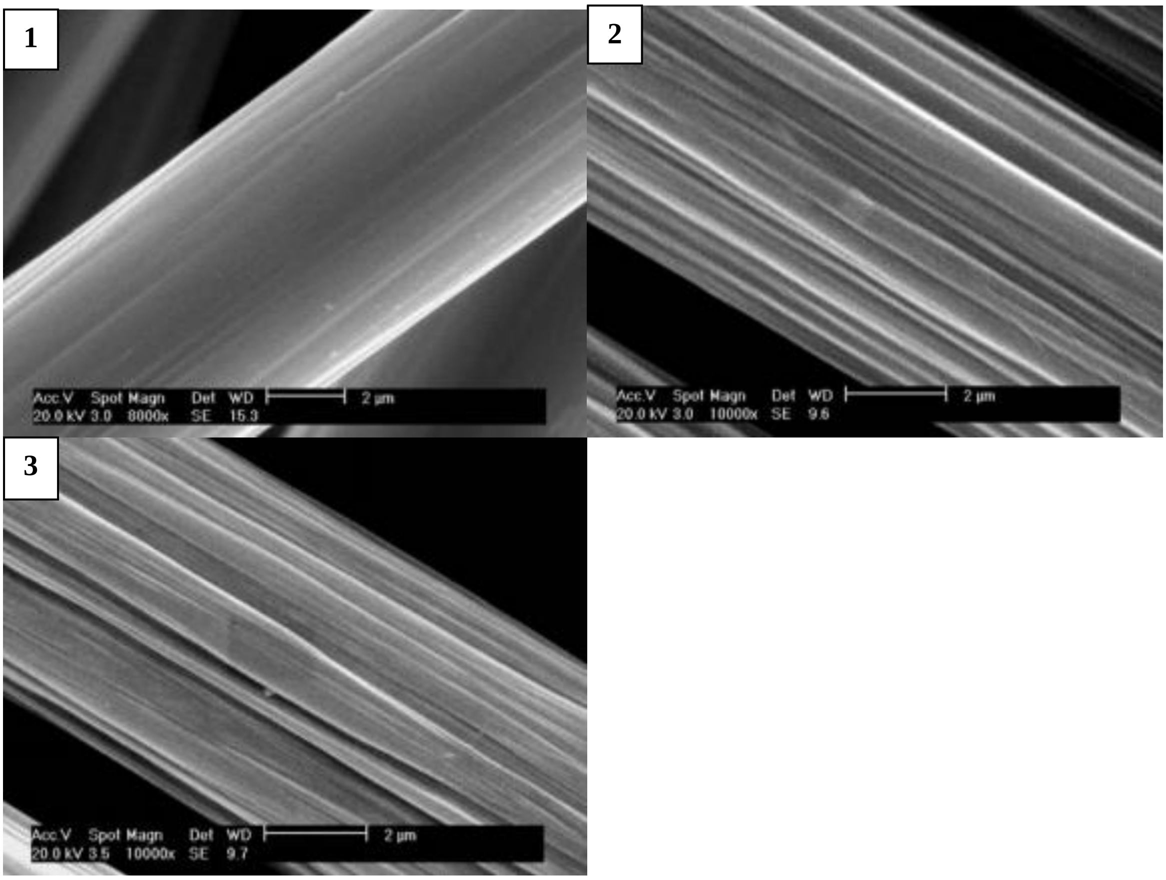

Fig. 2 : SEM photos of carbon fibers with different surface treatments: (1) untreated, (2) air-treated, (3) gamma-radiated [27] .

CONCLUSION

Surface treatment influence chemical and mechanical structure of carbon fibers and enhance chemical bonding with matrix. Increased roughness increases surface area on fiber surface to improve interactions between fiber and matrix Surface Different treatments have different influence on fiber surface. Optimization is required to select appropriate treatment method according to application and desired properties.

The study was done after approval of ethical board of Imam Abdurrahman Bin Faisal University.

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