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*Research article*

# Hemp extract as a multifunctional stabilizer for polyhydroxybutyrate (PHB) materials: Investigations into anti-aging properties and lifetime control

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**Abstract.** Biodegradable biopolymers like polyhydroxybutyrate (PHB) hold promise for sustainable packaging, but their inherent degradability reduces material stability. Synthetic stabilizers, though effective, raise environmental and potential toxicity concerns. This study explores a multifunctional natural anti-aging agent: a hemp extract rich in cannabidiol (CBD) and cannabichromene (CBC). PHB composites with varying hemp extract concentrations were prepared and subjected to thermooxidative and weathering aging. Characterization employed FTIR-ATR, carbonyl index, and spectrophotometry. Static mechanical properties, DSC, and surface free energy (SFE) were also assessed. Notably, the hemp extract exhibited stability under ambient conditions but showed migration with time and aging. The results suggest a plasticizing effect on PHB and highlight the contrasting roles of the extract: inhibiting thermooxidative aging while potentially accelerating aging under atmospheric conditions. This opens avenues for tailoring material durability, further evaluated by life cycle analysis (LCA). This work represents one of the first investigations into hemp extract as an anti-aging agent for eco-friendly polymers, expanding the knowledge base of natural multifunctional additives.

***Keywords:*** *hemp, extract, aging process, biodegradable polymers, aliphatic polyesters, degradation processes*

## 1. Introduction

The modern world is permeated by polymeric materials in diverse forms, ranging from rubbers and resins to thermoplastics. This ubiquity stems from the unique properties of these materials, including ease of processing, adaptability to specific requirements through simple composition modifications, lightness, strength, and affordability. Unfortunately, the latter two characteristics also contribute to the substantial accumulation of polymer waste. To counteract this trend, biodegradable polymers, frequently of dual green or natural origin, are gaining prominence in research and industrial applications. Polyhydroxyalkanoates (PHAs), a group of aliphatic polyesters, serve as an excellent example. PHAs can be produced using microbial organisms. Diverse strains of bacteria are employed for PHA production, with *Ralstonia eutropha*, *Azotobacter vinelandii*, and *Alcaligenes latus* being the most prevalent industrially [1–4]. They can contain up to 80% biopolyester in dry matter. Cultivation conditions vary depending on the microorganism used but can be broadly categorized into two types. For *Ralstonia eutropha*, stress conditions, such as reduced oxygen and nitrogen availability, are required to induce polymer production. An excess of carbon sources, such as glucose, is also provided. *Azotobacter vinelandii* and *Alcaligenes latus*, on the other hand, continuously produce polyhydroxybutyrate (PHB) throughout the growth cycle without nutrient limitation. Both groups of

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bacteria store carbon and energy as intracellular polyhydroxybutyrate granules. It is noteworthy that the medium composition during cultivation significantly influences the polymer chain crystallinity and structure. PHB exhibits numerous advantages but its high production cost remains a major drawback. To address this, researchers have explored utilizing industrial waste as a cultivation substrate for bacteria. Common examples include agricultural and food wastes such as sugar beet molasses, whey, and its hydrolysates, as well as glycerol, a byproduct of biofuel synthesis [5]. According to the latest literature, the cost of PHB production is variable and depends on the technology and substrates used [6]. The cheapest PHB unit production cost was $3.63/kg when fructose was used [7].

Polyhydroxybutyrate is a promising biopolymer with the potential to replace petroleum-based polymers. It possesses comparable characteristics to conventional polypropylene (PP), including thermoplasticity and a similar melting point of approximately 165–175 °C. However, PHB exhibits a significantly higher crystallinity, leading to enhanced stiffness and brittleness compared to PP. Despite its remarkable tensile strength of 3.5 GPa, PHB's elongation at break is relatively low, reaching only 5% compared to 150–600% for polypropylene [8]. The narrow processing temperature window can lead to polymer chain degradation, diminishing material properties. By employing appropriate plasticizers or blending PHB with compatible polymers, such as polylactide or hydroxyvalerate, we can mitigate these limitations [9]. A multitude of compelling properties, including biodegradability, exceptional thermo-mechanical and barrier characteristics, and biocompatibility, has fueled immense research interest in PHB. Moreover, PHB's inherent low oxygen permeability renders it a promising material for packaging applications, effectively extending product freshness by curtailing organic oxidation reactions [10]. Owing to these compelling attributes, PHB stands as a viable alternative to largely non-biodegradable disposable packaging materials, particularly in the food, pharmaceutical, and medical sectors [11, 12]. Despite its biodegradability, PHB requires stabilization against environmental factors, including water, light, temperature, oxygen, and microorganisms, for widespread application. Thermal degradation is believed to occur primarily through a random process of breaking chemical bonds within the polymer chain. This reaction, involving the removal of β-CH groups and the formation of a six-membered ring, leads to a significant decrease in molecular weight. However, some cleavages preferentially occur at the ends of long polymer chains. Consequently, a variety of degradation products are formed, including olefinic compounds, carboxylic acids, crotonic acid, and oligomers, which was described in the work by Turco *et al*. [13]. Kawalec *et al*. [14]. elucidated the precise mechanism of thermal degradation of PHB at moderate temperatures. They highlighted the possibility of regulating this process through modifications to the structure of chain end groups and by controlling the concentration of carboxylate end groups in PHB. Conventional synthetic stabilizers, however, are often cost-prohibitive and potentially toxic, hindering their industrial-scale implementation. Our research group is exploring the utilization of natural substances with eco-friendly anti-aging properties as an alternative to synthetic stabilizers. Polyphenols, a prominent group of compounds exhibiting anti-aging effects, have emerged as a promising candidate [15–18]. Previous studies on PHB and its stabilization using natural polyphenols have explored the use of compounds such as lignin, tannic acid, catechins, wine pomace extract, and tea extract, as shown in a review by Bonnenfant *et al*. [19]. In their research, Lopez-Rupio and Kirschweng demonstrated that β-carotene is an effective UV stabilizer for PHB-based materials. They established that the additive functions as a plasticizer for this material and further confirmed the maintenance of mechanical properties following simulated shooting under ultraviolet light [20, 21]. In this study, we primarily investigated hemp-derived compounds, with a particular focus on cannabidiol (CBD), as a promising natural multipurpose anti-aging agent [22]. The research will serve to expand the knowledge of new potential anti-aging agents in polymers, including biodegradable biopolymers.

## 2. Experimental

### 2.1. Materials

Polyhydroxybutyrate with the formula P(3HB-*co*-HB) was used in this study. It is a thermoplastic polymer belonging to the group of aliphatic polyesters (produced by SIMAGCHEM®, Xiamen, China). It is characterized by its biodegradability, especially under anaerobic conditions. Its melt flow rate is 18 g/10 min (443 K/2.16 kg).

The active ingredient with anti-aging properties is a hemp extract rich in cannabidiol (CBD) and cannabichromene (CBC), obtained through a supercritical extraction process using $CO_2$ as a solvent. These compounds are part of the cannabinoid group naturally present in hemp plants. The extract was acquired as a free sample from a friendly company specializing in the industrial extraction of CBD from hemp (supplier confidentiality clause, Lithuania). In light of this, the composition of the hemp extract employed was analyzed and is reported herein [23].

## 2.2. Methods

### 2.2.1. Preparation of sample

PHB in granular form was dried in a Binder® laboratory dryer for 24 h at 50 °C prior to processing to remove bound water due to the hygroscopic properties of this polymer. In the next step, a laboratory balance was used to weigh an aliquot of PHB and hemp extract in the appropriate proportions. Samples were prepared with 1.5 and 3.0 phr of hemp extract, and a reference sample without the bioadditive was also included All the reagents were placed in a beaker and pre-mixed by hand using a laboratory spoon. The resulting mixture was placed in the hopper of a laboratory extruder (Zamak Maercator, Skawin, Poland) using a single screw with an $L/D$ ratio of 24 and a diameter of 25 mm. Extrusion was carried out under the following conditions: temperature of 160 °C, pressure of 17 atm, screw speed of 40 rpm. Finally, a series of extrusions with a length of about 120 cm, a width of 25 mm, and a thickness of about 1.5 mm were produced. After extrusion, the samples were cooled to room temperature and conditioned for one week at room temperature.

### 2.2.2. The methodology for testing prepared samples

The methodologies for thermo-oxidative aging, weathering processes, spectroscopic measurements, carbonyl index (IC) determination, spectrophotometry, mechanical testing, and surface free energy (SFE) analysis were conducted as previously described [23].

### 2.2.3. Differential scanning calorimetry (DSC) analysis

Thermal analysis was performed using a Mettler Toledo DSC analyzer (Greifensee, Switzerland). The following thermal parameters of the polymer samples were determined: glass transition temperature ($T_g$), cold crystallization temperature ($T_c$), melting temperature of the crystalline phase ($T_m$), and oxidation onset temperature ($T_o$). Additionally, the enthalpy ($\Delta H$) associated with phase transitions and the specific heat capacity change at the glass transition ($\Delta C_p$) were investigated. Approximately 5 µg of each sample was loaded into open 100 µL aluminum pans. PHB materials were heated from 23 to 200 °C at a heating rate of 10 °C/min under an argon atmosphere. After isothermally maintaining the samples at 200 °C for 5 min, they were cooled to 0 °C. Subsequently, the atmosphere was switched from argon to air (flow rate 50 mL/min) for the oxidative stability test, followed by heating to 200 °C.

## 3. Results and discussion

### 3.1. Fourier transform infrared spectroscopy (FTIR) measurement results

To elucidate the physicochemical changes induced in the polymeric material upon exposure to hemp extract, its infrared spectrum was characterized beforehand [23].

A detailed analysis of the spectrum shown in Figure 1 reveals distinct functional groupings that correspond to specific wavenumbers. At 3416 cm$^{-1}$, intense absorption peaks indicate the presence of OH stretching vibrations, primarily associated with intramolecular bonds. The spectral range of 3068–2854 cm$^{-1}$ exhibits residual signals attributed to OH group vibrations from cannabidiol acid alongside prominent CH stretching vibrations in alkanes. The peaks at 1708, 1621, and 1578 cm$^{-1}$ are indicative of C=O and C=C stretching vibrations, which are corroborated by the structure of CBD and suggest the formation of an intramolecular pseudocyclic bond. Bending vibrations are observed for methyl groups at 1444 and 1376 cm$^{-1}$, while bending vibrations corresponding to OH groups in phenolic derivatives are evident at 1242–1028 cm$^{-1}$. The wavenumbers 887 and 723 cm$^{-1}$ correspond to C–O and C–O–H stretching vibrations in aromatic compounds, while benzene derivatives in substitution 1.2 and 1.3 exhibit absorption at these peaks. Gęskowski *et al.* [24] emphasize the significance of the bands around 1445 and 883 cm$^{-1}$ in determining CBD and other cannabinoids content in the extract [24, 25].

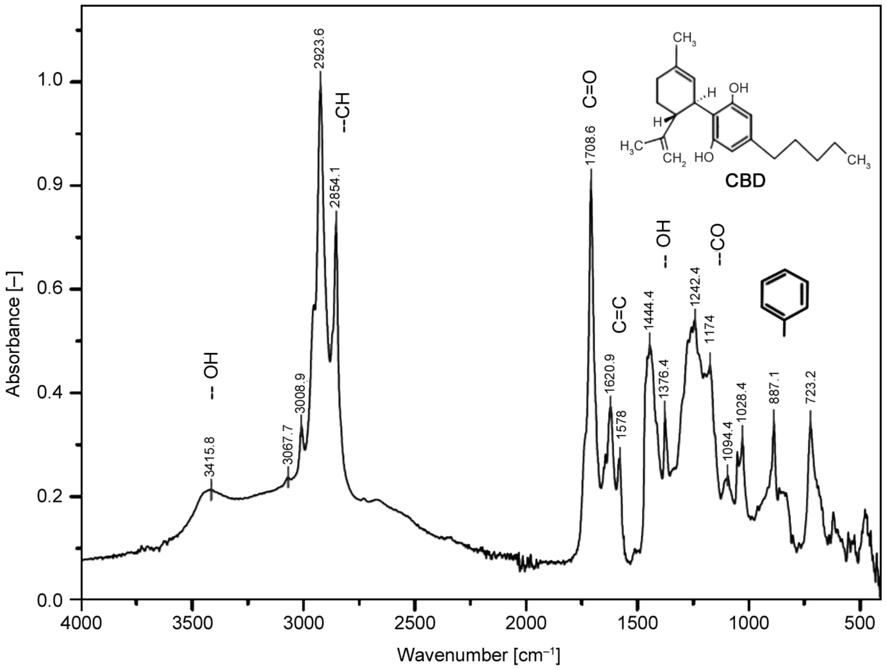

**Figure 1.** FTIR spectrum of hemp extract.

### 3.1.1. FTIR spectra analysis for PHB-based composites samples

Figure 2 presents a spectrum that depicts the spectroscopic changes observed in samples containing varying concentrations of hemp extract. Notably, the overall shape of the absorption curve remains largely unchanged, lacking distinct peaks attributable to the added phytoadditive. This observation signifies the efficient incorporation of the hemp extract into the polymer matrix during extrusion and the thermodynamic stability of the system under ambient conditions. With increasing hemp extract content, a gradual enhancement in the intensity of existing polyhydroxybutyrate (PHB) signals is apparent. A sharpening of peaks at 1748 cm$^{-1}$ (signatures of C=O stretching vibrations) suggests an expansion in the

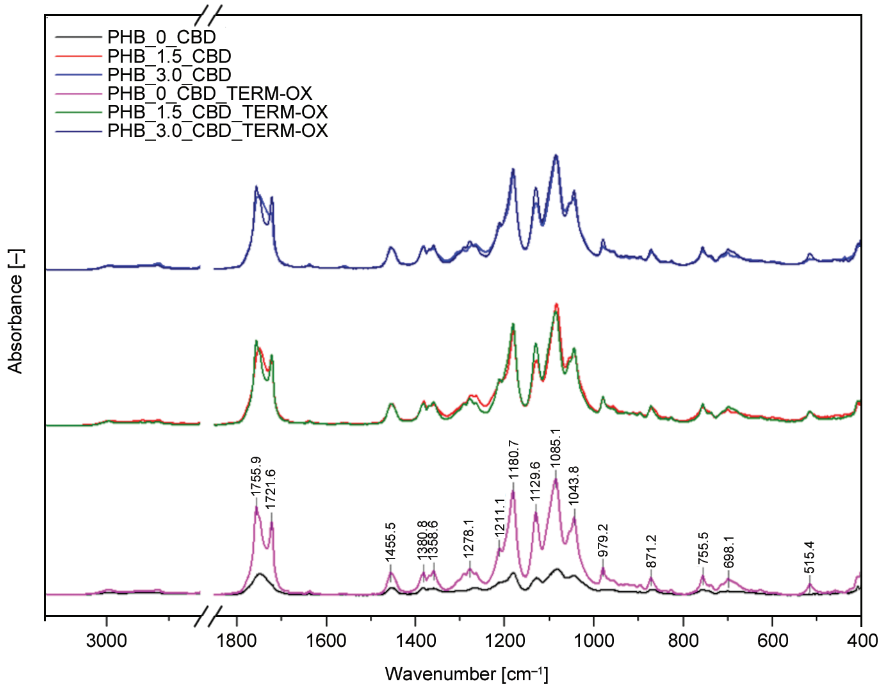

**Figure 2.** Comparative FTIR spectrum for PHB samples with different hemp extract content after 200 h of thermo-oxidative aging.

proportion of ester bonds, possibly arising from dehydration and esterification reactions of hemp extract compounds during high-temperature processing. Another intriguing peak emerges at 1284 cm$^{-1}$, potentially indicating the emergence of signals arising from the C–O structures of aromatic esters. The absorption spectrum also reveals a newly observed peak at 895 cm$^{-1}$ (C=C bending in alkenes). Additionally, a low-intensity peak for wavenumber 516 cm$^{-1}$ (–CH bending in substituents 1,4 or 1,2,3,4) is present. These data demonstrate that the sample surface exhibits predominantly PHB signals with minor peaks from the additive, indicating favorable miscibility of the employed system.

Figure 2 and Figure 3 present the spectra of samples subjected to 200 h of thermal oxidation and weathering, respectively. As evident from the spectra, the absorption curve of pure PHB undergoes a marked transformation. A distinct increase in the intensity of signals from C=O, C–O, and C–O-C groups is observed, signifying substantial oxidation and degradation of the material due to exposure to environmental factors, including light, temperature, air, and water. In contrast, the absorbance spectra of samples containing high-CBD and CBC hemp extract exhibit minimal alterations. For thermal oxidation, the pre- and post-aging spectra are almost indistinguishable. However, for weathering, slightly larger changes in signal intensity are observed, suggesting that the anti-aging phytonutrient is less resilient to environmental stressors such as water or light.

### 3.1.2. Calculation results and carbonyl index analysis

Employing data from Fourier transform infrared spectrometry (FTIR) analyses, the carbonyl index (IC) was determined. This is a quantitative measure of the degradation of polymeric samples due to aging. The carbonyl index was assessed for various samples with distinct hemp extract concentrations following each aging period and condition. The obtained data are presented graphically in the attached charts (Figure 4).

The carbonyl index (IC) was calculated to assess the oxidation and degradation behavior of PHB using FTIR-ATR spectroscopy. The IC values of PHB reference samples exhibited fluctuations during aging, reaching maxima after 100 h for weathering and 150 h for thermo-oxidative aging. The inclusion of 1.5 phr of hemp extract resulted in elevated IC values from the outset. This suggests a possible partial migration of the extract to the material's surface, leading to increased signal intensity. Nevertheless, the IC values of these samples decreased towards the end of the aging process, possibly due to the degradation of the phytocompounds themselves. For samples containing 3 phr of hemp extract, high IC values were observed from the beginning, with a substantial

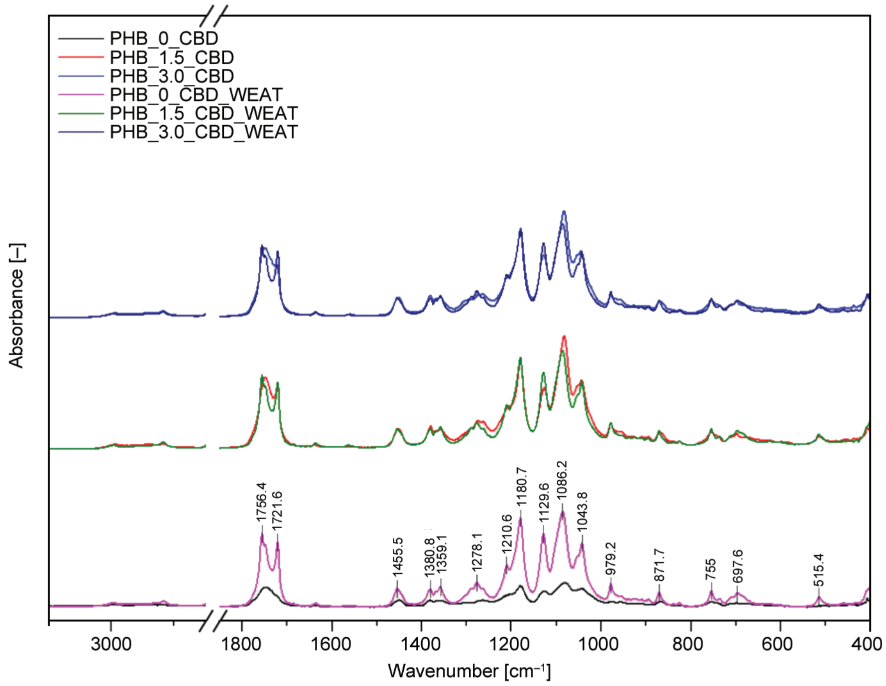

**Figure 3.** Comparative FTIR spectrum for PHB samples with different hemp extract content after 200 h weathering aging.

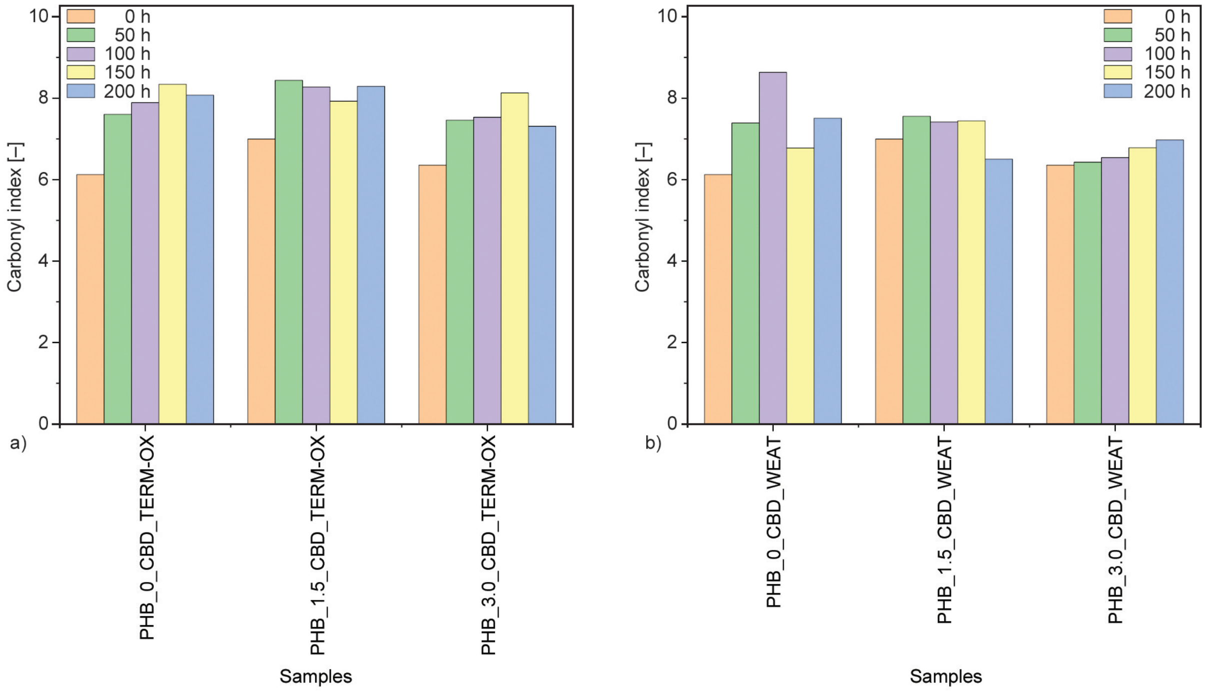

**Figure 4.** Graph of changes in the value of the carbonyl index for PHB samples, as a function of aging time and hemp extract concentration a) thermooxidative aging, b) weathering aging.

increase, particularly prominent for thermo-oxidative aging.

## 3.2. Analysis of static mechanical properties

Unaged samples exhibit a slight decrease in tensile at maximum given force ($T.F_{\max}$) values at peak load with rising hemp extract concentration, from 21.5 MPa for unmodified PHB to 18.5 MPa for samples containing 3.0 phr extract. Conversely, elongation at break (*Eb*) remains essentially unchanged within the standard deviation range for samples without extractant and those with 1.5 phr extract, which is presented in the attached Table 1. A substantial increase in *Eb* is observed with 3.0 phr extract, confirming its plasticization effect. A similar effect was observed for the addition of β-carotene to PHB in the study conducted by Lopez-Rupio and Lagaron [20]. Upon analyzing PHB samples with varying hemp extract

**Table 1.** Mechanical properties for PHB samples subjected to thermo-oxidative aging.

| Sample name | $T.F_{\max}$ [MPa] | $E.F_{\max}$ [%] | *TS* [MPa] | *Eb* [%] |
|---|---|---|---|---|
| PHB_0_CBD | 21.5±2.1 | 5.7±0.4 | 7.1±1.7 | 31.6±5.5 |
| PHB_0_CBD_TERM-OX_50h | 24.8±0.4 | 6.7±0.1 | 24.2±0.8 | 6.8±0.1 |
| PHB_0_CBD_TERM-OX_100h | × | × | × | × |
| PHB_0_CBD_TERM-OX_150h | × | × | × | × |
| PHB_0_CBD_TERM-OX_200h | × | × | × | × |
| PHB_1.5_CBD | 19.0±1.2 | 5.1±0.2 | 8.8±0.3 | 33.0±1.0 |
| PHB_1.5_CBD_TERM-OX_50h | 20.4±1.2 | 7.8±0.0 | 14.2±4.7 | 9.1±1.1 |
| PHB_1.5_CBD_TERM-OX_100h | 19.9±0.0 | 6.6±0.2 | 19.6±0.4 | 6.7±0.2 |
| PHB_1.5_CBD_TERM-OX_150h | 13.7±4.5 | 5.3±0.1 | 13.5±4.4 | 5.3±0.1 |
| PHB_1.5_CBD_TERM-OX_200h | × | × | × | × |
| PHB_3.0_CBD | 18.5±0.9 | 7.6±1.5 | 7.2±1.4 | 27.9±2.1 |
| PHB_3.0_CBD_TERM-OX_50h | 22.5±0.1 | 8.7±0.7 | 22.4±0.0 | 8.9±0.8 |
| PHB_3.0_CBD_TERM-OX_100h | 25.6±1.7 | 7.9±1.1 | 25.5±1.8 | 8.1±1.2 |
| PHB_3.0_CBD_TERM-OX_150h | 15.4±5.0 | 5.8±1.6 | 14.2±3.8 | 5.8±1.6 |
| PHB_3.0_CBD_TERM-OX_200h | 14.3 | 5.0 | 14.3 | 5.0 |

× – test result not conclusive due to excessive sample degradation concentrations, no clear correlation between *TS* and *Eb* was observed. Exposure to weathering conditions caused extensive degradation of all samples, leading to disintegration into numerous brittle fragments, rendering mechanical testing infeasible. This observation underscores the profound impact of external factors such as moisture and light on the degradation of PHB and hemp extract compared to thermo-oxidative aging. Notably, samples incorporating the additive exhibited significantly finer fragmentation and enhanced brittleness relative to pure PHB, suggesting a catalytic role in weathering-induced degradation. This can be attributed to the additive's plasticizing effect, which weakens interchain bonds, enabling water penetration and accelerating degradation.

### 3.2.1. PHB composite samples subjected to aging in thermo-oxidative conditions

Thermo-oxidative aging of polyhydroxybutyrate (PHB) samples revealed an intriguing effect of cannabinoids on the aging process itself. The higher the concentration of CBD and CBC, the greater the stability of the PHB samples, as evidenced by their extended durability. Samples without extract could only withstand static mechanical testing for a maximum of 50 h of thermo-oxidative aging. With 1.5 phr of additive, the time to failure increased to 150 h, and with 3.0 phr, it reached 200 h. The overall condition of the samples upon removal from the aging chamber further demonstrated the effectiveness of hemp extract as an anti-aging agent. Intriguingly, the stretch value of the samples decreased with increasing cannabinoid concentration after 50 h of aging. However, at the highest cannabinoid concentration, an initial increase followed by a decrease in the stretch value was observed. On the other hand, maximum tensile force increased with extract concentration but decreased with time.

These findings indicate a potent plasticizing and stabilizing effect of hemp extract, likely attributed to its interaction with PHB chains, as shown in Figure 5. CBD and CBC both possess highly polar functional groups, including hydroxyl groups, within their chemical structures. Moreover, they incorporate nonpolar elements, particularly extended aliphatic chains. This unique structural arrangement facilitates the formation of weak intermolecular interactions, such as those between the hydroxyl groups of CBCs and CBDs and the carboxyl groups of polyhydroxybutyrate. These interactions enhance the stability of the additive-polymer system. The introduction of these spatially extensive extractive compounds, including aliphatic chains and aromatic rings, into the interchain structure can lead to the disentanglement of PHB chains, thereby weakening interchain interactions and enabling enhanced mobility. This ultimately culminates in polymer plasticization, and the elongation at break data for PHB samples with varying CBD levels exhibited a similar trend.

Based on the data collected from the mechanical tests, the aging factor *K* was calculated and the results are presented in Figure 6. After 50 h of processing, the thermo-oxidative aging factor (*K*-factor) of PHB reference samples was 0.74. The addition of 1.5 phr

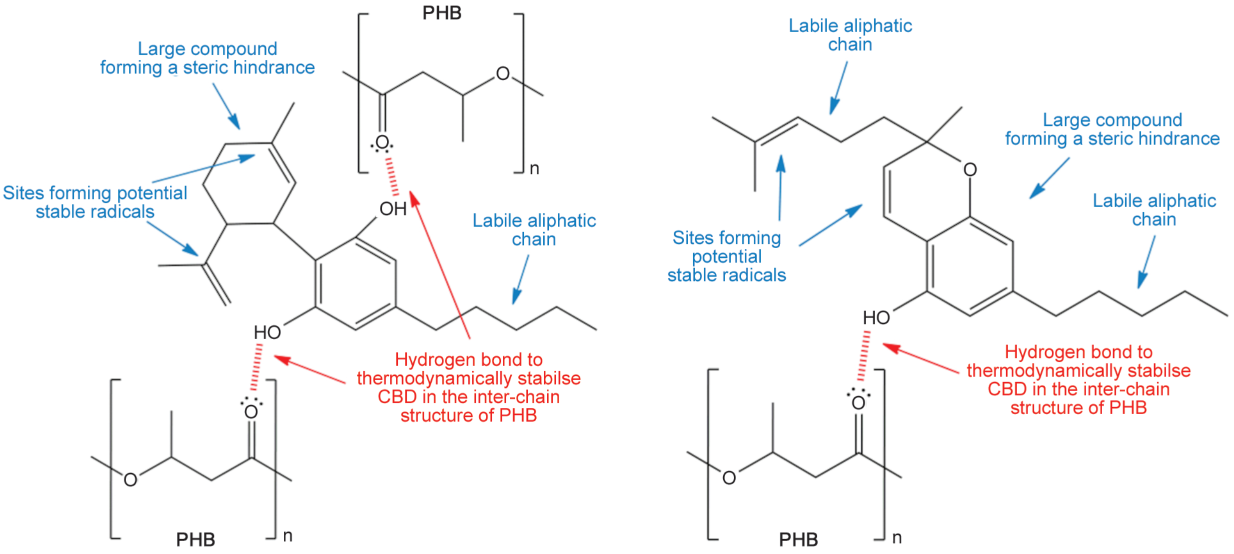

**Figure 5.** Hypothetical theoretical schemes for PHB plasticisation and thermodynamic stabilisation of CBD and CBC in interchain space.

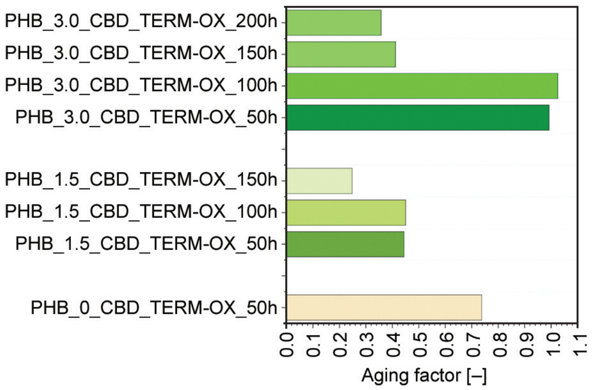

**Figure 6.** Change of the thermo-oxidative aging coefficient for samples of PHB composites.

extract extended sample durability to 150 h but reduced the *K*-factor to approximately 0.4. In contrast, the incorporation of 3.0 phr additive in the composite composition enabled sample stability over 200 h of degradation. During the first 100 h, the *K*-factor approached 1, but it subsequently decreased to a final value of 0.36. These results clearly demonstrate the inhibitory effect of CBD and CBC on PHB degradation, prolonging the material's lifespan under the influence of factors such as temperature and air.

### 3.3. Measurements and analysis of the results of the DSC test

Differential scanning calorimetry (DSC) analysis revealed a significant influence of hemp extract on the thermal properties of the polymer. The addition of 3 phr phytocannabinoids decreased the onset of the glass transition temperature ($T_g$) from 27 to 25 °C and broadened the glass transition region from 41.4 °C to approximately 52 °C. Moreover, the glass transition enthalpy ($\Delta C_p$) decreased from 1.0 to 0.6 J/(g·K) with increasing additive concentration, suggesting a reduced specific heat difference between the liquid and solid phases and a lower energy barrier for intermolecular mobility within the polymer. This is indicative of a plasticizing effect exerted by hemp extract on PHB. The wider glass transition temperature range and lower $\Delta C_p$ suggest that the transition between states requires less energy and is facilitated. As illustrated in Figure 7, the significant decrease in the glass transition endpoint values under different weathering modes highlights the potential for controlling material properties in various service environments. At a 3 phr additive content, $T_g$ was 15 °C lower for weathering aging compared to thermooxidative aging. Furthermore, a higher $\Delta C_p$ value was observed for the weathering-aged sample containing cannabinoids relative to the unadditive sample. This suggests degradation of the hemp extract under weathering conditions and a corresponding decrease in its ability to lower the energy barrier to glass transition.

The incorporation of these cannabinoids into PHB enhances intermolecular mobility, which concurrently promotes crystallization and lowers the crystallization temperature by 2 °C by decreasing the energy barrier for structural self-assembly. The change in the enthalpy of crystallization for the weathering-aged

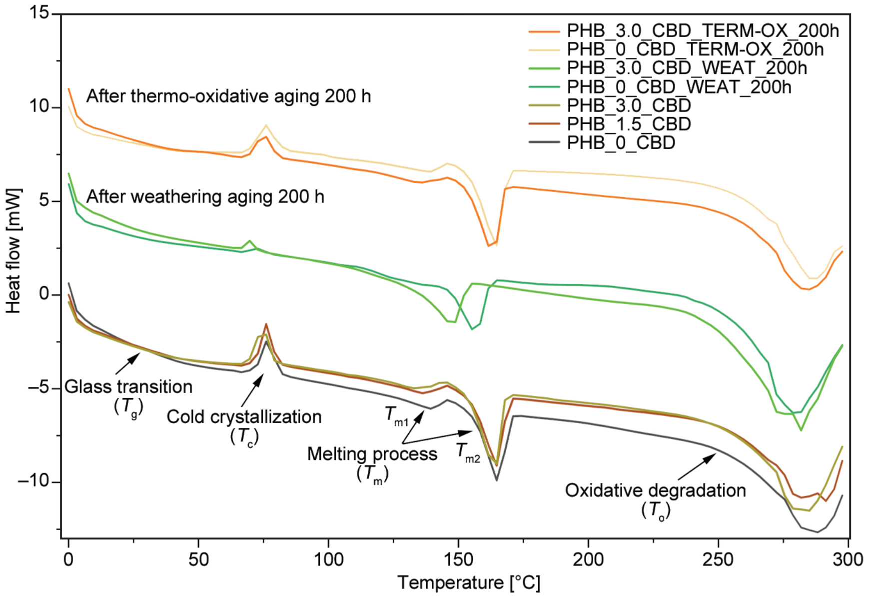

**Figure 7.** Results of DSC measurements of phase transition temperatures and heat for PHB samples with different hemp extract content before and after weathering and thermooxidative aging.

samples is most evident, as it was about 1.7 J/g, compared to 12.0 J/g for the reference sample before aging. Cannabis extract reduced the melting temperature ($T_{m1}$) by 3 and 6.5 °C for samples containing 1.5 and 3 phr of cannabinoids, respectively. The enthalpy of melting was also reduced, further emphasizing the plasticizing effect of the additive on PHB. While thermooxidative aging did not induce significant changes in the absence or presence of the additive, weathering aging caused a shift and overlap of the $T_{m1}$ and $T_{m2}$ peaks. As a consequence of aging, the total energy required to melt the sample increased. This behavior can be attributed to the increased content of the crystalline phase in the material after the degradation of the extract and the accelerated degradation of the amorphous phase. Samples containing hemp extract showed an oxidation temperature ($T_o$) of approximately 244 °C, which was about 40 °C higher than that of the reference samples. The oxidation enthalpy for the non-additive sample was 3.4 J/g, about 19-times lower than that of the samples containing hemp extract. Although thermooxidative aging showed a similar correlation between phytosubstance addition and increased thermal stabilization of the material, weathering aging yielded contrasting results. In this case, the oxidation temperature range showed little change after cannabinoids addition, and the required oxidation energy was 6-fold lower compared to the nonadditive reference material. These findings demonstrate the potential for tailoring the properties of hemp extract-containing materials based on specific environmental conditions and intended applications, emphasizing the plasticizing and stabilizing effects of the additive.

## 3.4. Measurements and analysis of the results of the spectrophotometric test

Upon sample preparation, a preliminary visual assessment of their appearance was performed. Thereafter, the study's progress on the efficacy of hemp extract as an anti-aging agent was evaluated following thermo-oxidative and weathering degradation. The PHB-based composites presented a creamy and homogeneous texture with a smooth surface. Upon incorporation of hemp extract, the samples developed a straw-colored hue, with intensity increasing with higher extract concentrations. Notably significant changes in the appearance of the prepared samples were observed under weathering conditions. The samples exhibited increased discoloration and developed numerous surface cracks, both as a function of aging duration and hemp extract content. This phenomenon, as previously discussed, can be attributed to the additive's plasticizing effect, which enhances water penetration.

### 3.4.1. Analysis of the PHB composites after thermal-oxidative aging

The incorporation of hemp extract into PHB composites significantly impacts their color and saturation characteristics, which was confirmed by the results in Figure 8. With increasing extract concentrations, color change and saturation index during aging diminish, indicative of cannabinoids' protective role against therm-oxidative degradation. As extract content rises, the whiteness index also declines, suggesting a modification in material properties. Additionally, the hue angle decreases upon the addition of the hemp derivative, implying a shift towards a more neutral color. These findings underscore the potential of CBD and CBC as natural antioxidants and degradation indicators in PHB composites.

### 3.4.2. Analysis of the PHB composites after weather aging

The weathering of aliphatic polyester samples resulted in substantial alterations in color, chroma, whiteness index, and hue angle, which is shown in Figure 9. These changes were governed by both aging duration and cannabidiol content. Samples with higher extract concentrations exhibited a more conspicuous shift in color and whiteness index, suggesting degradation-induced properties. For all samples, chroma underwent the most significant transformation within the initial 50 h of aging, indicating the instability of dye compounds within the extract under weather degradation conditions. Overall, incorporating hemp extract emerged as an effective indicator of aliphatic polyester degradation during weathering.

## 3.5. The results of testing and analysis of surface free energy (SFE)

The prepared samples exhibited no significant alteration in their SFE values, either with the pure polymer or upon incorporation of 1.5 phr extract. This observation suggests that the phytocompound exhibits excellent miscibility and thermodynamic stability with the polymer matrix in small quantities, and it does not exhibit any initial migration, as corroborated by the FTIR-ATR studies presented above.

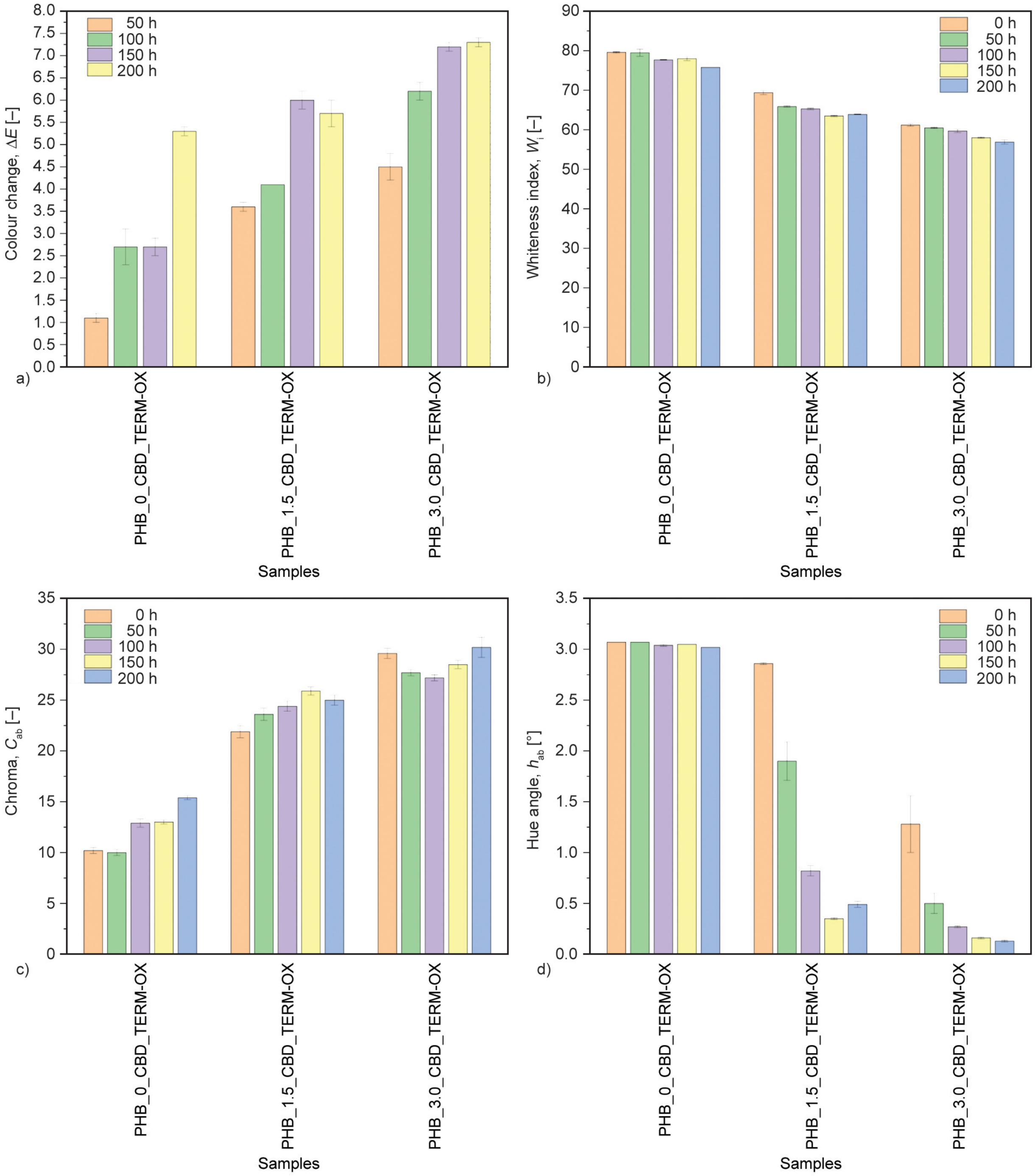

**Figure 8.** Spectrophotometric properties for PHB samples subjected to thermo-oxidative aging a) color change, b) whiteness index, c) chroma, d) hue angle.

However, a pronounced increase in both individual SFE components and the overall SFE value was observed following the addition of 3.0 phr hemp extract.

### 3.5.1. PHB composite samples subjected to aging in thermo-oxidative conditions

The reference PHB samples exhibited a reduction in both total and dispersive surface free energy during thermo-oxidative aging, which was confirmed by the results in Figure 10. However, the polar component increased after 100 and 150 h of aging before returning to its initial level. Composites containing 1.5 phr of natural additive demonstrated aging trends nearly identical to the reference samples. The only observed difference was a decrease in the disperse and cumulative components to their lowest values after 50 h, followed by a gradual increase over time, albeit not reaching the baseline values associated with aging. An even more pronounced decline in the value of the dispersion component and the total surface energy was

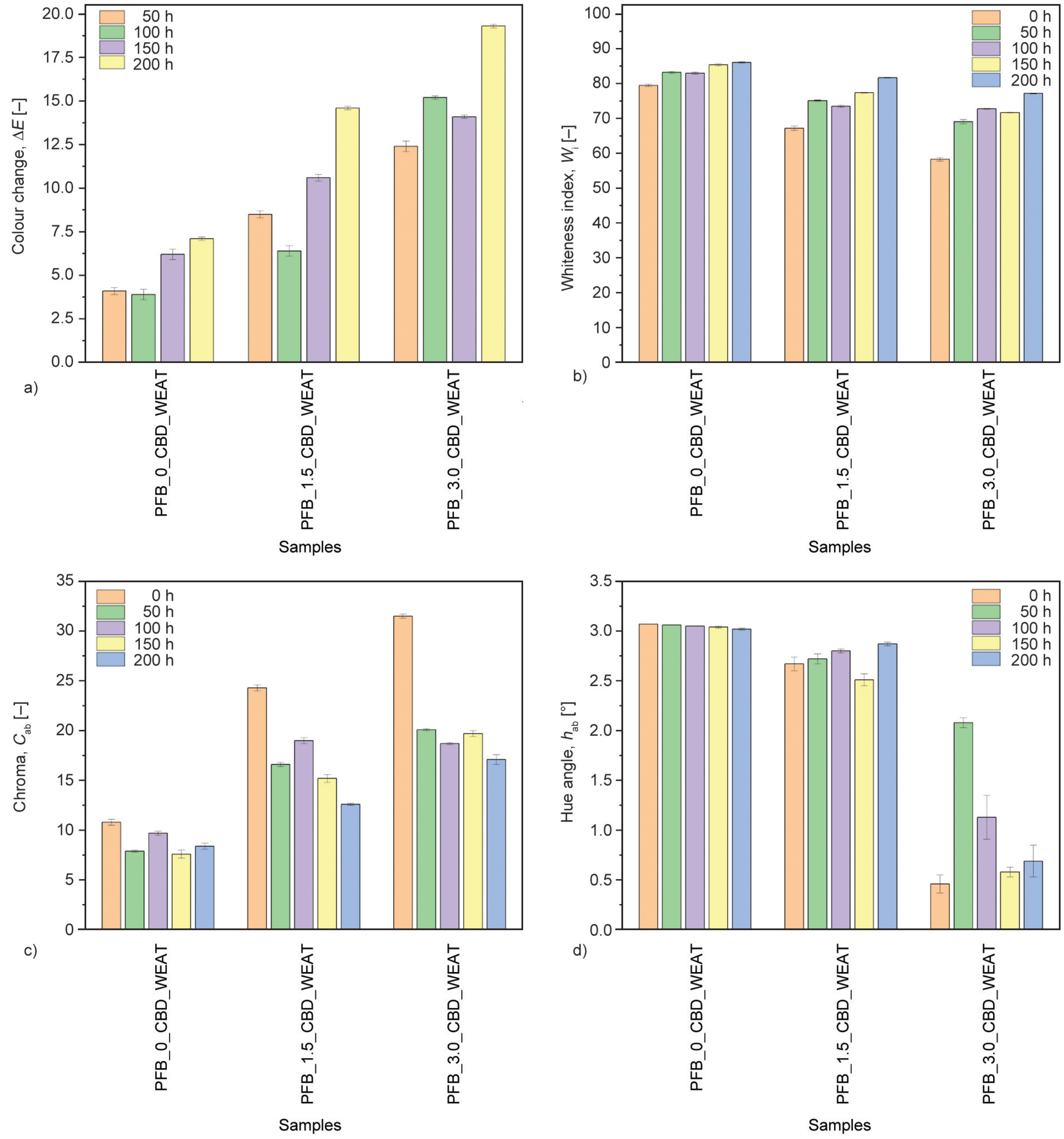

**Figure 9.** Spectrophotometric properties for PHB samples subjected to weathering a) color change, b) whiteness index, c) chroma, d) hue angle.

observed in the analysis of the PHB composite with 3.0 phr cannabidiol. This is likely attributed to the plasticizing effect of this compound on the material, resulting in a smoother extrudate surface. On the other hand, a persistent increase in the polar component may signal a disruption in the thermodynamic stability of the system and migration of the additive at elevated temperatures during aging. This can be corroborated by a significant rise in the polar component during degradation and the constant intensity of the absorption peaks previously observed in the FTIR spectrum.

### 3.5.2. PHB composite samples subjected to weather aging

The behavior of reference polyhydroxybutyrate samples under weathering conditions was also simulated. In this case, no clear trend was observed for changes in the values of the dispersed components and the total surface free energy during the aging process. However, the polar component exhibited a remarkable increase, approximately tenfold, in the final stage of aging for the reference sample. The incorporation of 1.5 phr extract resulted in an initial

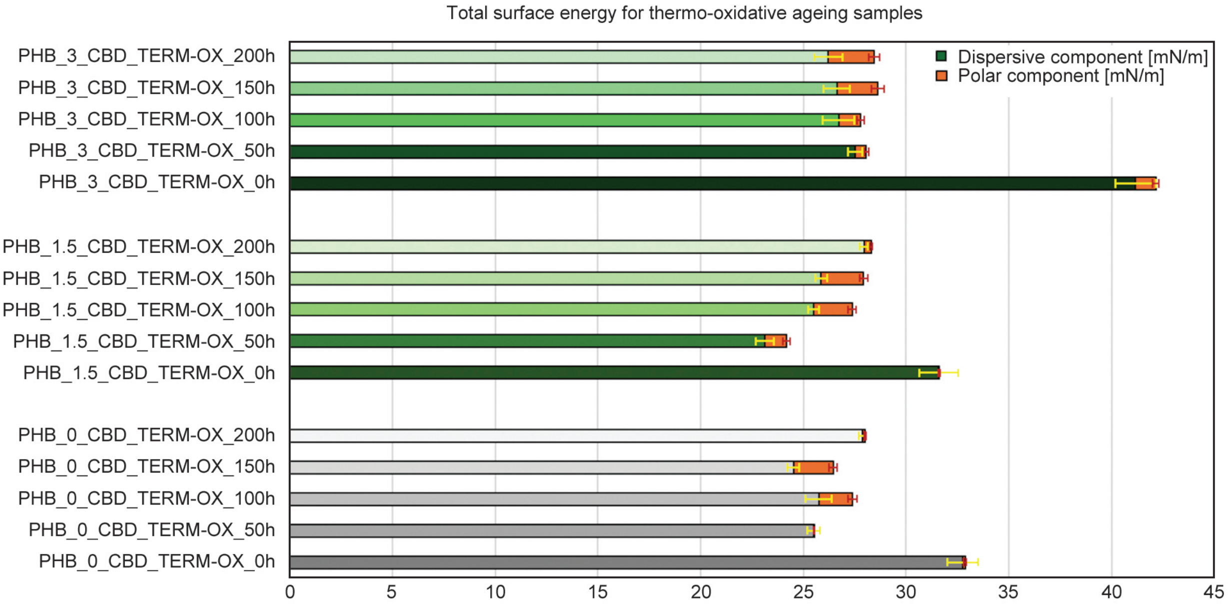

**Figure 10.** The distribution of surface free energy for PHB samples aged thermo-oxidatively.

increase in all SFE components, followed by a significant decrease in all but the polar component. This could be attributed to the disruption of the thermodynamic equilibrium in an initially stable system during weathering, leading to extract migration towards the composite surface. The increased polar component may also be indicative of the degradation of migrating additive at the surface, as further supported by the results obtained with 3.0 phr. In this case, a significant shift in SFE values occurred at 100 h of aging. Up to this point, all SFE components decreased, but after this time, they started increasing again, accompanied by a pronounced rise in the polar component, which can be observed in Figure 11. A comprehensive analysis of FTIR, IC, mechanical, spectrophotometric, and surface free energy (SFE) data suggests that CBD degradation proceeds via distinct mechanisms under thermo-oxidative and weathering conditions, leading to the formation of varying degradation products. However, further investigations are warranted to definitively establish whether the influence of water and light during hemp extract aging genuinely alters the degradation reaction pathways.

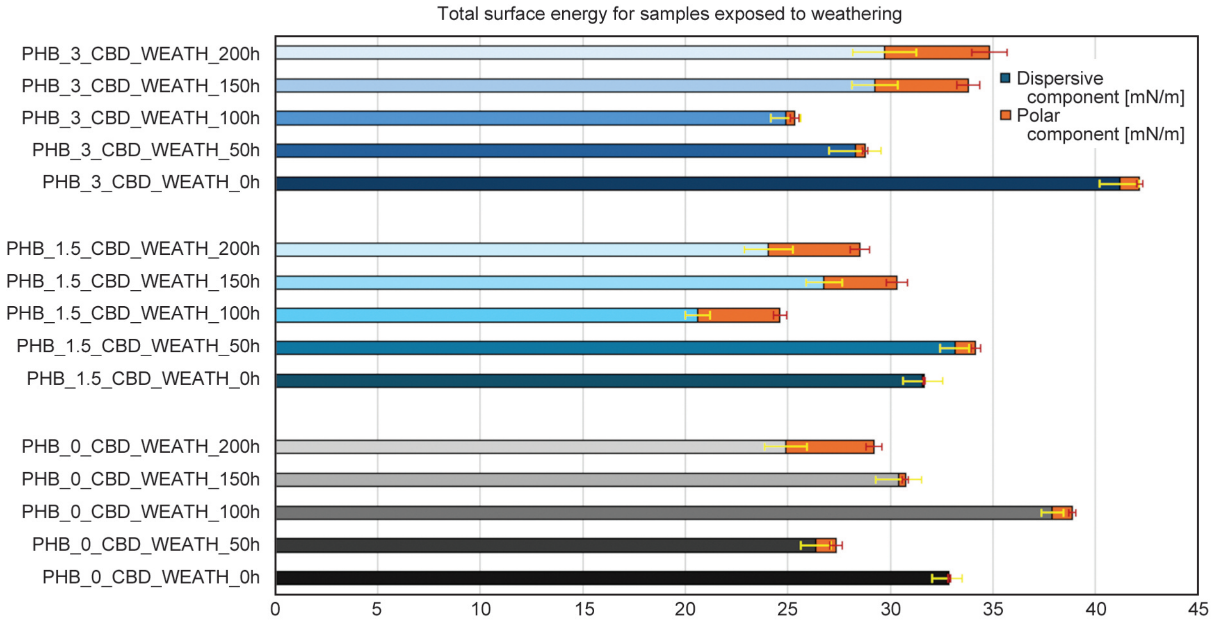

**Figure 11.** Surface free energy distribution for PHB samples subjected to weathering.

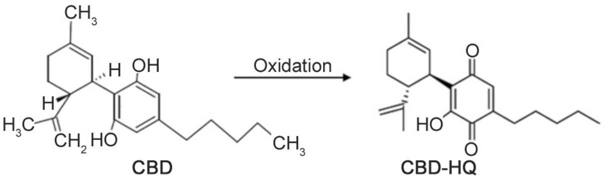

**Figure 12.** The potential oxidation reaction of CBD to CBD-HQ.

A noteworthy mechanism proposed by Caprioglio *et al*. [26] involves redox reactions of cannabinoids, yielding hydroxyquinones (CBC-HQ) and benzoquinones, which may possess oxidative properties, as illustrated in Figure 12. The possibility that these degradation products may significantly impact the degradation of the tested materials during later aging stages is highly probable. Based on the published findings, it is plausible to hypothesize that CBD undergoes oxidation to hydroxyquinone and then reduction to 1,4-*p*-benzoquinone. This reaction sequence may influence the reactions within the polymer-additive system, resulting in a sharp increase in the carbonyl index towards the end of the aging period. However, this hypothesis necessitates further in-depth research to thoroughly investigate the reaction mechanism and its products within the PHB-hemp extract system. Specifically, examining the effects of environmental factors like water and light, where derivatives react with water at elevated temperatures and are irradiated, is crucial [27, 28]. Thermo-oxidative aging may promote the formation of quinone compounds from CBD derivatives, contributing to the emergence of colorant substances that act as light absorbers. The incorporation of hemp extract as an additive in packaging materials represents a novel approach proposed by our research group. To date, there have been no published studies or commercial applications of this packaging additive, resulting in a dearth of specific regulations governing its use. While legislation pertaining to cannabinoids in pharmacology and the food industry exists, it varies widely across different jurisdictions, including major regulated markets such as the United States, the United Kingdom, and the European Union [29]. Hemp extract containing CBD is already utilized and permitted in various products, including dietary supplements, food additives, and cosmetics. Regarding the safety of oxidized forms of hemp extract additive components, there have been conflicting reports. While some studies have suggested potential negative effects on liver and kidney function, these claims have been refuted by subsequent research [30, 31]. Overall, these findings indicate the promising safety profile of hemp extract as an additive for polymeric packaging materials.

## 4. Conclusions

The findings presented in this study demonstrate that hemp extract, rich in cannabidiol and cannabichromene as natural antioxidants, exhibits a dual behavior, serving as a polymer degradation inhibitor under thermo-oxidative aging conditions while simultaneously acting as a catalyst for degradation in response to weathering factors [32, 33]. Notably, this observation was particularly evident in mechanical tests due to the significant material degradation induced by aging, rendering further testing impossible due to material breakdown. Spectral analysis of FTIR data and the calculated carbonyl index unequivocally confirm that both thermo-oxidative and weathering degradation of PHB composites supplemented with phytocompounds derived from hemp ultimately lead to alterations in the carbonyl index value relative to the reference sample subjected to extended testing. Evaluation of SFE revealed no significant difference in SFE values between hemp-extract-added samples after 200 h of thermo-oxidative aging and reference samples. However, under weathering conditions, SFE values exhibited greater temporal variability depending on the extract concentration. Intriguingly, these temporal variations in SFE components may serve as an indicator of the thermodynamic stability of the polymer-extract system. This assumption is supported by the holistic approach adopted in this study. The distinct thermodynamic stability and miscibility of these systems resulted in varying phase separation potentials, *i.e.*, different migration patterns of extract-borne compounds from the starting material to the surface of the samples. During migration, the value of the dispersed component typically decreased, while the value of the polar component generally increased. DSC analysis revealed a pronounced influence of hemp extract on the polymer's thermal properties. A marked decrease in the $T_g$ was observed, indicative of enhanced molecular mobility. Moreover, the $T_m$ exhibited a downward shift, accompanied by a reduction in the associated enthalpy, consistent with a plasticizing effect exerted by the extract. The lowered energy barrier for segmental motion, attributable to the presence of the extract, facilitated crystallization, potentially inducing morphological alterations in the material. Additionally, the onset temperature of oxidative degradation was elevated, signifying improved thermal stability. Collectively, these findings underscore the potential to tailor the polymer's properties through the incorporation of hemp extract, affording control over parameters such as processability and durability across a range of environmental conditions. Colored substances present in the extract function as efficient light absorbers, inducing structural modifications, redox reactions, and, ultimately, color changes. This mechanism may mitigate the impact of environmental factors on the tested polymer material. Analysis of color change outcomes corroborates this hypothesis. The main conclusion drawn from this research is the confirmation of the multi-faceted properties of hemp extract as an anti-aging and indicator agent in PHB-based materials under thermo-oxidative aging conditions. However, the most intriguing finding is its catalytic activity under aging conditions. This property presents an opportunity for tailoring the service life of manufactured polymer materials based on environmental exposure factors.

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