Surface Treatment of Carbon Fibers - A Review

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Abstract

Carbon Fibers (CFs) are widely used as reinforcement material in polymer composites. However, they are having inert surface and do not allow matrix material to make bonding with it. Surface treatment of fibers is one of the suggested methods to improve adhesion between the two. Present paper concentrates on various methods used to surface treat the CF and gives details on physical, chemical and morphological changes occur in fiber properties. These changes due to treatment lead to improved composite properties due to improved surface area on fiber surface, chemical bonding and adhesion between fiber and matrix. Mainly used surface treatment methods are acid oxidation, plasma treatment, rare earth treatment, gamma irradiation etc. comparative study of these methods help in selection of appropriate treatment method as per requirement.

Keywords: Carbon fibers; surface treatment; composites

1. Introduction

CFs are mainly used as reinforcements in composite materials such as CF reinforced plastics, carbon-carbon composite, CF reinforced materials, and CF reinforced cement. CF offer the highest specific modulus and highest specific strength of all reinforcing fibers. 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 [1, 2].

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The two main sectors of CFs applications are aerospace and nuclear engineering, and the general engineering and transportation sector, which includes engineering components such as bearings, gears, cams, fan blades, etc., and automobile bodies. CFs when used without surface treatment produce composites with low interlaminar shear strength (ILSS). This has been attributed to weak adhesion and poor bonding between the fiber and matrix [3]. Treatments increase the surface area and surface acidic functional groups and thus improve bonding between the fiber and the resin matrix [4, 5]. 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 [6] 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 [2].

2. Effect of surface treatment of CFs

CFs, though very expensive are most favoured for tailoring high performance composites and tribo-composites. Their surface, however, is chemically inert and leading to the most potential problem of inadequate adhesion and hence weaker composite than the expected one. 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 a large number 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. First effect called as positive effect leads to the enhancement in fiber-matrix 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 [9]:

- By increasing the wettability of the fiber surface by the matrix resin.
- By removing the weak boundary layer, e.g., 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.
- By allowing the matrix molecules physically to entangle with, or diffuse into, the molecular network of polymer coating applied on the fibers.
- By promoting mechanical interlocking between the fiber and the matrix. This can be achieved by creating surface porosity, into which resin molecules can penetrate.
- By increasing the number of active sites on the fiber surface for subsequent chemical bonding with the unreacted species in the matrix resin.
- By applying a thin layer of ’coupling agent' that will chemically bond to both; fiber and matrix.

3. Surface treatment methods

Various treatment methods used for CF are classified in two categories i.e. oxidative and non-oxidative methods. In these categories, mainly used methods are; acid (HNO₃) treatment, plasma treatment, rare earth treatment and gamma irradiation of CF. Major types of surface treatments for CFs are discussed in brief as follows.
3.1. Oxidation treatment

In this method, acidic functional groups are produced on the CFs surface. The effectiveness of treatment in improving the surface properties depends on the concentration of oxidative medium, treatment time and temperature as well as fiber itself. Generally oxidation is achieved with gases (by air, oxygen, ozone etc.) or liquids (by nitric acid, hydrochloric acid etc).

Sellitti et al. [10] 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. Wu et al. [11] oxidized CFs by immersing in the nitric acid at 115°C for a period of 20 to 90 minutes. The acidic capacities of CFs increased almost linearly with the oxidation time. 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. [12] 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. Rand and Robinson [13] oxidized CFs by refluxing 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. Jang and Yang [14] refluxed CFs in 60% nitric acid for 40, 60, 80 min at 100 °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. The O1s/C1s ratio increased with the acid treatment time, which represents the introduction of polar functional groups that usually aid good wetting. Zhang et al. [15] performed oxidation of PAN 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. After HNO3 oxidation, there were more active groups (–O–C=O, –O–C=O) 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. Li [16] oxidized 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 in the nature of the chemical functions, by the conversion of hydroxyl-type oxygen into carboxyl functions. Zhang et al. [17] perform the oxidation of pitch based CF by heating CFs in nitric acid (65–68%) at 90°C for 1.5 h and found after treatment a active groups or active sites for van der Waals and hydrogen bonding on the surfaces of CFs increased, which improved the interfacial adhesion between the fibers and the surrounding PI matrix. After oxidation, there were more active groups (–O–C=O, –C=O, –O–C=O) on the surfaces of the CFs, which increased total surface energy and their polarity and thus enhanced the wettability of the CFs with the PI matrix. Su et al. [18] modified carbon fabric by strong HNO3 etching by immersing in a 13 mol/L HNO3 solution for 2 h and observed the active groups produced during the oxidation process, which contributed to strengthen the bonding strength between the fabric and the adhesive. XPS analytical results showed that the etching lead to a little decrease in the C concentration and a minor increase in the O concentration on fabric. At the same time, the N concentration of the fabric dramatically significantly decreased by etching with HNO3.

Tiwari et al. [19] 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 (Fig. 1) 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. These groups increased its chemical reactivity and wettability with matrix. With increase in treatment time pick up of matrix by fabric (supporting enhanced fiber matrix adhesion) increased sharply upto 60 minutes followed by slow rise till 90 minutes time. Tensile force taken by fabric tow continuously decreased with increasing treatment time and load bearing capacity of fibers reduced by almost 40% after 3 hrs of oxidation.

3.2. Plasma treatment

Plasma is defined as an electrically conducting medium generally consisting of negatively charged electrons, positively charged ions, and neutral atoms or molecules or both. The main purpose of plasma 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].

Various adhesion mechanisms can be promoted by plasma treatments. These include: (a) possible removal of surface contaminants to provide better fiber/resin contact; (b) an enhanced degree of mechanical keying between the fiber and the matrix because of the increased fiber surface roughness; (c) an increased surface energy which would promote wetting of the fiber by the matrix; and (d) deposited functional groups for possible chemical interactions between the fiber and the matrix resin.

Sun et al. [21] treated surface of CFs by means of oxygen plasma and observed that higher reactivity between fiber surface and matrix as a result of an increase of COOH, --C--OH and =C=O groups on the fiber surface. The surface constitution was changed by the plasma treatment and improved the wetting properties of fiber surface. The contact angle between water and the CFs was decreased from 75° to 61°. Electron micrographs of CFs surface showed the surface striations and surface roughness were changed increasingly after plasma etching.

Jang and Yang [14] studied the effect of oxygen plasma treatment on surface morphology of CF for varying time from 1 min to 5 min and found that the BET surface area on the CF surface increased due to results from micro-pittings 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. However, the weak boundary layer of CF is removed by oxygen plasma treatment so that the increment of O1s to C1s ratio was relatively small.

Donnet et al. [22] investigated 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.

Su et al. [18] modified carbon fabric with air plasma bombardment at 130 V for 5 min and confirmed by XPS analysis that the air plasma bombardment led to a little decrease in the C concentration and a minor increase in the O
concentration of the carbon fabric. However N concentration of the carbon fabric dramatically increased after bombarded by air plasma. Tiwari et al. [23] studied effect of plasma by four types of CF viz. virgin (F0), treated with cold nitrogen plasma (FP1), mixture of cold nitrogen plasma with 0.5% O2 (FP2) and mixture of cold nitrogen plasma with 1% O2 (FP3). Fibers after treatment showed improved adhesion with the matrix as supported from adhesion test and SEM analysis of fiber morphology (Fig. 2). Almost 25% higher matrix pick up was observed in the case of FP3 CF. A nominal reduction in tensile strength of CFs tow was observed due to plasma surface treatment. Raman spectroscopic analysis indicated slight distortion in the graphitic structure of CF after treatment. Composite with highest O2 (1%) dosing proved the best in mechanical properties. Almost 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.

3.3. Gamma treatment

In this treatment, fibers are exposed to high-energy gamma-irradiation or laser irradiation which leads to surface roughening as well as addition of 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. Xu et al. [24] irradiated the mixture of CFs and 0.5 wt% water solution of praseodymium nitrate by gamma-ray for the dose of $3 \times 10^5$ 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. Wan et al. [25] irradiated CF to integral doses of 2kGy at a dose rate of 67 Gy/h, in oxygen atmosphere and ambient temperature. It was recognized that radiation affected the crystal lattice by displacement of atoms within the lattice or electronic excitation. The electrons stripped from the atoms were believed to cause dimensional (topographical) change of CFs and to create active sites on fiber surfaces which bonded with functional groups of bulk polymers. They found that oxygen content increased by 69% after gamma-ray radiation. Fibers showed a presence of the carboxyl group and hydroxyl group. Li et al. [26] Co60 gamma ray irradiation was used for modification of CFs surface. XPS analysis, indicated that the oxygen/carbon ratio increased rapidly. 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), but excessive irradiation (>250 kGy) was not beneficial for mechanical interlocking between CF and epoxy resin. 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.
Li et al. [27] gamma-ray irradiation graft technology was used in order to enhance the surface performance of the CF. XPS results showed that the value of O/C and the quantity of oxygen functional groups on CF surface were enhanced efficiently after treatment. The surface roughness of CF was greatly increased compared with the untreated CF. In addition, the specific surface area of CFs and the contact area between the CF and the resin was increased. These all promoted the formation of a good interface when fabricating composites. Tiwari [28] et al. performed treatment to carbon fabric by exposing it to Cobalt-60, γ-radiation source with activity of $1.3 \times 10^4$ Curie for three doses (100, 200 and 300 kGy) at the rate of 4.54 kGy/hr in air. SEM studies showed (Fig. 3) that with the increase in dose from 0-300 kGy, roughness of the fiber surface increase. The fabric treated with 300 kGy dose picked 22.8% higher amount of matrix as compared to the untreated fabric. Raman spectroscopy confirmed slight distortion in graphitic structure as indicated by the increased $I_D/I_G$ ratio. Maximum 35% increment was observed over $I_D/I_G$ ratio for untreated fabric in case of 300 kGy dose. The enhancement in adhesion between the matrix and CF led to the improvement in ILSS of all the composites. Almost 60% increase in ILSS was exhibited by CG3.

3.4. Rare earth treatment

According to the chemical bonding theory, it is suggested that rare earth elements are adsorbed onto both the CFs surface and the matrix through chemical bonding, which increases the concentration of reactive functional groups due to the chemical activity of rare earth elements [29]. These reactive functional groups can improve the compatibility between CFs and PI matrix and form a chemical combination between the CFs and PI matrix. So the interfacial adhesion between CFs and PI matrix is increased. Cheng and Shang-guan [30] argued that rare earth element has big effective nuclear charge and strong ability to attract electrons of other atoms around it. It is suggested that RE will firstly be adsorbed onto the CFs surface in the surface treatment. Then, RE will strongly attract the electrons in CC bond of CFs, resulting in the excursion of the electron cloud of CC bond and weakening the CC bond. Therefore, it is easier for functional groups to react with CFs, and more functional groups will be introduced on the fiber surfaces. When there is a strong bonding between fibers and the matrix resin, the load stress is effectively transmitted from the matrix to fibers, and fibers can successfully carry the load. The main mechanisms for surface treatment to improve the interfacial bonding of CFs composites are that surface functional groups are introduced on the fiber surfaces which interact with the matrix.

Qianqian and Xianhua [31] dipped CFs into an alcoholic solution of LaCl$_3$ (0.3 wt.%) for 3 h and showed by XPS study of CF surface that oxygen concentration increased after treatment and the amount of oxygen-containing groups were largely increased which a play important role in improving surface-free energy and adhesion between fiber and matrix. The untreated and RE treated fibers had the O1s/C1s ratio of 8.96% and 38.4% respectively.

Zhang et al. [32] investigated the influence of rare earth surface treatment on CF, soaked in an alcoholic solution of LaCl$_3$ (0.3 wt.%) for 5 h. The LaCl$_3$ solution etched the surface of CFs increased the surface roughness and possessed a larger surface area and formed more mechanical interlocking sites. In addition, the enhancement of the surface roughness reduced the contact angle between fibers and PI and hence increased the wettability. In XPS analysis, lower After rare earth treatment, the content of $-\text{C}=-\text{C}-$ decreased while the content of $-\text{C}=-\text{OH}$, $-\text{C}=-\text{O}$, Bridged structure, $\text{C}=\text{O}$ and $-\text{COOR}$ increased, which increased total surface energy and their polarity thus enhanced the wettability of the CF with the matrix. Zhiwei et al. [33] found that effect of soaking and irradiating in
praseodymium nitrate solution (0.1%-0.5% rare earth) lead to an increase of CFs surface roughness, improvement of oxygen-containing groups, enhancement of disorder degree and introduction of praseodymium element on CFs surface. As a result, the coordination linkage between fibers, praseodymium ion and matrix was formed.

Xu et al. [24] found that rare earth treatment introduced some degree of surface disorder measurable by Raman spectrometry. It was noticed that various peak parameters change somewhat upon rare earth etching and oxidation. Rare earth treatments brought about a slight rise in the $I_D/I_G$ and $W_D/W_G$ ratios, indicative of an increase in the degree of disorder, which occurred through the breaking of aromatic bonds and the reduction of surface crystallinity. CF surface became rougher and produced surface striations when soaked and irradiated in rare earth solution, both factors promoted mechanical keying or interlocking mechanism between the fibers and the matrix. Tiwari et al. [34] surface treated CF by suspension of YbF$_3$ in ethyl alcohol prepared with three doses (0.1, 0.3 and 0.5 % by wt.). YbF$_3$ treatment to CF led to the changes in surface topography of fibers (Fig. 4) and inclusion of oxygenated functional groups such as ether, carbonyl and carboxyl. Overall it was concluded that YbF$_3$ treatment to CF is beneficial only when employed judiciously. If treatment concentration exceeds a typical value (0.3wt% in this case), properties of composites start falling down to the extent that occasionally 0.5wt% YbF$_3$ treated composite was slightly poorer in performance than the untreated one. FESEM studies confirmed that the YbF$_3$ particles when adhere to the fibers in mono-molecular layer fashion, leads to the enhanced fiber-matrix adhesion. If multi-molecular layers are formed, in case of 0.5 wt%, adhesion is less and the composites developed from such fabrics show lower strength.

4. Conclusions

Based on study done by various researchers, this can be concluded that surface treatment of CFs is essential to improve its adhesion with various matrices. Treatment significantly influences fiber characteristics. Following observations are made;

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

References


