STM JOURNALS

International Journal of
Crystalline Materials

Volume 1, Issue 1, 2024
January—June
DOI (Journal): 10.37591/IJCM

https://journals.stmjournals.com/ijcm

Review IJCM

Direct Synthetic Routes of Mxenes and Their Application in Carbon Fiber Reinforced Plastics (Cfrps) As Supplementary Sizing Layer

Suresh Selvaraj[1,*], Dev Patel[2], Meetkumar Joshi[2], Yashraj Joshi[2] Indra Neel Pulidindi [3]

Abstract

Sized carbon fibers with a supplementary sizing layer of MXenes (synthesized via traditions MAX phases), bonded to carbon fibers (CFs) as well as the resin matrix via different kinds of physicochemical (van der Waals force, hydrogen bonding, covalent bonding) interactions enhanced the performance of the resulting carbon fiber reinforced plastic materials. This is because of the strong interface generated due to the appearance of MXene at the interface of the CF and the resin matrix. Excellent enhancement in the interfacial and mechanical properties of the CFRPs with MXene modified interfaces were highlighted. Use of new two dimensional (2D) layered crystalline MXene phases and morphologies, that were made possible with the advent of the new synthetic strategies (solid state as well as chemical vapour deposition) excluding the use of MAX phases, need to be exploited for the forming the supplementary sizing layer over the CFs for a breakthrough in the CFRP technology, The supplementary sizing layer of MXenes, synthesized through traditional MAX phases, not only reinforces the bond between the CFs and the matrix but also contributes to improved durability and mechanical properties. The unique properties of MXenes, including their high electrical conductivity and chemical stability, further amplify the functionality of CFRPs. Future research should focus on exploring novel MXene phases and morphologies, synthesized via innovative methods like solid-state techniques and chemical vapor deposition, to optimize the interfacial properties and achieve unprecedented performance in CFRPs. This approach holds promise for the next generation of high-performance composite materials, pushing the boundaries of current CFRP technology.

Keywords: MXenes, transition metal carbides/nitrides/carbonitrides, carbon fibers, sizing layer, carbon fiber reinforced plastics

INTRODUCTION

A google scholar search crossing the keywords, namely, MXenes and CFRPs yields 1140 results (as on 31st July 2024) indicating that the research area, though fertile, remained unexplored [1-10]. The advent of nanoscience has revolutionized every sphere of human activity, ranging from, agriculture, industry, health, climate, communications, security and energy needs. Innovation in nanoscience is huge with immense benefits to mankind. Nanomaterials play a vital role in improving the interfacial strength and the mechanical properties of the CFRP's increasing the sphere of their utility many a fold. Carbon nanomaterials like CNT's and oxygen functionalized CNT's were used for improving the polarity and chemical reactivity of CF's [11, 12, 13]. Modifying the sizing composition with COOH functionalized CNT lead to 9.5 % enhancement in IFSS [11]. Modification of vinyl sizing agent with NH_2 functionalized CNT

*Author for Correspondence
Suresh Selvaraj
E-mail: drssureshchem@gmail.com

[1]Associate professor, ACE Engineering College Ghatkesar, Secunderabad, Telangana, India
[2]Student, School of Chemical Sciences, GSFC University, Vadodara, India.
[3]Scientific consultant, Jesus' Scientific Consultancy for Industrial and Academic Research (JSCIAR),

Received Date: August 02, 2024
Accepted Date: August 08, 2024
Published Date: August 16, 2024

Citation: Suresh Selvaraj, Dev Patel, Meetkumar Joshi, Yashraj Joshi Indra Neel Pulidindi. Direct synthetic routes of MXenes and their application in carbon fiber reinforced plastics (CFRPs) as supplementary sizing layer. International Journal of Crystalline Materials. 2024; 1(1): 7–13p.

enhanced the ILSS and impact toughness of CF-unsaturated polyester composite by 32.2 and 55.2 % respectively [12]. Novel carbon materials like carbon dots are yet to be exploited as in situ fluorescent sensor to probe the CFRP interface as well as for the surface modification of CFs for improving the compatibility of CF's with resin matrix [14, 15]. Unconventional inorganic nanomaterials like Mxene nano compounds are being used to engineer the interface and for enhancing the mechanical performance of CFRPs [16]. Mxenes are inorganic analogues of graphene with 2D nano sheet like structures. Mxenes are 2D transition metal carbides and/or nitrides with the general formula of $M_{n+1}X_nT_x$, where M - early transition metal, X - C and/or N, and T – terminating group (O, OH and F). Owing to their unique structure and properties (electrical, thermal and mechanical), Mxene nanomaterials are applied in the fields of energy storage, adsorption and catalysis. Zhao et al., made a remarkable study on the use of Mxene nano compound (Titanium carbide with terminal functional groups, TiCT) as sizing compound to improve the interfacial adhesion of CFs with epoxy composite. As a result significant enhancement in the mechanical properties, namely, tensile, flexural, shear and impact strength were achieved [16; 17]. Systematic methodology employed for the amine functionalization of CF's with aminopropyl triethoxy silane and the subsequent self-assembly of NH_2-CF and Mxene nanomaterial wherein the Mxene compound form a supplementary sizing layer on the CF for better adhesion with the epoxy resin matrix is depicted in Fig. 14. Systematic method of synthesis of titanium carbide Mxene compound with terminal functional groups (T-O, OH and F) is shown in Figure 1 [16].

Uniform distribution of the terminal functional groups F, OH and COOH is visualized by the elemental mapping on the surface of Mxene compound, titanium carbide ($Ti_3C_2T_x$ nano sheets). Surface morphology and shape of the $Ti_3C_2T_x$ nano sheets were characterized by SEM analysis. EDAX spectrum and elemental composition deduced from EDAX spectrum showed the presence of terminal functional groups, namely, F and O (OH) and C (COOH) [16].

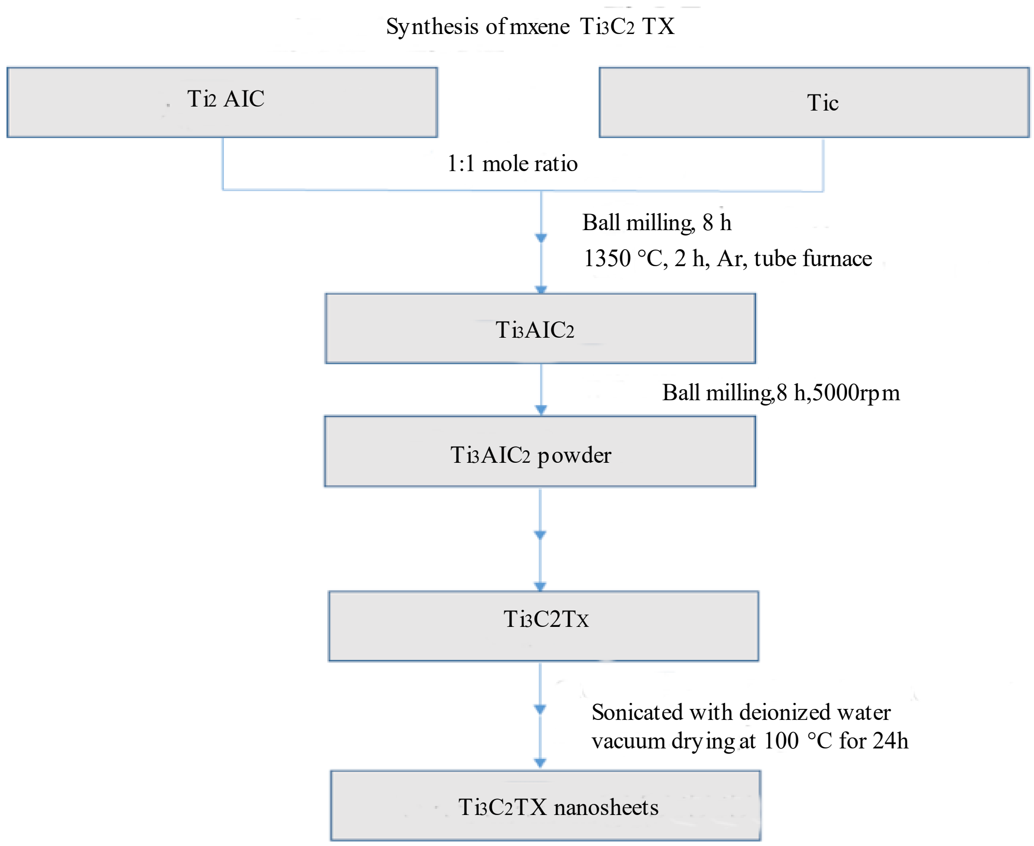

Figure 1. Method of synthesis of Mxene compound, $Ti_3C_2T_x$ (T-terminal functional groups like H, OH and F) [16].

Schematic steps involved in the sizing of CFs with Mxene is shown in Figure 2. The use of amine functionalized Mxene sized CFs as reinforcement in the epoxy matrix is depicted in Figure 3 [16].

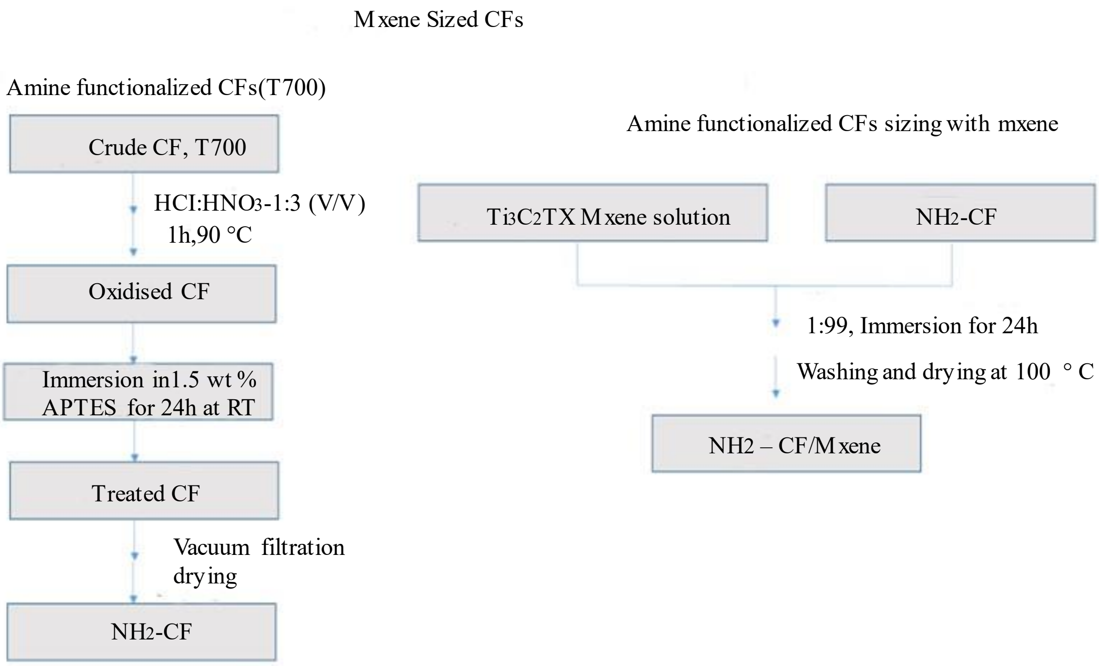

Figure 2. Schematic steps involved in the sizing of CF's with Mxene [16].

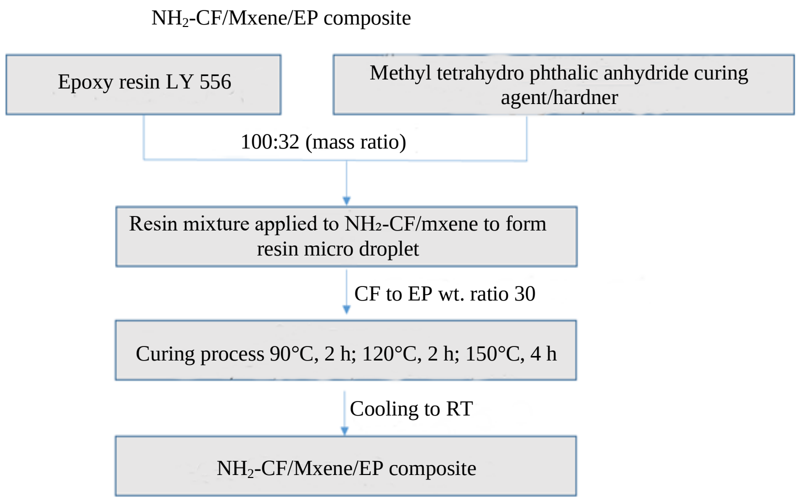

Figure 3. Method of synthesis of amine functionalized Mxene sized CF reinforced epoxy composite [16].

Because of the formation of supplementary interface by Mxene in the reinforcement, the mechanical properties of Mxene sized CF reinforced epoxy composite were improved. Tensile, flexural, shear and impact strengths of the resulting composite were enhanced by 40.8, 45.9, 74.4 and 38.5 % compared to crude CF-EP composite [16].

ADVANCES IN THE INTERFACE CHARACTERIZATION METHODS

Liu et al., reviewed the state of the art methods for characterizing the interface of CFRP's owing to the significance of such a study [18]. Conventional analytical methods are indispensable. XRD is the fundamental and primary analytical tool at the disposal of a chemist to know the bulk structure of solids, as in the present instance of CFRP's. The crystal plane spacing of carbon fiber changes as a result of the residual stress at the CFRP interface. This change in the interlayer spacing of carbon fiber is deduced from the famous Bragg diffraction equation: $\lambda = 2d\sin\theta$. The strain along the fiber axis is given by the following eq (1):

$$\varepsilon_z = \frac{d_z - d_z^0}{d_z^0} \quad (1)$$

Where, d_z = crystal place spacing perpendicular to the fiber axis in the CFRP d_z^0 = interplanar spacing perpendicular to the fiber axis of the free carbon fiber (measured on the free carbon fiber). ε_r is the measured strain when the crystal diffraction is measured parallel to the direction of the carbon fiber axis.

Likewise, the surface topology and roughness is deduced from the AFM analysis in various modes, namely nano indentation, force modulation and phase imaging. The chemical composition at the interface of the CFRP is examined by FT-IR, XPS, Auger electron spectroscopy (AES), secondary ion mass spectrometer (SIMS), electron energy loss spectroscopy (EELS), micro Raman spectroscopy (MRS) and extended X-ray absorption fine structure spectroscopy (EXAFS) [18]. Fluorescence microscopic methods need to be developed for viewing the interface structure using fluorescent probes like carbon dots [19]. Liu et al., could enlarge the region of interface in the CFRPs by 1.2 μm by doping sizing agent with upconversion luminescent nanoparticles [20]. The enlargement of interface of the CF/epoxy interface matrix was attributed to the inter diffusion between sizing layer and epoxy matrix. Luminescent nanoparticles resulted in a positive effect on the interfacial adhesion of CF/epoxy composites through chemical bonding among the luminescent nanoparticles, sizing layer and matrix [20]. Rather than using the expensive rare earth based upconversion luminiscent materials, strategies based on using carbon dot containing sizing agents for funtionalising and armoring the CF surface need to be developed, so that the adherence of the CFs with the polymer matrix is enhanced. Strategies like sonochemical deposition of carbon dots on CF makes the surface of CF's polar and fluorescent. Such a strategy not only enlarges the interface width but also improves the desired mechanical properties of strength, modulus and shear at the interface of the CFs and polymer matrix. These are only a representative examples of possible analytical methods to probe the interface and many more methods can be developed depending on the specific problem or material at hand. For instance, an unexplored analytical method EPR can be used both quantitatively and qualitatively to know the nature and magnitude of interaction and bonding of the CFs surface with the polymer matrix. Carbon materials owing to surface unsaturation have a specific concentration free electrons and so they show a very characteristic EPR signal. The area under the EPR signal is a measure of the free electron concentration. Once the CFs are bonded to the polymer resin matrix, there will be significant decrease in the concentration of the free electrons [21]. Such a change in free electron concentration can be a measure of bonding strength and adhesion of CFs to the resin matrix.

Future directions

As early as 1971, Jeffries has pointed out that cellulosic fiber derived carbon fibers are of no real value for CFPF production as such carbon fibers are either not strong or stiff. However, so as to have a sustainable and economically viable production process for CF's for the exponentially growing demand and applications of CFs as CFRPs, there should be a paradigm shift in the choice of the precursor for CF production. Currently, commercial CF production processes use either PAN or pitch as raw material. As almost all chemicals that are derived from fossil resources can be produced from biomass, methods should be developed for lignin biopolymer based CF production for CFRP application [22, 23]. In addition, developments took place for the synthesis of MXene compounds in direct routes [24, 25] which is elaborated in the subsection 3.1 below.

Simple and direct route for the synthesis of MXene compounds [24, 25]

Direct and clean synthetic routes for producing MXene compounds, excluding the traditional path of MAX phase, made possible the formation of new phases and morphologies (as exemplified in the specific case of Ti_2CCl_2). Such an advance facilitated surmounting the challenges of scalability and the use of hazardous chemicals. Robertson and Tolbert provided insights into such new pathways for the production of MXene compounds [24]. Conventionally MXenes have been synthesized from MAX phases, where A is typically aluminum (Al) with other possibilities as well. The element A is often removed with the use of hazardous chemicals in a process called etching. Owing to the generation of large amounts of chemical wastes, the large scale manufacturing of MXenes through the conventional route is limited. Recently, Wang et al., reported a clean, scalable and direct method of synthesis for MXene compounds without the use of MAX phases and thereby avoiding the step of etching with harsh chemicals used in the traditional route. Two methods of synthesis of MXene type compounds (Ti_2CCl_2), namely, the solid state synthesis and the chemical vapour deposition, were developed. Such an approach opened new avenue for the synthesis of these novel 2D layered crystallite materials with wide range of applications (energy storage, shielding material from electromagnetic interference, transparent conducting materials, biomedical applications) [25]. The use of such MXene compounds prepared in clean and direct routes with new phases and morphologies as sizing compounds for the functionalization of carbon fibers for application in advanced carbon fiber reinforced composites is awaited [26-29]. Unlike graphene, as MXene clays are hydrophilic these material finds enormous applications in materials science and technology.

CONCLUSION

99 is not 100. In no way the present review on understanding the interface of carbon fiber reinforced composites (CFRP's) is complete. However, a new and fresh perspective on the properties of carbon fibers, surface modification of carbon fibers by the process of sizing, the role of sizing process in forming the strong interface between CF and polymer matrix, methods of characterization of the interface of CFRP and the growing usefulness of CFRPs in high technology sectors is provided. Emphasis was laid on the potential of MXene compounds as supplementary sizing layer on the carbon surface resulting in a strong interface with the epoxy resin leading to improved performance of the CFRPs. Recent advances in the synthesis of MXene phases, without the use of MAX phases, in a clean and direct way were discussed.

Acknowledgements

Gratefulness is due to Professor Xinling Wang, SJTU, for introducing PIN, the fertile field of characterization of interface of carbon fiber reinforced composites as a part of his postdoctoral research. The generous postdoctoral fellowship provided to PIN by Professor Xinling Wang, SJTU for conducting research on carbon fiber reinforced composites is acknowledged. Indebtedness is due to Dr Ms Dandan Zhu, STJU, for her painstaking efforts that facilitated the successful completion of the project. Thanks are due to Dr Chongchong Yang for the steadfast support and guidance throughout the postdoctoral research of PIN in the research group of Professor Xinling Wang. Thankfulness is due to Professor Zhen Zheng for the fruitful discussions and for appearing in the weekly group meetings and providing timely advice. Indebtedness is due to the management of GSFC University, Vadodara for granting PIN an opportunity to teach and research as an assistant professor for 13 months.

REFERENCES

1 Hu Y, Chen JZ, Yang GY, Li YJ, Dong M, Zhang H, Bilotti E, Jiang JJ, Papageorgiou DG. Highly conductive and mechanically robust MXene@CF core-shell composites for in-situ damage sensing and electromagnetic interference shielding. Composites Science and Technology. 2024; 246:110356.
2 Hu SK, Han P, Meng C, Yu Y, Han SL, Wang HY, Wei G , Gu J. Comparative study of different bonding interactions on the interfacial adhesion and mechanical properties of MXene-decorated carbon fiber/ epoxy resin composite, Composites Science and Technology. 2024; 245:110352.
3 Duan NM, Li Y, Shi ZY, Wang JL, Zhang CP, Tang XF, Wang GL. A novel micromechanical model for predicting the shear properties of multilayer Ti3C2Tx MXene/carbon fiber fabric/epoxy composite. Polymer composites. 2024; 45 (10): 9196-208p.

4 Ye WB, Zhou YF, Liu W, Hou YB, Chu FK, Hu Y, Song L, Hu WZ. Fabricating advanced MXene-based hybrid materials to elevate fire safety and mechanical strength in carbon fiber-reinforced bismaleimide resins. Chemical Engineering Journal. 2024; 487:150456.
5 Guo ZW, Liu L, Ao YH. 2D/0D multiscale interfacial engineering of carbon fiber composites for simultaneous achieving high mechanical and electromagnetic interference shielding properties. Polymer composites. 2024; 45 (8):7507-518p.
6 Hu Y, Yang GY, Chen JZ, Li YJ, Dong M, Zhang H, Bilotti E, Jiang JJ, Papageorgiou DG. Interfacial engineering of hybrid MXene-Ni-CF tri-core–shell composites for electromagnetic interference shielding and E-heating applications. Composites Part A. 2024; 178: 107990.
7 Kumar K, Das S, Garg R, Goyat MS. A Comprehensive Review on Enhancing the Strength of CFRPs through nano-reinforcements: Applications, characterization, and challenges. J Fail. Anal. and Preven. 2024.
8 Wang X, Li SC, Xiang DW, Gao M, Zuo HM, Li DS. Flexural properties and failure mechanisms of short-carbon-fiber-reinforced polylactic acid composite modified with MXene and GO. Materials. 2024; 17:1389.
9 Huang MR, Huang Y, Yang H, Li WM. Ti3C2T x MXene/Fe3O4/carbon fiber fabric/water polyurethane composite fabrics for electromagnetic interference shielding and thermal management. ACS Applied Nano Materials. 2024.
10 Hu YZG, Jiang MQ, Cong XY, Liu GY, Yi XS, Liu XL. Lightweight, multifunctional recycled carbon fibre/MXene/PEDOT: PSS nonwoven veils with double-layered structure for excellent electromagnetic interference shielding. Chemical Engineering Journal. 2024; 489:151122.
11 Zhang, W., Deng, X., Sui, G., Yang, X., Improving interfacial and mechanical properties of carbon nanotube-sized carbon fiber/epoxy composites. Carbon, 145, 2019, 629-639.
12 Wu, Z., Cui, H., Chen, L., Jiang, D., Weng, L., Ma, Y., Li, X., Zhang, X., Liu, H., Wang, N., Zhang, J., Ma, Y., Zhang, M., Huang, Y., Guo, Z., Interfacially reinforced unsaturated polyester carbon fiber composites with a vinyl ester-carbon nanotubes sizing agent. Composites science and technology, 164, 2018, 195-203.
13 Elwathig A.M. Hassana, Lili Yang, Tienah H.H. Elagib, Dengteng Ge, Xiaowei Lv, Jianfeng Zhou, Muhuo Yu, Shu Zhu, Synergistic effect of hydrogen bonding and π-π stacking in interface of CF/ PEEK composites. Composites Part B, 171, 2019, 70–77.
14 Pulidindi, I. N., Gedanken, A., Carbon Nanoparticles based Glucose Sensor, International Journal of Analytical Environmental Chemistry, 94 (1), 2014, 28-35.
15 Mishra, R. K., Pulidindi, I. N., Kaba, E., and Gedanken, A., In situ formation of carbon dots aid ampicillin sensing. Analytical Methods, 8, 2016, 2441-2447.
16 Zhao, X., Qi, S., Liu, J., Han, X., Zhang, F., Preparation and mechanical performances of carbon fiber reinforced epoxy composites by Mxene nanosheets coating. Journal of materials science: Materials in Electronics, 30, 2019, 10516-10523.
17 Jin-Cheng Lei, Xu Zhang, Zhen Zhou, Recent advances in MXene: preparation, properties and applications. Front. Phys. 10, 2015, 107303.
18 Liu, L., Jia, C., He, J., Zhao, F., Fan, D., Xing, L., Wang, M., Wang, F., Jiang, Z., Huang, Y. Interfacial characterization of carbon fiber reinforced polymer composites. Composite Science and Technology, 121, 2015, 56-72.
19 Tzhayik, O., Pulidindi, I. N., Gedanken, A., Forming Nano Spherical Cellulose Containers, Industrial & Engineering Chemistry Research, 53, 2014, 13871-13880.
20 Liu, D., Li, B., Li, G., Leyu, W., Yang, X., Tagged and enhanced interface of carbon fiber/epoxy by doping sizing agent with upconversion luminescent nanoparticles. Materials Letters, 196, 2017, 37-41.
21 Viswanathan, B., Indra Neel, P., and Varadarajan, T. K. (2009) Development of carbon materials for energy and environmental applications, Catalysis Surveys from Asia, 13, 164-183.
22 Nisha, S. S., Nikzad, M., Kobaisi, Md. A., Truong, V. K., Sbarski, I., The role of ionic – liquid extracted lignin micro/nanoparticles for functionalization of an epoxy-based composite matrix. Composites Science and Technology, 174, 2019, 11-19.

23 Indra Neel Pulidindi, Aharon Gedanken (2019) Can Biofuels Alleviate the Energy and Environmental Crisis?, Book, Nova Science Publishers, Inc., New York, ISBN: 978-1-53615-050-6.
24 Daniel D. Robertson and Sarah H. Tolbert, A Direct And Clean Route To MXenes: New, scalable methods synthesize two-dimensional carbide and nitride materials, Science, 379 (6638), 2023, 1189-1190.
25 Di Wang, Chenkun Zhou, Alexander S. Filatov, Wooje Cho, Francisco Lagunas, Mingzhan Wang, Suriyanarayanan Vaikuntanathan, Chong Liu, Robert F. Klie, Dmitri V. Talapin1, Direct synthesis and chemical vapor deposition of 2D carbide and nitride MXenes, Science 379, 1242–1247 (2023).
26 Yang CC, Zhu DD, Sun CY, Chen BY, Li YH, Pulidindi IN, Zheng Z, Wang XL (2021) Electrothermal responsive self-healing for carbon fiber/epoxy interphase based on Diels-Alder adducts, Composites Science and Technology, 208, 108767.
27 Pulidindi, I.N.; Gedanken, A. Surface Modification of Carbon Fibers. Preprints 2023, 2023082053. https://doi.org/10.20944/preprints202308.2053.v1, 2023.
28 Pulidindi IN. Crystallinity of Commercial Carbon Fibers from X-ray Diffraction (XRD) Studies. International Journal of Photochemistry and Photochemical Research, 2024, Volume 1, Issue 1. 2024; 1(1): 17–27p.
29 Pulidindi IN, Raman spectroscopy of the determination of relative crystallinity of carbon fibers, International Journal of crystalline materials (submitted).

