Red-Beetroot-Extract in the Biodegradable Polymers

Subjects: Materials Science, Composites

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This study investigated the effect of natural antioxidants inherent to beetroot (Beta vulgaris var. Vulgaris) on the ageing of environmentally friendly plastics. Certain properties were examined in this context, comprising thermal, mechanical, and morphological properties. A visual evaluation of relevant changes in the given polymers (polylactide and polycaprolactone) was conducted during an ageing test in a UV chamber (45 °C, 70% humidity) for 720 h. The films were prepared by a casting process, in which samples with the extract of beetroot were additionally incorporated in a common filler (bentonite), this serving as a carrier for the extract. The results showed the effect of the incorporated antioxidant, which was added to stabilize the biodegradable films. Its efficiency during the ageing test in the polymers tended to exceed or be comparable to that of the reference sample.

Keywords: polylactide ; polycaprolactone ; beetroot ; antioxidant ; biodegradable polymer ; abiotic stability ; degradation

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[1]1. Introduction

Numerous synthetic AOs are available commercially, yet few suitable natural AOs exist for packaging purposes, especially for active packaging [2][3][4]. Examples of widely used synthetics include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tertiary butylated hydroquinone (TBHQ) [5][6][7]. Research on natural AOs have centered around phenolics, polyphenolics, bioactive pigments, and tannin substances commonly obtained from plant extracts, such as coffee, cocoa [8][9], tea [10], grapes [11], citrus fruits [12], spices and medicinal herbs [13], and agricultural waste products (berries fruits or tuberous vegetables) [14].

Chief examples of bioactive pigments include betalains, which are present in high concentrations in beetroot (BR) (*Beta vulgaris)*. Betalains are often utilized in foodstuffs as a natural water-soluble colorant. There are two forms of betalain in BR, betacyanins (red-violet pigments) and betaxanthins (yellow-orange pigments) [15][16]. The antioxidant effect of betalains is much higher than those of many flavonoids, ascorbic acid, and tocopherols. It has also been shown that betalamic acid, the basic structure of all betalains, is therefore able to donate two electrons to an oxidizing agent [17][18].

However, betalains show sensitivity to stability influenced by factors that include degradation by heat, light, enzymes, and oxygen. During storage and processing, betalains can degrade, causing changes in color and antioxidant effect [15][19].

2. Analysis on Research Results

2.1. Characterization of Beetroot Extract (BRE)

The polyphenol content of the extract was quantified by Folin–Ciocalteu reagent (FCR) and such an assay was performed for the entire BR bulb. The results were evaluated according to the calibration series prepared, through application of the gallic acid standard. The various sections of the BR constituted significant sources of polyphenol. Indeed, the entirety of the BRE contained 93 mg (expressed as mg of gallic acid equivalent per 100 g of BRE). The content of polyphenolic substances in the BRE, as prepared in the ethanol solution (70%), reached similar values to those in the literature. This BRE was seen to remain stable under conditions of storage at low temperature (4–8 °C) in darkness for at least one month, with no significant change in polyphenol content [20][21].

The antioxidant activity of the BRE was evaluated by the 2,2-diphenyl-1-picrylhydrazyl (DPPH), a scavenging method widely deployed for evaluating antioxidant activity for relatively short durations, compared to other methods. The main attribute of AO is the neutralization of free radicals by donating an electron or hydrogen atom. In particular, polyphenols more often act as direct radical scavengers of the lipid peroxidation chain reaction (chain-breakers). The cessation of the reaction chain and the formation of a stable radical occurs upon the supply of an electron from the chain-breaker to the free radical, which it neutralizes [22][23]. The reducing ability of the DPPH radicals was determined by diminishing its absorbance at 517 nm, as induced by the AOs. The subsequent measurements revealed that the antioxidant activity of

the BRE corresponded to 114 mg per the equivalent amount of 100 g of ascorbic acid. The value for antioxidant activity, herein converted to the amount of ascorbic acid, is influenced by various aspects such as the type of BR storage, conditions, the environment of its cultivation, and the technique of extract preparation. This explains the wide variance reported in other publications, i.e., from 20 to 170 mg (expressed as mg of ascorbic acid equivalent per 100 g of BRE) [24] [25][26].

Figure 1 shows a representative total ion chromatogram (TIC) for the BRE from mass spectrometry in positive ion mode. On integration, the TIC exhibited several peaks evaluated as ms/ms fragmentation obtained arising through collision-induced dissociation. The peak at 2.98 min, a $[M + H]^+$ molecular peak of m/z 549.1336, presented a fragment of m/z 387.0809 and was consistent with previous findings on the fragmentation of neobetanin (**Figure 2**A) published in references [27][28]. The molecular ion at 2.49 min had a value for m/z of 551.1509, which, on dissociation, yielded fragments of m/z 389.0976 (**Figure 2**B) typical for betanin or isobetanin (2.61 min) [27][28][29]. In coelution with betanin and isobetanin, the following were identified: 2′-O-glucosyl-betanin (t_R = 2.52 min; $[M + H]^+$ = 713.2034) and 2′-O-glucosyl-isobetanin (t_R = 2.63 min; $[M + H]^+$ = 340.1132) [28]. Tentative identification was also performed on feruloylglucose at 3.55 min ($[M + H]^+$ = 357.1175), 5,5′,6,6′-tetrahydroxy-3,3′-biindolyl at 3.74 min ($[M + H]^+$ = 297.0874), betavulgarin at 5.35 min ($[M + H]^+$ = 313.0704), and cochliophilin A at 6.23 min ($[M + H]^+$ = 283.0604) [27][28].
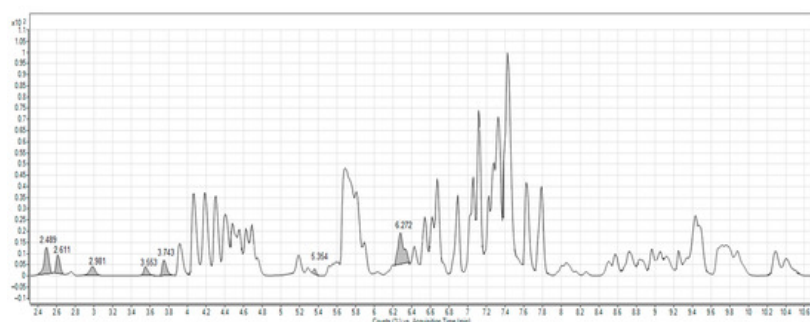

Figure 1. Representative TIC of diluted BRE; retention times were attributed by mass spectrometry analysis.
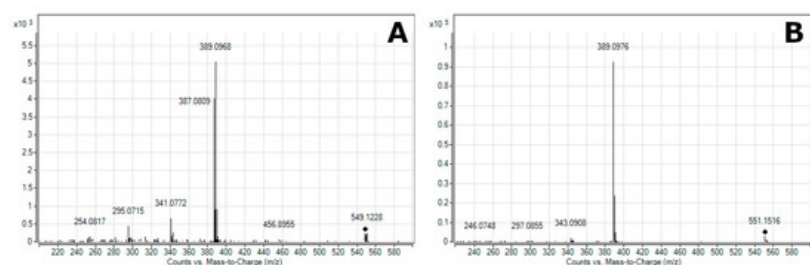

Figure 2. Positive electrospray tandem mass spectra for (**A**) neobetanin, and (**B**) betanin or isobetanin. The daughter ion of m/z 387.0809 was obtained by fragmentation of the parent ion of m/z 549.1228 of neobetanin. The daughter ion of m/z 389.0976 corresponds to protonated aglycone, and was obtained by fragmentation of the parent ion of m/z 551.1516 of betanin or isobetanin. The collision energy was 10 eV and 30 eV for (**A**) and (**B**), respectively.

2.2. Thermal Analysis

The applicability of polyphenol-containing BRE as a natural source of AOs added to polymers is crucially dictated by their thermal stability. The thermal properties of the prepared samples with natural AOs from BR were analyzed by DSC and TGA and were compared with the neat polymers (PLA and PCL) and these polymers with the BE carrier alone. A significant effect of ageing on the values of T_g for the PLA samples was observed after 720 h in the UV chamber (see **Table 1**). As a result of accelerated ageing, a clearly noticeable decrease in T_g values was observed for the neat PLA sample, potentially caused by two phenomena. First, low-molecular-weight compounds may have formed new macromolecules in the process of degradation, giving rise to plasticizing properties and lowering the glass transition temperature of the polymeric materials. Secondly, the macromolecules could have been shortened by breakage of the polymeric main chain. It is known that short macromolecules are characterized by low glass transition temperatures. As for the ageing study of semicrystalline PCL, it was not possible to compare the glass transition of the material (−60 °C) technically. Analysis of the PCL samples revealed that data on T_m could be evaluated, with neat PCL and PCL-BE samples showing two melting peaks (**Table 2**). The absolute values for the cold crystallization and enthalpy of melting of these samples are virtually identical, as ageing PCL often exhibits double-melting behavior, i.e., a stable melting structure at high temperatures and a less stable melting structure at lower temperatures [30].
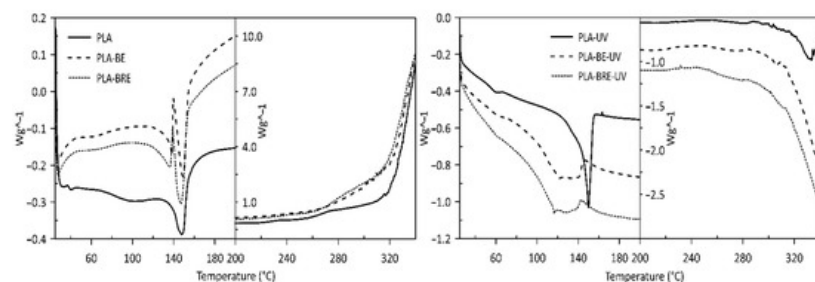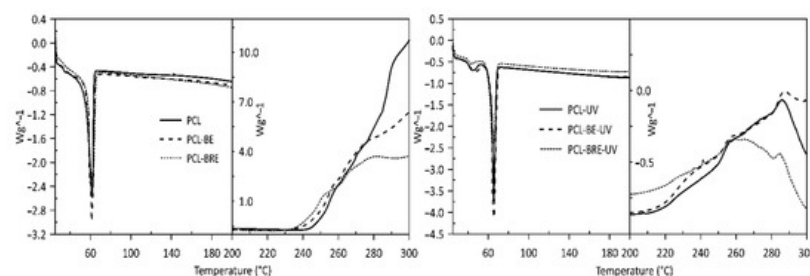
Table 1. DSC data for the neat PLA and PLA composites with bentonite and AO before and after the *UV ageing* test.

Sample	T_g [°C]	T_m [°C]	ΔH_m [J/g]	T_{onset} [°C]	T_{peak} [°C]	ΔH [J/g]
PLA	53	146	36	254	355	1805
PLA-BE	57	143	39	267	349	1564
PLA-BRE	57	145	38	265	347	1746
PLA-UV	49	151	42	212	-	-
PLA-BE-UV	53	133	37	216	-	-
PLA-BRE-UV	57	135	39	218	-	-

Table 2. DSC data for the neat PCL and PCL composites with bentonite and AO before and after the *UV ageing* test.

Sample	T_{m1} [°C]	T_{m2} [°C]	T_{cc} [°C]	ΔH_{cc} [J/g]	ΔH_m [J/g]	T_{onset} [°C]	T_{peak} [°C]	ΔH [J/g]
PCL	65	-	34	3	88	245	312	3168
PCL-BE	65	-	34	3	86	240	314	2254
PCL-BRE	66	-	35	3	90	236	281	1157
PCL-UV	66	39	26	3	92	215	286	254
PCL-BE-UV	64	38	36	3	99	216	288	307
PCL-BRE-UV	-	64	30	1	93	208	265	143

Visible changes were only observed in the thermal stability values of T_{peak} in the presence of oxygen, where samples with the carrier (bentonite) and the carrier with the AO demonstrated more rapid thermal degradation than samples comprising the pure polymers did. This phenomenon occurs to a lesser extent in the sample before PLA aging, especially in PLA-BE (**Table 1**, **Figure 3**). The primary difference between the polymers was the intrinsic enthalpy ΔH of the PCL-BRE samples (1157 J/g), which is by far the lowest. **Table 2** and **Figure 4** and reveal that the thermal degradation of the PCL-BRE samples proceeded slowly, more so than for the samples under comparison. In the case of PCL-BRE, the effect of the anti-degradant as an interrupter of the chain autooxidation reaction caused the formation of free radicals from the macromolecular chain to cease. Generally, the thermal decomposition of both polymers can be affected by several external abiotic factors, such as temperature, moisture content, or the presence of oxygen. Another important factor is that free radicals are responsible for the thermal degradation of these polymers. The thermal degradation of polymers is considered an inevitable effect under normal melt processing conditions. However, degradation can be prevented or slowed down by an inorganic filler or AOs [27][28].

Figure 3. DSC degradation test for the PLA samples under an oxygen atmosphere.

Figure 4. DSC degradation test for the PCL samples under an oxygen atmosphere.

The curves for the TGA, PLA, and PCL composites indicate the influence of not only bentonite, but also the AO on the stability of both materials after solar ageing. The PLA curves in **Figure 5** show that the initial release of moisture and other volatiles occurred first (a weight loss in the region below the thermal degradation). The onset of PLA-UV degradation was already apparent at 354 °C, appearing for PLA-BE-UV at 343 °C and PLA-BRE-UV at 347 °C. The main degradation peaks were visible at 340 °C for PLA-UV, at 331 °C for PLA-BE-UV, and at 335 °C for PLA-BRE-UV. Degradation was at a slower rate for PLA-BRE-UV manifested by an initially slower loss in mass (**Table 3**). The TGA curves in **Figure 6** describe the degradation process of the PCL materials. The effect of bentonite was obvious, reducing the rate of degradation for PCL-BE-UV to 367 °C and PCL-BRE-UV to 360 °C, whereas PCL-UV was evident at 335 °C [31][32].
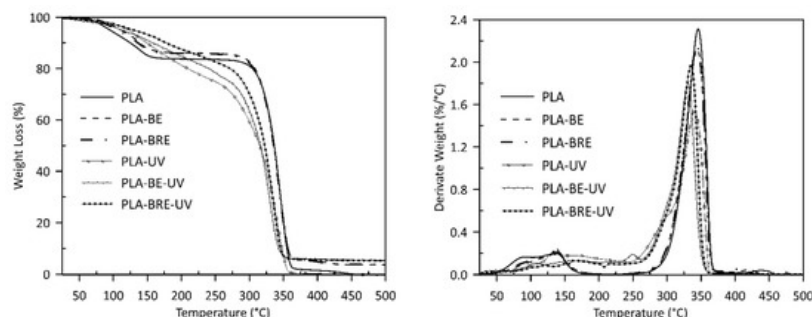

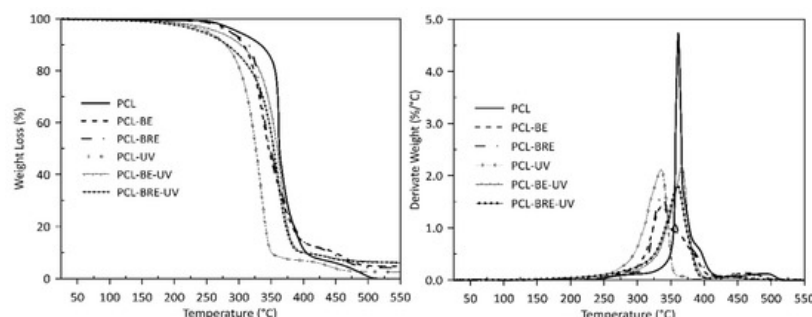**Figure 5.** Thermogravimetric response of PLA bentonite with AO alongside the reference samples.

Figure 6. Thermogravimetric response of PCL bentonite with AO alongside the reference samples.

Table 3. Summary of TGA curves for the PLA, PCL, and composites.

Samples	T_{onset} (°C)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	Mass Loss (%)
PLA	359	123	337	355	100
PLA-BE	358	140	336	357	95
PLA-BRE	357	136	335	356	95
PLA-UV	354	149	315	348	100
PLA-BE-UV	343	156	316	342	95
PLA-BRE-UV	347	175	322	346	95
PCL	368	333	363	350	100
PCL-BE	378	307	346	449	95
PCL-BRE	378	315	348	443	95
PCL-UV	350	278	326	350	99
PCL-BE-UV	381	302	359	397	95
PCL-BRE-UV	379	281	354	398	95

2.3. Mechanical Properties

The mechanical properties of the PLA and PCL composites were monitored prior to and following the artificial ageing test, and compared with the reference samples shown in **Figure 7** and **Figure 8**. The first of the parameters was monitored by Young's modulus (**Figure 7**). This parameter increased, especially in the case of aging PLA samples, where the material

became rigid and more brittle, caused mainly by the cleavage of the chains of macromolecules and the crosslinking. The maximum stress point (**Figure 8**) of the materials was also observed. A slight increase in this parameter was observed for composites with bentonite, which acted as a nucleation agent. Another important parameter concerned elongation at break (**Table 4**). For the PLA and PCL-based systems before ageing, adding a natural AO led to a rise in elastic modulus. The slight increase in elongation at break in all AO systems (PLA-BRE and PCL-BRE) in comparison with neat PLA and PCL and also PLA-BE and PCL-BE samples could be attributed to a plasticizing effect initiated by stabilizing molecules; indeed, it is known that low-molecular-weight molecules dispersed in polymeric matrices can increase the free volume of the system and reduce friction between macromolecules. PCL-BRE demonstrated a higher elongation of 1062% before aging, dropping to 375% after aging, and the reference sample showed a reduction from 1006% to 14%. The composite PLA-BRE prior to ageing exhibited 363%, and 9% afterward, whereas the relevant reference dropped from 357% to 24%. These types of chemical modifications of the polymeric materials, which occur in the photo-oxidation process due to decomposition reactions, are detrimental to the mechanical properties of the materials.
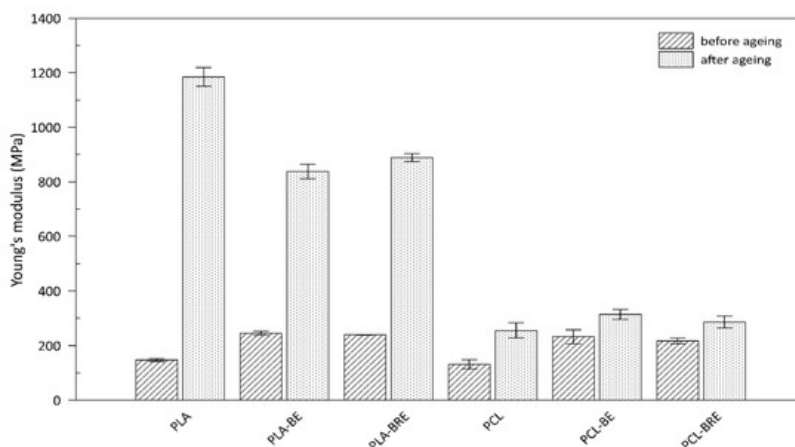

Figure 7. Mechanical properties of the PLA and PCL samples as per Young's modulus.
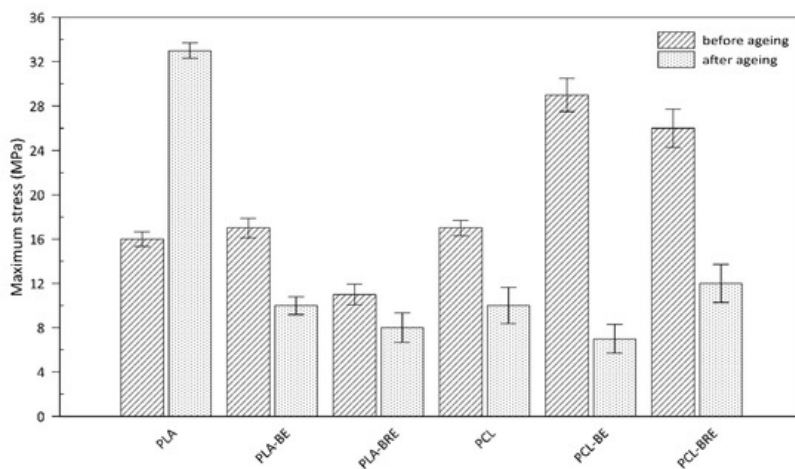

Figure 8. Mechanical properties of the PLA and PCL samples as per maximum stress.

Table 4. Comparison of the mechanical properties of the PLA and PCL composites prior to and following ageing; the ageing factor (A_f) was calculated according to Equation (1).

Samples	Before Solar Ageing		After Solar Ageing		A_f (−)
	σ (MPa)	ε (%)	σ (MPa)	ε (%)	
PLA	15 ± 1	354 ± 18	16 ± 2	24 ± 6	0.07 ± 0.01
PLA-BE	16 ± 2	301 ± 25	6 ± 2	5 ± 1	0.01 ± 0.00
PLA-BRE	10 ± 1	363 ± 14	1 ± 1	9 ± 1	0.00 ± 0.00
PCL	17 ± 1	1006 ± 9	8 ± 3	14 ± 6	0.01 ± 0.01
PCL-BE	22 ± 2	1008 ± 6	6 ± 3	8 ± 3	0.00 ± 0.01
PCL-BRE	22 ± 2	1062 ± 8	11± 3	375 ± 42	0.15 ± 0.00

According to the results illustrated in **Table 4** as per the ageing factor (A_f), the reference sample PLA appeared to be the most stable under extreme conditions in the climatic chamber. PCL samples supplemented with the AO from BRE also exhibited a suitable ageing factor (A_f). This study showed a low effect of natural AO from BR, i.e., BRE could reduce the amount of synthetic AO in degradable polymer formulations, especially PCL-based ones. Hydrolytic degradation of the chains in PLA occurs primarily on the surface and preferably in amorphous regions [32][33].

2.4. Colour Measurement

It is known that additives applied to change the color of polymeric materials in food packaging can affect the overall appearance and, thus, the consumer. In particular, light in the UV region can trigger photooxidation processes, with the potential rapid loss in quality or deterioration of the packaged foodstuffs as a consequence, making such a step undesirable [34], although unwanted alteration may occur in the original color during transport and storage. It is important to examine the effect of these additives on the individual properties of the materials. The results presented herein reveal the effect of current natural additions of bentonite and extract on the biopolymers (**Figure 9** and **Figure 10**). The altered color of all the films was immediately noticeable, in that they turned a shade of yellow. In the case of the PLA films, the change was most pronounced in the sample containing only bentonite. The color change index (ΔE) for this was 29, i.e., the same value for the neat PCL sample (**Figure 9**). In contrast, the lowest values were evident for the samples with BRE, and the color change index equaled 17 in both cases. During the ageing test, a significant alteration occurred in chromium (C_{ab}) in the biopolymer samples only supplemented with bentonite. The whiteness index (W_i) increased in all the samples due to a change in the transparency of the materials, and a slight haze appeared during ageing. For these reasons, incorporating such natural dyes in the given polymers would reveal the degree of degradation and could be used as indicators (**Figure 10**).
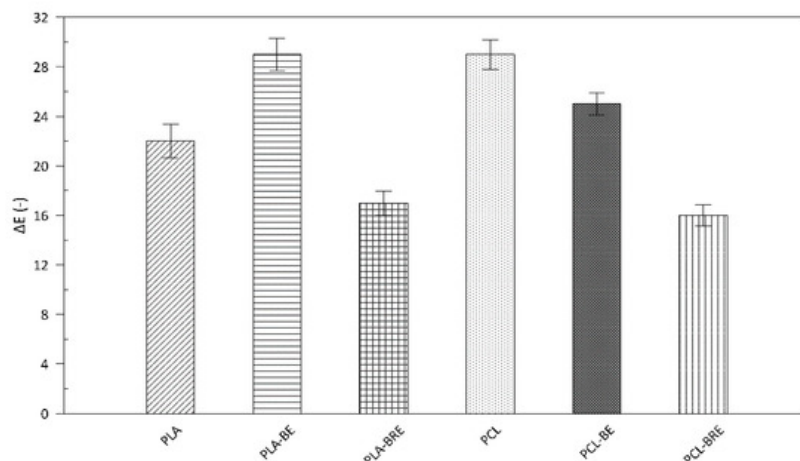

Figure 9. Color change (ΔE) in the PLA and PCL composites with bentonite and natural AOs, compared with the reference of pure PLA and PCL; calculations were performed according to Equation (2).
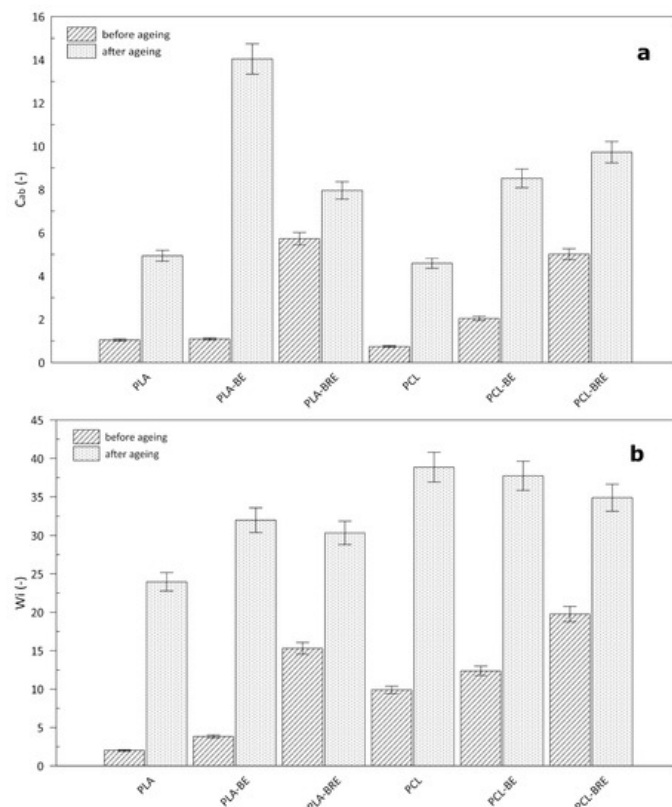
Figure 10. Impact of solar ageing on (**a**) chroma (C_{ab}) and (**b**) the whiteness index (W_i); calculations were performed according to Equations (3) and (4).

2.5. Fourier-Transform Infrared Spectroscopy (FT-IR)

The effect of ageing on the PLA and PCL films was determined by FTIR, thereby gauging the extent of alteration in chemical structure. The subject of this measurement was to monitor changes in structures due to the added BRE. **Figure 11** displays spectra for the PLA before and after exposure to UV. The ester bonds (C(=O)-O-C) of PLA located in the bands 1088 cm^{-1} and 1183 cm^{-1} represented sensitive groups mainly (C-O-C) in the process of solar aging. The bands observed at 1383 cm^{-1} and 1455 cm^{-1} were caused by CH_3 asymmetric and symmetric deformation. Other characteristic PLA peaks at 1756 cm^{-1} corresponded to (C=O) carbonyl groups. The intensity of the aforementioned sensitive bands decreased through UV radiation. To conclude, the samples of neat PLA demonstrated a significant decrease in the characteristic bands, mainly due to photodegradation or thermal degradation of the polymer structure. Certain peaks for PLA-UV in the region of 1654 cm^{-1} were also discerned, indicating the formation of anhydride groups upon degradation [35][36].
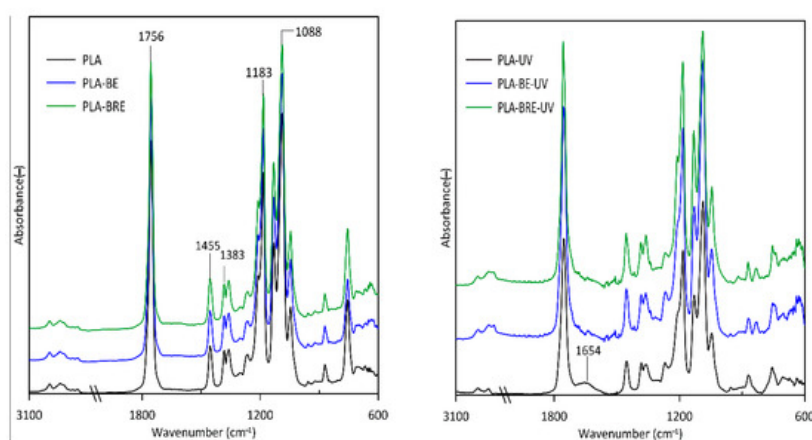

Figure 11. FTIR spectra for the PLA and PLA composite films prior to and following exposure in a UV chamber.

The main peaks characteristic of the PCL material (**Figure 12**) were found primarily in the regions of 2865 cm^{-1} and 2945 cm^{-1}, representing symmetric and asymmetric bending vibrations of the methylene unit. Another was a peak at 1724 cm^{-1} pertaining to the stretching of the carbonyl of the ester group. It is possible that C-O-C bands corresponded to the peaks at 1187 cm^{-1} and 1241 cm^{-1}. The PCL samples underwent degradation upon exposure to the UV chamber and

temperature, revealed through heightened peaks for the carbonyl groups, thereby suggesting the formation of radicals in the PCL macromolecules. In the case of PCL-UV, the main peak broadened at 1724 cm^{-1} [37][38].
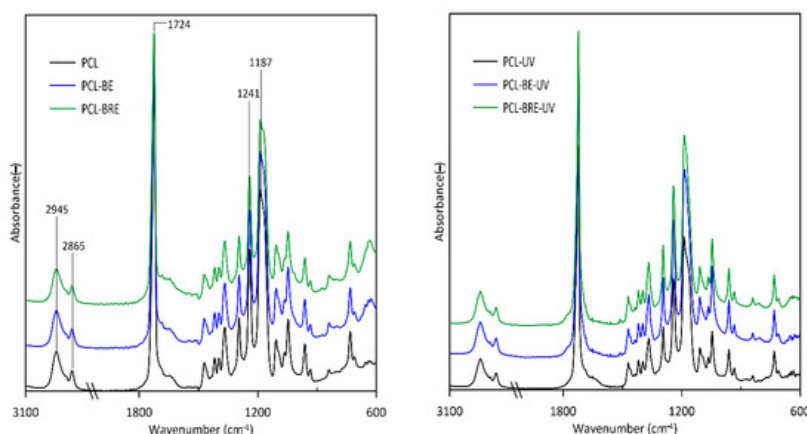

Figure 12. FTIR spectra for the PCL and PCL composite films prior to and following exposure in a UV chamber.

Although no structural chemical changes were observed in both matrices after the addition of BE and BRE (before the UV chamber), there were minor changes in individual cases after exposure to the UV chamber.

However, all the samples experienced partial degradation, additionally affected by the higher temperature in the UV chamber; this acted on the material for a relatively long time; therefore, it is not possible to directly deduce any unambiguous effect by the BRE.

2.6. Scanning Electron Microscopy (SEM)

SEM images of fracture surfaces of PLA and PCL samples (**Figure 13**A–F and **Figure 14**A–F) detail changes before and after exposure in the UV chamber, at 1000× magnification, but also sample surfaces after the UV chamber (G–I), at 270× magnification. SEM images made it possible to monitor the surface changes caused by the UV chamber environment. It was also possible to observe stratification and homogeneity of the added filler at the fractures of the samples. The degradation process was evident after four weeks in the UV chamber, with cracks, cavities, and peeling fragments visible in both materials [37][38]. However, PLA samples showed lower changes after exposure in the UV chamber than PCL samples did. Degradation was best observed on the surface of PCL, which was significantly degraded by visible cavities after exposure. Samples of PLA and PCL containing BRE also showed signs of degradation, although these manifestations were mild and affected only a thin surface layer.
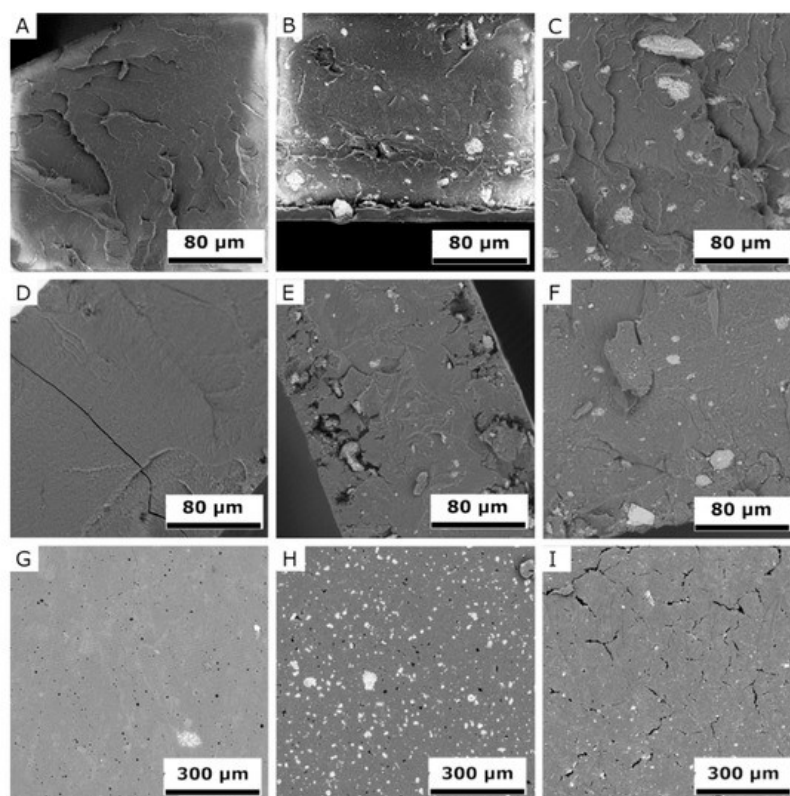
Figure 13. SEM images detailing change in the PLA samples prior to and following exposure in a UV chamber; the fracture surfaces of samples (**A**) PLA, (**B**) PLA-BE, (**C**) PLA-BRE, (**D**) PLA-UV, (**E**) PLA-BE-UV, and (**F**) PLA-BRE-UV; and the surfaces of the samples (**G**) PLA-UV, (**H**) PLA-BE-UV, and (**I**) PLA-BRE-UV.
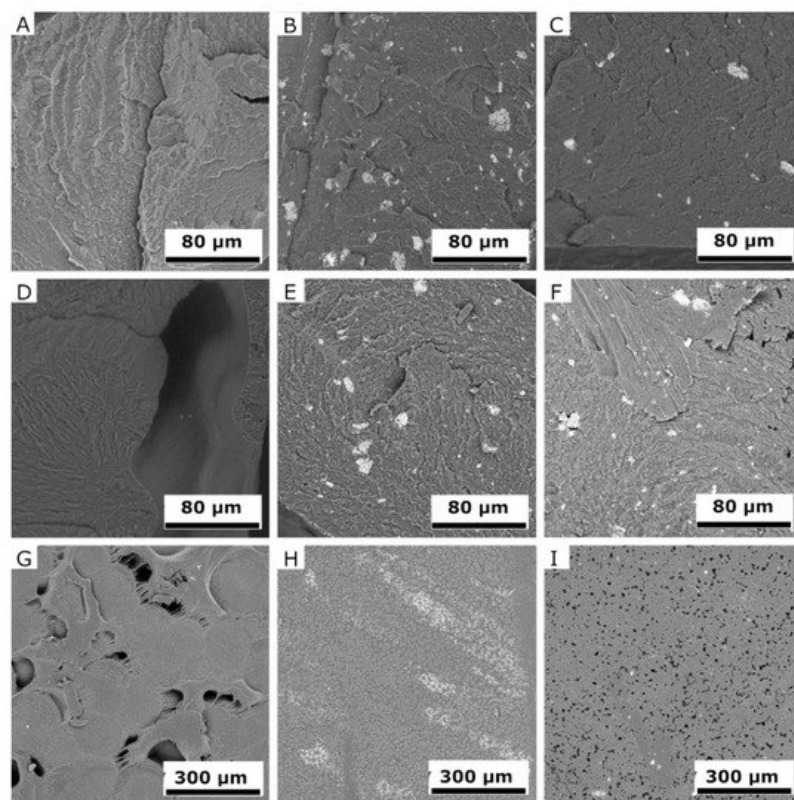

Figure 14. SEM images detailing change in the PCL samples prior to and following exposure in a UV chamber: the fracture surfaces of samples (**A**) PCL, (**B**) PCL-BE, (**C**) PCL-BRE, (**D**) PCL-UV, (**E**) PCL-BE-UV, and (**F**) PCL-BRE-UV; and the surfaces of samples (**G**) PCL-UV, (**H**) PCL-BE-UV, and (**I**) PCL-BRE-UV.

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