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Aging Effect of Plasma-Treated Carbon Fiber Surface: From an Engineering Point

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Abstract: Dielectric barrier discharge (DBD) plasma surface modification has certain aging effect. This article studies the aging effect of plasma (DBD) on the surface modification of carbon fibers. The test results show that plasma (DBD) treatment reduces the impurity particles on the surface of carbon fibers and makes the surface texture coarser. In addition, there is no significant change. After plasma (DBD) treatment, the content of C–O–C, C–O and C=O on the surface of carbon fibers increased from 3.20%, 7.76% and 1.64% to 7.06%, 21.50 and 6.08%, respectively. This is due to the high-energy particle bombardment of the fiber surface, which forms activated carbon atoms on the surface. The free electrons of these activated carbon atoms combine with ionized oxygen in the air. However, with the passage of time, the content of C–O–C, C–O and C=O gradually decreases to 3.31%, 8.57% and 1.77%, respectively. This is because some functional groups formed on the treated carbon fiber surface are not firmly bound, and some of these functional groups containing O_2 groups will combine with surrounding substances through irreversible chemical oxidation reactions to produce CO_2, which leaves the carbon fiber surface as a gas. The treated carbon fibers will immediately become hydrophilic, and the water contact angle decreases from 148.71° to 0°. With the passage of time, the water contact angle gradually increases to 118.16°, and the hydrophobicity recovers.

Keywords: surface modification; dielectric barrier discharge (DBD) plasma; carbon fiber; timeliness (aging effect)

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1. Introduction

Carbon fiber has attracted considerable attention and research from scholars due to its excellent physical and chemical properties and wide range of applications. Carbon fiber exhibits outstanding mechanical properties (such as high strength, high modulus and low density), high thermal conductivity, low thermal expansion coefficient, high electrical conductivity, high chemical stability and compatibility with metals. It plays a significant role in advanced composite materials, flexible conductive materials, catalysts, biomedical, automotive engineering, etc. [1–4]. Carbon fiber, however, has a smooth surface and very few active functional groups, which results in chemical inertness and hydrophobicity, making it difficult to be covered by coatings or resins uniformly. Enhancing the bonding interfacial strength between carbon fiber and the matrix and fully exploiting the excellent properties of carbon fiber are of great significance in improving the performance of composite materials.

In recent years, methods for surface modification of carbon fiber have become a focused areas. The most commonly used methods for the surface modification of carbon fiber are surface oxidation, surface sizing and plasma treatment. Surface oxidation involves placing the carbon fiber material in an oxidizing agent to undergo an oxidation reaction. Based on the types of oxidizing agents, surface oxidation can be divided into two categories. The first category is gas-phase oxidation, where carbon fiber material is exposed to F_2, O_2, CO_2 or O_3 under heating conditions to undergo an oxygen oxidation reaction, forming oxygen-containing polar functional groups, such as –O, –C, –OH and –COOH, on the surface. Polar

bonds can be formed on the matrix surface through polar functional groups, resulting in the effective enhancement of the interfacial bonding energy between carbon fiber and the matrix [5]. The second category is liquid-phase oxidation, where the carbon fiber surface is treated with oxidizing agents, such as $KMnO_4$, HNO_3 or HNO_3 solution or mixed solution. Although the surface oxidation process is relatively mature, the introduction of strong oxidants adsorbed on the fiber surface can cause serious damage to the fiber surface. Surface sizing involves uniformly attaching the slurry to the carbon fiber surface, forming a protective layer with about 10 nm thickness, aiming to reduce the phenomenon of fiber surface fuzzing and breakage, thereby improving the surface smoothness and overall strength of carbon fiber, followed by the enhancement of abrasion resistance and bundle ability [6]. The slurry can be classified as a solvent-based, water-based or emulsion-based type [7]. The key point in surface sizing is the degree of compatibility between the slurry and the matrix. The compatibility degree is positively correlated with the effectiveness of modification. If the sizing agent has a similar molecular structure to the matrix, the surface polarity of carbon fiber may not be effectively improved, and the wetting capability of the coating or resin on the carbon fiber surface may not be significantly enhanced. Therefore, the option of a sizing agent plays a crucial role in the sizing method. Plasma treatment is a method that uses high-energy electrons, particles and neutral particles produced by electrochemical discharge or high-frequency electromagnetic oscillation waves to bombard the carbon fiber surface. The carbon fiber surface molecules will be excited and ionized by the high-energy particles, leading to the breakage of chemical bonds [8]. Free radicals and polar functional groups can be generated on the surface, by which the wetting property can be increased [9]. Meanwhile, under the action of high-energy electrons, low-temperature active ions on the fiber surface produce the sputtering effect [8], indirectly cleaning the surface impurities and increasing the fiber texture. Adhesion between the fiber surface and the matrix can be improved by changing the chemical and physical properties of the fiber surface without significant impacts on carbon fiber properties [5,10].

The preceding overview highlights three widely employed techniques for the surface modification of carbon fiber. In comparison to the initial two methods, namely surface oxidation and surface sizing, the utilization of low-temperature plasma in plasma treatment stands out for its simplicity, efficiency and time-saving attributes. It has advantages, such as excellent treatment effect, no need for expensive vacuum equipment [11], low energy consumption [12] and low environmental pollution (no solvent). There are many studies on the surface modification of plasma, but there are few reports on its timeliness (aging effect) [13–16]. This research focuses on the modification of commercial carbon cloth surfaces using a dielectric barrier discharge (DBD [17]) device at room temperature and atmospheric pressure. Based on the experimental results, the timeliness (aging effect) of surface modification of carbon fiber was analyzed.

2. Materials and Methods

The carbon cloth (Taiwan Carbon Energy WS1009) was divided into 8 precise segments, each measuring 2 cm × 2 cm. Subsequently, these segments were thoroughly immersed in absolute ethanol to undergo a stringent ultrasonic cleaning process for a duration of 5 min. After that, it was rinsed by pure water three times. Subsequently, the segments were subjected to an additional ultrasonic cleaning stage utilizing ultra-pure water for a duration of 5 min, ensuring the highest level of cleanliness. At last, to facilitate the complete evaporation of any residual moisture, the segments were dried in an oven set at 70 °C, for a duration of 5 h. The 8 cleaned carbon cloths were subjected to plasma DBD treatment at room temperature and pressure for 5 min (as shown in Figure 1). After processing, they were placed at room temperature (298 K), atmospheric pressure (101.325 kPa) and normal humidity (50%) for 60 min, 90 min, 120 min, 150 min, 180 min, 210 min and 240 min, respectively, named as 0-C1s (no samples placed), 60-C1s, 90-C1s, 120-C1s, 150-C1s, 180-C1s, 210-C1s and 240-C1s.

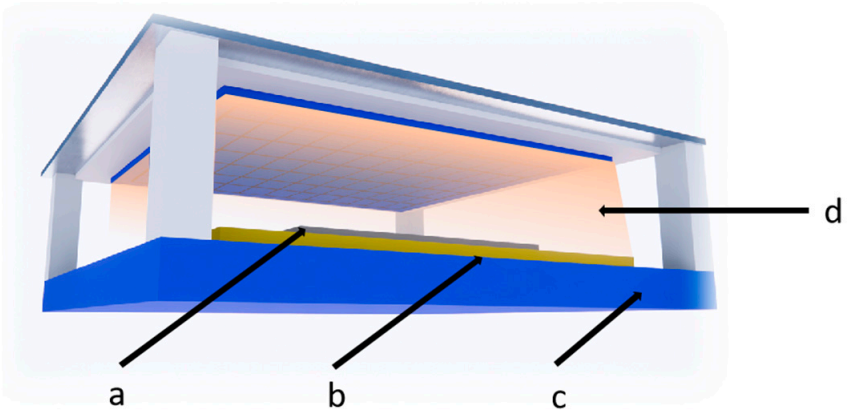

Figure 1. Schematic diagram of the plasma (DBD) generation device. (**a**) Carbon fiber sample, (**b**) substrate, (**c**) worktable, (**d**) plasma.

The surface morphology of the plasma treatment samples was observed and analyzed by an emission scanning electron microscope (SEM) with a Zeiss Supra 55, and the surface chemistry of the samples was determined using X-ray electron photoelectron spectroscopy (Thermo Fisher scientific, Waltham, MA, USA, ESCALAB 250Xi+) and calibrated based on the standard C1s (284.8 eV) binding energy. Sample surface water contact angles were measured by a Theta Lite instrument (WCA. Biolin Scientific, Gothenburg, Sweden) at 6 μL per droplet, and the results were used to assess sample surface wettability. All measurements were repeated five times in order to calculate the mean calibration error.

3. Results and Discussion

3.1. Surface Morphology

The SEM of the samples after plasma treatment is shown in Figure 2. Additionally, the raw, untreated samples are shown in Figure 2i, which are industrially prepared wet-spun fibers with distinctive smooth and flat stripes and grooves on the surface, which are axially parallel to the fibers on the surface of the samples [18]. The samples are coated with a polymer sizing layer, which protects the samples and facilitates the subsequent processing. A minor amount of contaminants may adhere to the surface during transportation, serving as the primary cause for the presence of impurity particles on the surface. The morphological changes resulting from plasma treatment are depicted in Figure 2a–h. Notably, the surface particles diminish, and the grooves, when compared to the original sample, become slightly clearer. This transformation is primarily attributed to the active particles in the plasma, which act on the sample surface, leading to the degradation and separation of the polymer sizing layer. Consequently, the original groove characteristics of the sample surface fibers gradually emerge. The observed reduction in impurity particles further substantiates the role of plasma in surface cleaning. Additionally, no other significant changes were observed [18,19].

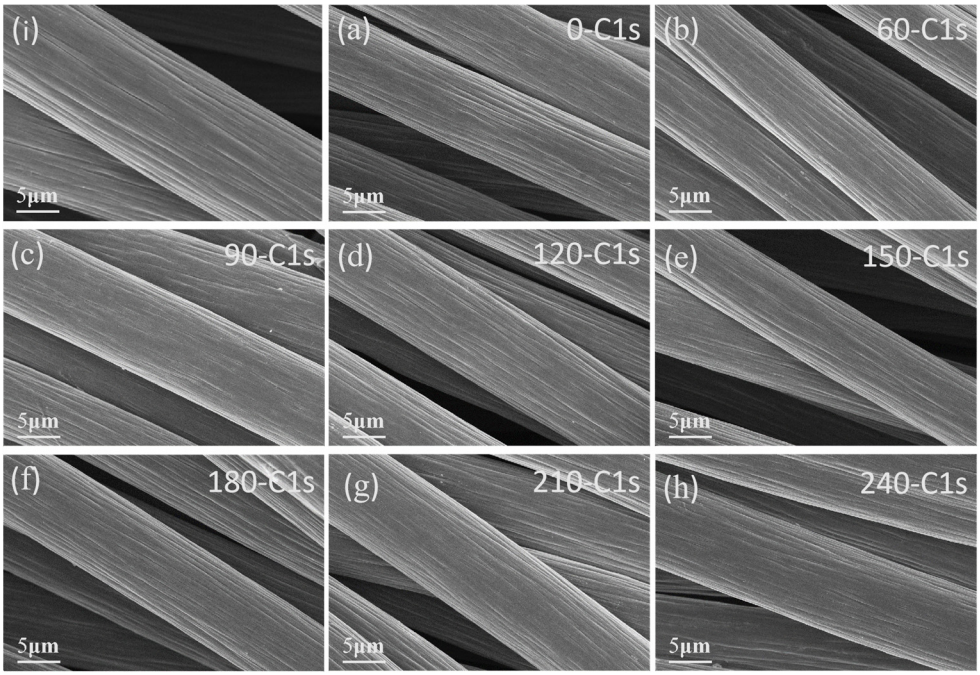

Figure 2. SEM image plots of samples. (**i**) Untreated sample. (**a**–**h**) Samples with aging time of 0–240 min.

3.2. Surface Chemical Assessment

In order to analyze the chemical composition and state of several samples, XPS was performed. C and O are the main elements in the samples. Figure 3 shows the high-resolution C1s spectra of several samples. It can be seen that the most prominent peak is 284.8 eV, relating to C–C. In the corresponding high-resolution spectra of the untreated raw samples, as shown in Supplementary Figure S1, it presents low contents of C–O–C, C–O and C=O, only 3.2%, 7.76% and 1.64%, respectively, which is most likely due to the air surrounding the samples. Figure 3a shows that the C–O–C, C–O and C=O groups on the surface of the sample after 5 min of plasma treatment increased to 7.06%, 21.50% and 6.08%, respectively. With the passage of time, the content of C–O–C, C–O and C=O groups gradually decreased, returning to the state before plasma treatment (the trend is shown in Figure 4). This indicates that the activated carbon atoms and oxygen-containing functional groups on the carbon fiber surface after plasma treatment are unstable. Due to the transient and efficient action of high-energy particles in plasma on the material surface [20], the activated carbon atoms and newly introduced oxygen-containing functional groups may gradually react with air molecules to form carbon dioxide gas and leave the sample surface.

3.3. Contact Angle

The hydrophilicity and hydrophobicity can be clearly reflected by the surface contact angle. The surface contact angle of carbon fiber samples was measured by the Theta Lite instrument. As can be seen from the Figure 5, the surface of the original sample without plasma treatment is hydrophobic, and the contact angle is 148.71°. After plasma treatment for 5 min, the sample presents hydrophilicity, and the contact angle decreases sharply to 0°, which is in agreement with the study of Rani K V et al. [21]. The contact angle was 0° until a placement time of 90 min. When the placement time reached 120 min, the contact angle changed to 50.82°. From 150 min to 180 min, the contact angle changed significantly from 65.2° to 102.32°. After 180 min, the contact angle presented a slight change and, finally, reached a maximum of 118.16° at 240 min. The above shows that the plasma treatment can significantly change the surface properties of the material. The hydrophilicity of the surface of the material can be changed by plasma treatment. With the increase in process time, the

hydrophilicity decreased significantly, and the hydrophobicity was restored, which was consistent with the results of Owen et al., Morra et al. and Riedl et al. [22–25].

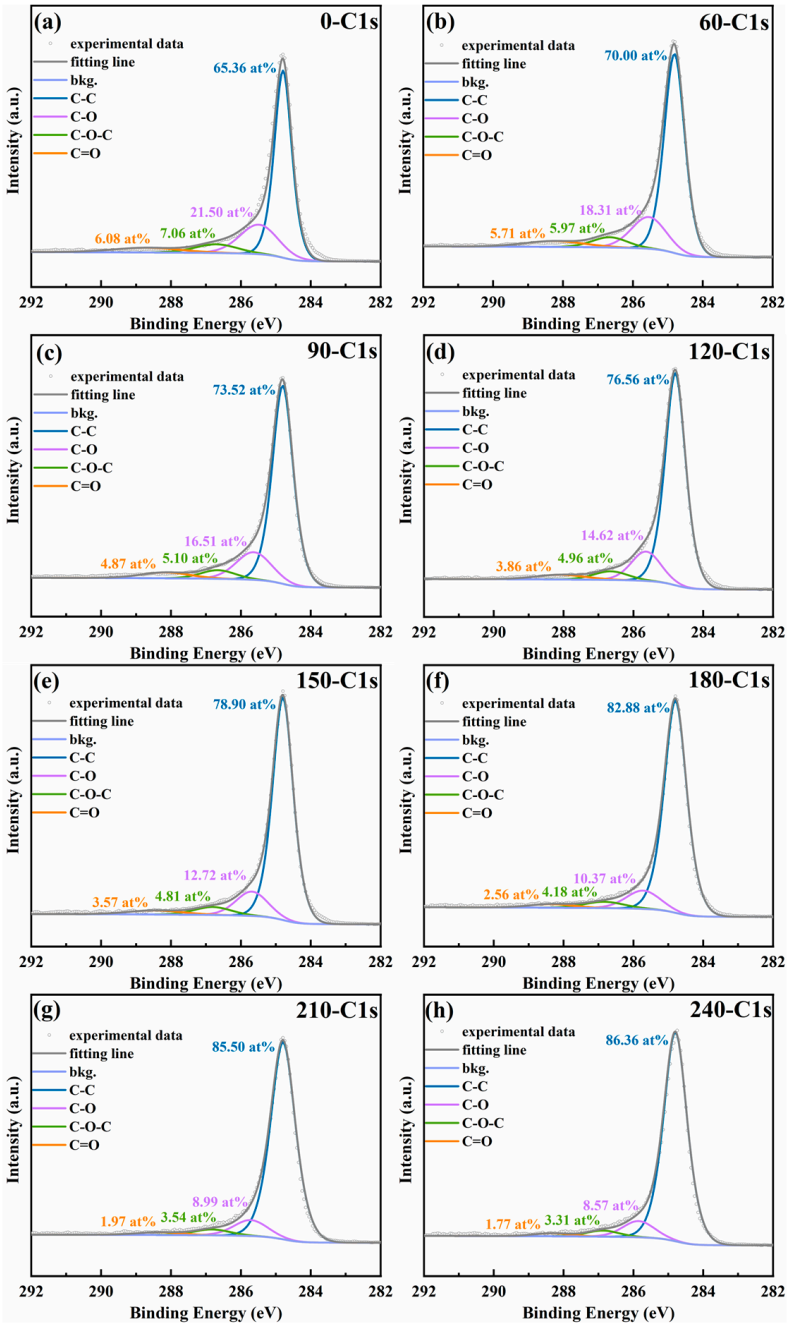

Figure 3. XPS spectra of samples. (**a**–**h**) Samples with aging time of 0–240 min.

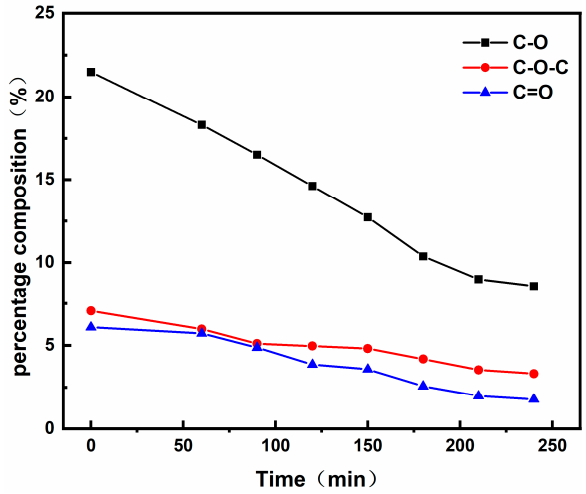

Figure 4. Change trend of O_2 groups.

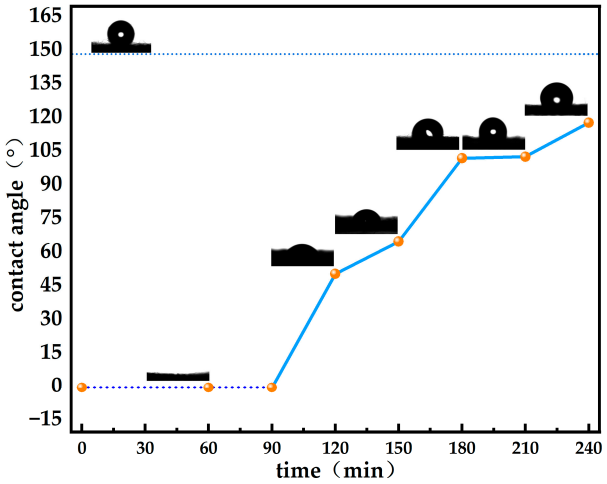

Figure 5. The change in contact occurs as the placement time is extended.

3.4. Mechanism Analysis

The surface edges of the sample treated with plasma generated many dangling bonds (resulting from the fracture of the sample caused by plasma bombardment). These dangling bonds form an unstable saturated state with the substances in the surrounding air (such as hydrocarbon compounds and water), as shown in Figure 6a. Meanwhile, the defects caused by plasma will also generate charge "traps" (charge holes) [26], which attract the incorporation of free radicals, resulting in charge neutralization [27]. The adsorption of these organic compounds occurs on the surface of carbon fibers. When carbon fibers are exposed to the surrounding environment, the content of O_2-containing groups will increase significantly. With the passage of time, the available active sites on the surface (such as dangling bonds) continue to react with substances in the surrounding environment (such as O_2) [28,29]. In this continuous reaction, C–H bonds will be replaced by C–O–C and C–O functional groups [30] (Figure 6b). The plasma treatment, being a surface modification technology, results in the generation of some functional groups on the carbon fiber surface that exhibit weak binding affinity. The parts of these functional groups containing O_2 will combine with substances in the surrounding environment, resulting in irreversible chemical oxidation reactions to produce CO_2 [31], which leaves the carbon fiber surface as a gas (Figure 6c).

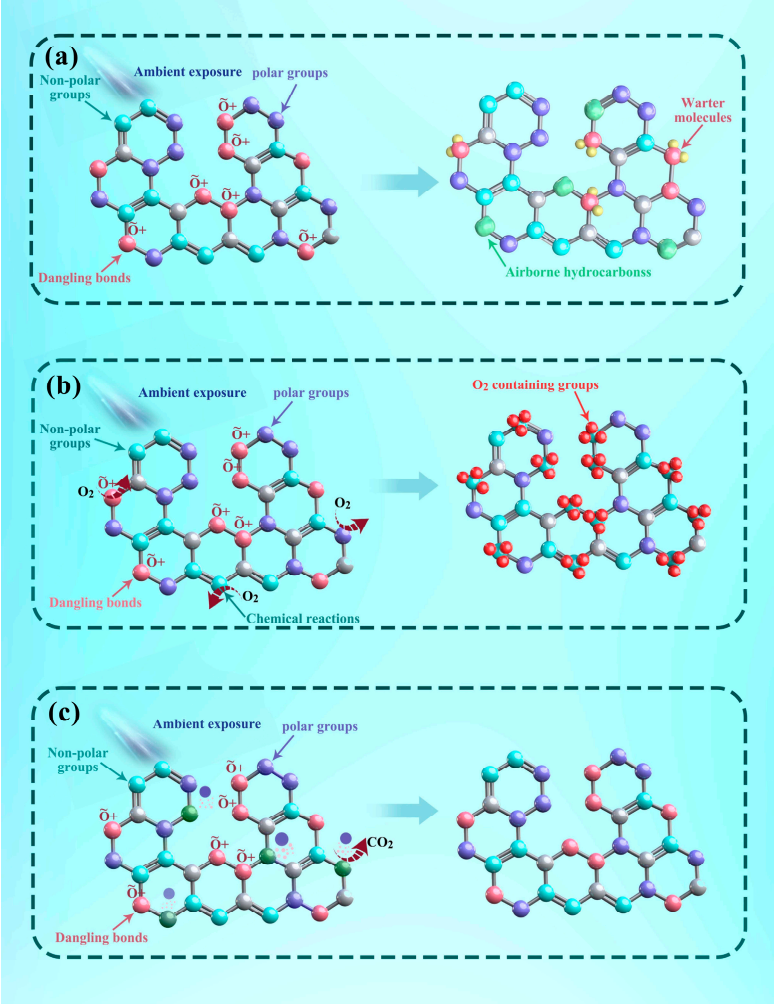

Figure 6. Possible mechanism. (**a**) Initial state after placement. (**b**) The intermediate state after placement. (**c**) Final state after placement.

4. Conclusions

Although the plasma surface modification of carbon fiber is short-term and efficient, its timeliness is also an important factor limiting its development. In this paper, plasma treatment (DBD) was used to modify the surface of carbon fiber, which had little effect on its surface morphology. The surface of the sample after plasma treatment significantly increased oxygen-containing groups, but it gradually decreased with the extension of the storage time. After plasma treatment, the surface of carbon fiber was highly hydrophilic, but with the extension of the storage time, the hydrophobicity gradually recovered. After four hours of storage, the contact angle reached a maximum of 118.16°, and the change curve of the contact angle with water indicated that the optimal application time frame of the material is within 160 min after treatment. There are many studies on various aspects of plasma surface modification, but there are few reports on its timeliness. The basic data measured in this paper about the timeliness can provide a reference for future research in this field.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings14010080/s1, Figure S1: XPS spectra of samples that have not been treated with plasma (DBD).

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References

1. Downs, W.B.; Baker, R.M. Novel Carbon Fiber-Carbon Filament Structures. *Carbon* **1991**, *29*, 1173–1179. [CrossRef]
2. Suzuki, M. Activated Carbon Fiber: Fundamentals and Applications. *Carbon* **1994**, *32*, 577–586. [CrossRef]
3. Huffman, M.L.; Venton, B.J. Carbon-Fiber Microelectrodes for in Vivo Applications. *Analyst* **2009**, *134*, 18–24. [CrossRef] [PubMed]
4. Lee, T.; Ooi, C.H.; Othman, R.; Yeoh, F.Y. Activated carbon fiber-the hybrid of carbon fiber and activated carbon. *Rev. Adv. Mater. Sci.* **2014**, *36*, 118–136.
5. Jin, Z.; Han, Z.; Chang, C.; Sun, S.; Fu, H. Review of Methods for Enhancing Interlaminar Mechanical Properties of Fiber-Reinforced Thermoplastic Composites: Interfacial Modification, Nano-Filling and Forming Technology. *Compos. Sci. Technol.* **2022**, *228*, 109660. [CrossRef]
6. Yu, G.; Wei, H.; Li, D. Research progress of carbon fiber sizing agent and its effects on interface properties of composites. *Eng. Plast. Appl.* **2019**, *47*, 143–147.
7. Hao, R.T.; Zhang, X.J.; Tian, Y.H. Research progress of heat-resistant thermoplastic sizing agents. *Chem. Ind. Eng. Prog.* **2018**, *37* (Suppl. S1), 117–124.
8. He, W.F.; Li, R.K.; Luo, S.H. Progress in plasma surface treatment on carbon fiber for composite material. *Surf. Technol.* **2020**, *49*, 76–89.
9. Unterweger, C.; Duchoslav, J.; Stifter, D.; Fürst, C. Characterization of Carbon Fiber Surfaces and Their Impact on the Mechanical Properties of Short Carbon Fiber Reinforced Polypropylene Composites. *Compos. Sci. Technol.* **2015**, *108*, 41–47. [CrossRef]
10. Wang, T.; Jiao, Y.; Mi, Z.; Li, J.; Wang, D.; Zhao, X.; Zhou, H.; Chen, C. PEEK Composites with Polyimide Sizing SCF as Reinforcement: Preparation, Characterization, and Mechanical Properties. *High Perform. Polym.* **2019**, *32*, 383–393. [CrossRef]
11. Saifutdinova, A.A.; Saifutdinov, A.I.; Gainullina, S.V.; Timerkaev, B.A. Modeling the Parameters of an Atmospheric Pressure Dielectric Barrier Discharge Controlled by the Shape of the Applied Voltage. *IEEE Trans. Plasma Sci.* **2022**, *50*, 1144–1156. [CrossRef]
12. Xia, G.; Chen, Z.; Saifutdinov, A.I.; Eliseev, S.I.; Hu, Y.; Kudryavtsev, A.A. Longer Microwave Plasma Jet with Different Discharge Performances Originated by Plasma-Surface Interactions. *IEEE Trans. Plasma Sci.* **2014**, *42*, 2768–2769. [CrossRef]
13. Hünnekens, B.; Krause, A.; Militz, H.; Viöl, W. Hydrophobic Recovery of Atmospheric Pressure Plasma Treated Surfaces of Wood-Polymer Composites (WPC). *Eur. J. Wood Wood Prod.* **2017**, *75*, 761–766. [CrossRef]
14. Pykönen, M.; Sundqvist, H.; Järnström, J.; Kaukoniemi, O.-V.; Tuominen, M.; Lahti, J.; Peltonen, J.; Fardim, P.; Toivakka, M. Effects of Atmospheric Plasma Activation on Surface Properties of Pigment-Coated and Surface-Sized Papers. *Appl. Surf. Sci.* **2008**, *255*, 3217–3229. [CrossRef]
15. Mendez-Linan, J.I.; Ortiz-Ortega, E.; Moreno, M.F.J.; Palma, M.I.M.; Martínez-Guerra, E.; Aguirre-Tostado, F.S.; Martínez-Chapa, S.O.; Hosseini, S.; Madou, M. Aging Effect of Plasma-Treated Carbon Surfaces: An Overlooked Phenomenon. *Carbon* **2020**, *169*, 32–44. [CrossRef]
16. Min, S.-J.; Kim, J.; Park, C.; Jin, J.-H.; Min, N.K. Long-Term Stability of Superhydrophilic Oxygen Plasma-Modified Single-Walled Carbon Nanotube Network Surfaces and the Influence on Ammonia Gas Detection. *Appl. Surf. Sci.* **2017**, *410*, 105–110. [CrossRef]
17. Desmet, T.; Morent, R.; De Geyter, N.; Leys, C.; Schacht, E.; Dubruel, P. Nonthermal Plasma Technology as a Versatile Strategy for Polymeric Biomaterials Surface Modification: A Review. *Biomacromolecules* **2009**, *10*, 2351–2378. [CrossRef]
18. Kim, S.; Oh, J.; Park, C.H. Development of Energy-Efficient Superhydrophobic Polypropylene Fabric by Oxygen Plasma Etching and Thermal Aging. *Polymers* **2020**, *12*, 2756. [CrossRef]
19. Egghe, T.; Ghobeira, R.; Morent, R.; Hoogenboom, R.; De Geyter, N. Comparative Study of the Aging Behavior of Plasma Activated Hexamethyldisiloxane-Based Plasma Polymers and Silicone Elastomer Thin Films. *Prog. Org. Coat.* **2022**, *172*, 107091. [CrossRef]
20. Mei, T.; Gao, M.; Liu, D.; Wang, Y.; Huang, Y. Enhanced Electrocatalytic Activity of Carbon Cloth by Synergetic Effect of Plasma and Acid Treatment. *Plasma Sci. Technol.* **2021**, *23*, 025504. [CrossRef]
21. Rani, K.V.; Chandwani, N.; Kikani, P.; Nema, S.K.; Sarma, A.; Sarma, B. Optimization and Surface Modification of Silk Fabric Using DBD Air Plasma for Improving Wicking Properties. *J. Text. Inst.* **2017**, *109*, 368–375. [CrossRef]
22. Owen, M.J.; Gentle, T.M.; Orbeck, T.; Williams, D.E. Dynamic wettability of hydrophobic polymers. In *Polymer Surface Dynamics*; Springer US: New York, NY, USA, 1988; pp. 101–110.

23. Morra, M.; Occhiello, E.; Gila, L.; Garbassi, F. Surface Dynamics vs. Adhesion in Oxygen Plasma Treated Polyolefins. *J. Adhes.* **1990**, *33*, 77–88. [CrossRef]
24. Riedl, B.; Angel, C.; Prégent, J.; Blanchet, P.; Stafford, L. Effect of Wood Surface Modification by Atmospheric-Pressure Plasma on Waterborne Coating Adhesion. *Bioresources* **2014**, *9*, 4908–4923. [CrossRef]
25. Vizireanu, S.; Ionita, M.D.; Ionita, R.E.; Stoica, S.D.; Teodorescu, C.M.; Husanu, M.-A.; Apostol, N.G.; Baibarac, M.; Panaitescu, D.M.; Dinescu, G. Aging Phenomena and Wettability Control of Plasma Deposited Carbon Nanowall Layers. *Plasma Process. Polym.* **2017**, *14*, 1700023. [CrossRef]
26. Cao, Y.; Hua, H.; Yang, P.; Chen, M.; Chen, W.; Wang, S. Investigation into the Reaction Mechanism Underlying the Atmospheric Low-Temperature Plasma-Induced Oxidation of Cellulose. *Carbohydr. Polym.* **2020**, *233*, 115632. [CrossRef]
27. Ortiz-Ortega, E.; Hosseini, S.; Martínez-Chapa, S.O.; Madou, M. Aging of Plasma-Activated Carbon Surfaces: Challenges and Opportunities. *Appl. Surf. Sci.* **2021**, *565*, 150362. [CrossRef]
28. Vandenbossche, M.; Hegemann, D. Recent Approaches to Reduce Aging Phenomena in Oxygen- and Nitrogen-Containing Plasma Polymer Films: An Overview. *Curr. Opin. Solid State Mater. Sci.* **2018**, *22*, 26–38. [CrossRef]
29. Bachmann, S.; Schulze, M.; Morasch, J.; Hesse, S.; Hussein, L.; Krell, L.; Schnagl, J.; Stark, R.W.; Narayan, S. Aging of oxygen and hydrogen plasma discharge treated aC: H and ta-C coatings. *Appl. Surf. Sci.* **2016**, *371*, 613–623. [CrossRef]
30. Guo, W.; Chen, B.; Lam, V.T.; Brink, G.H.T.; Kooi, B.J.; Svetovoy, V.B.; Palasantzas, G. Effect of Airborne Hydrocarbons on the Wettability of Phase Change Nanoparticle Decorated Surfaces. *ACS Nano* **2019**, *13*, 13430–13438. [CrossRef]
31. Sahoo, G.; Polaki, S.R.; Ghosh, S.; Krishna, N.G.; Kamruddin, M. Temporal-Stability of Plasma Functionalized Vertical Graphene Electrodes for Charge Storage. *J. Power Sources* **2018**, *401*, 37–48. [CrossRef]