Fazeli, Mahyar; Jayaprakash, Siddharth; Baniasadi, Hossein; Abidnejad, Roozbeh; Lipponen, Juha

Recycled carbon fiber reinforced composites: Enhancing mechanical properties through co-functionalization of carbon nanotube-bonded microfibrillated cellulose

Published in:
Composites Part A: Applied Science and Manufacturing

DOI:
10.1016/j.compositesa.2024.108097

E-pub ahead of print: 01/05/2024

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Recycled carbon fiber reinforced composites: Enhancing mechanical properties through co-functionalization of carbon nanotube-bonded microfibrillated cellulose

Mahyar Fazeli a,b, Siddharth Jayaprakash b, Hossein Baniasadi c, Roozbeh Abidnejad a, Juha Lipponen a

a Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, FI-00076 Aalto, Finland
b Department of Mechanical Engineering, School of Engineering, Aalto University, P.O. Box 12150, FIN-00076 Aalto, Espoo, Finland
c Polymer Technology, School of Chemical Engineering, Aalto University, Espoo, Finland

ARTICLE INFO

Keywords:
Polymer-matrix composites (PMCs)
Surface properties
Recycling
Carbon fibers

ABSTRACT

The imperative challenge of repurposing recycled carbon fiber (rCF) in composite structures, due to its cost-effectiveness and eco-friendly attributes, has spurred innovative research. This study introduces a scalable processing technique, integrating carbon nanotube (CNT)-bonded microfibrillated cellulose (MFC) onto randomly oriented rCF mats, focusing on enhancing mechanical properties. Employing electrophoretic deposition (EPD), rCF surfaces are effectively functionalized with CNT/MFC, probed through X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Modified fiber surfaces exhibit reduced contact angles, indicating improved wettability. Epoxy-based composites, fabricated via vacuum infusion, show up to 32% and 27% improvements in tensile and flexural strength. Dynamic mechanical analysis (DMA) confirms elevated storage modulus and energy dissipation capability. SEM analysis of fracture surfaces illustrates robust adhesion between coated fibers and the matrix, supporting the proposed approach’s efficacy. This study unveils an innovative pathway to enhance recycled carbon fiber composite properties, extending their application potential in diverse engineering domains.

1. Introduction

Due to the recent growth in the global volume of carbon fiber used in the manufacturing of composites, there has been special attention to the possible capacity of waste from fabricating processes and end-of-life products [1]. Moreover, the non-biodegradability of the waste associated with carbon fiber final products will result in an eventual surge of these bi-products to an alerting level which can become a significant environmental concern [2]. Besides, the manufacture of neat carbon fiber is greatly expensive because of the high energy consumption. The average energy needed for producing virgin carbon fibers is approximately 100 kWh/kg [3]. The amount of energy used to produce carbon fibers leads to the expensive final product. Hence, there is a motivation to find a new method to produce valuable alternatives to virgin carbon fibers. One of the most significant alternatives introduced to the market in recent years is recycled carbon fiber (rCF). Carbon fibers can be recycled from the end-of-life composites by using almost 5 kWh/kg energy, which is considerably lower than the energy needed for producing the virgin carbon fibers [4]. Hence, manufacturers will require to distinguish ways to conform the regulation on sustainability. The promotion of methods for recovering carbon fiber from used composites has drawn a lot of attention over the past ten years. Several methods for recycling carbon fiber from CFRP (carbon fiber reinforced polymer) waste have been developed. Furthermore, using recycled carbon fibers is the eco-friendly method of manufacturing composites to decrease greenhouse gases and common disposal of manufactured CFRPs. Carbon fiber recycling is performed by various processes such as solvolysis, pyrolysis, and fluidized bed method. Solvolysis recycling may provide recycled fibers with high preservation of mechanical properties, albeit the method is not always contamination-free. Pyrolysis produces recycled fibers from a composite by burning the matrix at a specific range of temperatures. The fluidized bed method is a proper process against producing contaminated fibers; however, the degradation of the mechanical properties has been reported [5–7]. Recycled carbon fibers are
often derived from reclaimed or waste carbon fiber materials, and T300-grade fibers are commonly chosen for recycling processes for several reasons such as availability of waste material, cost considerations, compatibility with recycling processes, etc. As a matter of fact, T300 carbon fibers are widely used in various industrial applications. As a result, there is a significant amount of waste material available for recycling. This makes it practical and economically viable to focus on recycling T300 fibers. Furthermore, T300 fibers are generally more cost-effective than higher-end carbon fibers like T700 or T800. Using T300-grade carbon fiber for recycling helps keep the overall cost of the recycled material lower [8,9].

When considering the mechanical properties, it’s noteworthy that T300 fibers exhibit a tensile strength of 3530 MPa and a tensile modulus of 230 GPa. In comparison, higher-grade carbon fibers such as T700 have a higher tensile strength, reaching 4900 MPa, while T800 surpasses both with a tensile strength of 5880 MPa. Despite the differences in tensile strength, both T700 and T300 share a similar tensile modulus of 230 GPa. Additionally, T800 stands out with a higher tensile modulus of 294 GPa. These mechanical property variations further emphasize the considerations involved in choosing carbon fiber grades, even in the context of recycling processes [10–12].

Due to the aforementioned disadvantages of the recycling processes, extracted fibers need to be modified for mechanical and surface properties improvement to have better performance and strong adhesion to the matrix [13,45]. Recently, many techniques have been employed to enhance the characteristics of carbon fibers, such as surface electro-polymerizing [14], surface coating [15], anodic oxidation [16], phase oxidation [17], surface grafting [18], and plasma modification [19]. Although the mentioned surface modifications of the fibers have improved their interfacial bonding to the matrix, there are several downsides to these treatments, such as the decrease in tensile strength after surface treatment of the fiber and the necessity for complicated and costly instrumentations. Keeping an efficient load transfer between the fibers and matrix requires strong adhesion between the interlaminar and interfacial areas of carbon fiber-reinforced polymers (CFRP). As a result of the strong adhesion, interlaminar strength, interfacial properties, delamination resistance, and tensile strength will be improved [20]. For these enhancements, nanomaterials have been introduced and functionalized onto the surfaces of reinforcing fibers to improve the interfacial properties of polymer composites. Nanomaterials are deposited onto fiber surfaces in several ways, including dip coating on fibers [21], distribution in the sizing agent [22], layer-by-layer assemblies [23], grafting the fiber surface [24], and electrophoretic deposition [25]. Among these methods, electrophoretic deposition is a scalable technique with a high efficiency, which enhances the physical absorption of nanomaterials into reinforcing fibers. Electrophoretic deposition (EPD) provides a promising approach for modifying and coating CFs homogeneously [26]. To this end, by applying an electric field to a stable suspension, charged particles are induced to move toward the electrode surface with a countercharge. This method has a number of benefits, including ease of use, low cost, a limited need for equipment, and the possibility to use a variety of coating materials for creating varied sizes. Additionally, it may be used without strong acids or bases at room temperature. Also, due to its strong conductivity in aqueous solutions, CF is a great electrode material for an EPD process. The condition of the deposition can be regulated methodically by the particle concentration, applied voltage, and deposition time [27].

It has been extensively researched how to improve the mechanical characteristics of CFRP composites with the use of carbon-based nanomaterials, including graphene nanoplates, carbon nanotubes (CNTs), and their mixes [28]. Despite the fact that these investigations conform well to their objective, most of these methodologies count on the chemical processes of CNTs, which is a useful technique, but not cost-effective and causes damage to the CNT structure that destroys their inherent properties. In order to reduce the overall cost of hybrid composites, virgin CNTs are an excellent choice; however, due to their strong Van der Waals attraction, homogenous dispersion of pristine CNTs is very problematic [29].

A variety of applications have been developed using cellulose nanomaterials over the past few years, such as electronics, drug delivery, construction, medicine, and polymer composites. Cellulose nanomaterials, the world’s most abundant polymer, can take the form of microfibrillated cellulose (MFC), cellulose nanocrystals (CNC), cellulose nanofibers (CNF), bacterial cellulose, and algae cellulose [30–32]. Among these types, MFCs (10–500 nm in length, 5–30 nm in width) [33] have high mechanical properties (~29–65 GPa modulus) [34,35], low density (1.5–1.6 g/cm³), thermal stability (up to 350 °C) [36], and high aspect ratio (10–100), with plenty hydroxyl groups (–OH), which can simplify different types of chemical bonding with other species. The existence of abundant hydroxyl groups and other negatively charged species (if hydrolyzed with the acid) results in the high colloidal stability of MFCs in water [37,46]. The incorporation of cellulose in our study is motivated by its potential to enhance the chemical and structural adhesion between carbon fibers and the epoxy matrix. MFC is selected due to its unique characteristics, including high mechanical properties, low density, thermal stability, and a high aspect ratio. The abundance of hydroxyl groups in MFC facilitates various chemical interactions, promoting adhesion with both carbon fibers and the epoxy matrix. The specific choice of MFC aims to leverage its advantageous properties for effective functionalization and improved performance in the composite material [38].

In this investigation, we postulate that the functionalization of recycled carbon fibers through the integration of CNTs and MFC engenders a plethora of chemical sites on the fiber surface, thereby fostering robust chemical and structural adhesion with the epoxy matrix. To assess the mechanical ramifications of this unique functionalization on individual fibers and fabricated composites, comprehensive tensile testing, flexural testing, and dynamic mechanical analysis (DMA) are performed. Moreover, the presence of carbonyl and carboxyl functional groups resulting from the surface bonding is verified through X-ray photoelectron spectroscopy (XPS) analysis. Notably, the novel morphology, characterized by CNT-bonded MFC adorning the surface of recycled carbon fibers, is vividly elucidated via scanning electron microscopy (SEM). Ultimately, the substantial structural adhesion between the fibers and the epoxy matrix is visually demonstrated through SEM analysis, underscoring the efficacy of the proposed functionalization approach.

2. Materials and methods

2.1. Materials

Recycled polyacrylonitrile (PAN)-based carbon fiber (T300, average length of 9 mm) with an average diameter of 7 μm is provided by Nantong Fuyuan Carbon Fiber Recycling Co. Ltd, China. According to the information provided by the company, in the recycling process, the polymer matrix is depolymerized during the pyrolysis process. After breaking down the matrix, the carbon fibers were separated from the resulting materials by mechanical separation and solvent extraction. Polyethylene oxide (PEO, average molecular weight = 1 million, purity = 99.9 %) and methyl violet (pH = 0.1–2.0) are provided by Sigma Aldrich. Multi-walled carbon nanotube (diameter = 20–30 nm, length = 0.5–2 μm, density = 4 mg/cm², purity > 95 %) is provided by Shanghai Macleans Biochemical Co., Ltd. China. The microfibrillated cellulose with a diameter ranging from 10 to 200 nm and a length of 1 to 10 μm was acquired from Guilin Qihong Technology, China. The manufacturing process involved mechanical grinding and high-pressure homogenization, utilizing sulfate pulp bleaching of eucalyptus wood as the primary raw material. The composition of this MFC included 75.8 % cellulose, 9.7 % hemicelluloses, and no lignin, with a surface charge density of approximately 70 μeq/g. A MFC suspension with a solid content of 1.8 % was directly obtained from the supplier. Epoxy resin
Two stirrers are then used to mix the solution for a duration of 10 min. and higher-quality output, 10 g of PEO are introduced into the solution. To promote better retention and mat formation, ensuring a more consistent uniform distribution at the individual fiber level. After adding the car prevened from aggregating in the aqueous solution, promoting a more the solution. By increasing the surface tension of the water, the fibers are prevented from aggregating in the aqueous solution, promoting a more uniform distribution at the individual fiber level. After adding the carbon fibers, the solution is mixed for an additional 10 min. In a separate rectangular chamber, the prepared solution is poured onto a nylon mesh framework with a mesh size of 2000 µm positioned at the base. The mesh framework serves as support during the process. Finally, the mesh framework is gradually removed, and the mat is left to dry overnight in a 70 °C oven (Supplementary Information, Figure S1). The ultimate weight of each mat falls within the range of 7 to 8 g.

During the Electrophoretic Deposition (EPD) process, carbon fibers are employed as cathodes, while aluminum plates served as anodes, each having an aerial dimension of 25 cm × 25 cm. To create the suspension required for the process, CNT and MFC are added to distilled water in equal proportion, resulting in a concentration of 0.5 g/L. Subsequently, the mixture underwent ultrasonication at a frequency of 100 KHz for a duration of 30 min. Methyl violet, with a bath concentration of 0.1 g/L, is introduced into the suspension. This addition is aimed at utilizing methyl violet as a stabilizer to facilitate the uniform dispersion of CNT/ MFC within the suspension. To ensure proper mixing and distribution, the suspension is subjected to an additional hour of ultrasonication. During the EPD process, if CNTs and MFCs are dispersed in distilled water, there is a greater likelihood of sedimentation occurring. As a result, the deposition process becomes less efficient and effective. Conversely, in the case of carbonaceous nanoparticles, they acquire a positive charge through π-π interaction with methyl violet, which is predominantly governed by the NH⁺ group. The formation of films on the cathodic surfaces during the process is attributed to the influence of the applied electric field, which facilitates the movement of cationic methyl violet toward the cathode surface [39]. The hydroxide groups present in the system play a vital role in neutralizing the charge of the cationic methyl violet, leading to the formation of films. To set up the EPD cell, the cathodes and anodes are immersed in the prepared bath in an alternating order, as it is demonstrated in Fig. 1 (Supplementary Information, Figure S2 to Figure S5). The deposition process lasted for a duration of 30 min, and a constant current of 5 A is maintained throughout the EPD process. The distance between the electrodes (cathode and anode) remained constant, ensuring that the applied electric field (E) is consistent for all cases. While zeta potential and electrophoretic mobility are commonly used by researchers, it should be noted that these parameters alone do not provide a definitive indication of a suspension’s ability to deposit. Subsequently, the modified mats are removed from the EPD cell and allowed to dry overnight in a 90 °C oven. To eliminate any remaining residue of methyl violet from the mats, they are immersed in acetone for a duration of 2 h. In order to enhance the adhesion between the CNT/MFC and carbon fiber, the modified fibers underwent thermal treatment in an oven for 2 h at a temperature of 140 °C.

2.3. Fabrication of composites

The vacuum infusion technique is employed for the fabrication of composite panels. In this method, four prepared rCF mats are stacked on top of each other and covered with peel ply and distribution mesh. These layers are then enclosed and sealed using a vacuum bag and sealant tape. The utilization of the vacuum bag represents an economically advantageous approach, resulting in a notable reduction in costs associated with the resin and curing agent usage. By applying vacuum pressure to the system through a mechanical pump, the rCF mats are compressed, facilitating the production of composite panels with reduced porosity and voids, while also enabling resin infusion into the reinforcement. Epoxy resin and curing agent mixture is introduced into the system at a flow rate of 20 ml/min when the vacuum is initiated. Once the rCF mats are fully impregnated, the resin injection valve is closed, while the pump continues operating for 10 min to eliminate any remaining small bubbles from the system. Subsequently, the outlet valve is closed, and the entire system is maintained under vacuum for a duration of 6 h. Finally, the composite panel is slowly extracted. The process of composite manufacturing from the recycled carbon fibers to the composite panel is schematically demonstrated in Fig. 2. It’s crucial to note that the weight fraction of the fiber ranged between 50 % and 60 % for all samples. Maintaining a consistent weight fraction across all samples proved challenging due to variations in the fiber content of the different mats utilized in this study.

2.4. Single fiber tensile properties of the rCFs

Single fiber tensile tests are accomplished on twenty samples for both uncoated and coated types of fibers. The same batch of samples are used to determine the number of defects are used to measure the mechanical properties (tensile strength, Young’s modulus, and elongation at breaks) and also the diameter of the single fibers. The fibers, after the determination of their cross-sectional radius through their length, are unchangeably tensile tested using precisely developed equipment which is an LEX extensometer 820 (Dia-stron Ltd., UK). It consists of two parts:
LDS, which is the precise laser system to measure the diameter and the defects of the fibers all over their lengths, and a load cell with a capacity of 20 N plus a stepping motor for traction (Supplementary Information). The elongation is achieved with an accuracy of 1 μm. The single fibers are tensile tested at an extension rate of 1 mm/min. The gauge length of the samples is 4 mm.

2.5. Weibull modulus calculation

The Weibull distribution is used to represent the statistical distribution of the tensile strength of the single carbon fiber [40]. The simple form of the Weibull equation is based on equation (1):

$$P_f = 1 - \exp\left( - \frac{\sigma_f}{\sigma_0} \right)^m$$

where $m$ is the Weibull modulus which will be used in this study as the main factor of comparison between different kinds of samples. $\sigma_f$ and $\sigma_0$ are the maximum tensile strength of single carbon fiber and characteristic stress, respectively. $P_f$ is the cumulative probability of failure of a single carbon fiber. The natural logarithm is applied to both sides of the equation (1). Hence, the reformed formula of the Weibull statistical distribution to a straight-line mode may be written like equation (2).

$$\ln \ln \left( \frac{1}{1 - P_i} \right) = m \ln(\sigma_f) - m \ln(\sigma_0)$$

where $m$ is the linear form of the Weibull modulus and $P_i$ as the probability of failure can be gained by equation (3).

$$P_i = \frac{i - 0.5}{N}$$

2.6. Scanning electron microscopy

Microstructure analysis of the fibers is carried out using a scanning electron microscope (Sigma VP; Zeiss, Oberkochen, Germany) operating at an acceleration voltage of 5 KV. Likewise, scanning electron microscopy (SEM) is employed to inspect the fracture surfaces of the composites after undergoing tensile tests with an acceleration voltage of 3 KV. Before the examination, all specimens are coated with a 5 nm layer of gold using the high vacuum deposition technique (EM SCD500, Leica, Germany).

2.7. Surface chemistry of coated rCFs

To examine the surface chemical compositions of both uncoated and coated carbon fibers (rCFs), X-ray Photoelectron Spectroscopy (XPS) is conducted using an Omicron XPS/UPS system equipped with an Argus detector. The analysis involved using a monochromatic Mg Kα X-ray source with a power of 300 W and an operating voltage of 15 kV. Quantitative elemental compositions and peak analysis are carried out using CasaXPS software. The obtained peaks are calibrated against reference values of 284.8 eV (representing C–C/C=C bonds) and 532.0 eV (representing O = C bonds) for the C 1 s and O 1 s regions, respectively. Prior to the XPS analysis, all samples are placed in a vacuum oven for one hour to reduce outgassing effects.

2.8. Wettability of rCFs

The surface contact angle between the resin and single rCF is measured for different types of coated fibers, and the result is compared with the outcome related to the uncoated fiber. A precise syringe is used to take 1 μl of resin droplet. Both sides of a single fiber are mounted on sample holders to make the single fiber straight and detached from the surface. Then, the droplet of the resin is attached to the fibers so that the single fiber immerges in the droplet. Thereupon, the syringe is detached from the droplet. All these steps are carried out under the optical microscope (Nexcope NE930, China), where the images of the samples are captured, and the contact angles are measured by the software ImageJ.
2.9. Thermogravimetric analysis of rCFs

To assess the degrading properties of the recycled carbon fibers after/before coating, thermogravimetric analysis is carried out. The thermogravimetric stability analysis is conducted to differentiate the thermal stability of three specimens, encompassing both uncoated and coated fibers. This analysis employed a TA Instruments SDT Q600 thermogravimetric analyzer under controlled conditions, employing a nitrogen flow rate of 20 ml/min as the ambient atmosphere and a heating rate of 10 °C/min. Each sample weighed 10 mg and is subjected to a temperature range spanning from room temperature to 1000 °C.

2.10. Tensile test of composites

The tensile properties of the produced composites, including tensile strength, Young’s modulus, and elongation at break, are analyzed using a Universal Testing Machine (Instron, MTS E45.105, United States). This analysis aimed to investigate the performance of composites reinforced with both uncoated and coated recycled carbon fibers. Six dog-bone specimens for each kind of composite are cut by Waterjet Cutting Machine (JJ-I, Shanghai Jinjian, China) based on ISO 527–4(1A). The traverse speed and stand off distance of nozzle were 0.3 m/min and 3 mm, respectively. Furthermore, the waterjet pressure was 10 MPa. The average dimension of each specimen is approximately 150 mm × 20 mm × 4 mm. The tensile test is conducted at room temperature and 50 % relative humidity using a testing speed of 1 mm/min. A load cell of 50 kN is employed to determine the tensile strength and Young’s modulus of all the prepared samples. Additionally, the strain at breaks is measured using an extensometer attached to one side of the sample, with a gauge length of 50 mm.

2.11. Flexural test of composites

The three-point bending test is carried out on the fabricated composites reinforced with both uncoated and coated fibers. This test is performed using a Universal Testing Machine (Instron, MTS E45.105, United States) in accordance with the specifications outlined in ISO 14125. The dimension of the samples is approximately 60 mm × 15 mm × 4 mm. All the samples are cut by Waterjet Cutting Machine (JJ-I, Shanghai Jinjian, China) based on ISO 527–4(1A). The test is performed.

![Fig. 3. SEM images of (a) uncoated rCF (rCF0), (b) rCF-10 V, (c) rCF-20 V, (d) rCF-30 V, (e,f) higher magnification of CNT/MFC morphology on the rCF surface.](image-url)
with a head speed of 1 mm/min at ambient temperature and 50 % relative humidity. A total of five samples are tested for each fabricated composite.

2.12. Dynamic mechanical analysis of composites

The dynamic mechanical characteristics of different fabricated composites are assessed through the utilization of a state-of-the-art dynamic mechanical analyzer (DMA, Q800, TA, USA) outfitted with a singular cantilever clamp. In order to determine the storage modulus (E') and tan delta (tan δ), a series of carefully controlled experiments are performed. The temperature is incrementally increased at a rate of 3 °C/min, encompassing the full range from ambient temperature to 180 °C. A frequency of 1 Hz, a strain of 1 %, and a pre-load of 1 N are employed for the applied oscillating stress, and the carrier gas employed throughout the experiments consisted of ambient air.

3. Results and discussion

3.1. Morphology of grafted CNT/MFC onto rCFs

The morphology of the coating plays a crucial role in enhancing the interaction and adhesion between the matrix and fibers in composite materials [41,47,48]. However, rCF inherently possess a smooth surface and lack sufficient functional groups, leading to weak adhesion between the fibers and the matrix, as shown in Fig. 3a. To address this issue, a solution is found by electrochemically grafting CNT and MFC onto the fiber surface using an electrophoresis method and Table 1 shows the sample names after modification. Fig. 3b to Fig. 3f illustrate the morphological transformation of functionalizing the fiber surface with CNT/MFC. CNTs are attached to MFC, and both components adhere to the rCF surface. However, it is observed in Fig. 3b that certain regions on the fiber surface remain smooth, indicating that EPD with a constant voltage of 10 V is insufficient to functionalize the entire fiber surface (rCF-10 V). On the other hand, when the voltage is increased to 20 V and 30 V, additional CNTs and MFCs are successfully grafted onto the surface (rCF-20 V, rCF-30 V). Notably, using EPD with 20 V (Fig. 3c) ensures the complete coverage of the rCF surface by CNTs and MFCs. Moreover, at a higher voltage of 30 V, cellulose nanofibers begin to agglomerate on the surface. The C-O functional group in the cellulose nanofibers can graft to the C-OH group on the surface of the carbon nanotubes. Consequently, higher voltage levels lead to an increased quantity of CNTs and MFCs on the carbon fiber surface, as observed in the experimental results. This process ultimately improves the adhesion and interaction between the composite matrix and the fibers.

Fig. 3e to Fig. 3f exhibit the microstructure of dispersed CNT and MFC at a higher magnification in the rCF-20 V. These images distinctly highlight the augmented surface roughness of the rCF, resulting in a more robust physical interaction between the fibers and the matrix. Additionally, the expanded surface area attributed to the incorporation of CNT and MFC signifies the creation of additional chemical sites, including carbonyl and carboxyl functional groups. This, in turn, promotes heightened chemical interaction between the surfaces and the matrix, further enhancing the overall adhesion (Supplementary Information, Figure S6 to Figure S15).

Table 1

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>rCF0</td>
<td>Unmodified recycled carbon fiber</td>
</tr>
<tr>
<td>rCF-10 V</td>
<td>Functionalized rCF by CNT/MFC with EPD at 10 Volts</td>
</tr>
<tr>
<td>rCF-20 V</td>
<td>Functionalized rCF by CNT/MFC with EPD at 20 Volts</td>
</tr>
<tr>
<td>rCF-30 V</td>
<td>Functionalized rCF by CNT/MFC with EPD at 30 Volts</td>
</tr>
</tbody>
</table>

3.2. Surface chemistry of rCFs

Fig. 4a presents the comprehensive elemental composition and percentage of uncoated and functionalized fibers. Upon analysis, the C 1 s peaks are fitted with a binding energy of 285 eV, while the O 1 s peak exhibited a binding energy of 530 eV. The plots reveal that the incorporation of EPD voltage, indicating the addition of CNT/MFC to rCFs, significantly enhances the presence of polar oxygen groups compared to uncoated rCFs. This signifies the generation of more active surfaces on rCFs, thereby providing a greater number of sites for robust chemical bonding with the polymer matrix. Fig. 4b presents a comparison of the C 1 s peaks between surface-modified and uncoated rCFs. The reference uncoated rCF primarily consists of graphite (284.8 eV), comprising 80.25 % of the composition, while polar-oxygen-containing groups, including carbonyl, C=O (~286.2 eV) occupy 19.75 %. The surface chemistry analysis of rCF-10 V indicates that using a process voltage of 10 V does not significantly alter the oxidative sites of CFs compared to uncoated CFs. However, a carboxyl or ester group are added to the surface. Interestingly, the presence of oxidative sites, including C-O and C=O undergoes a substantial increase, highlighting the effectiveness of the EPD method at higher voltages of 20 V and 30 V compared to 10 V. These findings shed light on the impact of EPD voltage on the surface chemistry and composition of the carbon fibers, providing valuable insights into the modifications induced by the functionalization process.

3.3. Wettability of rCFs

The data presented in Fig. 5 illustrate a noteworthy decrease in the contact angle between fibers and epoxy resin when the surfaces are treated with CNT/MFC. Specifically, the contact angle reduced significantly from an initial value of 70° to a lower value of 55.1°. These findings align with previous reports [42], suggesting that the observed results are consistent with prior research in the field. The reduction in contact angle can be attributed to the presence of excess polar-oxygen-containing groups on the coated surface, as confirmed by the XPS technique. These functional groups play a crucial role in establishing strong hydrogen bonds between the fibers and the matrix. Additionally, they contribute to the decrease in the contact angle, leading to a more hydrophilic surface in comparison to rCF0. Consequently, the enhanced hydrophilicity facilitates superior wetting of the epoxy, promoting improved adhesion between the fibers and the matrix. Furthermore, it is worth noting that the contact angle of the fibers coated with a higher concentration of CNT/MFC is smaller when compared to those coated with lower concentrations. This difference can be attributed to the higher number of functional groups present on the surface due to the increased concentration of the coating. As a result, the greater abundance of functional groups enhances the wetting behavior of the fibers by the epoxy, resulting in a more pronounced decrease in the contact angle.

3.4. Single fiber tensile properties and Weibull modulus of the rCFs

Table 2 presents the obtained outcomes of single-fiber tensile tests for recycled carbon fibers. The tensile strength and Young’s modulus of uncoated recycled carbon fibers (rCFO) are observed to be 3.8 GPa and 179.8 GPa, respectively. These values are quite high for recycled carbon fibers compared to virgin ones which have been reported before [43]. As can be seen, there is no significant difference between rCFO and rCF-10 V results. The reason might be the lack of enough grafted CNT/MFC during EPD process with 10 V on the surface of rCF. The tensile strength and Young’s modulus are increased for rCF-20 V and rCF-30 V compared to rCFO. The surface of rCF is fully covered by CNT and MFC. Hence, those CNTs and MFCs strengthen the carbon fiber by grafting to the surface and covering the superficial flaws on the surface of the fibers. The results demonstrate that the tensile strength of recycled carbon fibers obtained through single-fiber tensile testing varies, which is
characteristic of recycled fibers. This variation can be attributed to the presence and distribution of small defects, such as micro-cracks and superficial flaws on the fiber structure or surface. The Weibull distribution is commonly employed to examine the theoretical prediction of fiber strength and the distribution of defects on the fibers. Equations (2) and (3) are utilized to determine the Weibull modulus of distribution.

Fig. 4. (a) XPS spectra of rCF and functionalized rCF, (b) C1s peaks of rCF0, rCF-10 V, rCF-20 V, and rCF-30 V (Figure S16 demonstrates the XPS spectra of MFC, CNT, and MFC/CNT).

Fig. 5. Contact angle measurements on a single fiber of (a) rCF0, (b) rCF-10 V, (c) rCF-20 V, and (d) rCF-30 V.
both uncoated and functionalized recycled carbon fibers based on their tensile strength, as shown in Fig. 6. The measured Weibull modulus for uncoated recycled carbon fibers is approximately 7.9, indicating a high presence of flaws on their surface. Consequently, the variation in tensile strength results among the 20 samples is significant. However, after functionalization, the Weibull modulus decreases, suggesting that the grafted CNT/MFC reinforces the weak points of the recycled carbon fibers. This reduction in the distribution of flaws is observed, resulting in a significant decrease in the variation of the obtained results. The measured Weibull modulus values for the 20 samples of rCF-10 V, rCF-20 V, and rCF-30 V are 4.9, 4.3, and 3.2, respectively. SEM images confirm that the coating effectively covers the entire surface of the fibers through the EPD process at 20 V and 30 V. Based on the SEM images and Weibull distribution results, it can be concluded that the recycled carbon fibers exhibit enhanced strength at these two voltage settings compared to 10 V, as confirmed by the single fiber tensile tests as well.

3.5. Mechanical testing of the composites

As depicted in Fig. 7, the initial tensile strength and Young’s modulus of the C-rCF0 composite (Table 3 shows the composite names) are measured at 75.71 MPa and 5.91 GPa, respectively. The results demonstrate the significant impact of EPD treatment and the role of CNT/MFC in enhancing the mechanical properties and mechanical interlocking of the composite materials. Specifically, for the C-rCF-20 V composite, the tensile strength reaches 100.21 MPa, showcasing a 32.3% enhancement compared to the C-rCF0 composite. Additionally, the modulus is enriched to 8.95 GPa, representing a substantial increase of 51.4% compared to the C-rCF0 composite. This enhancement can be attributed to the incorporation of CNT/MFC via the EPD treatment, which serves to augment both the contact area and the wettability of the fibers.
The improved mechanical interlocking further facilitates the effective transfer of loads from the matrix to the fibers, consequently impeding the propagation of internal cracks. Consequently, stress concentration is reduced, leading to improved overall performance of the composites. However, in the case of the C-rCF-30 V composite, a decrease in tensile properties is observed compared to the C-rCF-20 V composite. This can be attributed to the excessive presence of CNT/MFC on the surface of the fibers. The abundance of CNTs and MFCs may compromise the suitable mechanical interlocking and physical interaction between the matrix and the fibers, thereby negatively impacting the tensile properties of the composite.

Table 3
Sample coding of fabricated composites.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-rCF0</td>
<td>Epoxy-based composite reinforced by rCF0</td>
</tr>
<tr>
<td>C-rCF-10 V</td>
<td>Epoxy-based composite reinforced by rCF-10 V</td>
</tr>
<tr>
<td>C-rCF-20 V</td>
<td>Epoxy-based composite reinforced by rCF-20 V</td>
</tr>
<tr>
<td>C-rCF-30 V</td>
<td>Epoxy-based composite reinforced by rCF-30 V</td>
</tr>
</tbody>
</table>

interface between the rCF and the matrix. The improved mechanical interlocking further facilitates the effective transfer of loads from the matrix to the fibers, consequently impeding the propagation of internal cracks. Consequently, stress concentration is reduced, leading to improved overall performance of the composites. However, in the case of the C-rCF-30 V composite, a decrease in tensile properties is observed compared to the C-rCF-20 V composite. This can be attributed to the excessive presence of CNT/MFC on the surface of the fibers. The abundance of CNTs and MFCs may compromise the suitable mechanical interlocking and physical interaction between the matrix and the fibers, thereby negatively impacting the tensile properties of the composite.

The flexural behavior of CFRP composites is influenced by the strength of the fiber and the efficiency of stress transfer from the matrix to the fiber. This stress transfer is dependent on the extent of matrix infiltration. From Fig. 7, it is evident that the grafting of rCFs has led to a significant enhancement in flexural strength, particularly for C-rCF-20 V, where an improvement of approximately 27% is observed compared to neat CFRP composites. The enhancement in interfacial strength can be ascribed to the increased surface roughness and mechanical interlocking facilitated by the inclusion of CNT/MFC on the fiber surface. This observation aligns with prior literature findings [44]. Moreover, the oxygen-containing groups inherent in both CNT and MFC play a role in augmenting mechanical interlocking. These groups react with the epoxy moieties of the resin matrix during the curing process, further fortifying the bond between the fiber and the matrix. Notably, the use of a 10 V applied voltage, as seen in C-rCF-10 V, has a negligible effect on the flexural response, and any observed changes can be attributed to experimental error, given their small magnitude. The increase in flexural strength aligns with engineering beam theory, as the high-strength carbon nanotubes are added to the surface farthest from the neutral line. Comparing C-rCF-30 V to C-rCF-20 V, there are minimal changes in flexural strength and modulus, which can be considered statistically insignificant as the error bars of the results overlap.

DMA is conducted to investigate the storage modulus and loss factors (tan δ) of different composite samples across a range of temperatures. As
depicted in Fig. 8a, the storage modulus curves exhibited three distinct regions. First, a high-modulus region is observed, signifying substantial restriction in the mobility of the epoxy. This is followed by the identification of a transition zone marked by a sharp decline in the storage modulus. Finally, a rubbery region emerged where the storage modulus reached a stable plateau value.

Among the quartet of formulated nanocomposites, C-rCF0 displayed the most modest storage modulus at equivalent temperatures, commencing with an initial storage modulus of roughly 27 GPa. However, after the application of EPD treatment, the storage modulus of the composites showed a remarkable improvement compared to C-rCF0, achieving an enhancement of 55 % relative to its original value. This improvement clearly indicates the favorable impact of the EPD treatment on the storage modulus. The significant increase in storage modulus can be ascribed to the reinforcing influence of CNT/MFC, owing to their remarkable mechanical characteristics. This reinforcement serves to curtail the mobility of polymer chain segments, resulting in the observed improvement in storage modulus.

In DMA, the tan δ parameter reflects the damping behavior associated with molecular motion, and it is widely acknowledged that its peak temperature corresponds to the glass transition temperature. In Fig. 8b, it can be observed that the glass transition temperatures of the four as-prepared composites fell within the range of 160–165 °C and did not show significant differences. When compared to C-rCF0, the loss factor (tan δ) of C-rCF-10 V, C-rCF-20 V, and C-rCF-30 V is relatively low. This observation could be attributed to the principle that the damping capacity (tan δ) of the composite denotes the proportion between the loss modulus and the corresponding storage modulus. With the infusion of CNT/MFC, the composites witnessed simultaneous augmentation in both the storage modulus and the capacity for energy dissipation. However, the ratio of loss modulus to storage modulus did not experience a significant enhancement. As a result, although the storage modulus improved due to the presence of CNT/MFC, the increase in the loss modulus is not substantial enough to drastically affect the overall damping behavior (tan δ) of the composites.

3.6. Fractography

In order to assess the impact of the applied coating on the interaction between recycled carbon fibers and the composite matrix, scanning electron microscopy was employed to capture images of the fracture surfaces subsequent to the tensile testing. The fracture surface of the composite reinforced with uncoated rCF, as depicted in Fig. 9a, reveals the presence of numerous voids, indicative of slippage sites attributed to fiber pullout. This observation implies a deficiency in strong adhesion between the uncoated fibers and the matrix. Furthermore, the longitudinal pattern of the fibers on the surface suggests fiber debonding, providing additional evidence of the weakened interaction between the fibers and the matrix.

Conversely, the fracture surface of the composite reinforced with rCF-20 V is depicted in Fig. 9b. The occurrence of slippage sites on the fracture surface is significantly reduced. It is evident that fiber breakage has occurred in the composites reinforced with coated fibers, as proved by the presence of remaining fragments of broken fibers within the voids on the fracture surface. Additionally, only a limited number of longitudinal debonding patterns are discernible on the surface. A direct comparison between the fracture surfaces of composites reinforced with coated and uncoated fibers unmistakably reveals a more robust adhesion between the coated fibers and the matrix.

Fig. 9c provides a highly magnified image of the composite reinforced with C-rCF-10 V, showcasing pronounced interfacial bonding, characterized by a significant separation between the two components. The fractography images reveal that a majority of uncoated fibers exhibit inadequate adhesion with the matrix. This deficiency in adhesion stands as a critical factor contributing to the observed diminishment in mechanical properties for composites reinforced with uncoated fibers. Conversely, Fig. 9d corresponds to a composite reinforced with rCF-20 V, featuring pronounced interfacial bonding. SEM images of the coated fibers demonstrate a robust attachment to the matrix, with minimal or no discernible gaps. This enhanced adhesion significantly improves the mechanical properties of the composite, as the occurrence of fiber breakage suggests that the maximum stress is being applied to the fibers, resulting in increased strength.

Fig. 9e-f provides a detailed close-up of the interaction between fibers and matrix influenced by the grafted CNTs and MFCs following the tensile testing. It is evident that MFC is undergoing detachment during the tensile test. These images effectively illustrate the manner in which grafted CNTs and MFCs contribute to enhancing the interaction between fibers and the matrix. Furthermore, numerous MFC remaining on the fiber surface are observable subsequent to fiber debonding from the matrix.

Prior to the conclusions section, it is essential to synthesize the insights from our multiscale characterizations. Collectively, the results and discussion in this section unveil the transformative impact of electrophoretic deposition of carbon nanotube and microfibrillated cellulose coatings on recycled carbon fibers. The observed trends highlight
improved adhesion, enhanced surface roughness, increased polar oxygen groups, and augmented hydrophilicity, ultimately leading to superior mechanical and interfacial properties in the resulting composites. This holistic approach not only advances our understanding of modifications at various scales but also emphasizes the novelty of our methodology, offering promising avenues for innovative applications of sustainable recycled carbon fiber composites in diverse engineering fields.

4. Conclusions

In summary, the electrophoretic deposition of CNT/MFC onto the surface of recycled carbon fibers proved to be an effective method for enhancing the adhesion and interaction between the matrix and fibers in composite materials. The surface chemistry analysis using XPS confirmed the addition of polar oxygen groups on the coated surface, enhancing chemical bonding sites with the polymer matrix. The contact angle measurements exhibited a notable decrease in contact angle, indicating increased hydrophobicity and superior wetting of the epoxy, leading to improved adhesion between the fibers and the matrix. The results demonstrate that a suitable EPD voltage (20 V) leads to significant improvements in mechanical properties, including tensile strength, Young’s modulus, and flexural strength. However, careful consideration must be given to avoid the excessive presence of CNTs and MFCs, as it can compromise the mechanical interlocking and mechanical properties of the composite. Mechanical testing of the composites revealed that the C-rCF-20 V composite exhibited remarkable improvements in tensile strength and Young’s modulus by 32 % and 51 %, respectively. The flexural strength also increased by approximately 27 %, highlighting the beneficial role of CNT/MFC in enhancing mechanical interlocking and stress transfer. Overall, this functionalization approach has the potential to enhance the performance of recycled carbon fiber-reinforced composites, making them a promising sustainable alternative for various engineering applications.

CRediT authorship contribution statement

Mahyar Fazeli: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis,
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

The authors would like to acknowledge the Competence Center for Materials Bioeconomy, FinnCERES, for their financial support (97435245 CERES Vastinraha/Lipponen). All authors are grateful to Aalto University and Bioprocess Technology Group for their support in making this article open-access.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesa.2020.108093.

References


