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Crystallinity of Commercial Carbon Fibers from X-ray Diffraction (XRD) Studies †

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Abstract

Sized carbon fibers have commercial significance. Such carbon fibers serves as an excellent reinforcing material with the polymer resin filler matrix leading to the formation of carbon fiber reinforced composites (CFRCs). Polarized carbon fibers find applications in the realms of health, energy, environment, defence, catalysis and smart materials. For brevities' sake, the focus of the current research paper is only on the structural characterization of carbon fibers using XRD. The structure of the pitch derived (NX90, NX100) and polyacrylonitrile, PAN, (T700SC) derived sized commercial carbon fibers (CFs) were analysed using X-ray diffraction (XRD) technique. The inter layer spacing (d_{002}) of NX90, NX100, T700SC and graphite were 0.3388, 0.3395, 0.3514 and 0.3350 respectively. Likewise, the average crystallite size (d_{002}) along the c-axis for NX90, NX100, T700SC and graphite were 14.10, 14.26, 1.33, and 0.06708 nm respectively while the average crystallite sizes along a-axis for NX90, NX100, T700SC and graphite were 29.16, 29.25, 2.75, 0.2461 nm respectively. Thus pitch based carbon fibers (NX90, NX100) exhibited polycrystalline graphitic structure while polyacrylonitrile (PAN) based fibers (T700SC) have turbostratic graphitic carbon structure. Such changes in structure will have implications on the performance of CFRPs ultimately produced using the carbon fibers reported here.

Keywords: Carbon fibers, pitch, polyacrylonitrile, characterization, structure, crystallinity, XRD

INTRODUCTION

Commercial carbon fibers (CFs) can be produced, mainly either from pitch or polyacrylonitrile (PAN). As such carbon fibers are no better than wood or stones. Yet, they can be made as valuable as silver by surface functionalization (to induce surface polarity and multifunctionality) and as precious as gold by compositing the surface modified carbon fibers with either carbon materials or resin based matrices. This is analogous to the promise of hope found in the book of Isaiah that "For brass I will bring gold; and for iron, I will bring silver and for wood brass, and for stones iron, Isaiah 60:17." Industrial process of preparation of commercial carbon fibers involves various vital steps. After the formation of the fibers from the raw material, the fibers will be treated by a process called sizing. This process will enhance the polarity of the surface of the carbon fibers, mainly, by enriching oxygen surface functional groups on the surface. Apart from sizing, another vital process involved in the production of carbon fibers is treatment with oil agent to induce exceptional strength to the carbon fibers.

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Carbon Fibers

Carbon fibers are the main load bearing component of the CFRPs' is the carbon fiber owing to high specific strength and light weight of the CFs'. However, the surface of CF's is chemically inert making compatibility between CF surface and polymer matrix a problem. As a result there is week bonding at the interface between the CF surface and the polymer matrix. To overcome this problem, methods for the surface functionalization of carbon fibers to generate surface polarity, grafting molecules with oxygen functionality, were developed, that have revolutionized the applicability of carbon fibers many a fold.

Surface Modified Carbon Fibers

Innovative strategies are being developed to modify the surface of CFs to make the surface rough and chemically reactive and to design a strong interfacial bonding between the CF surface and polymer matrix leading to the increase in the usefulness of the CFRPs' many a fold due to enhancement in critical properties of the CFRP's like interfacial shear strength (IFSS). State of the art developments in the surface modification of carbon fibers enhancing the applicability of carbon fibers many a fold were systematically compiled in a review [1].

Application of Surface Modified Carbon Fibers

Materials based on surface modified carbon fibers find applications in diverse fields of human activity, ranging from, health, energy, environment, defence, catalysis and smart materials as shown in Figures 1–6. Other vital sectors of human endeavours, namely, agriculture, construction, transportation, communication, and space exploration are also being immensely benefited with the advances in carbon fiber surface modification methods.

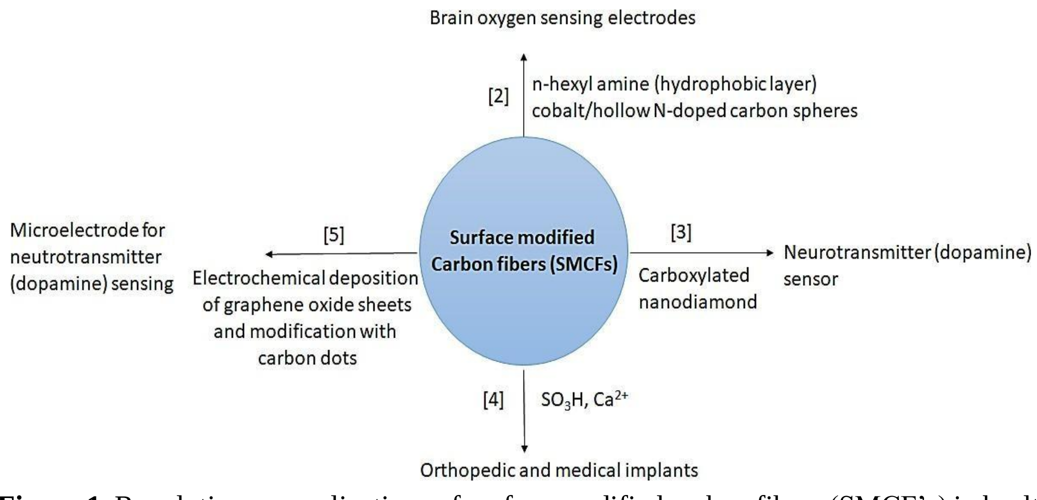

Figure 1. Revolutionary applications of surface modified carbon fibers (SMCF's) in health [2–5].

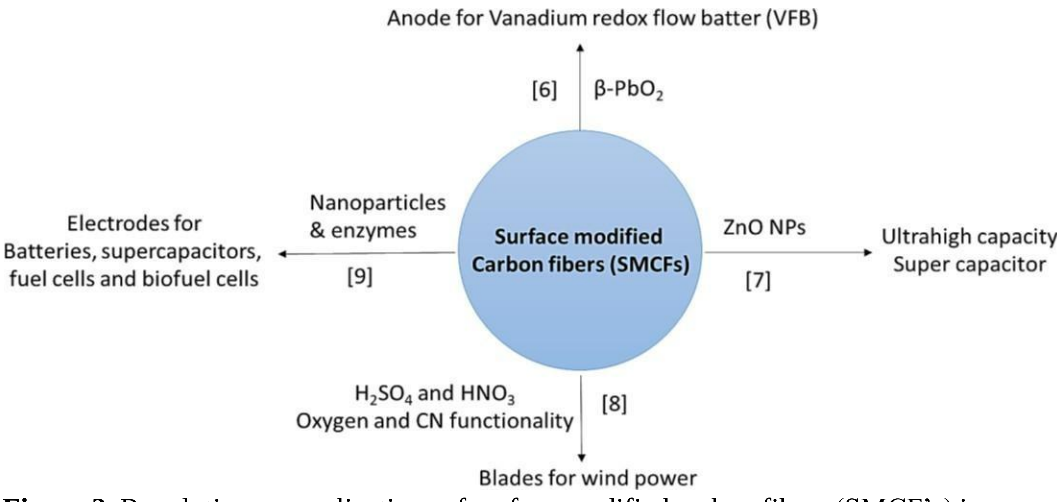

Figure 2. Revolutionary applications of surface modified carbon fibers (SMCF's) in energy [6–9].

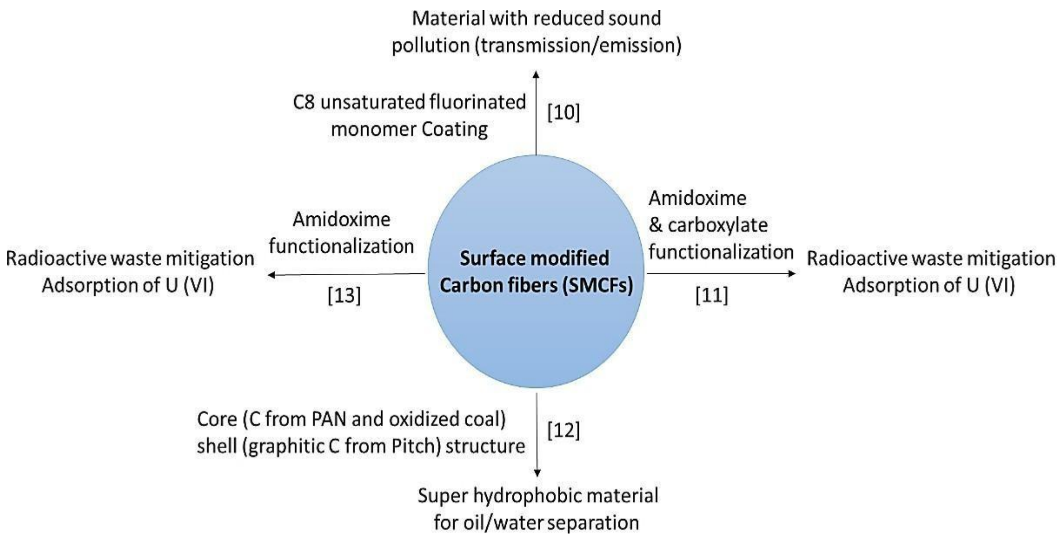

Figure 3. Revolutionary applications of surface modified carbon fibers (SMCF's) in environment [10–13].

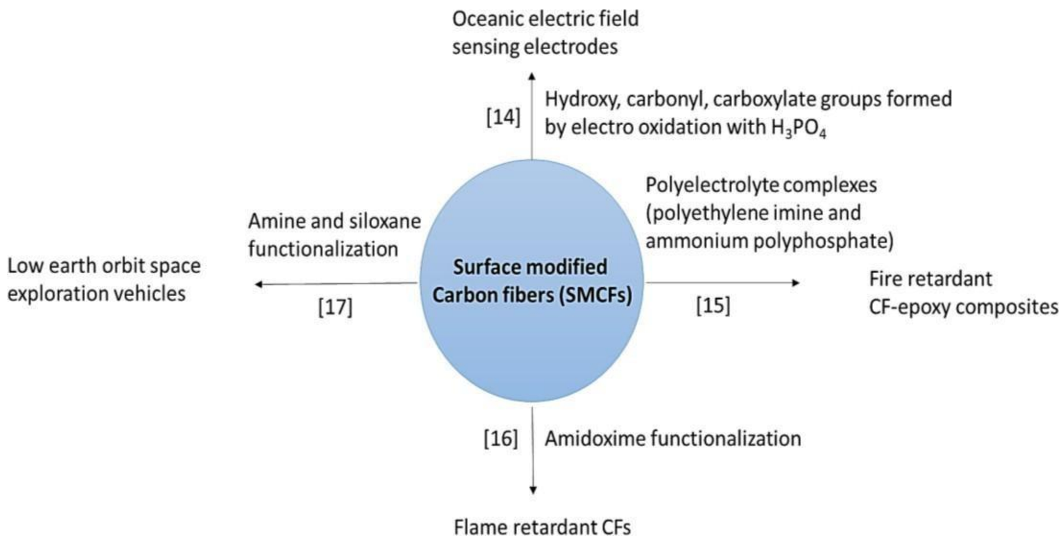

Figure 4. Revolutionary applications of surface modified carbon fibers (SMCF's) in defence [14–17].

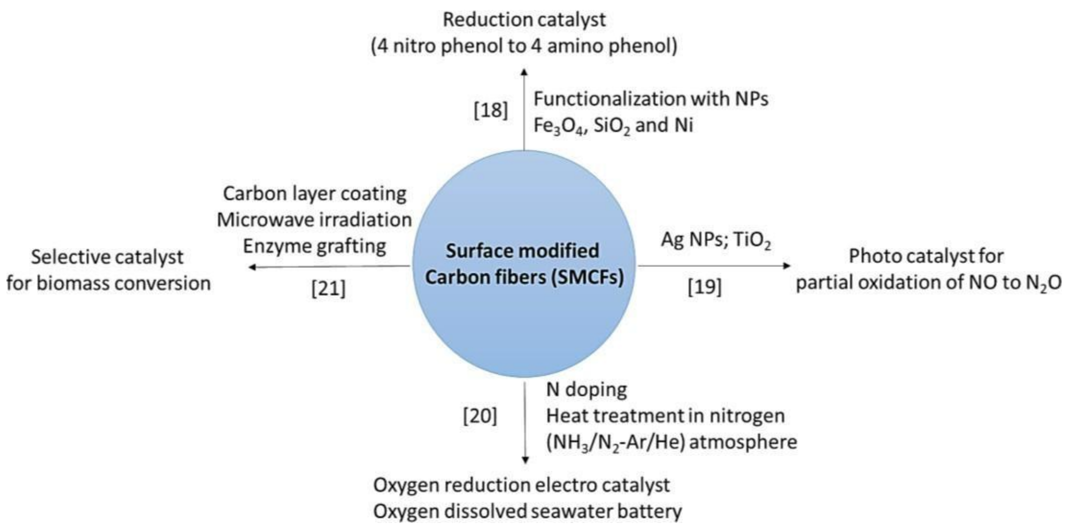

Figure 5. Revolutionary applications of surface modified carbon fibers (SMCF's) in catalysis [18–21].

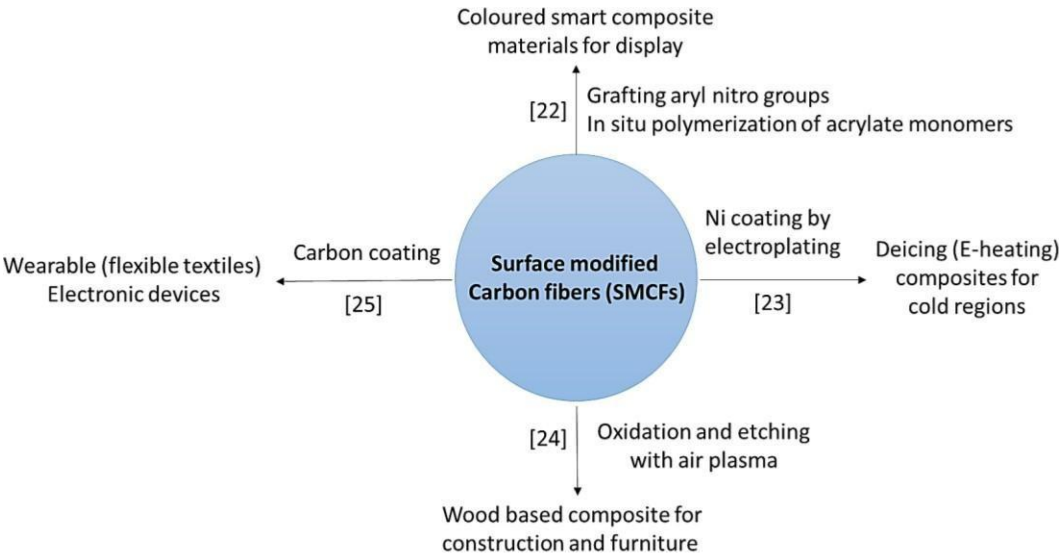

Figure 6. Revolutionary applications of surface modified carbon fibers (SMCFs) in smart materials [22–25].

Thus the surface modification of CFs increased the sphere of usefulness of CFs many a fold and their application domain was enlarged covering many sectors of human activity ranging from health, energy, environment, defence, catalysis and smart materials. Owing to the growing applications of surface modified carbon fibers (commercial carbon fibers), it is necessary to have an in depth understanding of their structural properties. The objective of the current work is to systematically characterize the pitch (NX90 and NX100) and polyacrylonitrile, PAN based carbon fibers (T700SC) for understanding their structure using X-ray diffraction. Such a study will facilitate establishing structure-property-application relationship.

EXPERIMENTAL

Materials and Methods

PAN based sized carbon fibers (T700SC-24K series) were provided by Toray industries Inc., Pitch based carbon fibers (NX90 and NX100) were procured from Nippon graphite fiber Co., Samples of carbon fibers (NX90, NX100 and T700SC) for powder XRD analysis were prepared by grinding the carbon fibers in a mortor and pistle by the addition of few mL of ethanol. As pitch based fibers are brittle, making powder of pitch based fibers (NX90, NX100) is easier than that of PAN based fibers (T700SC). Addition of ethanol greatly eases the process of grinding carbon fibers to fine powder suitable for XRD analysis. Not only for forming the power, but also for obtaining single fibers from the brittle pitch based carbon fibers (NX90, NX100) addition of few drops of ethanol is helpful and saves time and effort.

Calculation of the Structural Parameters of Sized Carbon Fibers

Quantitative treatment of the XRD data is carried out by calculating the interplanar spacing using Bragg equation (1) as shown below [26]:

$$d = n\lambda/2Sin\theta \ldots \quad (1)$$

where λ is the wave length of the radiation (CuKα) used = 0.15405 nm
θ is the diffraction angle for the peak position.

Likewise, the average crystallite size along the "c" axis (L_c) and along "a" axis (L_a) were calculated using Scherrer equation (2) shown below:

$$L = K\lambda/\beta Cos\theta \quad (2)$$

where L = L_c and L_a are the crystallite size along “c” and “a” axes

β is the half-width of the peak in radians and K is the shape factor. The shape factor K depends on the lattice dimension. The K values of 0.9 and 1.84 were used respectively for calculating L_c and L_a values [26].

RESULTS AND DISCUSSION

Structural Characterization of Carbon Fibers with X-ray Diffraction (XRD) Technique

X-ray diffraction is the first and foremost technique that is of immense use for the analysis of inorganic solids. Strangely, purely, organic materials belonging to the class of carbon materials, like carbon fibers, too can be characterized by XRD to gain insights into the structural details. XRD plots of cabron fibers NX90, NX100 and T700SC were shown in Figure 7, 8 and 9 respectively. Full width at half maxima (FWHM) of the d_{002} reflection is a measure of the crystallinity of the carbon material. The sharper the peak, the greater is the crystallinity. Simple observation, by an expert eye, of the d_{002} reflection from NX90, NX100 and T700SC; leads to a conclusion that the pitch based carbon fibers are more crystalline than the PAN based carbon fibers (Figures. 7–9)

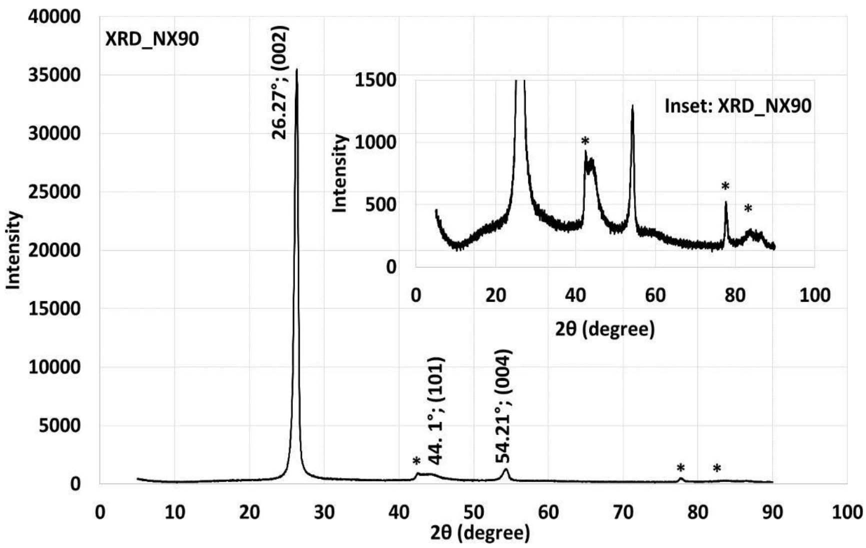

Figure 7. XRD pattern of pitch based carbon fibers NX90.

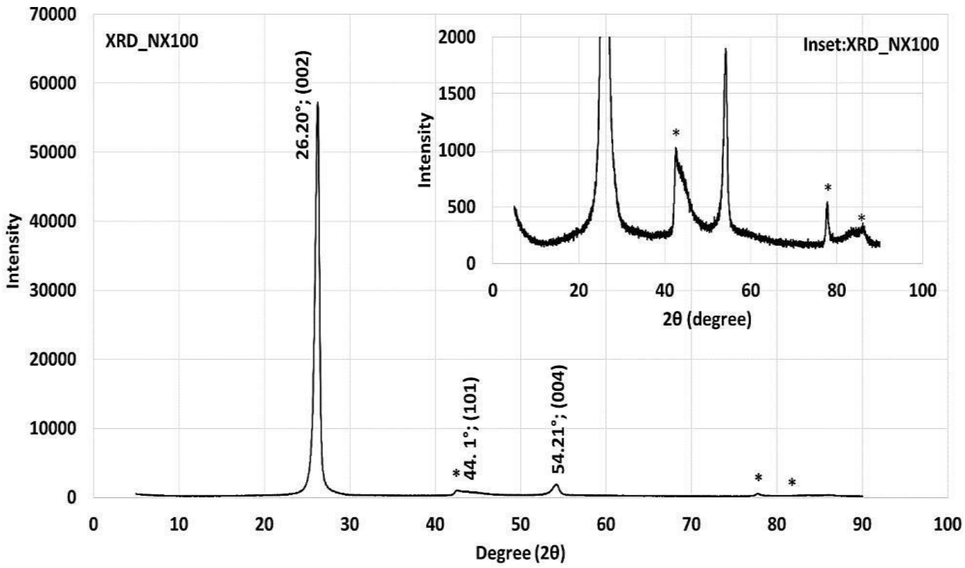

Figure 8. XRD pattern of pitch based carbon fibers NX100.

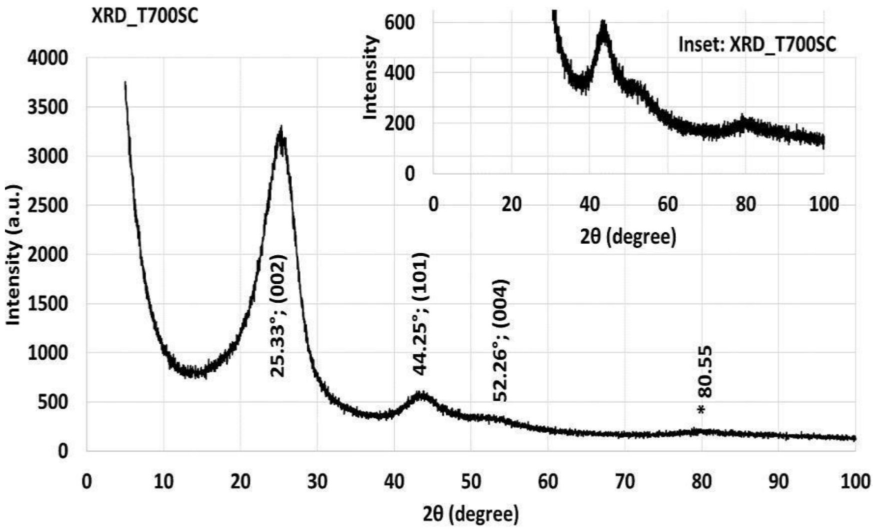

Figure 9. XRD pattern of polyacrylonitrile (PAN) based carbon fibers T700SC.

Irrespective of the carbon source (pitch or polyacrylonitrile, PAN) of all the carbon fibers NX90, NX100 and T700SC tested showed graphitic carbon structure. However, the fibers prepared from pitch are more crystalline than those prepared from PAN, as expected. Pitch has inherent aromatic structure while polyacrylonitrile (PAN) has a linear carbon chain structure Figure 10 [26]. This results in higher degree of graphitization in pitch based carbon fibers compared to PAN based fibers upon carbonization. Such higher degree of graphitization of pitch based fibers is reflected by the sharpness of XRD peaks.

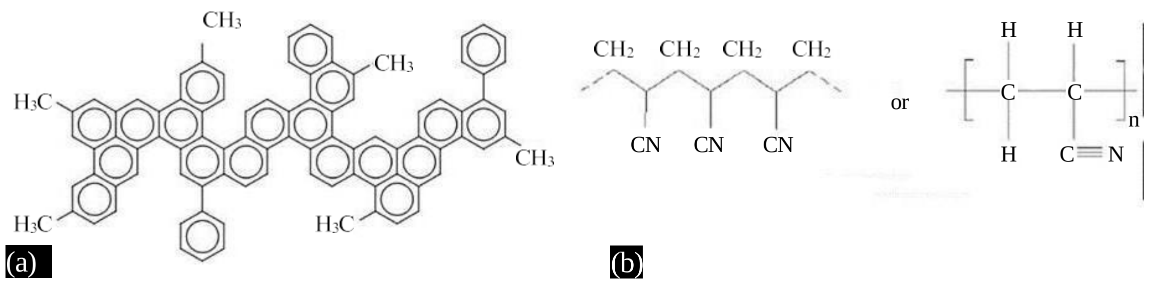

Figure 10. Structure of (a) Pitch and (b) Polyacrylonitrile (PAN<>).

Diffraction peaks in the XRD pattern of NX90 and NX100 at ~26.27, 44.1 and 54.21° are indexed to the (002), (101) and (004) planes of graphitic carbon (Figures. 7 and 8) Likewise, the diffraction peaks in the XRD pattern of T700SC at 25.33, 44.25 and 52.26° as well are indexed to the (002), (101) and (004) planes of graphitic carbon (Figure 9). Interesting observation is that in additional to the signals typical of graphitic carbon materials, additional signals of lower intensity were observed (shown in the inset of Figures. 7, 8 and 9 by magnifying the X-axis) and those peaks are marked with the symbol "*". These signals are attribute to those planes in the graphitic strucutre at the curvature of the carbon fiber. Unlike regular graphene which is comprised of layered structure of hexagonal arrangement of carbon atoms, in carbon fibers these graphene sheets are folded in the form of cylinders and so they will have curvature at the folding. The graphitic planes at the curvature are marked with the symbol "*". Infact such diffraction peaks are noticed in the XRD pattern of similar carbon structures like multiwalled carbon nanotubes [27].

For making the comparison of the peak areas perceptible, the overlaid XRD plots for the carbon fibers (NX90, NX100 and T700SC) is shown in Figure 11.

As can be seen, the peak indexed to the (002) graphitic plane of the carbon structure of pitch based CFs (NX90, NX100) is sharper and intense compared to the corresponding peak in the PAN based (T700S) Ccarbon structure. The full width at half maxima of the peak indexed as (002) is a measure of the crystallite size of the graphtic planes ordered along the c-axis and a-axis. The ordering of the graphene sheets along the “c” and “a” axes in graphitic carbon structure were shown in Figure 12.

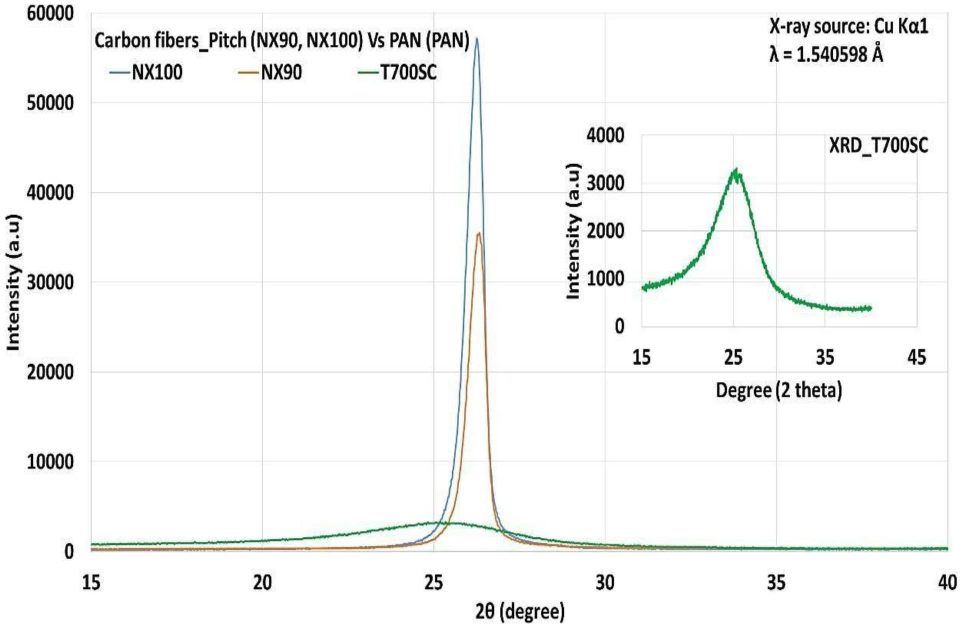

Figure 11. XRD pattern of NX90, NX100 and T700SC – A comparison.

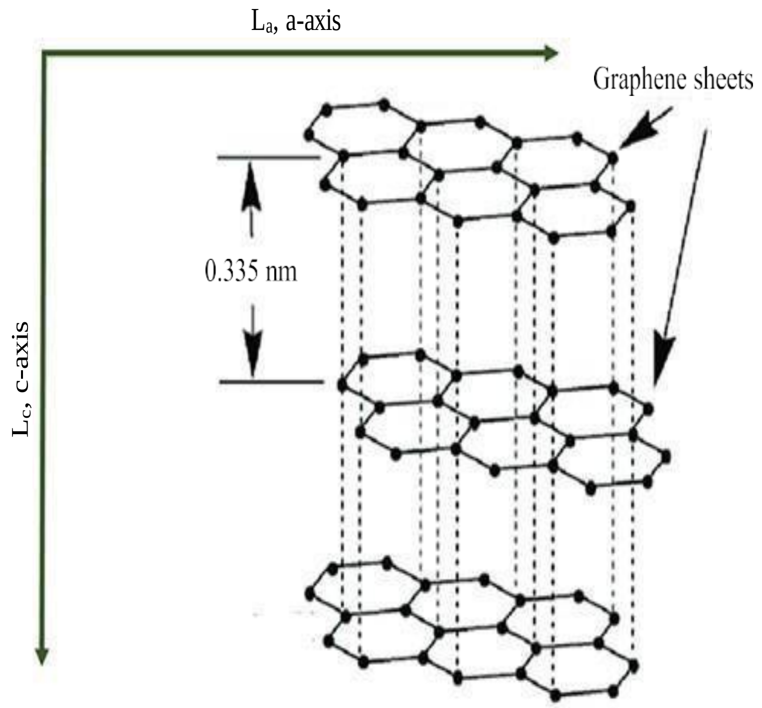

Figure 12. Ordering of graphene sheets along the “c” and “a” axis in a graphitic carbon structure.

For comparision, the XRD peak patterns of the pitch based (YSH50A) and PAN based (M46J) CFs from literature were shown in Figure 13.

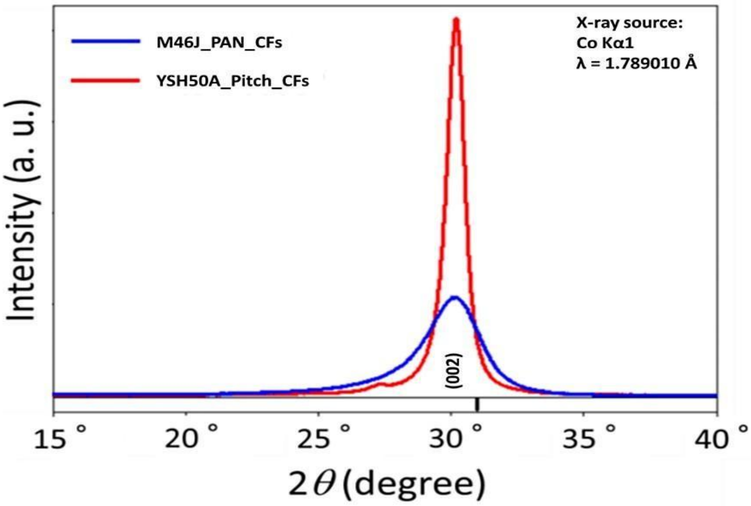

Figure 13. XRD pattern of pitch based (YSH50A) Vs PAN (M46J) based carbon fibers – A comparison [adapted with permission from MDPI, reference 28].

Determination of Structural Parameters and Crystallinity of Carbon Fibers Using XRD

Information on the relative degree of crystallinity and the dimensions of the crystallite sizes of the carbon fibers (NX90, NX100 and T700SC) along the 'c' and 'a' axis were deduced by comparing area of the peak under the peak indexed to the (002) plane of the graphitic structure. For making the comparison of the peak areas perceptible, the overlay XRD plots for the carbon fibers (NX90, NX100 and T700SC) is shown in Figure 12. As can be seen, the peak indexed to the (002) graphitic plane of the carbon structure in the pitch based CFs (NX90, NX100) is sharper and intense compared to the corresponding peak in the PAN based (T700S) Ccarbon structure. The full width at half maxima of the peak indexed as (002) is a measure of the crystallite size of the graphitic planes ordered along the c-axis and a-axis. The alignmnet of the graphene sheets along the "c" and "a" axes in graphitic carbon structure is shown in Figure 12. Masao Kimua and coworkers carriedout some fundamental work on the structural determination of carbon fibers using XRD and such a study served as a reference to the author of this work [28]. In their paper, the peak pattern of the pitch based (YSH50A) and PAN based (M46J) CFs were published with appropriate interpretation [28]. The XRD peak patterns of the carbon fibers (NX90, NX100 and T700SC) examined in the present study matched well with the literature reported XRD pattern meaning that the pitch based fibers are more crystalline than the PAN based fibers [28].

The interlayer spacing calculated from the Bragg equation and the values of average crystallite size along the c-axis (stacking axis), L_c and along the "a – axis", L_a, determined using Scherrer equation were summarized in Table 1. The values of the interlayer spacing and crystallite sizes of the carbon fibers tested in the present study (NX90, NX100 and T700SC) were compared to those values reported in literature [28]. Moreover, the corresponding values for pure graphitic carbon structure were also shown for comparison (Table 1).

Table 1. Inter planar spacing (d_{002}) and average crystallite sizes (L) of carbon fibers.

Carbon fibers	d_{002} (nm)	L_c (nm)	L_a (nm)
NX-90, Pitch	0.3388	14.10	29.16
NX-100, Pitch	0.3395	14.26	29.25
YSH50A, Pitch#	0.3440	12.00	-
T700SC, PAN	0.3514	1.33	2.75
M46J, PAN#	0.3460	4.1	-
Pure graphite*	0.3350	0.06708	0.2461

Data adapted from literature [26]* and [28]# and for comparison

As shown in Table 1, the interlayer spacing (d_{002}, nm) of pitch based fibers are close to that of pure graphite while the same for the PAN based fibers is higher than that of the graphitic carbon, meaning that pitch based carbon fibers resemble graphitic carbon more closely while the PAN based fibers, in general, have a turbostratic graphitic structure [26]. Moreover the average crystallite sizes along "c" and "a" axis in the pitch based fibers are nearly an order of magnitude higher than that of PAN based fibers. Similar trend of interlayer spacing and crystallite size values for the pitch and PAN based fibers were reported in literature [28].

CONCLUSION

T700SC has a a turbostratic graphitic structure with an interwoven network of carbon "ribbons" containing hexagonally arrayed carbon layers with the interlayer spacing value higher than that present in the pure graphitic carbon structures. In contrast, the pitch based carbon fibers have highly crystalline graphitic structure with the inter planar spacing close to pure graphite. Further structural investigation using sophisticated analytical tools like Raman spectroscopy as well X-ray microscopy (XRM) is warranted. Sub-atomic level characterization using [13] C MAS NMR and EPR too offers a wealth of information into the structural features of carbon fibers which will be a subject of discussion in future communications.

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REFERENCES

1 Pulidindi IN, Gedanken A. Surface Modification of Carbon Fibers. Preprints. 2023; 2023082053. https://doi.org/10.20944/preprints202308.2053.v1, 2023.
2 Mao LQ, Pan C, Xue YF, et al. Microelectrode for detecting oxygen in brain, comprises carbon fiber electrode, hydrophobic modified layer formed on outer surface of carbon fiber electrode and catalyst layer. 14 Feb 2020; China, CN110794012-A.
3 Puthongkham P, Venton BJ. Nanodiamond coating improves the sensitivity and antifouling properties of carbon fiber microelectrodes. ACS Sensors. 2019; 4 (9): 2403–11p.
4 Cheng YM, Liu PF, Xiao P, et al. Effect of surface chemical modification on the bioactivity of carbon fibers reinforced epoxy. Surf. Coat. Tech. 2019; 377: 1–10p.
5 Fang J, Xie ZG, Wallace G, et al., Co-deposition of carbon dots and reduced graphene oxide nano sheets on carbon –fiber micro electrode surface for selective detection of dopamine. Appl. Surf. Sci. 2017; 412: 131-7p.
6 Sun H., Yao C. Method for modifying carbon fiber that is utilized in anode material of vanadium redox flow battery, involves preprocessing carbon fiber fabric, depositing beta-lead oxide particles,

and scanning fiber fabric for multiple times. CN104064781-A, 24 Sep 2014; CN104064781-B, 4 Jan 2017.
7 Joo SW, Dillip GR, Kim CS. Carbon fiber/metal oxide complex composite used in electrode for ultrahigh capacity capacitor, comprises carbon fiber, and at least one metal oxide bonded to the carbon fiber. KR2018082799-A, 19 July 2018; KR1960154-B1, 4 Jul 2019.
8 Li M. Improved power generation efficiency of a wind power generator and reducing noise, comprises choosing carbon fiber blade of wind power generator, subjecting the activation treatment, surface modification, and applying a performance coating. CN108864457-A, 23 Nov 2018.
9 Kakhki RM. A review to recent developments in identification of carbon fiber electrodes. Arab. J. Chem. 2019; 12 (7): 1783–94p.
10 Regner, S. Drechsler, K. Sentpali, S. Modification of the fiber/matrix bonding by a plasma treatment to reduce the structure-borne sound transmission. Applied Acoustics. 2019; 153: 78–86p.
11 Wang F, Wang XL, Jiang YJ, et al. Study of adsorption performance and adsorption mechanism for U (VI) ion on modified polyacrylonitrile fibers. Journal of radio analytical and nuclear chemistry. 2020; 323(1): 365–77p.
12 Feng SZ, Luo WX, Wang LX, et al. Preparation and property of extremely stable superhydrophobic carbon fibers with core-shell structure. Carbon. 2019; 150: 284–91p.
13 Ashrafi Fl, Firouzzare M, Ahmad SJ, et al. Preparation and modification of force spin polypropylene nanofibers adsorption of uranium (VI) from simulated seawater. Ecotox. Environ. Safe. 2019; 186: Article No. UNSP 109746, 1–9p.
14 Zai XR, Liu A, Tian YH, et al. Oxidation modification of polyacrylonitrile based carbon fiber and its electro-chemical performance as marine electrode for electric field test. J. Ocean U. China. 2020; 19 (2): 361-68p.
15 Shi XH, Chen L, Zhao Q, et al. Epoxy resin composites reinforced and fire-retarded by surficially-treated carbon fibers via a tunable and facile process. Compos Sci Technol. 2020; 187; 1–7p.
16 Sun XL, Song JY, Zhang, et al. Effects of chemical pretreatment on structure and property of polyacrylonitrile based pre-oxidized fibers. J Eng Fibers Fabr. 2020; 15; 1-8p.
17 Zhao D, He JM, Zheng N, et al. Improved atomic oxygen erosion resistance of the carbon fiber-epoxy interface with polyhedral oligomeric silsesquioxane. High perform. polym. 2020.
18 Zhang M, Ding L, Zheng J, et al. Surface modification of carbon fibers with hydrophilic Fe3O4 nanoparticles for nickel based multifunctional composites. Appl Surf Sci. 2020:;509: 1–11p.
19 Kusiak-Nejman E, Czyzewski A, Wanag A. Dubicki M. Sadlowski M. Wrobel RJ. Morawski AW. Photocatalytic oxidation of nitric oxide over AgNPs/TiO2 loaded carbon fiber cloths. J Environ Manag. 2020; 262; 1–10p.
20 Ren L, Sang, Ding F, et al. Preparation of cathode used for oxygen dissolved seawater battery, involves forming surface active layer by subjecting poly acrylonitrile carbon fiber material surface matrix core to surface modification treatment and heat-treating surface. CN106654163, 10 May 2017.
21 Wang L, Chang Z, Wei Q, et al. Modifying immobilized enzyme vector by using microwave assisted method comprises e.g. pretreatment of enzyme vector, using organic reagents for carbon fiber surface treatment and drying, stirring and washing. CN107058280-A, 18 Aug 2017.
22 Eyckens DJ, Arnold CL., Randall JD, et al. Fiber with butterfly wings: Creating colored carbon fibers increased strength, adhesion, and reversible malleability. ACS Appl Mater and Interfaces. 2019; 11 (44): 41617-25p.
23 Cao YH, Farha FI, Ge DS, et al. Highly effective E-heating performance of nickel coated carbon fiber and its composites for de-icing application. Composites. 2019; 229: 1–7p.
24 Zhang W, Cao YZ, Yang P, et al. Manufacturing and interfacial bonding behavior of plasma-treated carbon fiber reinforced veneer based composites. Compos struct. 2019; 226:
25 Fang C, Hu P, Dong S, et al. An efficient hydrothermal transformation approach for construction of controllable carbon coating on carbon fiber from renewable carbohydrate. Appl. Surf. Sci. 2019; 491; 478–87p.

26 Pulidindi IN. Development and exploitation of carbon materials from plant sources. Ph D thesis, IIT Madras, India. December 2009.
27 Mirnezami SA, Zahedi A, Nejad AS. Thermal optimization of a novel solar/hydro/biomass hybrid renewable system for production of low-cost, high-yield, and environmental-friendly biodiesel. Energy. 2020; 202: 117562.
28 Harano T, Takeichi Y, Usui M, et al. Observation of distribution of π-orbital-oriented domains in PAN- and Pitch-Based carbon fibers using scanning transmission X-ray Microscopy. Appl. Sci. 2020; 10: 4836.

