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Surface modification and grafting of carbon fibers: A route to better interface

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ABSTRACT

This review is an audit of various Carbon fibers (CF) surface modification techniques that have been attempted and which produced results with an enhancement in the interfacial characteristics of CFRP systems. An introduction to the CF surface morphology, various techniques of modifications, their results and challenges are discussed here. CFs are emerging as the most promising materials for designing many technologically significant materials for current and future generations. In order to extract all the physic-mechanical properties of CF, it is essential to modulate a suitable environment through which good interfacial relation is achieved between the CF and the matrix. The interface has the utmost significance in composites and hybrid materials since tension at the interface can result in a deterioration of the fundamental properties. This review is aimed to provide a detailed understanding of the CF structure, its possible ways of modification, and the influence of interfacial compatibility in physic-mechanical and tribological properties. Both physical and chemical modifications are illustrated with specific examples, in addition to the characterization methods. Overall, this article provides key information about the CF based composite fabrication and their many applications in aerospace and electronics-where light weight and excellent mechanical strength are required.

1. Introduction

Since the creation of high performance carbon fibers(CF) in 1958 by Roger Bacon, it has been the wonder material of the 21st Century [1–3]. The CF is very light with low specific gravity and exhibits attractive mechanical properties such as high specific elastic modulus and tensile strength, in addition to the low thermal expansion coefficient, high thermal shock resistance, heat conductivity, electrical conductivity, chemical stability, self-lubrication property, etc. [3–10]. As a result, this new breed of high strength material has paramount significance in designing many devices for aerospace (commercial and military aircraft, in particular), sports goods, automotive industries, etc. Cfs are obtained by the controlled pyrolysis of various fibers containing 90% Carbon. Reports show more than 60% of consumption of CF by the United States for different industries. It has recently reported that Japan is the highest producer of this particular material [11–15].

Polymer composites and their applications need no introduction and Cfs have taken a supreme role as the primary load bearing constituent in advanced composite applications [16]. CF is used to fabricate the composite having light weight, stiffness, high temperature and damping resistance, chemical inertness, and outstanding fatigue properties. It is expected that the CF reinforced composites (CFRP) would produce august results if the composite system is a synergistic heterogeneous mixture. The interfacial characteristics of CF and matrix or any adjunct plays a pivotal role for the composite's application [17–20]. The CF surface is non-polar, has poor wet ability and comprises highly crystallized graphitic basal planes with inert structures. Also, the inert and smooth characteristic of the CF surface yields to the low interfacial strength as there is a lack of interfacial covalent bonds [1], which had been a major issue as this affected the ultimate mechanical properties of

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CFRP composite systems. Hence, the need for surface treatment of CF such as plasma modification [2–9], chemical oxidation [10–13], electrochemical treatments [14,15,17–19], high temperature atmospheric oxidation [20–23], radical trapping grafting [24–26] and surface functional group grafting procedures [27–29,3] have augmented and dedicated research groups have reported their findings. It was also observed that the surface density, surface morphology, roughness and the functional groups present on the surface arbitrates the adhesion between the fiber and the binder phase [30–32].

Over the last decade the production of carbon fibers have increased from 15,000 mt to 40,000 mt. There has been a surge of growing interest in the carbon fiber community to develop innovative, efficient, high-yielding methods of surface modifications of CF. In view of the magnitude of improvements in properties these modifications provide scaling up to industrial technology will be a challenge on its own but will surely be the ultimate goal of these studies. Numerous reports have already come out about the supreme applications of CFRP, by minimizing the effect of interfacial tension [30–35]. Understanding the complete perspective of the CFRP system mechanics of which CF is the climacteric entity becomes a pre-requisite. Thus, a study explaining the structural and functional characteristics of CF and various methods to improve its surface properties is the need of the time. A review has come out on the surface treatments of CF [33]; However, a detailed and up-to-date survey on this hot topic will be helpful to solve several issues of CFRP and modified CFRP manufacture yielding supreme materials.

2. Structural features of carbon fiber

The interaction between the binder and fiber can be well understood if we are familiar with the surface structure, which correlates to the internal structure of CF. It was sought to be as a concoction of highly oriented interconnected heaving submicron size ribbons in the early model [36], which was then later modified substantially through the studies of Diefendorf and Tokarsky [37]. Thereby, continued by the plasma etching work of Barnet and Norr [38], and the identification of phase heterogeneity also including the possible presence of 3-dimensional graphite phase [39,40]. From these studies, it is proved that the high modulus CF possesses two phases- turbostratic graphitic ribbons and 3d graphite inclusions-specifically reported when it is thermally treated to about 2000 °C. These turbostatic phases consist of wider, thicker, more axially oriented ribbons and narrower, less oriented, intertwined fibrils. Both phases contained several microcracks, microvoids, and lattice faults as well. The phase orientation was found to be less in the center or core of the fiber, whereas in the outside sheath more highly oriented perfect ribbons were seen. A mixture of these two variants are usually present in between the center and the sheath [40].

The skeletal structure of CF (polyacrylonitrile, PAN based CF) is represented in Fig. 1 [38]. From the figure, it can be observed that the highest orientations are found at the surface, but it contains exposed edge planes and basal planes. The high energy panes comprise of sp^2 carbons which have a free bond and thus can form very strong carbon – oxygen complex by chemisorbing oxygen [41] which would bond further with the binder resin. The low energy basal planes can also interact, but the bonds formed at the surface will not be so strong due to the weaker πinteractions. The other surface exhibits microporosity, cleavage cracks, crystallite boundaries, fibrillar microtexture, foreign inclusions and fracture inducing flaws which also affect the fiber resin adhesion. Therefore, surface characterizations are required to assess their significance.

The influence of CF structure on the processing temperature and mode of extraction has an adverse impact on its mechanical properties. In CFRP composites, this fact pronounces more as the CF again faces several experimental conditions during the composite manufacture. The CF may not have real interaction with the selected polymer [42,43]. All these factors point towards the various ways of surface treatment by which the utmost properties of CF can be extracted and fully utilized in

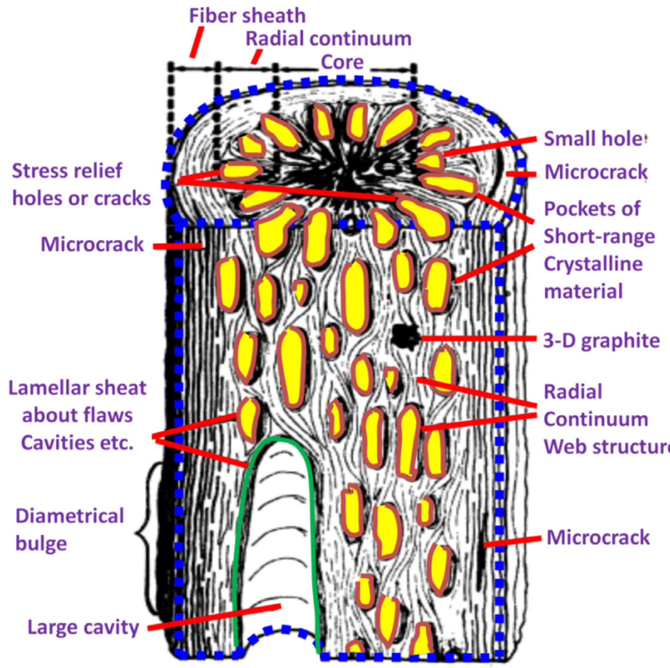

Fig. 1. Skeletal representation of Poly AcryloNitrile(PAN) based CF surface [38].

the CFRP composites.

3. Changing the surface

CF's are compatible with various matrices making them versatile reinforcements in composites. It is well established that, on application of load to any composite system, the transfer of stresses between reinforcements (CF filaments in this case) is achieved via the matrix demanding a strong fiber-resin bonding [44]. A weak fiber-resin bonding will be detrimental to the composite's mechanical properties, such as low inter laminar shear strength (ILSS). Thus, resolving surface treatment of fibers CF is needed apart from or along with the matrix modifications. The optimization of the surface treatment is imperative, as the composite will remain weak if the treatment is inadequate or will turn out to be brittle if too strong. Among the different classes, high modulus (HM) CFs will require the maximum treatment [45–47].

The surface treatment, in general, can be classified into two, a physical modification to the surface by enhancing roughness which results in the increase of surface area i.e. more number of contact points, micro-pores on the already porous surface of CFs. The second involves functionalizing (chemical modifications) the CFs with reactive functional groups which covalently bonds with the other phase, both enhancing the interface adhesion. Most of the methods encompass both the changes. Apparently, any surface treatment method which results in etching of the fiber's surface also adversely affects the fiber strength. Thus, the final strength of the composite and success of the treatment depends on the optimization of the treatment to get the maximum possible enhancement. A successful surface treatment is bound to [33]:

a. Increase the wet ability of the fiber surface to the matrix resin which involves the removal of the weak boundary layer, for instance, contaminant species or gas molecules adsorbed on the surface.
b. Ensure the significant level of van der Waals interactions, which allow the matrix molecules to physically entangle with, or diffuse into, the molecular network of polymer coating/ chemical adjunct applied onto the fibers.
c. Promote mechanical interlocking between the fiber and the matrix, usually done by creating surface porosity into which resin molecules