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Hygrothermal Aging of Glass Fiber-Reinforced Benzoxazine Composites

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Abstract: Glass fiber-reinforced polymer (GFRP) composites are widely utilized across industries, particularly in structural components exposed to hygrothermal environments characterized by elevated temperature and moisture. Such conditions can significantly degrade the mechanical properties and structural integrity of GFRP composites. Therefore, it is essential to utilize effective methods for assessing their hygrothermal aging. Traditional approaches to hygrothermal aging evaluation are hindered by several limitations, including time intensity, high costs, labor demands, and constraints on specimen size due to laboratory space. This study addresses these challenges by introducing a facile and efficient alternative that evaluates GFRP degradation under hygrothermal conditions through surface wettability analysis. Herein, a glass fiber-reinforced benzoxazine (BZ) composite was fabricated using the vacuum-assisted resin transfer molding (VARTM) method and was aged in a controlled humidity and temperature chamber for up to 5 weeks. When analyzing the wettability characteristics of the composite, notable changes in the contact angle (CA) and contact angle hysteresis (CAH) were 21.77% and 90.90%, respectively. Impact droplet dynamics further demonstrated reduced wetting length and faster droplet equilibrium times with the prolonged aging duration, indicating a progressive decline in surface characteristics. These changes correlated with reductions in flexural strength, highlighting the surface's heightened sensitivity to environmental degradation compared with internal structural integrity. This study emphasizes the critical role of surface characterization in predicting the overall integrity of GFRP composites.

Keywords: hygrothermal aging; surface wettability; glass fiber-reinforced composite

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1. Introduction

Fiber-reinforced polymers (FRPs) are extensively used across various industries, including marine, aerospace, automotive, renewable energy, medical, aviation, electronics, and construction [1–3]. These composites are fabricated by reinforcing fibers such as carbon, aramid, and glass within resin matrix materials like epoxy, polyester, vinyl ester, and polyurethane [4]. The choice of reinforcement and resin matrix is typically based on the desired performance and manufacturing cost [5]. The mechanical properties of FRP composites are primarily governed by the fiber's strength and stiffness, chemical stability, matrix strength, and the adhesion at the fiber–matrix interface. With appropriate compositions and fiber orientations, FRP composites can offer properties comparable to metals at a significantly lower weight [2]. Additionally, FRP composites are known for their excellent specific stiffness and strength, as well as their resistance to degradation, particularly in harsh environments [2,5–8]. Glass fiber is often chosen as a primary structural component due to its cost-effectiveness and corrosion resistance, especially in moist environments with high relative humidity, where metals are prone to corrosion and rust over time [7–9]. However, glass fiber-reinforced polymer (GFRP) structures can still experience some degradation after years of service. Therefore, addressing the durability of GFRP composites under long-term environmental effects is crucial to ensure their integrity and promote their broader application [5,7].

Polymer matrix composites, including GFRP composites, tend to degrade over time when exposed to moisture and elevated temperatures during their service life [1,10]. This process is known as "aging", which affects microstructural and morphological transformation of the materials over time and leads to a detrimental change in physical, chemical, and mechanical properties of the materials [1,9,11]. The long-term reliability of composites is crucial for ensuring the safety of life and property, particularly in applications where environmental conditions play a significant role [12,13]. GFRP composites are highly sensitive to moisture and temperature. Water absorption in these materials leads to swelling due to differential expansion between fibers and the matrix, detrimentally impacting mechanical properties and durability [9–12]. The moisture absorption and temperature-driven aging of GFRP composites are based on two fundamental processes: (1) immersion in water (hydro) and (2) exposure to humid air (hygro) at an elevated temperature [1]. Based on the existing studies, it was found that the evolution of mechanical properties for materials under hygrothermal or hydrothermal aging was a result of jointly synergistic environmental effects with complex mechanisms [14]. The hygrothermal environment, characterized by water molecule diffusion and high or fluctuating temperatures, accelerates the degradation process through plasticization, hydrolysis, matrix swelling, and fiber–matrix interface debonding [3,9,14–16]. These effects can manifest as reductions in flexural stress, tensile strength, modulus of elasticity, and other key mechanical properties, ultimately limiting the structural integrity of the composites [10,17]. Moisture uptake occurs through diffusion into the polymer matrix and capillary action in voids and microcracks, further exacerbating structural degradation [1,14]. High temperatures amplify these effects by facilitating moisture penetration and accelerating chemical and physical changes within the composite [6,7,14]. Experimental studies have identified critical degradation mechanisms such as matrix cracking, fiber failure, and anelastic deformation, all of which directly weaken the composite's strength and stiffness [5,15]. Accelerated aging tests have been widely adopted to simulate long-term environmental exposure, revealing significant impacts from combined effects such as UV radiation, freeze–thaw cycles, and hygrothermal conditions [5,7]. Notably, moisture's interaction with fiber–matrix interfaces and resin molecules is a key factor, leading to irreversible chemical and physical changes that compromise durability and performance [12,13]. Despite extensive research, a lack of long-term performance data continues to hinder the broader application of FRP composites, especially in outdoor and marine environments [9,11]. Understanding the interplay between environmental stressors and material structure remains a priority to enable more accurate life predictions, enhanced durability designs, and better control methods for composite applications [12,13,17].

Several studies have explored the effects of hygrothermal aging on fiber-reinforced polymer composites, with a focus on both mechanical properties and degradation mechanisms. Angrizani et al. [15] investigated the influence of mechanical loading and hygrothermal aging, isolated and combined, on epoxy/glass unidirectional composites. They observed that hygrothermal aging had a greater impact on mechanical properties than mechanical loading, primarily due to the chemical degradation of the matrix (plasticization) and the loss of fiber/matrix adhesion. Gupta et al. [7], using the vacuum-assisted resin infusion microwave curing (VARIMC) technique, fabricated polymer composites reinforced with glass fibers and subjected them to hygrothermal aging in seawater. Their findings highlighted reductions in ultimate tensile strength, modulus of elasticity, and interlaminar shear strength (ILSS), attributing these degradations to fiber–matrix debonding, matrix hydrolysis, and moisture-induced swelling. Sukur et al. [1] examined fabric defects and micro-cracks in glass/epoxy laminates manufactured via vacuum infusion, applying acoustic emission techniques to analyze the effects of hygrothermal aging on the mechanical properties. They found that hygrothermal aging not only diminished the composite's flexural and tensile strength but also degraded its thermo-mechanical properties, including storage modulus, loss modulus, and glass transition temperature (T_g). Zhuang et al. [12] focused on the role of interface structure in hydrothermal aging resistance, revealing that different interface structures influence the interlaminar shear properties of CFRPs. Similarly, Y. Wang et al. [16] explored carbon nanofibers (CNFs)' effects on hygrothermal aging in CNF/epoxy composites, aiming to understand aging mechanisms at the molecular level. They found that incorporating CNFs into epoxy resin reduced water absorption, the diffusion coefficient, and permeability, thereby improving tensile properties and T_g while enhancing the composites' durability against hygrothermal aging. P. Wang et al. [8,17] combined experimental studies and numerical simulations to model water diffusion and its degradation effects on GFRP composites, demonstrating the accuracy of their approach through tensile strength and water absorption tests on GFRP rebar. Meanwhile, an empirical model based on Langmuir parameters was used to predict the relationship between hygrothermal aging strength and immersion time, emphasizing the role of multidirectional stacking sequences in enhancing moisture absorption and equilibrium content [18]. K. Wang et al. [14] investigated the aging behavior of 3D-printed continuous fiber-reinforced composites (CGFRCs). Using fused filament fabrication (FFF), they prepared specimens with varied stacking sequences and observed that hygrothermal aging over 30 days reduced interlayer adhesion, caused glass fiber breakage, and degraded matrix properties. These collective studies provide a comprehensive understanding of hygrothermal aging, highlighting its detrimental effects on mechanical performance and structural integrity across various composite systems.

The choice of resin system plays a critical role in determining the durability and service life of glass fiber-reinforced polymers (GFRPs) [10]. Epoxy resins, widely used in various applications, offer excellent chemical resistance, low shrinkage upon curing, and high specific strength, making them a popular choice as the matrix material in fiber-reinforced composites [2,16]. However, their inherent flammability and the release of harmful halogen compounds during combustion present significant environmental and safety concerns. This has led to increased interest in developing halogen-free, flame-retardant alternatives such as benzoxazine-based resins. Benzoxazine (BZ) resins exhibit unique properties, including dimensional stability, near-zero shrinkage, superior heat and water resistance, electrical insulation, and exceptional flame resistance [19]. Additionally, these resins do not require strong acid catalysts for curing, produce no by-products, and allow for remarkable molecular design flexibility to tailor properties such as low water absorption, high char yield, and non-toxic curing [19,20]. BZ monomers, synthesized from phenol, formaldehyde, and amines, have shown promise in GFRP applications, though research on their implementation remains limited [19]. Moreover, the mechanical properties of all polymeric composites, including those based on epoxy and BZ resins, are highly dependent on temperature, necessitating thorough investigation into their dynamic stability under both cold and elevated temperature conditions [2].

The effect of forming and process-induced defects on the mechanical performance of composites is a significant subject for research, particularly for composite materials subjected to hygrothermal aging at high temperatures [1]. Because the real-time evaluation of GFRP structures is not suitable due to it being time-consuming (several months to years), labor-intensive, and costly, the long-term performance is usually quantified experimentally within a reasonable amount of time via an "accelerated aging test" [7,10,17]. Although there have been few experimental investigations into the effects of mesoscopic defects on the mechanical performance of FRPs, their impact on aging performance has not been extensively studied [1,9,11,17]. To the best of the author's knowledge, the majority of research studies focus on traditionally used thermosetting resins (i.e., epoxy) while comprehensive studies on the effect of hygrothermal aging on the mechanical and wettability properties of glass fiber-reinforced BZ composites remain limited. To address this gap, further investigation into the behavior of the glass fiber-reinforced BZ composites under hygrothermal aging is essential, along with the development of a fast and simple method for evaluating the degradation of GFRP structures in such conditions. This can potentially be achieved by the utilization of surface science in predicting and evaluating the integrity of the aged GFRP composites. Up to the present, there are very few research studies that have focused on the hygrothermal aging of GFRP composites, particularly on the role of surface wettability and its relationship with mechanical performance [21]. The effect of surface and interface structure on the durability of GFRPs under hygrothermal conditions remains to be further understood, and more work is needed to explore the hygrothermal aging behavior of GFRPs with different interfaces. Additionally, as degradation is not uniform across the member section, experimental results for a specific GFRP composite member are not applicable to others with different shapes, geometries, or fiber contents, making surface wettability tests necessary. The degradation of GFRP composites varies with size, which can be attributed to more severe degradation near the surface of the member [17].

The objective of this study was to build upon our previous works on the investigation of extreme environmental aging (i.e., thermal and acid exposures [22,23]) on glass fiber-reinforced BZ composite via hygrothermal aging for up to 5 weeks in a controlled temperature and humidity chamber and to analyze alterations in both physical and flexural properties. Analyzing the surface wettability of the hygrothermally aged GFRP composite was introduced in this study to overcome a limitation in predicting and evaluating the quality of large and complex composite structures. Contact angle (CA), contact angle hysteresis (CAH), and droplet impact dynamics were evaluated on both unaged and weekly aged samples to demonstrate the effectiveness of using surface wettability science as an innovative approach to accelerate testing methods for hygrothermally aged GFRP composite. A correlation could be drawn from the shared trend between the surface wettability and flexural strength analysis for the composite, highlighting the robustness of this new analytical approach.

2. Materials and Methods

2.1. Composite Fabrication and Hygrothermal Aging

The composite samples were prepared using a vacuum-assisted resin transfer molding (VARTM) process. This involved setting up twelve plain weave dry glass fiber plies (300 gsm) with dimensions of 30 cm × 30 cm, as depicted in Figure 1. The plies were arranged in a single direction and infused at 110 °C with a resin system of Loctite BZ 9110 Aero (Henkel, Bay Point, CA, USA) with medium toughness and service temperature at 121 °C, and the laminates were cured at 180 °C for 2 h [24]. After curing, the panels were cut into dimensions in accordance with ASTM D790-17 [25] and 5 cm × 5 cm square samples. The samples were then hygrothermally aged in a programmable humidity-controlled oven (ESPEC, Hudsonville, MI, USA) in accordance with ASTM D5229-20 [26] at temperatures of 70 °C and 85% relative humidity (RH) using deionized water for 5 weeks.

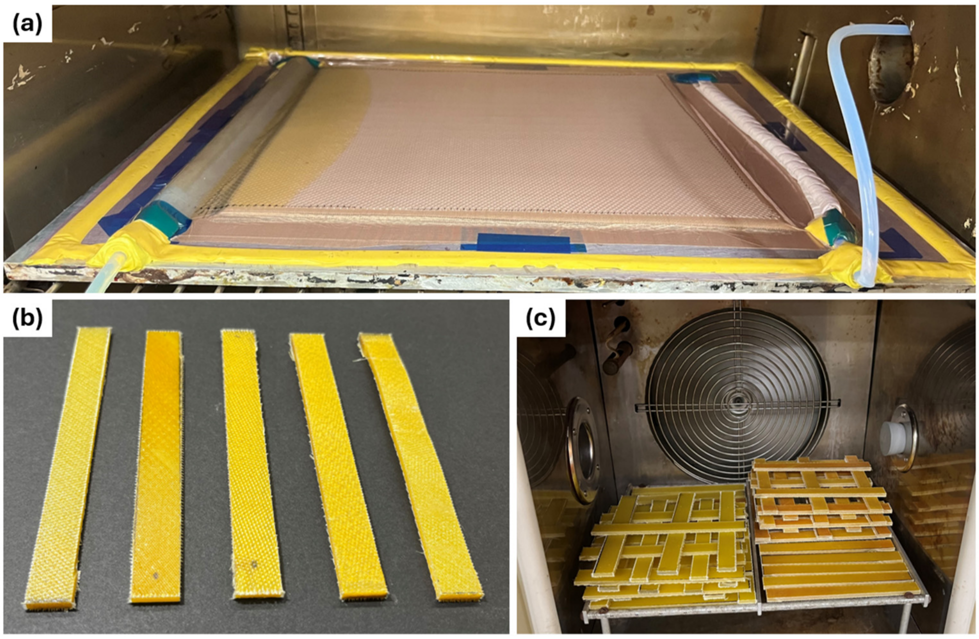

Figure 1. (**a**) Glass fiber-reinforced BZ composite fabrication via a vacuum-assisted transfer molding (VARTM) method. (**b**) Cured test specimens. (**c**) Hygrothermal aging of the samples in a programmable humidity-controlled oven up to 5 weeks.

2.2. Weight Change and Optical Microscopy

One set of three samples was dedicated for weighing purposes only, in order to ensure accuracy. Before weighing the sample following the aging process, the sample was placed in a desiccator to remove any absorbed moisture, without any coverage on either side. The samples were then weighed weekly using a microbalance with a four-digit precision at least three times, and the average values were reported. A change in weight due to hygrothermal aging was calculated using Equation (1) [6,7,11]:

$$W_t(\%) = \left(\frac{w_t - w_0}{w_0}\right) \times 100\% \tag{1}$$

where W_t (%) denotes the percentage moisture content of the specimen at time t, w_t is the weight of the sample after time t, and w_0 is the initial weight of the specimen at the dry state. Subsequently, a 5× trinocular boom-stand stereo microscope (AmScope, Irvine, CA, USA) was employed to examine the sample. This allowed for detailed observation of the effects of hygrothermal aging on the surface characteristics of the GFRP, specifically focusing on cracking phenomena, crack initiation, crack density, and the number of cracks.

2.3. Characterization of Flexural Properties

The flexural strength was evaluated following ASTM D790-17 standards using a three-point bending test, as shown in Figure 2a. The samples were prepared with dimensions of 14 mm in width, 130 mm in length, and 3.5 mm in thickness. Testing was performed with a universal testing machine (AGS-X, Shimadzu, Kyoto, Japan) equipped with a 10 kN load cell. The span length was maintained at 56 mm, and the crosshead displacement rate was set to 1.27 mm/min. For each sample set, five specimens were tested, and the average flexural strength was reported.

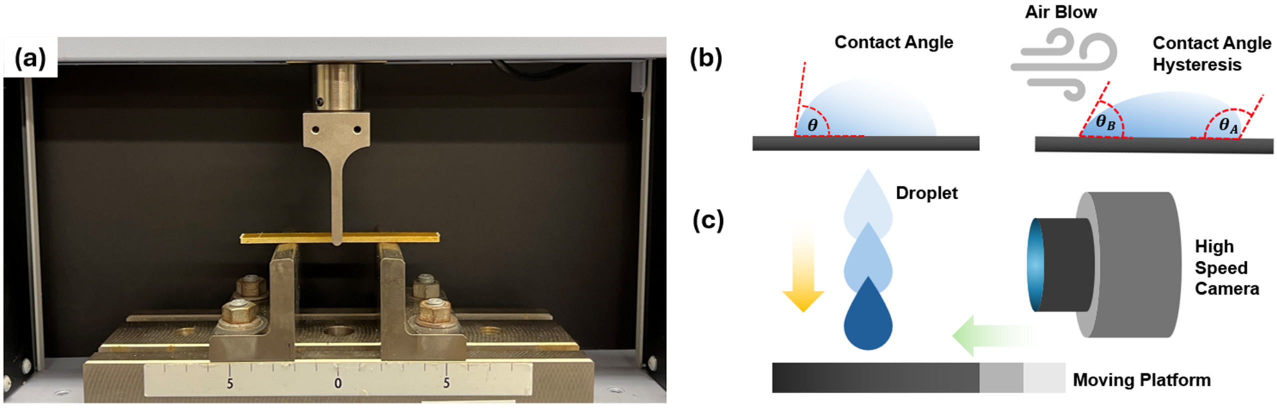

Figure 2. (**a**) Flexural testing of the cured specimen. (**b**) Measurement of a contact angle and contact angle hysteresis. (**c**) Characterization of the stationary and dynamic droplet impact with a high-speed camera.

2.4. Characterization of Contact Angle, Contact Angle Hysteresis, and Droplet Impact Dynamics

A customized experimental apparatus was developed to measure contact angle, contact angle hysteresis, and impact phenomena. The setup included a 0.3 m stroke pneumatic air cylinder (Parker-Hannifin, Buena Park, CA, USA) with a custom sample holder attached to the piston rod for the GFRP samples. The cylinder was mounted on a wooden block to prevent movement upon release and equipped with quick exhaust valves (Parker Legris, Mesa, AZ, USA) to adjust rod speed. Actuation was controlled by a 5-way solenoid valve (U.S. Solid, Cleveland, OH, USA), connected to a 6-gallon air compressor (DeWalt, Baltimore, MD, USA) and triggered by an Arduino Uno (Arduino, Somerville, MA, USA) based on input from an infrared sensor that detected passing droplets. Droplets (with an average volume of 7.24 mm^3) were dispensed using a sterilized syringe with a 0.3 mm needle, and data were recorded at 6400 FPS using a high-speed camera (Photron Fastcam, San Diego, CA, USA) with shadowgraphy, illuminated by an LED light with a diffuser (GS Vitec GmbH, Bad Soden Salmünster, Germany). The contact angle (CA) was quantified using the sessile droplet technique under static conditions. Initially, a liquid droplet was dispensed from a syringe onto the surface of GFRP samples. A high-speed camera captured an image of the sessile droplet immediately after deposition. The contact angle, which characterizes surface wettability, was measured as the angle between the droplet and the surface. Contact angle hysteresis (CAH), a parameter indicative of liquid mobility on the surface, was assessed by aerodynamic forces generated by controlled airflow, which was suitable for simulating ice accretion mechanisms on aircraft surfaces and water flow on automotive surfaces [27]. This process was recorded by a high-speed camera. CAH was determined as the difference between the advancing angle (θ_A) and the receding angle (θ_B), calculated as $\Delta\theta = \theta_A - \theta_B$ (refer to Figure 2b). A smaller hysteresis value ($\Delta\theta$) signifies easier droplet movement on the surface. Both the CA and CAH measurements were analyzed using Photron FASTCAM Viewer 4 (PFV4) software (version 4.2.0.0). At least five measurements were taken per frame for each CA and CAH, with the average values reported.

In the stationary and dynamic impact, the droplet was dispensed from a ring stand at a height of 30 cm (Figure 2c). In the stationary impact, no actuation of the cylinder was involved, and thus the droplet was able to be dispensed and fell vertically onto the GFRP. In the moving impact, the cylinder was actuated with 100 PSIG to gain a velocity of 3 m/s, and the droplet was timed through programmed delay in the code in order to obtain a solenoid activation and subsequent rod extension that was aligned with the time at which the droplet reached the height of the moving surface. These trials were post-processed in PFV4 to capture the wetting length over time, L_w, beginning at the moment of impact

($t = 0$), and ending upon the observation of the droplet returning to equilibrium or breaking into multiple rivulets. At least five measurements were taken per frame, and the average values were reported.

3. Results and Discussion

3.1. Weight Change

Understanding the dynamics of weight change in response to hygrothermal aging is crucial for assessing the overall integrity and reliability of the glass fiber-reinforced BZ composite. The hygrothermally aged composite exhibited a consistent increase in weight from week 0 to week 5. This change was particularly pronounced between week 0 and week 1, where the percentage of weight change was highest, at 0.15%, as illustrated in Figure 3a. This initial spike in weight suggests a significant absorption of moisture during the early stages of hygrothermal aging, indicating that the composite is highly responsive to environmental conditions. This observation corresponds with previous studies, in which a sharp increase in the overall weight of the GFRP composite was observed due to rapid moisture absorption into the specimen [6,28]. The gradual increase in weight observed in the subsequent weeks further corroborates the notion of water penetration into the composite material. Each weekly measurement reflects the ongoing interaction between the composite and the humid environment in which it was aged, highlighting the composite's susceptibility to moisture uptake. The increase in weight was found to slow down during week 4 and week 5, with only 0.05% and 0.01%, respectively, from the previous week. This indicates a tendency towards saturation [1,6,28]. This experimental behavior corresponded with a trend predicted using Fickian and Langmuir models of the moisture uptake, where the moisture rapidly increases at an early stage and progressively increases with time until the saturation point is reached, after which the moisture content tends to remain nearly constant [29].

The effects of heat and humidity on the composite's structural integrity were significant and readily apparent, as shown in Figure 3b–m. Over time, the hygrothermal aging process resulted in observable changes, particularly characterized by the appearance of deposits of reflective areas between the weavings of the glass fiber, as indicated by green arrows in Figure 3e,g,i,k,m. These reflective areas indicate that the resin has undergone alterations, likely due to the degradation of the matrix caused by the combination of heat and moisture. These resin-rich regions could contain micro- and meso-voids, generate micro-cracks, and accelerate the aging process by increasing water absorption due to the hydrophilic nature of micro-cracks and voids [1]. Though glass fibers generally do not absorb moisture due to their inert nature, the GFRP composite still absorbs the moisture through three mechanisms: (1) diffusion of water molecules into the matrix due to concentration gradient, (2) diffusion of water molecules through voids and micro-cracks within the matrix, and (3) transportation of moisture through flaws at the interface between the fiber and matrix due to poor wetting [1,11,12]. As hygrothermal aging progressed, the humid air circulating within the oven effectively penetrated and permeated the composite material, especially at an elevated temperature, which increased the moisture absorption content of the GFRP [13]. The diffusion process caused noticeable changes in the surface appearance, progressively revealing the texture of the glass fibers as aging progressed, as shown in Figures S1 and S2. The increasing prominence of the fiber texture indicates deterioration of the resin matrix, resulting in reduced structural homogeneity and microcrack formation. With each successive week, the GFRP laminate exhibited gradual alterations in surface roughness, highlighting the continuous degradation of the composite. This change corresponded with the accumulation of resin deposits in the gaps between the fiber weavings. The accumulation of these resin deposits not only alters the aesthetic characteristics of the surface but also suggests changes in the material's mechanical properties [6]. Moreover, a noticeable darkening in the color of the GFRP composite due to the moisture absorption was also visually observed (Figure S3), which corresponded with the observation reported in the previous study by Sukur et al. [1].

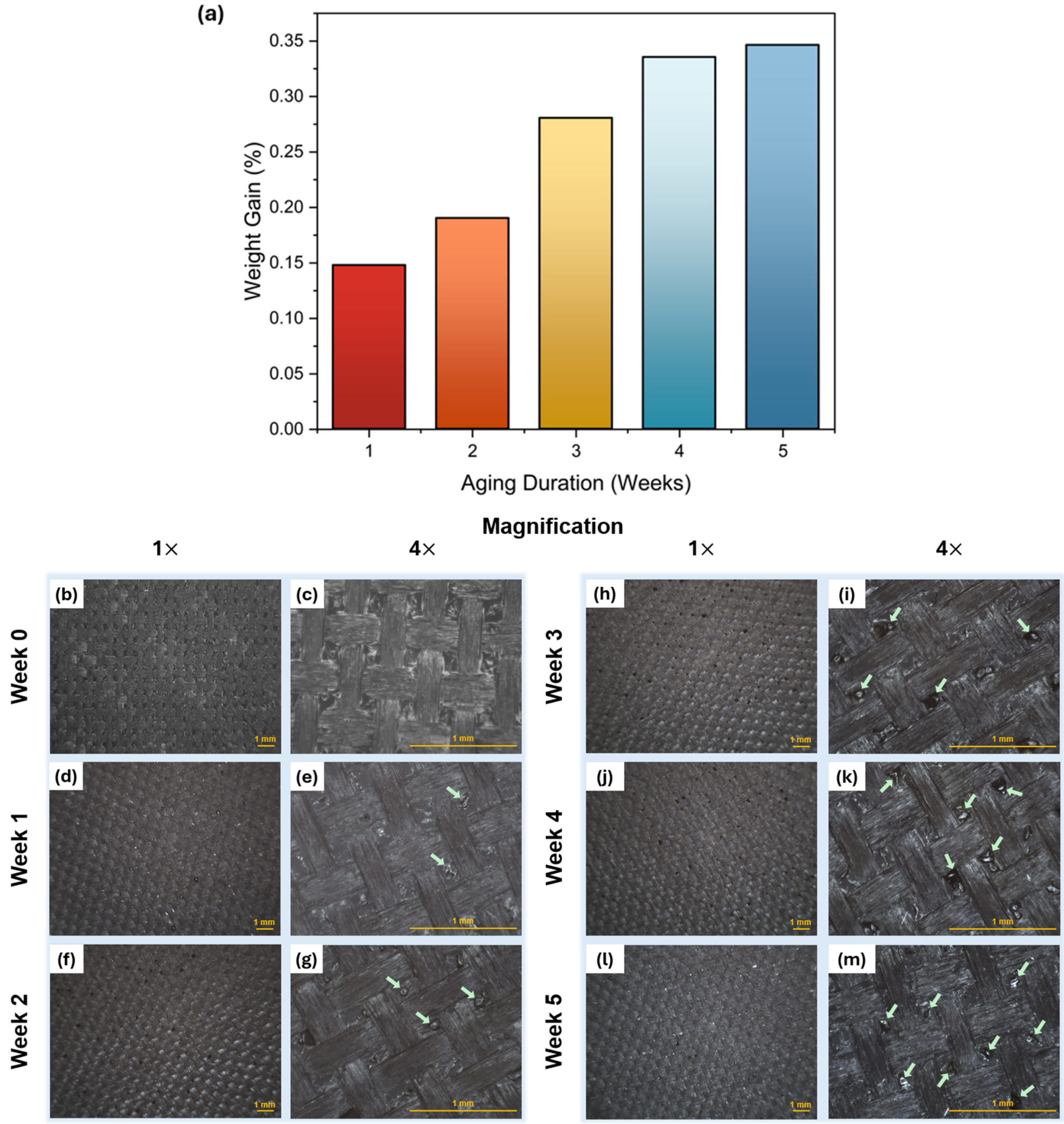

Figure 3. (**a**) Weight changes of the weekly hygrothermally aged glass fiber-reinforced BZ composite. The measurement errors range between 0.0001 and 0.0002 g. (**b**–**m**) Microscopic images of the weekly hygrothermally aged composite's surfaces with the appearance of deposits of reflective areas between the weavings of the glass fiber (green arrows).

3.2. Flexural Strength

Flexural strength analysis was performed to assess the overall strength characteristics of the manufactured composite by subjecting the composite against a three-point bending force, to measure the GFRP composite's capacity to withstand bending forces. This evaluation is crucial for understanding how the material performs under mechanical stress in practical applications. As illustrated in Figure 4a, the decrease in flexural strength revealed that the most significant drop in strength occurs during the first week of aging, a 46.75% reduction from the unaged stage. This initial decline suggests a rapid alteration in the material properties as the composite begins to respond to environmental factors. With prolonged hygrothermal aging duration, the flexural strength was continuously decreased but not as pronounced as the first week, with 5.48%, 4.11%, 0.49%, and 2.41%, respectively, for week 2 to week 5 from each previous week. After 5 weeks of hygrothermal aging of GFRP composite, its total flexural strength was found to significantly reduce, by 53.13% from its unaged stage. The decrease in flexural strength with increasing aging duration was also observed in multiple previous studies [1,28,29]. This was primarily due to a significant reduction in the strength of the resin and degradation of the interface adhesion between fiber and matrix from water absorption [28,29].

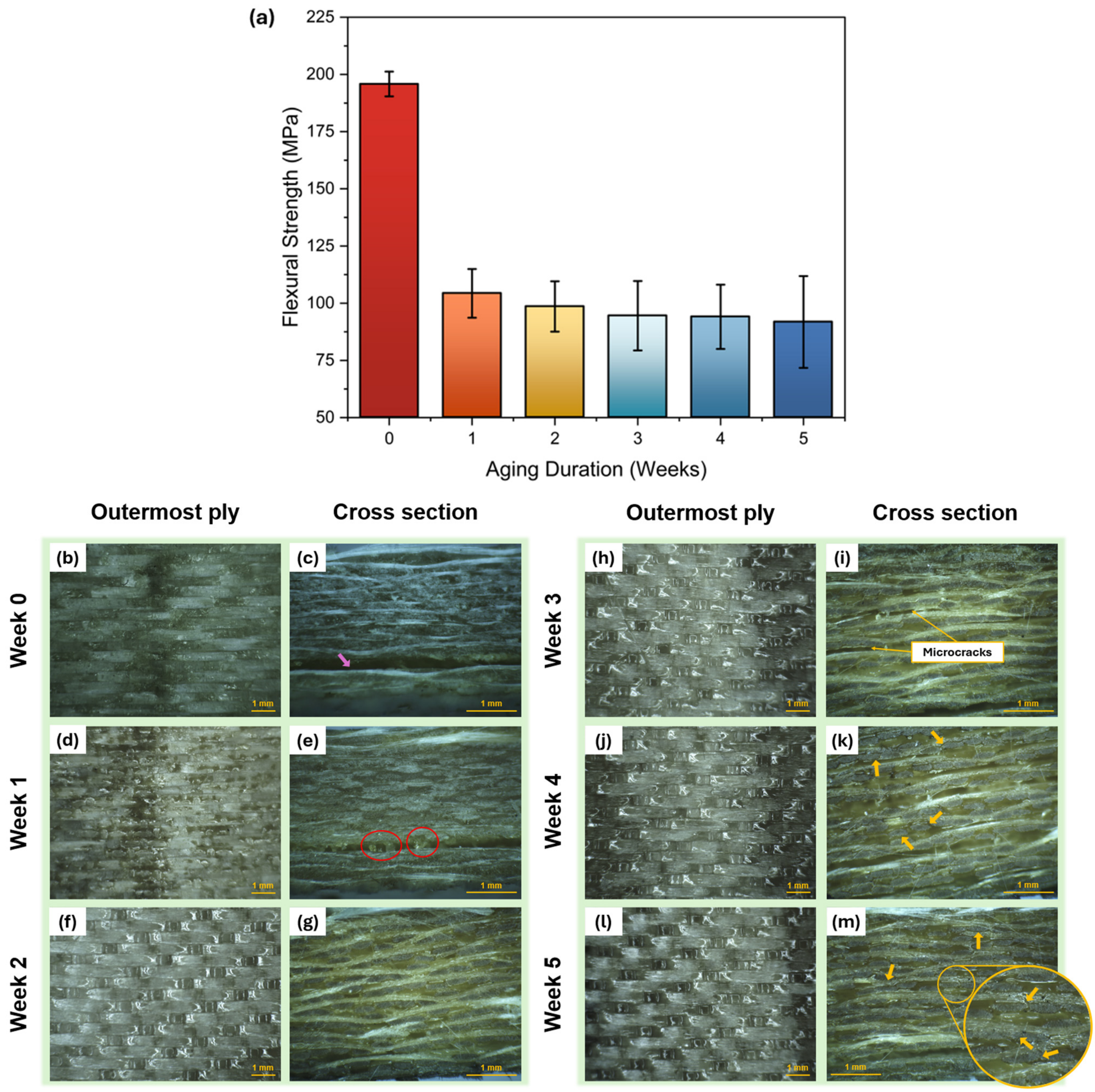

Figure 4. (**a**) Flexural strength comparison of weekly hygrothermally aged composite. (**b**–**m**) The outermost ply and cross-sectional fracture surfaces of the weekly hygrothermally aged samples. The purple arrow indicates a linear crack propagation path along an interphase. The yellow arrows denote microcracks between the glass fiber and matrix resin.

Microscopy images of the fracture patterns, as shown in Figure 4b–m, provided valuable insights into the behavior of the composite upon failure. Notably, only the samples from week 0 displayed a linear crack propagation path (purple arrow in Figure 4c) along an interphase, indicating a more brittle failure mode. In contrast, after 1 week of aging, a significant increase in plasticization of the BZ matrix could be observed along the crack propagation path (red circles in Figure 4e), suggesting a shift in material behavior due to the high moisture absorption. This trend indicates that the glass fiber-reinforced composite became increasingly flexible and less stiff because of hygrothermal aging. These findings align with those reported by Hsu and Hwang [30], who observed significant moisture uptake in the glass fiber/BZ composite after one week of exposure. Water infiltration, driven by capillary effects, weakened the fiber–matrix interface, leading to a deterioration in mechanical properties. Furthermore, in this study, the glass fiber/BZ composite was thermally aged at an elevated temperature of 70 °C, which could extensively accelerate matrix cracking and increase moisture uptake. This resulted in more severe mechanical degradation compared with previous observations [21,30]. Additionally, the calculated fiber volume fraction of the glass fiber/BZ composite was 44.56%, suggesting insufficient compression pressure during the VARTM process, which relied solely on vacuum pressure. This may have led to entrapped air and voids within the BZ matrix and at the interfaces. While both glass fiber and BZ are inherently hydrophobic, with low moisture absorption, the presence of trapped air and voids, which exhibit hydrophilic behavior, likely contributed to increased moisture uptake and further deterioration of the composite's mechanical performance. As the composite undergoes further aging, its internal structure likely evolves, allowing for greater deformation before failure, which is reflected in the changing fracture patterns. Additionally, similar observations, such as lines along the glass fibers in the aged specimens, indicating microcracks (yellow arrows) between the glass fiber and matrix resin (see Figure 4i,k,m), and the appearance of surface degradation (see Figure 4f,h,j,l) on the aged GFRP specimens in this study, correspond with the observations reported in the previous studies [3,28,31].

Inorganic fibers, such as glass fibers, typically do not absorb water; however, the surrounding matrix plays a crucial role in water absorption from the environment through diffusion and capillary processes [5,9]. This absorbed water leads to matrix swelling, which generates internal stresses, often initiating microcracks within the material [9]. As moisture accumulation increases, hydrostatic pressure may develop at the crack tips in GFRP composites, accelerating crack propagation. Over time, these microcracks may coalesce into macrocracks, compromising the thermosetting resin's microstructure and causing irreversible physical, chemical, and mechanical changes [1,5,32].

Key degradation mechanisms include plasticization and hydrolysis. Plasticization occurs when absorbed water disrupts the matrix's inter-chain Van der Waals forces and hydrogen bonds, which leads to resin softening, reduction of mechanical rigidity, and decrease in the glass transition temperature [5,9,13]. Hydrolysis, on the other hand, involves condensation polymerization caused by water molecules, leading to chain scission and diminished molecular bonding forces, which are often primary contributors to the reduction in GFRP flexural properties [5,9].

Another critical mechanism is the degradation of the fiber–matrix interface, where chemical inhomogeneities in the GFRP composite facilitate water ingress. Water absorption along this interface can induce differential swelling, exacerbate existing microcracks, or initiate new cracks due to the mismatched thermal expansion coefficients of the resin and fibers. This process not only increases water uptake but also promotes interface debonding and delamination. Such debonding significantly reduces adhesion between the fibers and matrix, impairing load transfer and overall mechanical integrity [1,3,5,9,11–13].

Furthermore, elevated temperatures can accelerate GFRP degradation by enhancing both moisture absorption and uptake rates. This aging process amplifies the aforementioned degradation mechanisms, ultimately leading to a significant reduction in the composite's mechanical properties [1,5,13,33].

3.3. Contact Angle

Surface analysis serves as an effective preliminary assessment tool for evaluating composite strength. By examining the condition of the outermost layer and its interactions with water droplets, researchers can gain insights into the material's properties prior to the destructive testing. As reported in the previous study by Zhuang et al. [12], which investigated the hygrothermal aging of composite, the hydrolytic degradation of thermosetting resin could result in the debonding of interface and matrix pulverization, potentially causing the matrix on the outermost layer to gradually crack and fall off. In addition, they also found that the failure of composites is not a simple process from surface to interior; instead, the surface and internal damage could occur at the same time. Therefore, in this study, the amount of BZ resin on the surface of the GFRP was observed to decrease continuously with the aging duration and fiber exposure tended to increase with aging duration, the surface characterization could be a good indication in determining the quality and integrity of the composite. According to our previous study [21], the wettability of the BZ resin became more hydrophilic with increasing thermal aging duration. In the same study, the elevated aging temperature led to a surface crack and microcrack formation within the matrix due to thermal oxidation after the first week of exposure. These cracks not only induced moisture infiltration but also potentially altered the wettability of the GFRP composite with the aging duration. The contact angle measurements thus serve as a crucial metric for quantifying the changes in wettability that occur because of hygrothermal aging. As illustrated in Figure 5a, the behavior of sessile droplets on the composite sample surfaces varies over time, reflecting the impact of increased hygrothermal aging. These static contact angle measurements provide a clear and detailed perspective on a surface's wettability, effectively indicating how readily the material interacts with water.

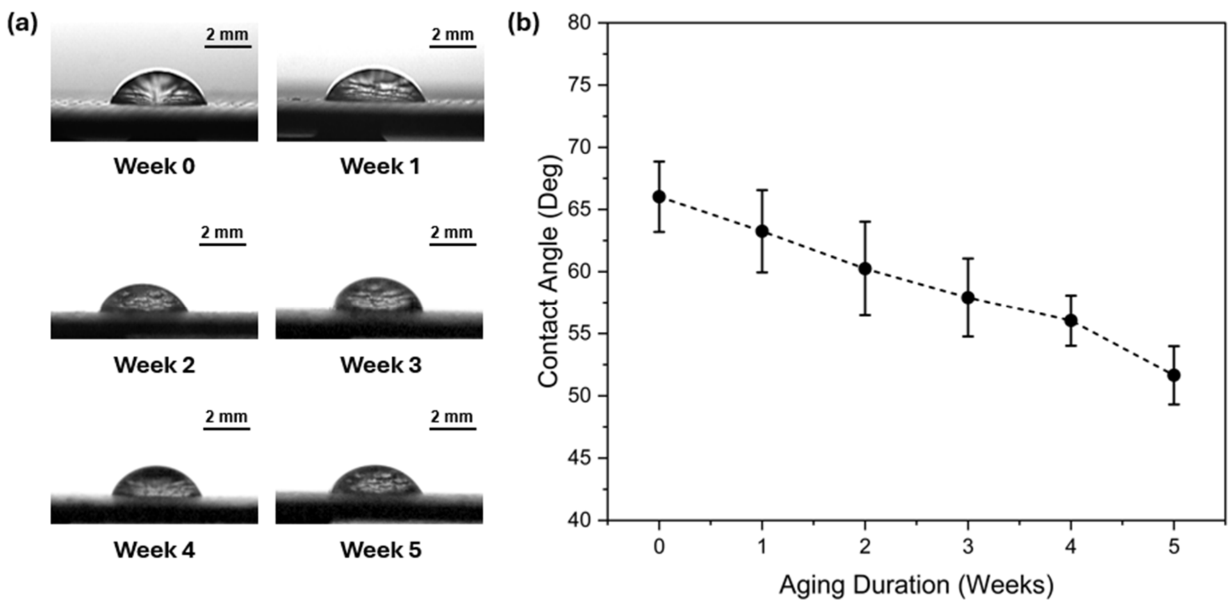

Figure 5. (**a**) Contact angle characterization on the weekly hygrothermally aged composite. (**b**) Change in the static contact angle with respect to the hygrothermally aged duration.

In the case of the glass fiber-reinforced BZ composite, there is a continuous decrease in contact angle when compared with the unaged sample taken at week 0, as shown in

Figure 5b. This trend highlights the progressive nature of the changes in wettability as aging time increases with a change in CA between 3% and 4% for each week of aging from week 1 to week 4. Notably, there is a significant drop in contact angle of 7.83% observed from week 4 to week 5 and a total change in CA of 21.77% from the unaged stage, which suggests a critical transition in the material's properties. During this period, the surface of the sample exhibits various areas with more extensive microcracking, plasticization of the BZ resin, and increase in surface roughness, as observed in Figures S1 and S2. This result not only demonstrates the increasing hydrophilicity of the GFRP composite as the aging process continues, but it also supports the observation that the week 5 specimen showed unexpected results during droplet impact tests. The conditions of the week 5 surface suggest that it may reach its maximum aging time, as indicated by the irregularities and changes in behavior noted in the static and dynamic droplet impact results in the subsequent sections. Furthermore, this observation in CA corresponds with the weight change that reached the saturation of the moisture uptake while being nearly constant in flexural strength reduction and which was discussed in the previous sections.

3.4. Contact Angle Hysteresis

The glass fiber-reinforced BZ composite exhibits a heterogeneous surface, which is characterized by a complex interplay of different textures and material properties [34]. Due to this heterogeneity, traditional contact angle hysteresis methods that rely on surface tilting are ineffective for assessing wettability in these samples. Moreover, it is also unsuitable for simulating ice accretion mechanisms on aircraft surfaces and water flow on automotive surfaces. To address this challenge, an alternative technique that employs an air blowing device was developed. This device consistently expels a fixed amount of air directed at the water droplet placed atop the composite surface, allowing for a more reliable measurement of contact angle hysteresis (Figure 6a).

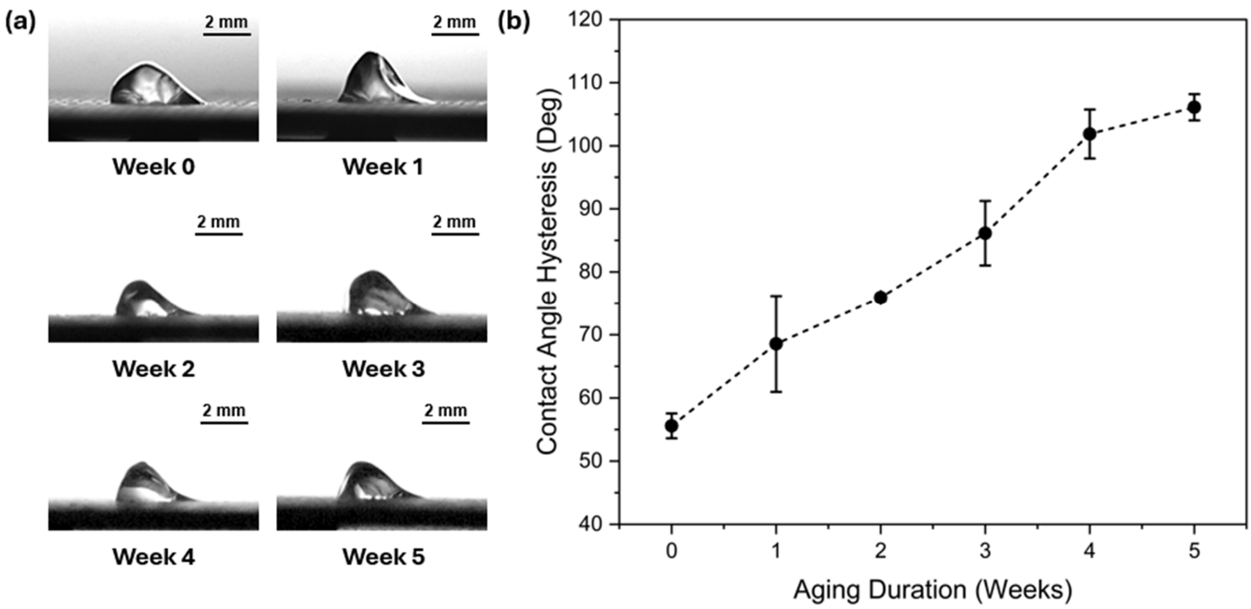

Figure 6. (**a**) Contact angle hysteresis characterization on the weekly hygrothermally aged composite. (**b**) Change in the contact angle hysteresis with respect to the hygrothermally aged duration.

As shown in Figure 6b, the measurements indicate that the contact angle hysteresis increased with extended aging time. This trend aligns with the findings from the contact angle analysis, which suggests that the composite surface becomes increasingly hydrophilic as it undergoes hygrothermal aging. The exposure of the glass fibers during this aging process plays a crucial role in enhancing the surface's affinity for water. As the aging progresses week by week, the water droplet demonstrates a stronger attachment to the composite surface, primarily due to the increased surface energy that develops in the material. This rise in surface energy is indicative of the changes that occur as the surface becomes more hydrophilic. Notably, as the hydrophilicity of the surface increases, it requires more energy to mobilize the water droplet. After 5 weeks of hygrothermal aging, the GFRP composite exhibited a significant change in CAH of 90.90% as compared with the unaged specimen. This pronounced change in the surface wettability behavior between unaged and aged specimens, in correspondence with the weight change and flexural properties, highlights the usability of the surface characterization as an indicator and predictor of the GFRP composite's integrity and condition.

3.5. Static Droplet Impact

The analysis of droplet shape and wetting length from impact on the surface of the composite was conducted for specimens that underwent hygrothermal aging over a 4-week period in the oven. As the aging time increased, a notable increase in the wetting length of the static droplet impact was observed, as shown in Figure 7a. This trend parallels the behavior seen in dynamic contact angle measurements, where the overall wetting length increases over time. Specifically, the longer the composite was subjected to hygrothermal aging, the more pronounced this extension in wetting length became. As the aging process progressed, variations in surface roughness—caused by plasticization and microcrack formation—and the hydrophilicity of the BZ resin became increasingly unevenly distributed across the composite surface (Figure 7b). This uneven distribution resulted in areas where the resin gathered in between the GF weavings, creating a heterogeneous surface that exhibited hydrophilic characteristics. The presence of these resin deposits influenced the behavior of the water droplets upon impact, as the droplets interacted with the varying surface properties. Furthermore, the droplets were observed to reach equilibrium longer with increased aging time. The specimens from week 0 demonstrated a noticeably shorter duration to attain equilibrium compared with those from subsequent weeks. The rough texture increases the complexity of the droplet's interaction with the surface, contributing to the slower equilibrium time for the aged composite [34].

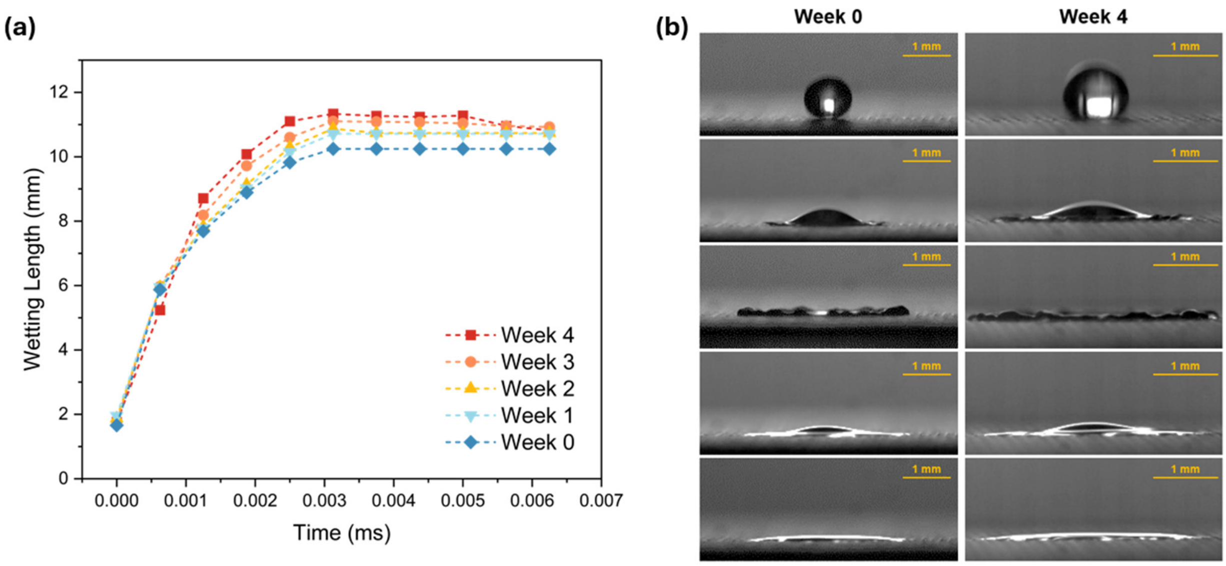

Figure 7. (**a**) Change in the wetting length of the static droplet impact with respect to the hygrothermally aged duration. The measurement errors are within 0.1 mm. (**b**) Sequential frame-by-frame observation of water droplet impacts on unaged sample (**left**) compared with the sample that was aged hygrothermally for 4 weeks (**right**).

3.6. Dynamic Droplet Impact

The dynamics of droplet impact on the fiber-reinforced BZ composite surface were systematically studied by allowing water droplets to fall from a height of 30 cm onto the samples (Figure 8), which were simultaneously moved horizontally on a piston at a speed of 3 m/s. This experimental setup enabled a detailed examination of how the droplet behavior changes with hygrothermal aging over a 4-week period. Throughout this time frame, a noticeable increase in wetting length was observed on the sample surfaces, indicating that the wettability of the composite became progressively more hydrophilic in behavior as the aging duration increased, as shown in Figure 8a–c. The observed change in hydrophilicity could be attributed to the degradation of the surface of the samples. As aging continued, the BZ matrix became more hydrophilic, which resulted in decreased resistance to the horizontal motion of the water droplets [21]. This change suggested that the surface characteristics of the composite were significantly altered by the aging process, leading to a more pronounced hydrophilic effect. The trend of increasing wetting length appeared to plateau after week 4. The stagnation in the increase of wetting length, as shown in Figure 8d, suggested that the surface aging of the composite at week 5 reached a maximum threshold for hygrothermal aging. Consequently, the wetting length measurements for week 5 were unmeasurable, indicating that the material's surface properties had changed in such a way that further assessment had become impractical.

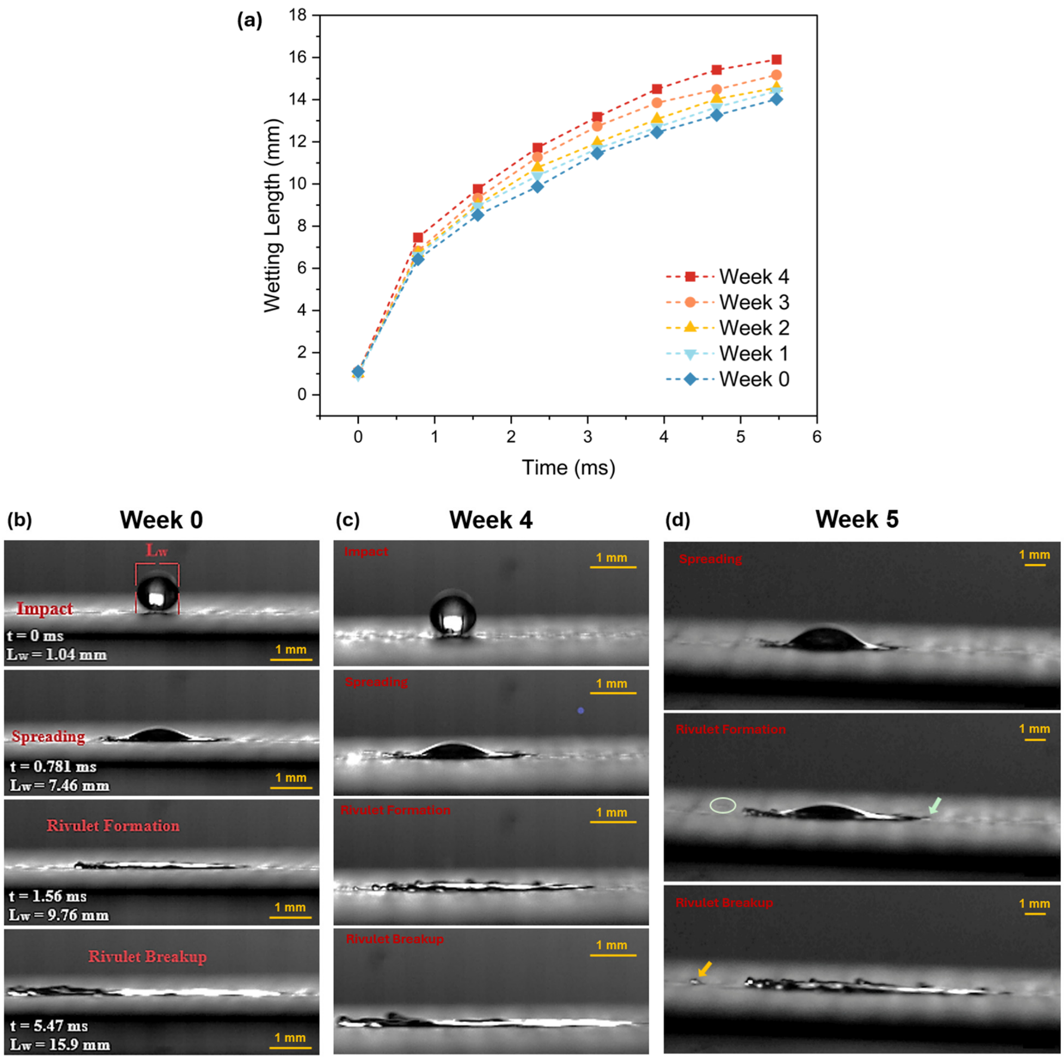

Figure 8. (**a**) Change in the wetting length of the dynamic droplet impact with respect to the hygrothermally aged duration. The measurement errors are within 0.1 mm. (**b**) Sequential frame-by-

frame observation of dynamic water droplet impacts on the unaged sample. (**c**) Sequential frame-by-frame observation of dynamic water droplet impacts on the 4-week aged sample. (**d**) Dynamic water droplet impact sequences on the 5-week aged sample on a rough surface, leading to a loss in droplet volume due to splashing and detachment (green arrow and circle). The yellow arrow indicates a complete separation of the detached droplet from the main droplet.

The results from CA and CAH correspond with the observations of the droplet impact dynamics, showing that the GFRP composite became increasingly hydrophilic as the weeks progressed. It is essential to consider that, while the BZ resin is inherently hydrophobic, it becomes more hydrophilic with the increasing aging duration. Multiple factors contribute to the overall results showing a variation in dynamic surface wetting length with hydrophilic behavior as the weeks progressed. One significant factor is that of the areas of the surface with increased roughness, which influences the resistance to the fluid motion of the droplet. This roughness can create turbulent interactions that change the regular movement of the water. Additionally, another key reason for the observed variation in wetting length is the accumulation of BZ resin in between the glass fiber weavings. This grouping together of the resin results in larger areas of rough surface, which also influences the travel length of the water droplets. The presence of these resin deposits can alter the dynamics of droplet impact, causing the droplets to vary in volume as they break up and bounce away when maneuvering over regions of the surface that exhibit the most pronounced signs of aging, as indicated by the arrows and circle in Figure 8d.

4. Conclusions

Hygrothermal environment can significantly reduce the mechanical strength of FRP composites and affect their structural integrity and performance over time. As the weight of the composite increases, its internal structure is likely to undergo changes that degrade mechanical properties, particularly its strength. This interplay between heat, humidity, and the composite's structure underscores the overall effects of hygrothermal aging. As the aging process progresses, the structural integrity of the composite is adversely affected, as shown in the significant reduction of 53.13% in flexural strength after 5 weeks of aging as compared with the unaged sample, which has significant implications for its performance and longevity in real-world applications. Understanding these changes is crucial for optimizing the material's formulation and enhancing its durability, particularly in environments prone to moisture and temperature fluctuations. Notably, the impact of hygrothermal aging on the wettability characteristics of glass fiber-reinforced BZ composites is profound. CA and CAH were observed to significantly change up to 21.77% and 90.90%, respectively, as compared with the unaged samples. These significant changes in the surface wettability behavior between unaged and aged specimens, in correspondence with the weight change and flexural properties, highlighted the usability of the surface characterization as an indicator and predictor of the GFRP composite's integrity and condition. In addition, observations, such as the increase in wetting length and longer duration to reach equilibrium, indicate the degradation in surface properties and strength as aging continues. These dynamics highlight the importance of monitoring wettability over time, especially in industries where materials face diverse environmental conditions. Knowing how hydrophobicity of surfaces changes with longer aging time can guide product design, performance, and longevity decisions.

Overall, these findings emphasize the nature of the composite's surface characteristics and the crucial relationship between aging processes and surface properties. By understanding how hygrothermal aging affects wettability, researchers and engineers can make better decisions about the composite's use and potential modifications to enhance performance. This comprehensive approach—combining flexural strength testing with surface analysis—offers valuable insights for optimizing glass fiber-reinforced composites in practical applications. The methodology can then be scaled to full structural dimensions, offering a time- and resource-efficient solution while enabling non-invasive assessment of real-world performance. This proposed surface wettability characterization can thereby be used to detect the degradation at early stages.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/eng6030060/s1, Figure S1: Surface characteristics of the unaged (week 0) GFRP composite samples on the vacuum-bag (left) and tool (right) side; Figure S2: Surface characteristics of the 5-week hygrothermally aged GFRP composite samples on the vacuum-bag (left) and tool (right) side; Figure S3: Change in color comparison between the unaged (left) and 5-week hygrothermally aged (right) GFRP composite.

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