# Scalable Non-Destructive Surface Modification of Polyacrylonitrile-Based Carbon Fibers for Carbon Fiber Reinforced Composites

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*Abstract –* Carbon fiber (CF) reinforced composites are highly valued for their exceptional thermal, mechanical, and chemical properties, making them widely applicable across various industries. Polyacrylonitrile (PAN)-based carbon fiber composites are sought after for their superior strength and stability. However, the interfacial bond between the fiber and matrix is susceptible to degradation, especially at high temperatures due to oxidation. Surface coatings like sizing are applied to protect fibers during manufacturing. These fibers, widely recognized for their high performance in commercial, military, and aerospace applications, often experience delamination due to inadequate interfacial properties caused by protective sizing agents. Therefore, optimizing fiber-matrix adhesion is crucial to maintain the performance of advanced composite materials. This study investigated a scalable, non-destructive methodology for desizing polyacrylonitrile-based CFs, enhancing their performance in CF-reinforced composites. The suggested procedure included cleaning, drying, and thermally treating carbon fabrics to remove this sizing and improve fiber-matrix adhesion. Scanning electron microscopy (SEM) revealed smoother surfaces for sized fibers and rougher textures for desized fibers. X-ray diffraction identified a new peak at 7.5°, and an increased intensity of peaks of desized CF, indicating structural changes. Fourier-transform infrared spectroscopy (FTIR) revealed the removal of polymeric sizing agents and the formation of carbon-oxygen functional groups, which provide active sites on the fiber surface. Contact angle analysis demonstrated improved hydrophilicity, with desized material exhibiting practically zero angle at 0-second intervals. This approach maintains fiber integrity while improving composite mechanical properties, suggesting potential for widespread industrial application.

*Keywords – Carbon Fiber, Surface Modification, Desizing, Wettability, CFRP.*

## I. INTRODUCTION

The increasing demand for lightweight and strong materials has greatly extended the relevance and application of fiber-reinforced composites [1]. CF reinforced polymers (CFRP), known for their superior strength-to-weight ratio, high stiffness, and corrosion resistance, are increasingly replacing traditional materials like steel in structural components [2]. Additionally, CF offer advantages such as excellent

electrical conductivity, effective damping, and low thermal expansion. These unique mechanical and electrical properties make CFs ideal for advanced composites in electric vehicle applications [3], [4].

CFs based on polyacrylonitrile (PAN) are acknowledged as high-performance fibers due to the need in the aerospace, military, and commercial industries [5]. While composites reinforced with CFs serve as crucial structural materials, they are susceptible to delamination due to insufficient interfacial adhesion[6], [7]. One important aspect that prevents fiber-matrix bonding during the production process is the sizing agent used as a protective measure. Earlier studies to improve fiber/matrix interfaces were frequently ineffective or unable to scale. [4], [8]–[10].

The adhesion between CFs and the matrix has a significant impact on the mechanical strength of CFRP composite materials. [6], [10]–[12]. Poor adhesion can lead to delamination and crack propagation, which compromise the composite's performance [7]–[9], [13], [14]. Studies by [15] and [16] highlighted that composite failure often occurs due to weak fiber-matrix adhesion, resulting in stress concentration, matrix debonding, and fiber pull-out. Surface alterations including adding polar functional groups and roughening the surface are advised to improve adherence. These changes enhance the mechanical anchoring and load transfer between the CFs and matrix.

The hydrophilic nature and improved wettability of the CF with the epoxy resin are indicated by the smaller contact angle and barrel-shaped epoxy droplet for the fiber [17]. Surface modification leads to the diminution of the contact angle because the coarseness and functional addition in the fiber are more intense. The enhanced surface roughness and development of new functional groups on the fiber surface culminated in a greater total surface area and elevated surface free energy. Consequently, this contributed to the improved wettability exhibited by the modified carbon fibers. The surface tension of the CF is roughly 40 mJ/m$^2$, making it very hydrophobic due to high-temperature carbonization and graphitization during production. [18].

Li et al. investigated how PAN-mechanical CF's qualities were affected by chemical treatment [19]. For five hours, the CF used in the investigation was submerged in an HNO3 solution at 120 °C. The treated CF's O/C ratio rose by 14%, according to the XPS data. According to the results of the tensile test, the treated CF/polyimide composite's TS and TM increased by 14% and 11%, respectively. The author also checked how the mechanical properties of the PAN-CF were affected by the chemical treatment [20]. The researchers used the $HNO_3/H_2SO_4$ solution to treat the CF at 60ºC mainly for 30 minutes. The XPS analysis revealed that the CF surface was modified through amines and acetic acid. The chemical bonding between the CF and the epoxy resin interface was made stronger for the composite to have an ILSS of 38 MPa which is quite a significant improvement over 16 MPa. Li et al. studied the effect of ammonia and $HNO_3$ treatment on CF [20]. The CF was first given an ammonia solution for 24 hours by the authors and then it was heated at 115 °C with $HNO_3$ for 10 minutes. The Oxygen concentration rose from 13% to 15%, as reported by the XPS analysis. Atomic force microscopy (AFM) showed that the CF's surface roughness rose by 54% following treatment. The researchers also observed that the IFSS of the composite made from treated CF/epoxy resin increased by 46%.

This analysis tends to a non-destructive desizing process for carbon fabrics which comprises washing, drying, and heat treatment. The desizing method's efficacy was confirmed using XRD, SEM, and contact angle measurements. The desized fibers exhibited increased hydrophilicity and structural modifications, as evidenced by SEM and XRD results. FTIR analysis revealed the formation of carbon-oxygen functional groups, enhancing adhesion sites on the fiber surface. This study offers a promising solution to improve composite performance without compromising fiber integrity.

## II. MATERIALS AND METHOD

### A. *Materials preparation*

PAN-based carbon fabric (TI3101, Grade: T300) with a 2x2 twill weave pattern, consisting of 3k filaments, a weight of 200 GSM, a width of 1000 mm, and a thickness of 0.2 mm, was utilized along with ethanol. The fabrics were cut into 8x8 inch samples.

The desizing process employed both chemical and thermal treatments. Initially, the carbon fabric samples were placed in a tray and fully immersed in ethanol. The soaked fabrics were then placed in a drying oven and heated at 55°C for 24 hours. Following this, the fabrics underwent a second ethanol wash and were subsequently dried in the oven at 120°C for 1 hour.

After drying, the fabrics were subjected to thermal treatment in a muffle furnace (nabertherm GmbH, 400V, 50/60Hz, 64 kW) at 385°C for 1 hour to further modify the fabric. The samples were allowed to cool inside the furnace post-treatment.

B. *Characterization*

The microstructure of the fibers was examined using a SEM ( model JEOL-6490A). To assess the crystal structure XRD using CuKα radiation was conducted. FTIR was employed to identify organic, polymeric, and select inorganic materials by analyzing their chemical functional groups. For FTIR analysis, the fibers were prepared by cutting them into small pieces and compressing them into potassium bromide (KBr) pellets.

The contact angle measuring method was used to determine the fiber surface's wettability. In this process, a controlled-size water droplet was deposited onto the carbon fabric using a syringe. The sessile drop method was utilized, where the droplet was released onto the sample surface at a controlled velocity. High-resolution images of the droplet and the fabric's surface were captured immediately after deposition called as 0 sec interval, as well as at 30 and 60 seconds. The contact angle was calculated by analyzing the droplet's profile using software that applied Young's equation to determine the angle formed between the liquid droplet and the fiber surface.
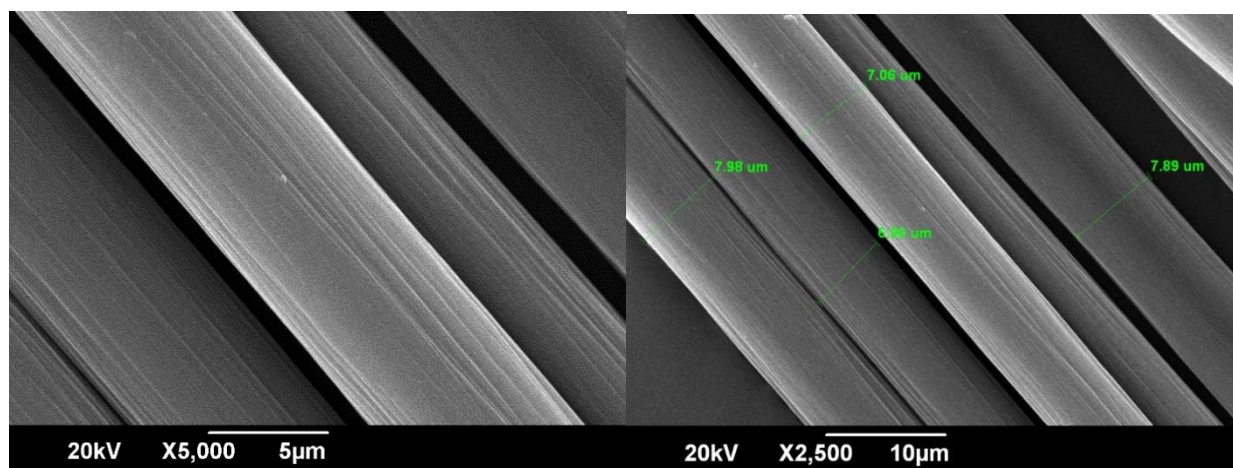
III.     RESULTS



Fig. 1 *SEM micrographs of sized CF*

The SEM micrographs presented in Fig. 1 show the as-received CFs which have a smooth surface morphology. A thin, uniform coating or sizing agent can be observed on the fiber surfaces. This sizing layer appears to have a smooth texture with fine longitudinal ridges or striations running along the fiber axis, likely a result of the fiber manufacturing and/or coating process. The diameter of the as-received CFs was measured to be approximately 7-8 µm, which was consistent with typical CF dimensions used in composite applications.

In contrast, the SEM micrographs Fig. 2 reveal the morphology of the CFs after a desizing process. These images show that the continuous sizing film has been effectively removed, exposing the underlying CF surface. The fiber surfaces now exhibit a rougher, more irregular topography, with small chunks or delaminated layers of material present. This change in surface appearance confirms the successful removal of the sizing agent, leaving behind the bare CF structure.

The XRD spectrum of the as-received (sized) CFs (Fig. 3) exhibited the characteristic peaks associated with a graphitic carbon structure. The prominent peak at a diffraction angle of approximately 25.6°

corresponded to the (002) crystallographic plane, which is a universal feature of graphitic materials. This strong and sharp (002) peak indicated a well-ordered, highly aligned graphitic structure within the CFs. Additionally, a less intense peak at around 43° was observed, which could be attributed to the (100) plane. The presence of this (100) peak suggested a good in-plane order of the carbon atoms within the graphitic layers. The significantly stronger intensity of the (002) peak compared to the (100) peak further confirmed the high degree of crystallinity and preferred orientation of the graphitic layers along the fiber axis.
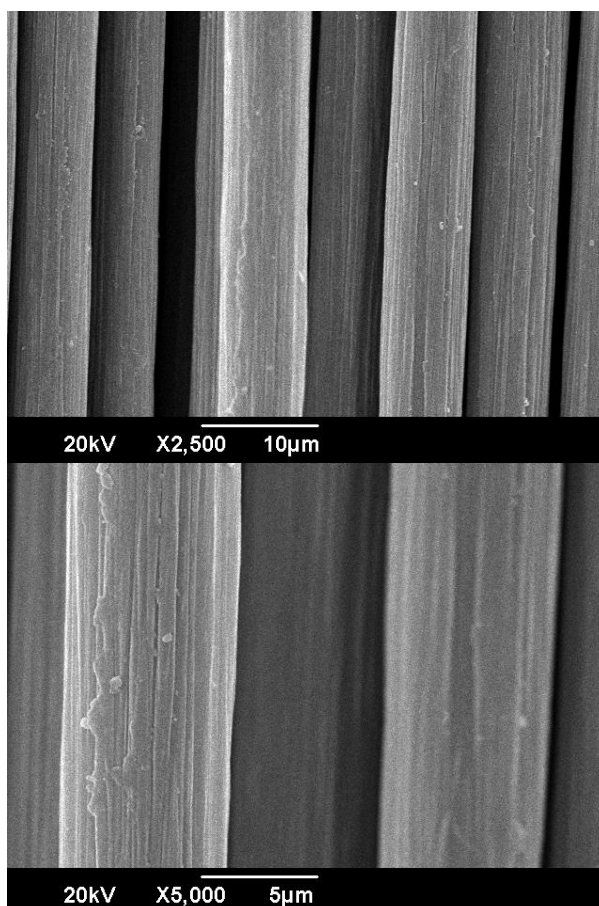


Fig. 2 *SEM micrographs of desized CF.*

The XRD pattern of the desized CFs (Fig. 4) showed some notable changes. An asymmetric peak centred around 7.5° had emerged, which was commonly associated with the (002) plane of graphitic carbon. This peak corresponded to the interlayer spacing between the graphene sheets, typically around 1.18 Å, as calculated using Bragg's law. This spacing was close to the interlayer distance in well-ordered graphitic materials, indicating the presence of a highly graphitic structure in the desized fibers.

The FTIR spectrum of the as-received sized CF (Fig. 5) exhibited several characteristic peaks, indicating the presence of various functional groups introduced by the sizing agent. The broad peak observed in the range of 3200-3600 $cm^{-1}$ was attributed to the stretching vibrations of hydroxyl (-OH) groups, likely originating from the sizing agent. The peaks at 2923 $cm^{-1}$ corresponded to the stretching vibrations of aliphatic C-H bonds, further confirming the presence of organic compounds from the sizing material.
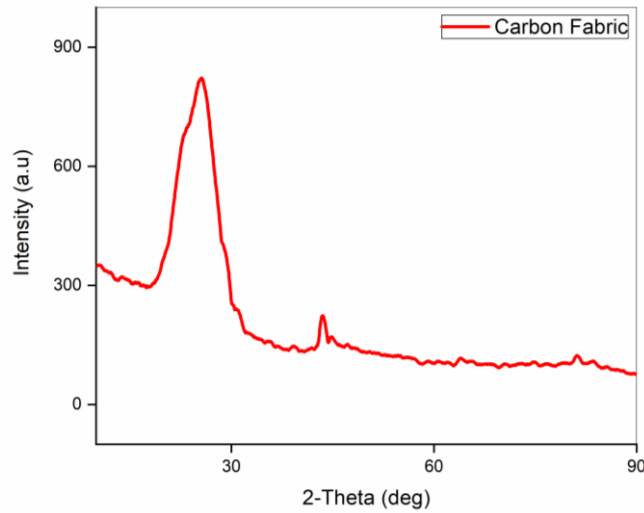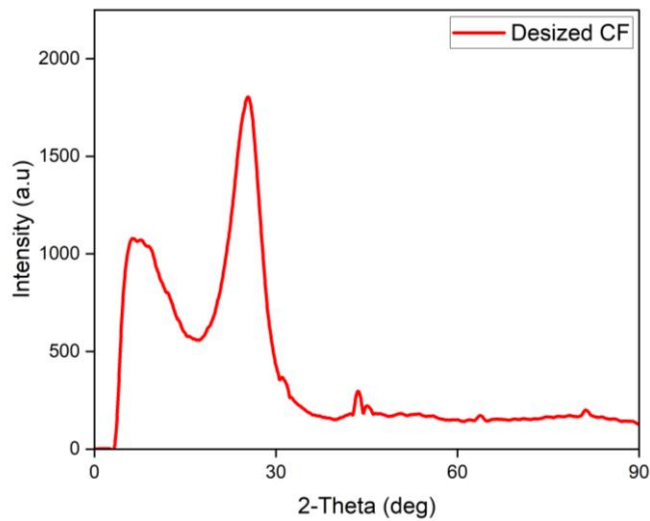
Fig. 3 *XRD pattern of PAN-based sized CF*



Fig. 4 *XRD pattern of PAN-based desized CF*

The peak at 1251 cm⁻¹ was assigned to the stretching vibrations of C-O bonds, which are commonly associated with ether or ester functionalities present in many sizing agents. Additionally, the peak at 1625 cm⁻¹ was attributed to the stretching vibrations of C=C or C=N groups, suggesting the incorporation of unsaturated bonds or aromatic moieties in the sizing formulation.
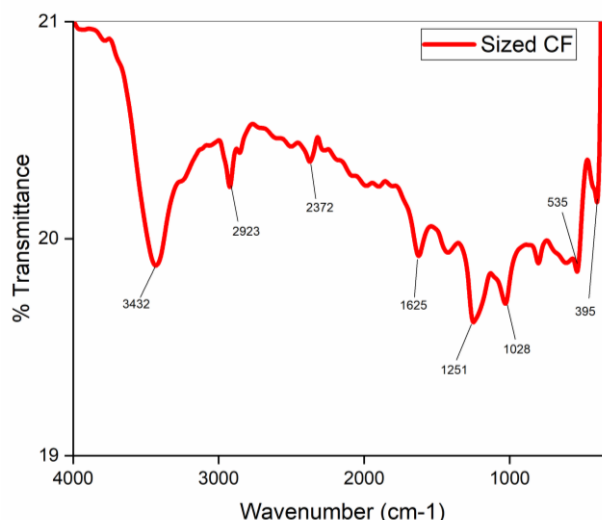
Fig. 5 *FTIR spectra of sized CF*

In contrast, the FTIR spectrum of the desized CFs (**Fig. 5**) exhibited a significantly different profile, indicating the removal of the sizing agent and the exposure of the underlying CF surface. The appearance of a strong, broad band centred at 3426 cm$^{-1}$ was attributed to the stretching vibrations of surface hydroxyl (-OH) groups, likely originating from adsorbed atmospheric moisture or residual polar functional groups on the desized fiber surface. The peak in the range of 2800-3000 cm$^{-1}$ was assigned to the asymmetric stretching of aliphatic C-H bonds, suggesting the presence of minor amounts of organic contaminants or sizing residues.
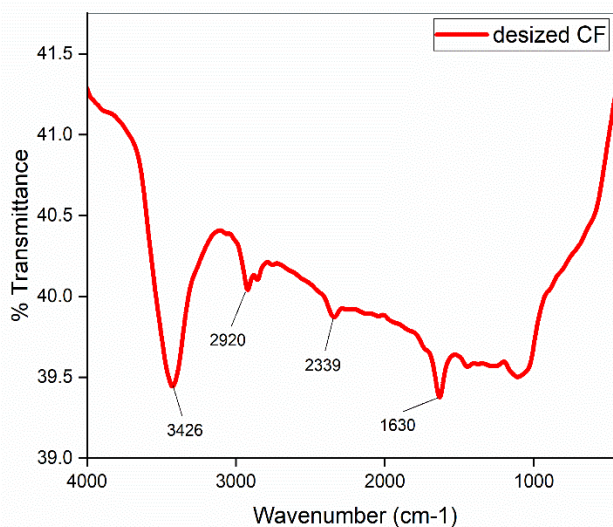


Fig. 6 *FTIR spectra of desized CF*

The peak at 1630 cm$^{-1}$ was attributed to the stretching vibrations of C=C bonds, which could be associated with the inherent graphitic structure of the CFs.

A comparative analysis of the FTIR spectra of the sized and desized CF (Fig. 7) further highlighted the changes induced by the desizing process. The overall shift in the transmittance range towards higher intensities for the desized fibers indicated a reduction in the amount of organic surface functionalities, as the sizing agent was effectively removed. Moreover, the increase in the intensity of certain peaks, such as those corresponding to C-O and C=C bonds, suggested an enhanced exposure of the underlying CF structure and a more pronounced graphitic character after the desizing treatment.
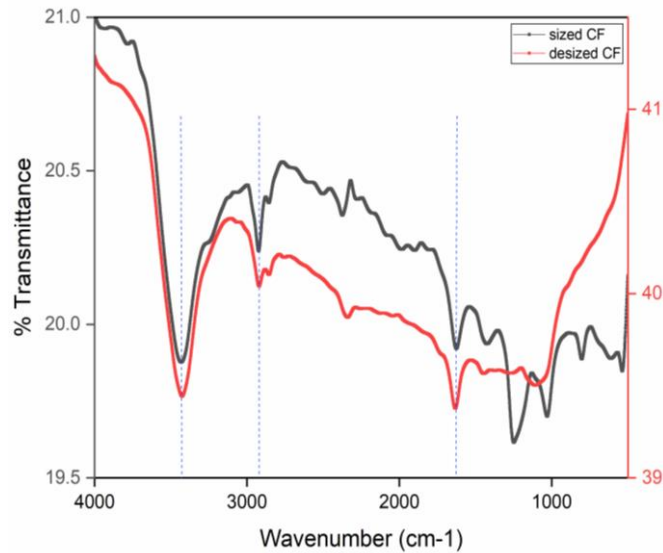
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Fig. 8 *Combined FTIR spectra of sized and desized CF*

The contact angle measurements were performed on both the sized and desized CF samples to assess the impact of the desizing treatment on the surface wettability. The initial contact angle measurements revealed distinct differences between the two samples.
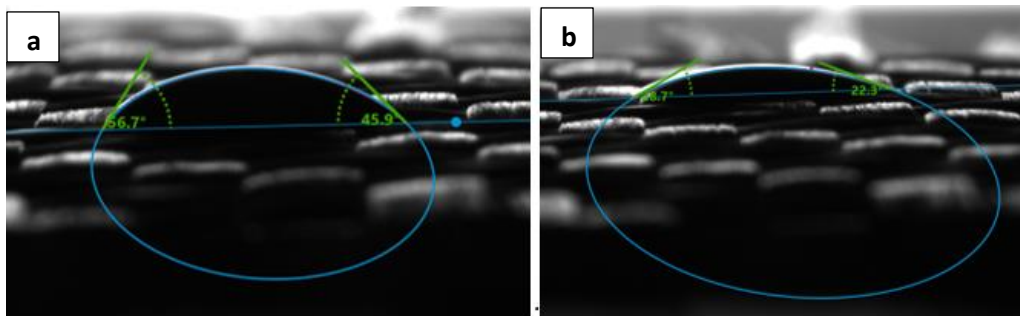


Fig. 9 *The contact angle of sized CF after (a) 0 seconds and (b) 30 seconds by droplet fall method*

The as-received-sized CF exhibited a contact angle of 56.7° on one side and 49.5° on the other side of the fabric *(*Fig. 10). This difference in contact angles can be attributed to the unique topographical features of the woven CF fabric, which exhibited a distinct valley-like structure due to the weaving pattern. The presence of the sizing agent on the CF surfaces contributed to the relatively higher contact angles, indicating a moderate wettability and surface energy. However, after a 30-second interval, the contact angles on the sized CF samples decreased significantly, with the left and right-side angles receding to 28.7° and 22.3°, respectively. The more pronounced reduction in the left-side contact angle was likely due to the liquid droplet spreading more readily toward the spaces between the warp and weft yarns of the woven fabric. This behavior suggested an enhancement in the wettability and spreading characteristics of the
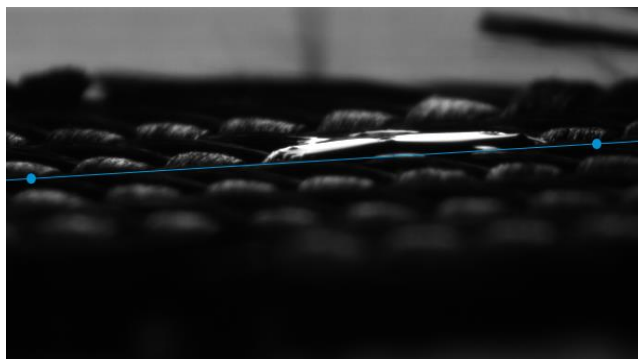
Fig. 11 *The droplet with a non-detected minimal angle on the desized CF*

sized CFs over time, which can be attributed to the gradual penetration of the liquid droplet into the porous fabric structure. The desizing treatment of the CFs resulted in a dramatic improvement in wettability, as evidenced by the near-complete absorption of the water droplet on the desized CF fabric (Fig. 12). The contact angle was virtually undetectable, approaching a value close to 0°, indicating an excellent wetting behavior. This significant enhancement in wettability can be directly correlated to the changes in the chemical composition and surface functionalities of the CFs, as revealed by the FTIR analysis.

## IV.    DISCUSSION

The desizing procedure successfully disclosed the highly graphitic nature of the CFs, as evidenced by the observed alterations in the XRD patterns, including the appearance of the distinctive (002) peak and the enhanced intensity of the graphitic characteristics. When integrated into composite materials, the improved graphitic order and crystallinity should help to enhance the targeted CFs' mechanical properties.

The FTIR results, in conjunction with the XRD findings, demonstrated that the desizing process effectively removed the sizing agent from the CF surfaces, revealing the inherent graphitic and polar characteristics of the CFs. This surface modification is of crucial importance in the context of composite applications, as it can significantly improve the adhesion and wettability between the CFs and the polymer matrix, leading to enhanced interfacial interactions and improved mechanical performance of the resulting composites. The FTIR analysis of the desized CF samples revealed a decrease in the strength of the distinctive peaks linked to the organic functional groups that the sizing agent had added. The significant increase in wettability seen in the contact angle measurements was probably caused by this decrease in surface polarity and the exposing of the CFs' intrinsic graphitic nature. The CF fabric's weave, which has a porous structure by nature, made it easier for the liquid droplet to absorb and disseminate quickly across the surfaces of the desized fibers.

These results show that the residual sizing agent from the CF surfaces was successfully eliminated by the desizing process, improving surface wettability and possibly improving interfacial adhesion between the CFs and the polymer matrix in composite applications. The enhanced wetting behaviour of the desized CFs was facilitated by the combination of reduced surface polarity and increased roughness. This is an important factor in the creation of high-performance composite materials.

## V. CONCLUSION

1. Wettability and surface chemistry of the fibers changed significantly when CFs were successfully treated with a straightforward, environmentally friendly chemical-thermal procedure.

2. SEM confirmed the usefulness of the desizing treatment, which removed the residual sizing agent and exposed the pristine surface of the CFs. Importantly, the cross-sectional shape, carbon content, and overall quality of the fibers were not adversely affected by the treatment, preserving the essential properties of the CFs.

3. The contact angle measurements showed that the desized CFs' wettability had significantly improved; in fact, the contact angle was almost zero, indicating good liquid spreading and absorption. As

verified by the FTIR study, this increased wettability was ascribed to the elimination of the sizing agent and the exposure of the CFs' intrinsic graphitic character.

4. The combination of reduced surface polarity and increased surface roughness, as a result of the desizing treatment, contributed to the superior wetting behavior of the modified CFs. This enhanced wettability is a crucial parameter for improving the interfacial adhesion between the CFs and the polymer matrix in composite materials, ultimately leading to enhanced mechanical and durability performance.

5. The simple and sustainable chemical-thermal treatment developed in this study provides a viable approach for the surface modification of CFs, paving the way for the fabrication of high-performance composite materials with improved interfacial characteristics and overall performance.

ACKNOWLEDGMENT

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