Timeliness of Cold Plasma Treatment on Surface Modification of Polylactic Acid Fibers

Yingxuan Chen[1], Haiyan Liu[1], Shuni Ying[2], Huihuang Ma[1], Jianfei Gao[3] and Xiaodong Zhou[1,*]

[1]*Shanghai Engineering Research Center of Hierarchical Nanomaterials, East China University of Science and Technology, Shanghai, 200237, China*

[2]*Shanghai Weixing New Building Materials Co., LTD, Shanghai, 201400, China*

[3]*School of Chemisty and Chemical Engineering, Henan University of Technology, Zhengzhou, Henan, 450001, China*

Abstract: Polylactic acid (PLA) fiber is a promising material due to its biodegradability, excellent mechanical properties, and good biocompatibility. However, its surface is chemically inert and has poor interfacial compatibility with gases due to a low number of polar groups. To address this issue, this study utilized cold plasma and solution wet pretreatment with varying pH levels to modify the surface of PLA fibers. The use of solution wet pretreatment helped mitigate the negative effects of plasma treatment on the timeliness, which improved the long-term stability of the PLA fibers surface properties. These modifications increased the suitability of the material for various applications. The surface of PLA fibers was modified using cold plasma and wet pretreatment with pH solutions of varying degrees. The surface chemical composition and hydrophilicity of modified fibers remained relatively stable for up to 120 days. Conversely, unpretreated fibers reverted to their original chemically inert state after 14 days.

Keywords: PLA fiber, Cold plasma, Solution pretreatment, Surface morphology, Timeliness.

1. INTRODUCTION

Polylactic acid (PLA) fiber composite materials have emerged as a prominent area of research in the field of new materials due to their biodegradability. These materials offer great potential for development and application. PLA represents a promising biodegradable polymer for research and application, given its outstanding mechanical properties, good thermoplastic processing performance, excellent biocompatibility, and biodegradability. Surface morphology, porosity, and chemical composition are critical features of PLA materials in medical applications. Specific molecular structures can produce PLA with excellent performance [1]. Furthermore, the degradation products of PLA are non-toxic and environmentally friendly, supporting its practical application in biomedical fields by promoting a natural cycle [2]. The surface of PLA fibers is highly inert and does not form a strong interfacial structure when combined with thermoplastic starch resin. Therefore, chemical or physical methods are required to modify the fiber surface, increase the presence of active groups on the fiber surface, enhance the hydrophilicity of the fiber surface, and improve the surface roughness of the fiber. This will lead to improved interfacial adhesion between PLA fibers and thermoplastic starch. Cold plasma technology is utilized to modify or coat the surface of fibers, aiming to enhance the interface performance of high-performance fiber composite materials and improve the bonding between high-performance fibers and the matrix. In comparison to traditional coating modification techniques, plasma modification technology offers several advantages including low reaction temperature, rapid processing speed, and uniform surface treatment [3-6].

Cold plasma treatment extends to various material forms, including particles, fibers, fabric structures, and composite materials [7]. It is instrumental in enhancing the interfacial bonding performance among fillers, fibers, and resins. Recently, cold plasma technology has been employed to enhance the functionality and interface properties of biopolymers. Serving as an eco-friendly alternative to current chemical and physical modification methods [8], cold plasma introduces polar functional groups to the surface of biological composite materials, thereby enhancing roughness, printability, adhesion, and contact angle, and improving overall surface properties. High-energy electron collisions with different polymer materials improve material interface bonding, resulting in clearly defined composite material interfaces [9]. Similarly, when high-energy electrons interact with certain inert materials, it fine-tunes the surface properties, generating new functional groups and forming defects that facilitate material bonding [10].

---

*Address correspondence to this author at the Shanghai Engineering Research Center of Hierarchical Nanomaterials, East China University of Science and Technology, Shanghai, 200237, China; E-mail: xdzhouecust@126.com

E-ISSN: 2311-8717/23

Investigating the timeliness of plasma modification has become a significant aspect of material modification research, playing a vital role in the widespread application of plasma technology in production. Currently, there is limited research on the timeliness of low-pressure cold plasma-modified PLA fibers in air atmospheres, both domestically and internationally. Most studies concentrate on plasma modification in various gas atmospheres like N_2, NH_3, O_2, etc. The research primarily focuses on the impact of different working gas atmospheres on the surface properties of plasma-modified fibers. However, there is a lack of reports on the influence of wet pretreatment on the timeliness of plasma-modified PLA fibers.

This study examined the durability of cold plasma as a surface performance modifier of PLA fibers, focusing on the timeliness of plasma modification. The PLA fibers treated with plasma were stored for 120 days to analyze any changes in surface morphology and chemical composition. Additionally, we tested the contact angle of the PLA fibers after cold plasma modification and various storage durations.

2. EXPERIMENTAL

2.1. Materials

The PLA fiber, with specifications of 75D/72F PLA FDY, was procured from Xinxiang Rixin Ecological Textile Garment Co., Ltd. in China. Analytical grade ethanol (C_2H_5OH), sodium hydroxide (NaOH), and acetic acid were sourced from Sinopharm Chemical Reagent Co., Ltd. in China. Deionized water was prepared in-house in the laboratory.

2.2. Solution Wet Pretreatment of PLA Fibers

Cut the PLA fibers to around 10 cm in length and agitate them using a custom-made stirrer to guarantee thorough dispersion and contact with the solution. Create three distinct solutions containing acetic acid, deionized water, and NaOH at pH levels of 5, 7, and 9 for pretreating PLA fibers. Next, the loose bundles of PLA fibers were submerged and agitated in anhydrous ethanol for 60 minutes, then washed in an ultrasonic cleaner for 30 min. Rinse the PLA fibers with deionized water, dry them using a 35 °C hot air blower, and store them in a sealed bag post-drying.

2.3. Cold Plasma Modification of PLA Fibers

Figure **1** illustrates the schematic diagram of the cold plasma modification treatment applied to PLA fibers. Evenly distribute the preprocessed PLA fibers on the glass table within the vacuum chamber. Utilize two electromagnetic vacuum pumps to regulate the pressure within the vacuum chamber, maintaining a consistent level of approximately 10.0 Pa. Throughout the entirety of the plasma treatment process, the RSG500RF generator (China) was employed to control and adjust the output power to 200W. Establish a glow discharge time of 180 seconds while operating in the presence of air (20.9% O_2, 79.1% N_2). Once the processing is complete, extract the PLA fibers, seal them, and proceed to dry them for storage. The processed samples were stored under controlled conditions of 55% relative humidity and a temperature of 27 °C to assess the timeliness effects of plasma modification.

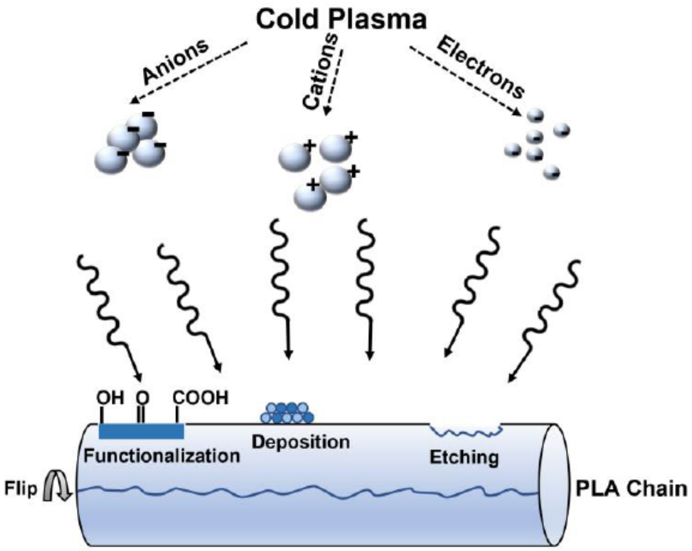

Figure 1: Schematic diagram of plasma modified PLA fiber surface.

2.4. Characterization

The surface morphology of PLA fibers was observed before and after treatment using an S-3400N scanning electron microscope (HITACHI, Japan). The surface chemical composition of the modified PLA fibers was analyzed using X-ray photoelectron spectroscopy (XPS, AXIS UltraDLD 220 spectrometer, Kratos Shimadzu, Japan). The analysis was conducted using AlK X-ray with a power of 150 W and α (hv=0.48 eV). The alterations in the hydrophilicity of PLA fibers due to surface modification were assessed using a contact angle measuring instrument (DSA25, Kruss, Germany).

3. RESULTS AND DISCUSSION

3.1. Surface Morphology of PLA Fibers

As depicted in Figure **2**, the surface morphology of PLA fibers that had been stored for 120 days exhibited minimal alterations. The surface morphology of PLA

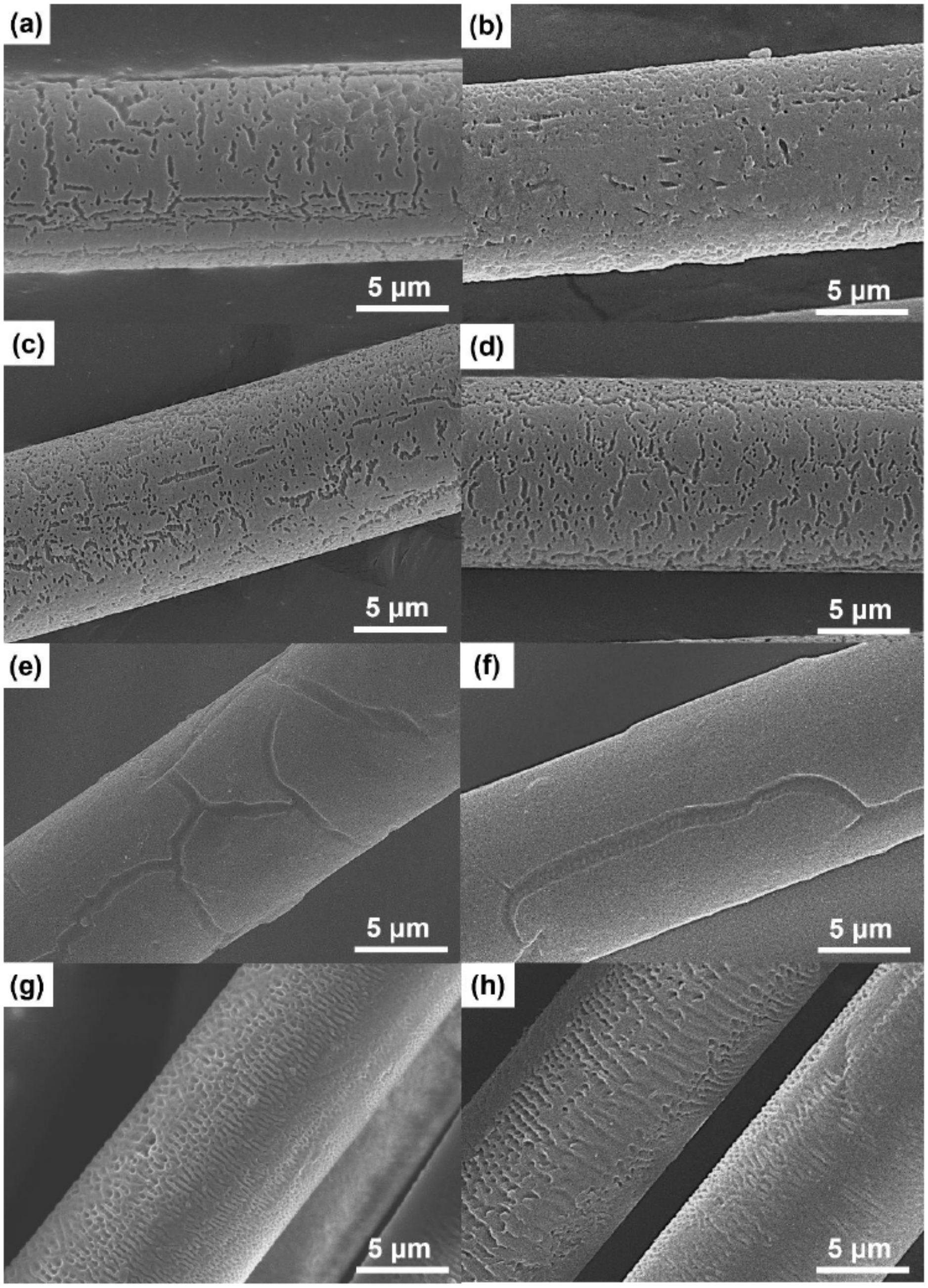

Figure 2: SEM images of PLA fibers modified by cold plasma after wet pretreatment. (**a**) pH=5, (**b**) pH=7, (**c**) pH=9, (**d**) untreated, (**e**) pH=5 and stored for 120 days, (**f**) pH=7 and stored for 120 days, (**g**) pH=9 and stored for 120 days, (h) untreated and stored for 120 days.

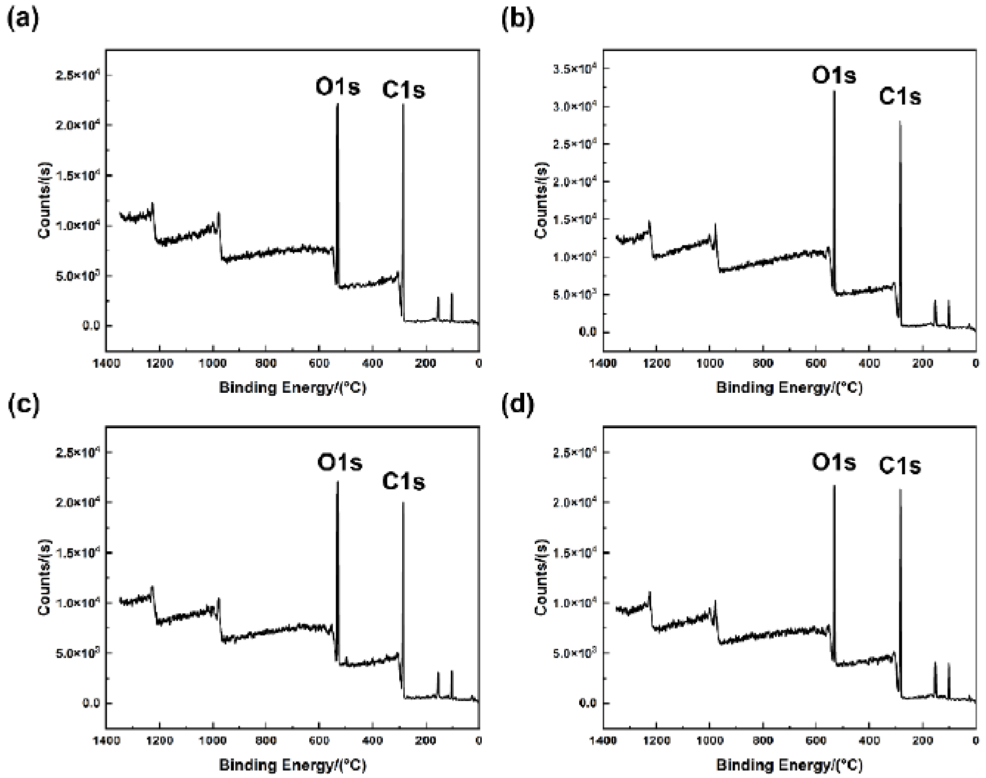

Figure 3: XPS element spectrum on the surface of PLA fiber: (**a**) untreated, (**b**) modified, (**c**) modified and stored for 7 days, (**d**) modified and stored for 14 days.

fibers remains largely unaffected by both cold plasma treatment and wet pretreatment using varying acidity and alkalinity levels. Furthermore, the interface performance of PLA fibers appears to be independent of the factors responsible for any morphological changes resulting from fluctuations in storage time.

3.2. The Effect of Chemical Composition on the Surface of PLA Fibers

The scanning peak spectra of surface elements on PLA fibers, obtained after 7 and 14 days of storage following cold plasma modification treatment using a power of 200 W in a NaOH solution with pH=9, are illustrated in Figure **3**. Table **1** presents the surface chemical element composition and the carbon-oxygen element ratio of PLA fibers stored for varying durations subsequent to plasma modification.

The oxygen-to-carbon ratio on the surface of untreated PLA fibers is 0.25. Following pre-treatment with an alkaline solution and subsequent plasma modification, the oxygen-to-carbon ratio on the surface of PLA fibers increased to 0.48, representing a relative increase of 47.92% compared to the untreated fibers. Plasma modification introduces additional oxygen-containing active groups on the surface of PLA fibers, while the alkaline solution hydrolyzes the fibers' molecular chains, leading to the breakdown of ester groups (-COO-) and the conversion of carbonyl groups (CO-) to hydroxyl groups, forming carboxyl groups (-COOH). Consequently, the oxygen content on the surface of PLA fibers increases. Following 7 days of storage in an environment with a temperature of 27 °C and a relative humidity of 55%, the oxygen-to-carbon ratio on the surface of PLA fibers exhibited minimal change, decreasing slightly to 0.46. Subsequently, after 14 days of storage, the oxygen-to-carbon ratio on the surface of PLA fibers remained unchanged at 0.46. Based on the findings of this experiment, it can be concluded that cold plasma treatment did not exhibit a significant decline in effectiveness following wet pretreatment with an alkaline solution. Additionally, wet pretreatment proves effective in slowing down the aging process of plasma-modified PLA fibers. Moreover, this treatment method is simple, efficient, and does not generate toxic or harmful by-products during the process.

We conducted a Gaussian Lorentz combination function to fit the C1s spectral peaks obtained from XPS of PLA fibers for further analysis of their surface functional groups. The binding energy analysis of XPS

Table 1: Analysis of Chemical Elements on the Surface of PLA Fiber

Sample	O/%	C/%	N/%	O/C Ratio
Untreated	19.7	80.2	0.1	0.24564
Modified	32.3	67	0.7	0.48209
Modified and stored for 7 days	31.2	68.4	0.4	0.45614
Modified and stored for 14 days	31.2	68.2	0.6	0.45748

revealed three peaks: C-C (248.8 eV), C-O-C (286.2 eV), and C=O (288.4 eV). Figure **4** illustrates the C element peak spectrum on the surface of PLA fibers. Cold plasma treatment significantly increased the -C=O groups content and slightly decreased the C-O-C groups content on the surface of PLA fibers exposed to w*et al*kali solution.

The peak area of the C1s peak spectrum in Figure **4** represents the content of various functional groups on the surface of modified PLA fibers. Table **2** displays the content of functional groups on the surface of PLA fibers at various storage times. Analysis of Table **2** reveals a 21.43% reduction in C-O-C group content on PLA fibers treated with w*et al*kali solution after cold plasma treatment, in comparison to unmodified fibers. This can be attributed to the hydrolysis reaction of molecular chains on the surface of PLA fibers in alkaline solution, resulting in a reduction of ester groups content and a significant increase of 71.43% in C=O group content. Cold plasma treatment introduces numerous oxygen-containing groups to the surface of PLA fibers. The table suggests that the majority of these groups are -C=O. The content of functional groups on the surface of PLA fibers treated with cold plasma after w*et al*kali treatment remained relatively stable after 7 and 14 days of storage. Thus, it can be concluded that the chemical composition of the surface of w*et al*kali-treated PLA fibers remains relatively stable after plasma treatment. XPS test results indicate that the wet pretreatment positively affects the durability and stability of the fiber's surface properties after plasma treatment.

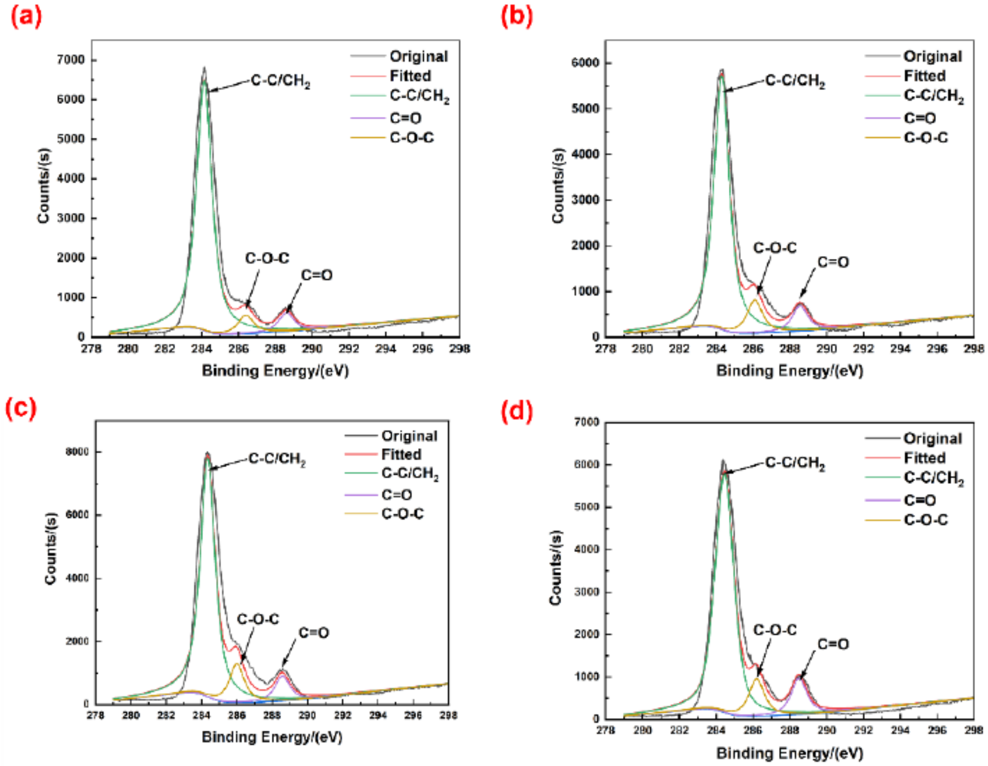

Figure 4: C1s peak spectrum of XPS on the surface of PLA fiber: (**a**) untreated, (**b**) modified, (**c**) modified and stored for 7 days, (**d**) modified and stored for 14 days.

Table 2: Contents of Different Functional Groups in C1s Peak Spectra on the Surface of PLA Fibers

Sample	C-C	C=O	C-O-C
Untreated	0.71	0.14	0.14
Modified	0.65	0.24	0.11
Modified and stored for 7 days	0.68	0.21	0.11
Modified and stored for 14 days	0.66	0.22	0.12

3.3. The Effect of Surface Hydrophilicity of PLA Fibers

Figure **5** depicts the contact angle photos of PLA fibers subjected to various modifications. The initial surface contact angle of unmodified PLA fibers remained consistent at 84.5° to 84.7°. Following plasma modification at a power level of 200 W, the surface contact angle of the PLA fibers, when tested within one hour, is 68.9°. This change can be attributed to the increase in surface roughness induced by the plasma modification, and the introduction of oxygen-containing polar groups on the fiber surface. Subsequently, after one day of storage, the contact angle increased to a range of 76.7° to 80.3°. This suggests that the surface performance of the cold plasma-modified sample exhibits timeliness, and the introduced oxygen-containing polar groups do not remain stable on the surface of PLA fibers. As materials tend to reach a stable state with low surface energy, the introduction of polar groups by plasma leads to an increase in surface energy. Consequently, the molecular chains with polar groups tend to reorient towards the material's interior, resulting in the surface stabilizing at a lower energy state.

According to Figure **6**, wet pretreatment of PLA fibers with an acid-base solution results in a relatively stable surface contact angle over time. Conversely, fibers untreated with a solution or deionized water demonstrate an increase in contact angle within 7 days of plasma treatment, followed by gradual stabilization. This can be attributed to polar groups from the plasma treatment penetrating the fiber's interior, causing a decrease in surface polarity, hydrophilicity, and subsequent increase in contact angle. Once the fiber's surface state stabilizes, the contact angle remains unchanged. Surface contact angle tests of PLA fibers indicate that pre-treatment with an acid-base solution prior to plasma modification effectively addresses plasma modification aging and preserves the surface hydrophilicity stability of PLA fibers post plasma treatment.

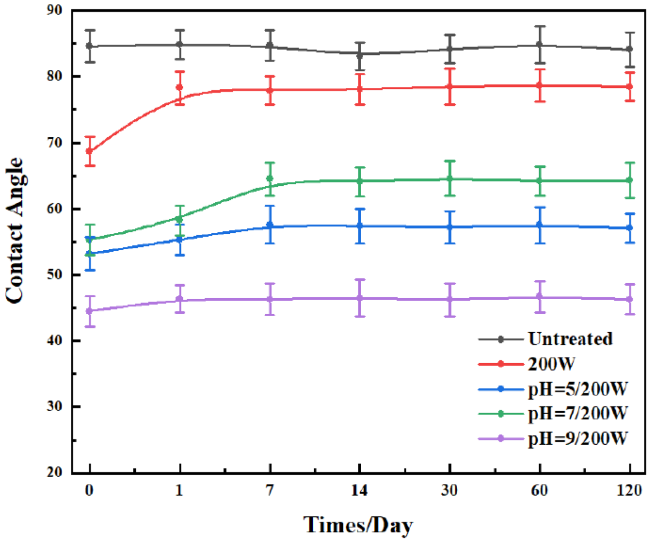

Figure 6: Contact angle of PLA fiber surface as a function of storage time.

4. CONCLUSIONS

The morphology of PLA fibers is minimally affected by storage time. The surface morphology of PLA fibers

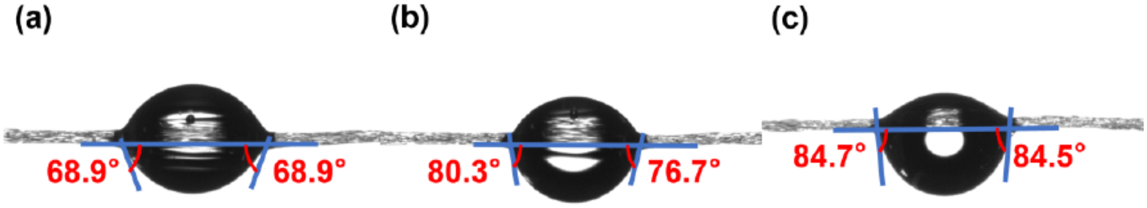

Figure 5: Surface contact angle diagrams of modified PLA fibers after plasma power treatment of 200w: (**a**) stored for 1 h, (**b**) stored for 1 day, (**c**) untreated.

remained nearly unchanged after 120 days of storage following solution pretreatment and cold plasma modification. Plasma modification of PLA fibers after solution wet pretreatment resulted in notable changes in carbon and oxygen content, characterized by an increase in oxygen content and a decrease in carbon content. The chemical element content and various functional groups on the surface of PLA fibers remained largely unchanged after 14 days of storage. Cold plasma modification alone results in a time-dependent effect on the water contact angle of PLA fibers, causing a decrease in their hydrophilicity over an extended storage period.

DECLARATION OF 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 STATEMENT

Data will be made available on request.

ACKNOWLEDGEMENTS

This research supported by “Fundamental Research Funds for the Central Universities”.

REFERENCES

[1] H.R. Kricheldorf, I. Kreiser-Saunders, C. Jürgens, D. Wolter, Polylactides - synthesis, characterization and medical application, Macromolecular Symposia. 1996; 103: 85-102. https://doi.org/10.1002/masy.19961030110

[2] J.P. Penning, H. Dijkstra, A.J. Pennings, Preparation and properties of absorbable fibres from l-lactide copolymers, Polymer. 1993; 34: 942-951. https://doi.org/10.1016/0032-3861(93)90212-S

[3] O. Kaynan, Y. Atescan, E. Ozden-Yenigun, H. Cebeci, Mixed Mode delamination in carbon nanotube/nanofiber interlayered composites, Composites Part B: Engineering. 2018; 154: 186-194. https://doi.org/10.1016/j.compositesb.2018.07.032

[4] S.U. Khan, J.-K. Kim, Improved interlaminar shear properties of multiscale carbon fiber composites with bucky paper interleaves made from carbon nanofibers, Carbon. 2012; 50: 5265-5277. https://doi.org/10.1016/j.carbon.2012.07.011

[5] Z. Chen, T. Yu, Y.H. Kim, Z. Yang, Y. Li, T. Yu, Different-structured nanoclays incorporated composites: Computational and experimental analysis on mechanical properties, Composites Science and Technology. 2021; 203: 108612. https://doi.org/10.1016/j.compscitech.2020.108612

[6] H. Yao, G. Zhou, W. Wang, M. Peng, Effect of polymer-grafted carbon nanofibers and nanotubes on the interlaminar shear strength and flexural strength of carbon fiber/epoxy multiscale composites, Composite Structures. 2018; 195: 288-296. https://doi.org/10.1016/j.compstruct.2018.04.082

[7] N. Encinas, M. Lavat-Gil, R.G. Dillingham, J. Abenojar, M.A. Martínez, Cold plasma effect on short glass fibre reinforced composites adhesion properties, International Journal of Adhesion and Adhesives. 2014; 48: 85-91. https://doi.org/10.1016/j.ijadhadh.2013.09.026

[8] S. Beikzadeh, A. Khezerlou, S.M. Jafari, Z. Pilevar, A.M. Mortazavian, Seed mucilages as the functional ingredients for biodegradable films and edible coatings in the food industry, Advances in Colloid and Interface Science. 2020; 280: 102164. https://doi.org/10.1016/j.cis.2020.102164

[9] Y.X. Pan, C.-J. Liu, P. Shi, Preparation and characterization of coke resistant Ni/SiO2 catalyst for carbon dioxide reforming of methane, Journal of Power Sources. 2008; 176: 46-53. https://doi.org/10.1016/j.jpowsour.2007.10.039

[10] Y.X. Pan, H.P. Cong, Y.L. Men, S. Xin, Z.Q. Sun, C.J. Liu, S.H. Yu, Peptide Self-Assembled Biofilm with Unique Electron Transfer Flexibility for Highly Efficient Visible-Light-Driven Photocatalysis, ACS Nano. 2015; 9: 11258-11265. https://doi.org/10.1021/acsnano.5b04884

Received on 07-12-2023 Accepted on 11-12-2023 Published on 20-12-2023

DOI: https://doi.org/10.12974/2311-8717.2023.11.05