

Biodegradable PLA-based materials modified by hemp extract

Karol Tutek

Lodz University of Technology

A.M. Masek (✉ anna.masek@p.lodz.pl)

Lodz University of Technology

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Abstract

Biodegradable and compostable polymers are sensitive to environmental factors. For this reason, they require stabilisers that inhibit ageing and degradation processes. Until now, synthetic stabilisers have been used in the polymer industry, but in recent years, in the era of environmentally friendly solutions, naturally occurring compounds have started to be used. It has become increasingly popular to create composites that are entirely of natural origin. An example of a natural stabiliser is hemp extract, which is presented and studied in this paper. It was applied to a polymer matrix made of polylactide. The samples were subjected to weathering and thermo-oxidative ageing, followed by infrared spectroscopic, spectrophotometric, static-mechanical and surface-free energy analyses. The results obtained confirm the validity of the assumption of an inhibitory ageing effect of hemp extract in the case of thermo-oxidative ageing and, very interestingly, of a catalytic effect in the case of weathering. Research on the use of this type of stabiliser in polymer composites is a scientific novelty that no one has investigated in polymer materials to date. This topic needs to be explored further due to the increasing interest and importance of hemp and its derivatives as materials and functional substances.

1. Introduction

Polymeric materials have defined tremendous human progress from the second half of the 20th century to the present day. A branch of this science and industry has been developing smoothly and continuously for decades, affecting everyone's life and development. Polymers are now the most popular material used around the world due to a number of their specific properties such as lightness, ease of processing, durability, simplicity of customization and, above all, low price. These qualities are like two sides of a coin, they are not only advantages but also disadvantages. Because of them, over the past decades their production, especially of disposable packaging, has increased on an unimaginable scale, which has caused a waste problem that is ubiquitous both in landfills and everywhere on land and in the sea. For this reason, current research is focusing on creating usable polymeric materials that would combine the best features of traditional polymers and be more easily, and preferably also controllably, biodegradable. One approach to the development of environmentally friendly polymeric materials is the use of substances derived from fauna and flora in composites[1–4]. For this reason, more and more research work is focusing on the use of biopolymers, e.g. cellulose, gelatin, agar, and chitin. It is also possible to create materials from polymers of natural origin, which can be obtained by biotechnology from products that are typically wasted in other industries. Examples of such materials are polyalkanoates (PHA), polylactide (PLA), poly(butylene succinate) (PBS), or polycaprolactone (PCL). All of the aforementioned polymers have satisfactory compostability or biodegradability[5–8]. However, their durability during use is uneven, and for this reason, they often require modification. One such possible modification is the introduction of various types of stabilizers to protect the polymers from environmental factors such as moisture, temperature, light, microorganisms and oxygen. It is possible to use synthetic stabilizers which are expensive and often toxic, precluding their use in food contact or medical products. In recent years, however, there has been a trend toward the use of natural plant-derived stabilizers based on polyphenols:

phenolic acids, stilbenes, anthocyanins or flavonoids[9–13]. In the research for the ninth article, we leaned on hemp seed extract containing such groups of compounds as monoterpenes, sesquiterpenes, terpenoids, cannabinoids, and unsaturated and saturated fatty acids[14–20].

Hemp extracts have recently become a popular addition to cosmetics to slow down the ageing process, as dietary supplements or additives to so-called superfoods. The premise of the study was to use crude hemp extract as a polylactide stabilizer against environmental conditions, which exhibits strong anti-inflammatory and antioxidant effects due to its polyphenolic compounds[22–24]. It is also a safe additive with health-promoting properties. As indicated in the publication "Hemp and its Derivatives as a Universal Industrial Raw Material. "Hemp and Its Derivatives as a Universal Industrial Raw Material (with Particular Emphasis on the Polymer Industry)-A Review", hemp is a raw material with possibly an extremely wide range of feedstocks, and the polymer industry could be one of its biggest beneficiaries[21]. To date, the effect of hemp extract as a stabiliser on the biopolymer matrix has not been investigated more extensively, something we have chosen to undertake successfully as the first in our research for this article.

2. Experimental

2.1 Materials

PLA is a thermoplastic polymer manufactured by NatureWorks LLC[®], Minnetonka, USA. Biopolymer with the trade name Ingeo[™] 4043D. This material is polylactide with CAS number 9051-89-2. This polylactide is characterized by a density of 1.24g/cm³, a glass transition temperature of 328-333K, a pour point of 418-433K and a melt flow index MFI of 6g / 10min at a nominal load of 2.16 kg and a temperature of 483K.

The active substance used to functionalize the above-mentioned polymers was a hemp extract obtained by extraction under supercritical conditions and containing significant amounts of cannabidiol (CBD). It is a natural compound from the cannabinoid family found commonly in the cannabis plant. It was provided as a commercial sample in cooperation with a Lithuanian company dealing with the production of CBD.

2.2 Methods

2.2.1 Preparation of sample

For the PLA thermoplastic-based samples, the granules were pre-dried for 24 hours in a laboratory dryer at 50°C to get rid of excess moisture from the hydrophilic granules. After this time, appropriate amounts of granules (data are given in the table below) and hemp extract were measured on a laboratory balance, which was premixed manually with a laboratory spoon in a beaker, and the resulting mixture was placed in a laboratory extruder equipped with a single screw with a diameter of 25 mm and a length to diameter ratio of L / D 24 (Zamak Maercator, Skawin, Poland). The extrusion process parameters for PLA-based

samples were as follows: extrusion temperature 180°C, pressure 17 atm. and screw speed 40 rpm. The extrusion resulted in flat strip-shaped samples about 1250 mm long, about 25 mm wide and about 1.5 mm thick. The samples were cooled at room temperature and then conditioned for 7 days under the same conditions.

Table 1
Composition and processing conditions
for PLA materials.

Component	Poly lactide (PLA)
Cannabidiol (CBD) [phr]	0.0
	1.5
	3.0
Temp. extrusion [°C]	180

2.2.2 The process of the weather ageing

Some of the samples were aged using a Weather-Ometer Ci 4000 chamber with a xenon lamp by Atlas Material Testing Technology LLC (Chicago, IL, USA) following the PN-EN 4892-2 standard. Ageing was divided into 2 day and night segments which were repeated one after the other. The first one lasted 900 minutes, during which the radiation intensity was 60.4W/m² and the relative humidity was 80%. The chamber temperature was 70°C and the panel temperature was 60°C. Rainfall was ruled out. The second episode lasted 600 minutes. During its duration, the radiation was turned off and the relative humidity dropped to 70%. The chamber temperature was 40°C and the panel temperature was 50°C. The rainfall simulation function was still turned off. The PLA-based samples were kept in the chamber for 50, 100, 150 and 200 hours.

2.2.3 The process of the thermo-oxidative ageing

The thermo-oxidative ageing was carried out in a Binden FD series dryer (Tuttlingen, Germany). Samples of individual polymer materials were suspended vertically with clips, which is important that each was exposed to free air circulation. The temperature of the chamber interior during the entire process was 75°C, these samples were aged in an air atmosphere that contained oxygen, and in the absence of light and excessive humidity. The PLA-based materials were aged at intervals of 50, 100, 150 and 200 hours.

Table 2
Parameters for ageing processes.

Component	Poly lactide
Abbreviation	[PLA]
Ageing time [h]	0
	50
	100
	150
	200
Ageing type	Unaged
	Weathering
	Thermo-oxidative [75°C]

2.2.4 Fourier Transform Infrared Spectroscopy Attenuated Reflectance (FTIR- ATR) Analysis

The previously prepared reference and aged samples of polymer composites with the two above-mentioned methods were tested for the content of functional groups using the Thermo Scientific Nicolet 6700 FT-IR spectrophotometer, which performs absorption measurements with the Fourier transform in the spectrum with a wave number of 4000-400cm⁻¹ using an adapter diamond Smart Orbit ATR attachment in absorption mode and 64 scans with a resolution of 4cm⁻¹. The results of the research were spectra, and their analysis allowed for the assessment of changes in the intensity of the occurrence of various types of functional groups as a result of changes in the composition through the addition of hemp extract and as a result of ageing weathering and thermo-oxidative ageing.

Additionally, the research allowed for the analysis of changes in the intensity of signals from the carbonyl band (C = O). As a result, based on the obtained spectrum, the carbonyl index (CI) was calculated for the samples before and after the ageing simulations. Based on the following equation, the values of the individual carbonyl indices were calculated:

$$CI = \frac{I_{C=O}}{I_{C-H}}$$

Where:

- CI - carbonyl index [-]
- $I_{(C=O)}$ - the total intensity of peaks corresponding to signals from carboxyl groups (C = O) in the wavenumber range from 1600 to 1865cm⁻¹

- $I_{(C-H)}$ - the total peak intensity corresponding to the signals from groups (C-H) in the wavenumber range from 2800 to 3040 cm^{-1} for samples based on thermoplastics

2.2.5 Measurement using spectrophotometry

As part of a series of tests, an analysis of the colour change of previously made samples of extrudates before and after the ageing processes was carried out following the PN-EN ISO 105-J01 standard. For this purpose, the Konica Minolta Sensing Inc. UV-VIS CM-3600d spectrometer was used. (Osaka, Japan). Three tests were performed for each analyzed material. The range of spectral spectrum was in the range of 360 to 740 nm, and its source was a xenon lamp performing four pulses. This apparatus measures the signal that is reflected from the surface of the test object and converts it into a result expressed by the colour perceived by the human eye. The obtained results were data on the CIE-Lab scale. It is based on the following parameters:

- The "a" coordinate axis for which positive values correspond to red and negative values correspond to green
- the "b" coordinate axis for which positive values correspond to yellow and negative to blue
- the "L" coordinate axis where the value of 100 corresponds to the brightest indicator and the value of 0 corresponds to black

Thanks to the obtained measurement data, it was possible to convert the obtained results into more widely used indicators of colour change, such as:

- the colour difference (dE)
- chroma (C_{ab})
- whiteness index (W_i)
- hue angle (h_{ab})

These indicators express the following formulas:

$$dE = \sqrt{(\Delta a)^2 + (\Delta b)^2 + (L)^2}$$

$$C_{ab} = \sqrt{a^2 + b^2}$$

$$W_i = \sqrt{a^2 + b^2 + (100 - L)^2}$$

$$h_{ab} = \begin{cases} \arctg\left(\frac{b}{a}\right) & as(a > 0 \cap b > 0) \\ 180^\circ + \arctg\left(\frac{b}{a}\right) & as(a < 0 \cap b > 0) \cup (a < 0 \cap b < 0) \\ 360^\circ + \arctg\left(\frac{b}{a}\right) & as(a > 0 \cap b < 0) \end{cases}$$

2.2.6 The analysis of the static mechanical properties

Testing of mechanical strength under static conditions of specimens made of PLA, "dumbbell" shapes with the above-mentioned dimensions were made, but the measurements were carried out on a Zwick-Roell Z005 machine intended for thermoplastics. In this case, 2 tests were performed for each material sample. Extrudate samples with a gauge length of 75 mm were measured with a thickness gauge and the width was measured with a calliper. The samples placed between the jaws of the apparatus were stretched at a speed of 50 mm/min. The parameters of the maximum tensile strength (T_{Fmax}), ultimate tensile strength (TS), elongation at break (Eb) and elongation at maximum strength (E_{Fmax}) were determined for the PLA-based samples.

Additionally, based on the obtained data, the ageing coefficient of the polymer (K) was calculated from the obtained TS and EB data before and after ageing based on the following formula:

$$K = \frac{(TS \bullet Eb)_{afteraging}}{(TS \bullet Eb)_{beforeaging}}$$

Where:

- K – Ageing coefficient [-]
- TS – Tensile strength [MPa]
- Eb – Elongation at break

2.2.7 Determination of Surface Free Energy (SFE)

Apart from the research mentioned in the previous section, surface free energy (SFE) was also determined. It was measured by determining the contact angle of previously prepared samples before and after the ageing processes. The SEF was determined using an OCA 15EC goniometer from DataPhysics Instruments GmbH (Filderstadt, Germany) and SCA 20 software for analysis of results and calculations. The device is equipped with a Braun DS-D 1000 SF syringe with a needle 38.1 mm long, an external diameter of 0.52 mm and an internal diameter of 0.25 mm. The obtained drops were a volume of 1 μ l. For each sample prepared, at least 10 results were obtained.

For the determination of the surface free energy and calculations according to the Owens-Wendt-Rabel-Kaelble method (OWRK), in which the geometric mean of the dispersion and polar components of the

surface tension of a liquid and the same components of the surface energy of the solid are included and shown in the equation below. The following 3 types of liquids were used for SFE measurements:

- Water – surface free energy 72.6 (mJ/m²)
- Ethylene glycol - surface free energy 47.7 (mJ/m²)
- Diiodomethane - surface free energy 50.8 (mJ/m²)

$$\gamma_s = \gamma_s^P + \gamma_s^D$$

$$(\gamma_s^P)^{0,5} = \frac{\gamma_w \cdot (\cos\theta_w + 1) - 2 \cdot 2 \cdot \sqrt{\gamma_w^D - \gamma_s^D}}{2 \cdot \sqrt{\gamma_w^P}}$$

$$(\gamma_s^D)^{0,5} = \frac{\gamma_D \cdot (\cos\theta_D + 1) - \sqrt{\frac{\gamma_D^P}{\gamma_w^P}} \cdot \gamma_w \cdot (\cos\theta_w + 1)}{2 \cdot \left[\sqrt{\gamma_D^D} - \sqrt{\gamma_D^P \cdot \frac{\gamma_w^D}{\gamma_w^P}} \right]}$$

Where:

- γ_s – total surface free energy of the sample [(mJ)/m²]
- γ_s^P – polar component of the sample's surface free energy [(mJ)/m²]
- γ_s^D – dispersion component of the sample surface free energy [(mJ)/m²]
- θ – contact angle [°]
- γ_w - total free surface energy of water 72.6 [(mJ)/m²]
- γ_w^P, γ_w^D - respectively: polar (51.0) and dispersive (21.6) components of the surface free energy of water [(mJ)/m²]
- γ_D - total surface tension of diiodomethane 50.8 [(mJ)/m²]
- γ_D^P, γ_D^D - respectively: polar (2.3) and dispersive (48.5) components of the surface free energy of diiodomethane [(mJ)/m²]

3. Results And Discussion

3.1 Fourier transform infrared spectroscopy (FTIR) measurement results

The correct interpretation of absorbance spectra from the relevant chemical groups present in the material requires knowledge of the wavenumbers at which peaks from characteristics of their functional

groups. The analysis of the FTIR spectrum focused on signals from carbonyl groups, which are one of the most important indicators of degradation of polymeric materials. For this reason, the infrared spectrum analysis using the Fourier transform was used to show and approximate the likely degradation processes that may have occurred during appropriate ageing.

The figure above shows the spectrum of CBD-containing hemp extract. Peaks from 3067 to 2854cm^{-1} are visible, probably indicative of strong CH-stretching vibrations in alkanes and alkenes and -OH in intramolecular bonds. In the peak for wave number 1708cm^{-1} , there is a stretching vibration of the C = O groupings. At the peaks between 1708 and 1578cm^{-1} , C = O and C = C stretching vibrations in alkenes are most likely shown (as may be indicated by the structure of CBD and the formation of an intramolecular cyclic bond). In 1444cm^{-1} methyl bending vibrations and similarly in 1376cm^{-1} -OH bending in phenolic derivatives. The peaks between wavenumber 1242 and 1028cm^{-1} are likely indicative of a -CO tensile drag. Peaks between 887 and 801cm^{-1} indicate 1,3 substitutions and 731cm^{-1} indicate 1,2 substitutions or derivatives of benzene. Analysis of the FTIR spectrum shows that the main component of the cannabis extract used is cannabidiol, which gives characteristic signals in the absorbance curve presented above.

3.1.1 FTIR spectra analysis for PLA-based composites samples

The peaks around 2900cm^{-1} are characteristic of the CH stretching vibrations in PLA, while the 1746cm^{-1} signal the vibrations stretching C = O aldehydes/lactones/esters. The peaks for the wavenumber 1451 and 1359cm^{-1} are the C-H bending vibrations in aldehydes and alkanes and the methyl group. The peaks at 1266 and 1080 and 1043cm^{-1} are C-O stretching vibrations (especially in the ethers). In the case of PLA composites with a hemp derivative, the characteristic bands of this substance are not visible in the spectrum. There is only an increase in intensity, without the appearance of new peaks, which eliminates the direct analysis of changes in the presence of active compounds contained in the extract on the spectra visible for PLA. However, the addition of cannabis extract causes an increase in the intensity of signals in the FTIR spectrum, especially visible for the bands with wavelengths 1746 , 1179 and 1078cm^{-1} , which correspond to the signals from the C = O group. The addition of 1.5 phr causes an average increase of these intensities by about 80%, and the addition of 3.0 phr CBD by about 220% compared to the reference sample. Such a result may indicate the migration of the hemp extract to the surface of the sample.

Thermo-oxidative ageing has an interesting effect on the PLA composite with the addition of a hemp derivative. The lowest intensity values - about 35% of the reference sample value - are obtained after adding 1.5 phr of the extract, slightly higher values of 45% of the reference sample peak intensity for 3.0 phr of added cannabidiol and much more intense without addition. This may indicate the stabilizing effect of CBD on PLA during thermo-oxidative ageing. However, at 1.5 phr CBD is most likely completely degraded, and at 3.0 phr some undegraded compound remains on the surface of the composite. Based

on the obtained results, it is possible to postulate a process in which the anti-ageing compound, which is cannabidiol, is decomposed first, and then the polymer is degraded.

In the case of the ageing process of the weather degradation process, we can see that the intensity of the peaks in the spectrum increases with the increase in the content of the hemp derivative in the composition of the PLA-based composite. Correspondingly, for the addition of 1.5 phr cannabidiol on average 145% and for the addition of 3.0 phr CBD about 165% compared to the reference sample. Comparing the simulation results of both types of ageing, it can be concluded that the increased amount of moisture and access to light cause different reactions during ageing. This can occur through the different degradation mechanisms of the cannabis derivative due to these different environmental conditions.

3.1.2 Calculation results and carbonyl index analysis

Based on the data collected during the Fourier transform infrared spectrometry (FTIR) studies, it was possible to calculate the carbonyl index (IC), which is a measure of the progression of degradation of polymer samples as a result of ageing. The carbonyl index was calculated for all types of samples with different hemp extract content after each time and type of ageing. The obtained results are summarized in the table and presented in the diagrams below.

In the case of standard PLA samples, it can be seen that there is a continuous gradual increase in the carboxylic coefficient value during weathering, while there are significant fluctuations during thermo-oxidative ageing, but ultimately after 200h, after both ageing processes, the IC value is comparable. The addition of 1.5 phr of extract in the case of weathering did not change the trend towards a stabilizing effect but enhanced it by increasing the coefficient value. In the case of thermo-oxidative ageing, there is a noticeable increase in IC up to 100h and a decrease thereafter, which may be correlated with the discolouration of the samples that was evident in the sample images presented in the article. This is probably due to the fact that the natural additive degrades and its effect on IC is limited. When 3 phr of hemp derivative is added, we observe an increase in IC up to 100h for both weathering and thermo-oxidative ageing, followed by a decrease - which may also be due to the rapid degradation of the hemp extract. The IC in this case is significantly lower for thermo-oxidative ageing than for weathering, and ultimately also lower than for the reference samples.

3.2 Analysis of static mechanical properties

3.2.1 PLA composites not subjected to ageing processes

Table 3
Mechanical properties for PLA reference samples

SAMPLE NAME	T.F _{max} [MPa]	E.F _{max} [%]	TS [MPa]	Eb [%]
PLA_0_CBD_REF	54.1 ± 3.7	6.9 ± 0.5	49.1 ± 0.8	8.6 ± 1.7
PLA_1.5_CBD_REF	53.2 ± 1.5	6.2 ± 0.4	41.9 ± 1.0	9.1 ± 1.3
PLA_3.0_CBD_REF	48.9 ± 1.3	5.2 ± 0.3	39.4 ± 5.1	7.1 ± 1.4

An important test to assess the condition of materials before and after ageing is static mechanical testing. In this case, a maximum tensile force analysis was carried out for PLA samples. The addition of cannabidiol reduced it, which may indicate the plasticizing effect of this substance on polymeric materials. However, the elongation at the maximum applied force decreased with increasing CBD concentration in the composite. Tensile strength also decreased in the same trend, while elongation at the break did not change, taking into account the measurement error. This could mean that the phyto-additives will reduce the inter-chain interactions occurring in the polymer matrix. This results in a greater ability for the chains to slide against each other with less use of force.

3.2.2 PLA composite samples subjected to ageing in thermo-oxidative conditions

Table 4
Mechanical properties for PLA samples subjected to thermo-oxidative ageing

SAMPLE NAME	T.F _{max}	E.F _{max}	TS	Eb
	[MPa]	[%]	[MPa]	[%]
PLA_0_CBD_REF	54.1	6.9	49.1	8.6
PLA_0_CBD_TERM-OX_50h	60.8	6.3	58.1	6.4
PLA_0_CBD_TERM-OX_100h	63.9	6.9	63.8	7.0
PLA_0_CBD_TERM-OX_150h	56.3	7.9	54.2	8.3
PLA_0_CBD_TERM-OX_200h	63.0	6.5	63.0	6.5
PLA_1.5_CBD_REF	53.2	6.2	41.9	9.1
PLA_1.5_CBD_TERM-OX_50h	62.8	6.9	62.3	7.1
PLA_1.5_CBD_TERM-OX_100h	56.2	6.1	45.2	8.4
PLA_1.5_CBD_TERM-OX_150h	57.4	6	54.6	6.2
PLA_1.5_CBD_TERM-OX_200h	63.1	6.7	57.4	7
PLA_3.0_CBD_REF	48.9	5.2	39.4	7.1
PLA_3.0_CBD_TERM-OX_50h	53.6	5.1	52.6	5.3
PLA_3.0_CBD_TERM-OX_100h	55.5	5.5	49	6.1
PLA_3.0_CBD_TERM-OX_150h	55.8	5.2	48.3	6.1
PLA_3.0_CBD_TERM-OX_200h	58	5.4	55.9	5.5

PLA samples with different CBD contents, subjected to thermo-oxidative ageing, showed an increase in tensile strength, however, a decrease in this parameter was also observed with an increase in phytoantioxidant concentration. As in the previous case for the reference samples, those after thermo-oxidative ageing also showed the same trend regarding the maximum force at elongation. As the concentration increased, the coefficient decreased, and the ageing time itself showed no unambiguous changes during the process. On the other hand, ageing time had a visible and strong effect on tensile strength, as the values increased with longer exposure time for each concentration, but from lower levels for samples with higher cannabidiol content. Elongation at break initially decreased significantly during the first 50 hours of the process, and then increased until the final times, where the trend was again downward. An increase in concentration harmed elongation at break values for PLA composites with CBD. In addition, the K-factor was determined, which indicates the degradation potential. In this case, for PLA composites without CBD content, the value of this coefficient in the initial phase decreases to a value of 0.88, which most likely indicates the progress of degradation of the lower molecular weight polymer

fraction, and initially increases, stabilizing at a level close to 1. The composite containing 1, 5 phr of CBD shows the opposite trend, meaning that in the initial 50 hours of the ageing process the K-factor increases to a value of 1.17, after which it decreases and stabilizes at a level close to 1. The sample containing 3.0 phr of cannabidiol in the initial period of thermo-oxidative ageing is characterized by an ageing factor close to unity, which increases over time to a level of 1.09 after 200 hours of the process. The increase in K-factor for PLA composites may be due to an increase in the degree of crystallinity of the material, as translational movements of macromolecules are facilitated at elevated temperatures, and the addition of CBD as a potential plasticizer may increase the possibility of this movement with a lower energy barrier minimized by reduced friction between chains.

3.2.3 PLA composite samples subjected to weather ageing

Table 5
Mechanical properties for PLA samples subjected to weather ageing

SAMPLE NAME	T.F _{max} [MPa]	E.F _{max} [%]	TS [MPa]	Eb [%]
PLA_0_CBD_REF	54.1 ± 3.7	6.9 ± 0.5	49.1 ± 0.8	8.6 ± 1.7
PLA_0_CBD_WEAT_50h	58.4 ± 1.4	7.7 ± 0.3	56.2 ± 1.4	7.7 ± 0.3
PLA_0_CBD_WEAT_100h	29.3 ± 3.8	4.9 ± 0.3	28.9 ± 4.1	4.9 ± 0.3
PLA_0_CBD_WEAT_150h	3.0	1.8	2.9	1.8
PLA_0_CBD_WEAT_200h	1.0	0.8	-	-
PLA_1,5_CBD_REF	53.2 ± 1.5	6.2 ± 0.4	41.9 ± 1.0	9.1 ± 1.3
PLA_1,5_CBD_WEAT_50h	32.7 ± 15.5	4.1 ± 1.0	32.7 ± 15.5	4.1 ± 1.0
PLA_1,5_CBD_WEAT_100h	8.1 ± 1.6	2.9 ± 0.4	8.0 ± 1.5	2.9 ± 0.4
PLA_1,5_CBD_WEAT_150h	2.2 ± 0.4	1.6 ± 0.1	2.1 ± 0.3	1.6 ± 0.1
PLA_3,0_CBD_REF	48.9 ± 1.3	5.2 ± 0.3	39.4 ± 5.1	7.1 ± 1.4
PLA_3,0_CBD_WEAT_50h	17.1 ± 4.2	3.0 ± 0.6	17.0 ± 4.1	3.0 ± 0.6
PLA_3,0_CBD_WEAT_100h	3.2 ± 0.0	0.9 ± 0.3	1.2 ± 0.6	1.7 ± 0.2

Weathering resulted in the most interesting samples and results of mechanical analysis of PLA composites with cannabidiol. All samples showed a decrease in tensile values at maximum force, but interestingly, the higher the CBD content in the composite, the stronger and faster the decrease in values occurred during the ageing process. For the 1.5 phr content, it was not possible to take measurements for the sample after 200 hours of ageing, and for the 3.0 phr CBD content, the samples disintegrated after 150 hours of weathering, which was even visible in the photos in earlier sections of this dissertation. This indicates the catalytic effect of cannabidiol as an additive to PLA on weathering processes. The same

conclusions can also be drawn for parameters such as elongation at break at the highest applied force, tensile strength and elongation at break. This opens a very interesting field for further research on a compound with antagonistic inhibitory and catalytic properties for PLA depending on environmental conditions. The ageing coefficient for PLA composites subjected to weathering ageing shows very strong changes. The reference sample initially shows a slight increase in value above unity, followed by a decrease to a value close to the 150h test time. Samples containing 1.5 phr of cannabidiol showed a faster decrease in the ageing factor K value than samples without this additive. Even more, pronounced changes are seen for the composite containing the highest amount of the tested hemp derivative in the composition. In this case, after 100 hours of atmospheric degradation, the ageing coefficient is close to 0. The decrease in K-factor values with increasing CBD content may have several different explanations. One may be based on increased mobility through plasticization and thus easier penetration of water as a factor leading to material destruction. Another is likely to be CBD degradation processes proceeding differently depending on environmental factors such as light and water. The resulting derivatives can probably catalyse the oxidation and reduction processes of polymers.

3.3 Measurements and analysis of the results of the spectrophotometric test

One of the first steps in testing after the samples were prepared was to analyze their appearance. The PLA-based composites were highly transparent and the surface was smooth. After adding the hemp extract, the samples obtained a tea colour, the intensity of which increased with increasing concentration of the extract.

In the next stage, an analysis of the research progress on the effect of hemp extract as an anti-ageing substance after the end of thermo-oxidative and atmospheric degradation was carried out. In the photos below you can see the appearance of the samples and analyze the changes taking place.

In the course of thermo-oxidative ageing, an increase in the level of turbidity of PLA samples is visible, probably resulting from an increase in the degree of crystallinity, which increased due to the possibility of making more free movements of segmental polymer macrochains at higher temperatures. The CBD-containing samples initially darkened during the process and discoloured as they aged further, indicating the potential use of the extract as an ageing indicator.

During weathering, the reference samples turned milky after 50h, which may indicate a transition to a semi-crystalline form. This photo also shows scratches and cracks in samples containing hemp extract after 150h and 200h of weathering, which indicates a weakening of mechanical properties, and greater brittleness - which may result from an increase in the degree of crystallinity and progress in degradation of polymer macromolecules. Interestingly, the samples with the addition of the hemp derivative have a smoother surface and are slightly more flexible than the reference samples.

3.3.1 Analysis of the PLA composites after thermal-oxidative ageing

Table 6
Spectrophotometric properties for PLA samples subjected to thermo-oxidative ageing

SAMPLE NAME	COLOUR CHANGE (ΔE) [·]	WHITNESS INDEX (W_i) [·]	CHROMA (C_{ab}) [·]	HUE ANGLE (h_{ab}) [°]
PLA_0_CBD_TERM-OX_REF	-	88.3 ± 1.4	3.6 ± 0.1	3.04 ± 0.01
PLA_0_CBD_TERM-OX_50h	11.6 ± 0.5	76.0 ± 0.5	5.7 ± 0.1	1.07 ± 0.11
PLA_0_CBD_TERM-OX_100h	12.2 ± 0.2	75.4 ± 0.2	5.5 ± 0.1	2.43 ± 0.17
PLA_0_CBD_TERM-OX_150h	28.7 ± 0.4	59.2 ± 0.4	3.5 ± 0.1	2.99 ± 0.01
PLA_0_CBD_TERM-OX_200h	12.0 ± 0.2	75.6 ± 0.2	5.2 ± 0.2	2.26 ± 0.23
PLA_1.5_CBD_TERM-OX_REF	-	74.1 ± 0.4	19.6 ± 0.5	3.01 ± 0.00
PLA_1.5_CBD_TERM-OX_50h	8.6 ± 0.2	67.8 ± 0.2	19.7 ± 0.2	2.88 ± 0.00
PLA_1.5_CBD_TERM-OX_100h	14.8 ± 0.2	59.8 ± 0.2	26.7 ± 0.8	2.80 ± 0.06
PLA_1.5_CBD_TERM-OX_150h	11.2 ± 0.2	63.6 ± 0.2	25.9 ± 0.4	0.36 ± 0.01
PLA_1.5_CBD_TERM-OX_200h	9.6 ± 0.3	67.1 ± 0.3	19.5 ± 0.2	2.93 ± 0.00
PLA_3.0_CBD_TERM-OX_REF	-	57.0 ± 0.9	39.5 ± 1.0	2.89 ± 0.01
PLA_3.0_CBD_TERM-OX_50h	15.0 ± 0.2	54.5 ± 0.8	33.8 ± 0.7	1.67 ± 0.00
PLA_3.0_CBD_TERM-OX_100h	14.9 ± 0.2	58.6 ± 0.7	30.2 ± 0.4	2.52 ± 0.06
PLA_3.0_CBD_TERM-OX_150h	16.6 ± 0.3	56.6 ± 0.5	30.7 ± 0.4	2.32 ± 0.09
PLA_3.0_CBD_TERM-OX_200h	16.9 ± 0.2	59.5 ± 0.1	28.1 ± 0.1	2.71 ± 0.01

The study of changes in the optical properties of samples can provide many answers to the surface ageing processes of polymer composites and vulcanizates. The most important parameters, such as colour change, saturation, whiteness index and hue angle, make it possible to evaluate the influence of particular additional factors on the change of colour, intensity or brightness of the tested materials. In this case, we can see the results of the change analysis in the above charts in these parameters for PLA samples with variable hemp derivative content to simulate thermo-oxidative ageing. The colour change of polylactide samples without natural additives is insignificant during ageing because after 50 hours of the degradation process the colour change is 11.6 and slightly increases by 0.5 until the last stage. The sample deviation after the 150-hour ageing period shown in the graph may be due to sample deformation and inadequate adhesion to the measuring cell. In the case of samples with 1.5 phr CBD, greater changes can be observed during the ageing process, because after 50 hours of the process the colour change

compared to the reference sample is 8.6, after 100 hours it increases to 14.8, which indicates the presence of oxidant degradation, and then it slowly drops to 9.6 after 200h. In this case, it may be due to a parameter change in the context of the degradation of the low content of the natural anti-ageing substance. The same process can probably be observed also for PLA samples containing 3.0 phr of extract. The colour change parameters in the ageing process increase from 15 to 16.9 along with the further course of oxidation in the thermo-oxidative ageing process. On the other hand, the chroma parameter changes dramatically as the CBD content in the tested materials increases. There are also tendencies that the samples to lose colour as the age of the samples, and the saturation value decreases for samples without extract, with values ranging from 3.5 to 5.7. For PLA samples containing 1.5 phr, the reference value is 19.6, after 100h of thermo-oxidative degradation, this coefficient increases to 26.6, and with further ageing it will gradually decrease to the final value of 19.5. With 3.0 phr of the natural antiageing agent in the composite, an even greater initial increase in the value of the saturation factor to 39.5 for the reference sample occurs, with gradually decreasing ageing time, the value of the colour saturation index to the level of 28.1. This indicates a discolouration of the sample due to the degradation of the added CBD. The whiteness index shows the highest values for PLA samples without extract and is initially about 88, then after 50h it drops to about 76 and remains at this level until the end of ageing. Samples with the addition of a natural multifunctional phytosubstance are darker, which indicates a decrease in the whiteness index, which for 1.5 phr of the additive is initially 74 and drops after 100h to the lowest value of 60, and then increases again to 67. This may be due to complete degradation. of this natural component after 100h and the return to the original brightness of the colour typical for a pure polymer. The addition of more and more of this natural antioxidant in the amount of 3.0 phr reduces the value of this index to about 57 and shows no significant changes in the course of ageing. For the parameter called colour angle, there are no visible trends for all samples that oscillate without a clear trend around a hue angle value of 0.5 to 3.0 - the shade of red on the colour wheel.

3.3.2 Analysis of the PLA composites after weather ageing

Table 7
Spectrophotometric properties for PLA samples subjected to weather ageing

SAMPLE NAME	COLOUR CHANGE (ΔE) [-]	WHITNESS INDEX (W.i) [-]	CHROMA (C.ab) [-]	HUE ANGLE (h.ab) [°]
PLA_0_CBD_WEAT_REF	-	86.0 ± 0.3	3.4 ± 0.2	3.05 ± 0.01
PLA_0_CBD_WEAT_50h	3.5 ± 0.4	82.7 ± 0.4	3.7 ± 0.1	3.11 ± 0.00
PLA_0_CBD_WEAT_100h	3.0 ± 0.2	83.5 ± 0.2	3.1 ± 0.1	3.12 ± 0.00
PLA_0_CBD_WEAT_150h	3.1 ± 0.4	83.4 ± 0.4	3.2 ± 0.1	3.12 ± 0.00
PLA_0_CBD_WEAT_200h	4.5 ± 0.3	81.9 ± 0.3	3.4 ± 0.1	3.12 ± 0.00
PLA_1.5_CBD_WEAT_REF	-	73.5 ± 0.3	20.2 ± 0.6	3.01 ± 0.00
PLA_1.5_CBD_WEAT_50h	16.0 ± 0.1	58.8 ± 0.2	26.7 ± 0.4	2.72 ± 0.06
PLA_1.5_CBD_WEAT_100h	9.6 ± 0.1	64.6 ± 0.2	24.7 ± 0.6	2.90 ± 0.00
PLA_1.5_CBD_WEAT_150h	10.5 ± 0.3	64.7 ± 0.1	22.6 ± 0.4	2.94 ± 0.01
PLA_1.5_CBD_WEAT_200h	9.2 ± 0.5	66.4 ± 0.7	21.1 ± 0.6	2.97 ± 0.01
PLA_3.0_CBD_WEAT_REF	-	56.0 ± 0.3	40.5 ± 0.3	2.87 ± 0.01
PLA_3.0_CBD_WEAT_50h	18.8 ± 0.2	54.3 ± 1.1	31.2 ± 1.0	1.80 ± 0.08
PLA_3.0_CBD_WEAT_100h	16.5 ± 0.4	52.1 ± 0.6	35.8 ± 0.8	0.47 ± 0.05
PLA_3.0_CBD_WEAT_150h	18.7 ± 0.3	50.4 ± 1.3	35.5 ± 1.2	0.37 ± 0.06
PLA_3.0_CBD_WEAT_200h	17.3 ± 0.2	63.6 ± 1.6	25.8 ± 1.0	0.37 ± 0.16

PLA samples with different hemp extract content changed significantly as the weather age. The colour change parameter for this material showed a value of about 3.0 for the reference sample, was maintained to the end and increased to a value of 4.5 after the entire ageing cycle. The colour changes increased with the increase in the content of the hemp derivative, with the amount of 1.5 phr, the reference sample reached the value of about 16.0 after 50 hours of the process, but in the next step, this value dropped to about 10 and remained at this level until the end of the process. This may indicate the degradation of the additive after the first stage of ageing. Composites containing 3.0 phr of natural antioxidants had even greater colour change values, ranging from 16.5 to almost 19 during the ageing process. This amount of this natural additive probably did not degrade as rapidly as no strong colour change was observed. The colour saturation index for these samples changes analogously to those described for thermo-oxidative ageing. Samples without the extract do not significantly change this parameter during the degradation process, and the value of the saturation parameter for them is about 3.0, however, a small addition of 1.5 phr of hemp extract causes a significant increase in the value to 20 in the first 50 hours, which reaches the maximum values of approx. 27 after 100h and drops to 21 over

time, which indicates the staining of the sample. The content of 3.0 phr of the additive raises the value of the chrominance index to about 40.5, and in this case, there is also a decrease in these values, but in this case the most noticeable drops occur in the last stage of ageing to the level of about 29. This is probably due to slower degradation of the substance and may be related to its concentration in the polymer matrix. The whiteness index for PLA composite samples subjected to weathering decreases with increasing concentration of CBD extract in the composite. Samples without the addition of a natural antioxidant of hemp origin show the highest value of the whiteness index at the level of about 80, the addition of 1.5 phr lowers this parameter to the value of about 70 for the reference sample and drops significantly in the first 50 hours to the value of 59, and for the subsequent stages of ageing the value again rises to 66, possibly due to degradation of the natural antioxidant and discolouration of the material. For PLA samples with 3.0 phr of hemp extract, the value of the whiteness index for the reference sample drops to about 56 and decreases with the ageing rate, which may be related to the migration of cannabidiol to the surface of the composite, and in the last stage, after 200 hours of climatic ageing, a sudden increase in the value to the level of about 63, which means, similarly to the previous case, discolouration of the sample as a result of the degradation of the addition of CBD. The change in hue angle for the current samples without the hemp derivative and 1.5 phr does not change significantly, the values, in this case, remain at 3.0 degrees. Only the addition of 3 parts by weight manifests itself in significant changes in the colour angle parameter. In this case, during the first 100 hours of ageing, significant decreases in the values from 2.8 to 1.8 are visible, followed by stabilization at a level 7 times lower than the reference sample.

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

3.4.1 PLA composites not subjected to ageing processes

Another of the studies conducted was the analysis of changes in the surface free energy of the prepared materials. The total value and individual components of this energy fluctuate strongly as a result of simulated ageing processes. By analysing these changes, it is possible to determine the progress of material degradation and observe the effect of the additive on the course of these changes.

For PLA reference samples with different cannabidiol contents, a decrease in both the total surface energy and the dispersion component can be observed. There is also a pronounced increase in the polar component, in the case of the 3.0 phr CBD content, up to 10-fold compared to the sample devoid of this phytosubstance. This may indicate poor miscibility of CBD with polylactide and migration of this compound to the surface, as the structure of CBD indicates that the compound is polar.

3.2.2 PLA composite samples subjected to ageing in thermo-oxidative conditions

Table 8
The distribution of surface energy for PLA samples aged thermo-oxidatively

SAMPLE NAME	TOTAL SURFACE ENERGY	DISPERSIVE COMPONENT	POLAR COMPONENT
	[mN/m]	[mN/m]	[mN/m]
PLA_0_CBD_REF	33.9 ± 0.6	33.7 ± 0.6	0.2 ± 0.1
PLA_0_CBD_TERM-OX_50h	28.6 ± 0.5	28.1 ± 0.5	0.4 ± 0.1
PLA_0_CBD_TERMOX_100h	32.2 ± 0.8	32.0 ± 0.8	0.2 ± 0.1
PLA_0_CBD_TERM-OX_150h	30.4 ± 1.2	30.3 ± 1.2	0.1 ± 0.1
PLA_0_CBD_TERM-OX_200h	32.8 ± 0.4	32.8 ± 0.4	0.0 ± 0.0
PLA_1,5_CBD_REF	32.0 ± 0.4	30.7 ± 0.4	1.3 ± 0.1
PLA_1,5_CBD_TERM-OX_50h	32.1 ± 0.3	32.0 ± 0.3	0.1 ± 0.0
PLA_1,5_CBD_TERM-OX_100h	31.4 ± 0.9	28.9 ± 0.8	2.5 ± 0.4
PLA_1,5_CBD_TERM-OX_150h	31.2 ± 0.6	29.9 ± 0.5	1.3 ± 0.4
PLA_1,5_CBD_TERM-OX_200h	30.6 ± 0.7	29.9 ± 0.7	0.7 ± 0.1
PLA_3,0_CBD_REF	33.2 ± 0.3	31.3 ± 0.3	1.9 ± 0.1
PLA_3,0_CBD_TERM-OX_50h	32.4 ± 0.5	30.7 ± 0.4	1.7 ± 0.2
PLA_3,0_CBD_TERM-OX_100h	32.9 ± 0.3	32.7 ± 0.3	0.2 ± 0.0
PLA_3,0_CBD_TERM-OX_150h	31.7 ± 0.4	31.1 ± 0.4	0.6 ± 0.2
PLA_3,0_CBD_TERM-OX_200h	32.2 ± 0.6	32.0 ± 0.6	0.2 ± 0.1

PLA-based composite samples subjected to thermo-oxidative ageing were analyzed, and the results are summarized in the graphs shown above. For the composite without CBD in the mix, little fluctuation can be observed over time in the value of the total and dispersive components of the surface energy. Only the polar component tends to fluctuate over time, as it increases after 50 hours of ageing and then decreases significantly, while the addition of 1.5 phr of cannabidiol causes more interesting changes. In this case, during thermo-oxidative ageing, both the dispersive and polar components of surface free energy decrease, which translates into a decrease in their total value. This may be due to the degradation in the

first place of the hemp derivative additive on the surface, which stabilizes and slows down the ageing process of the polymer material. In the case of PLA samples with the addition of 3.0 phr of cannabidiol, a similar trend can be observed as in the case of samples with the addition of 1.5 phr.

3.4.3 PLA composite samples subjected to weather ageing

Table 9
Surface energy distribution for PLA samples subjected to weather ageing

SAMPLE NAME	TOTAL SURFACE ENERGY [mN/m]	DISPERSIVE COMPONENT [mN/m]	POLAR COMPONENT [mN/m]
PLA_0_CBD_REF	33.9 ± 0.6	33.7 ± 0.6	0.2 ± 0.1
PLA_0_CBD_WEAT_50h	31.0 ± 0.5	28.2 ± 0.5	2.8 ± 0.3
PLA_0_CBD_WEAT_100h	32.4 ± 01.1	27.2 ± 0.9	5.2 ± 0.5
PLA_0_CBD_WEAT_150h	31.6 ± 0.9	25.8 ± 0.8	5.8 ± 0.5
PLA_0_CBD_WEAT_200h	34.0 ± 1.0	29.5 ± 0.8	4.5 ± 0.6
PLA_1,5_CBD_REF	32.0 ± 0.4	30.7 ± 0.4	1.3 ± 0.1
PLA_1,5_CBD_WEAT_50h	35.5 ± 1.3	31.5 ± 1.2	4.0 ± 0.5
PLA_1,5_CBD_WEAT_100h	34.5 ± 1.1	30.6 ± 1.0	3.9 ± 0.4
PLA_1,5_CBD_WEAT_150h	36.7 ± 0.8	32.5 ± 0.6	4.2 ± 0.4
PLA_1,5_CBD_WEAT_200h	34.3 ± 0.8	25.2 ± 0.6	9.1 ± 0.4
PLA_3,0_CBD_REF	33.2 ± 0.3	31.3 ± 0.3	1.9 ± 0.1
PLA_3,0_CBD_WEAT_50h	36.6 ± 0.7	34.1 ± 0.7	2.5 ± 0.3
PLA_3,0_CBD_WEAT_100h	37.6 ± 0.8	31.2 ± 0.6	6.4 ± 0.5
PLA_3,0_CBD_WEAT_150h	34.9 ± 1.2	28.2 ± 1.0	6.7 ± 0.7
PLA_3,0_CBD_WEAT_200h	42.2 ± 1.5	23.3 ± 1.0	18.9 ± 1.1

Weathering for samples based on the reference PLA showed that the polar component increases with time and the dispersive component decreases, with small variations in the total surface free energy. This may be due to the degradation of the PLA fraction from high to low molecular weight. With the addition of CBD in the amount of 1.5 phr, the contribution of components to the surface free energy changes considerably. The value of the polar component, which increases significantly with ageing and decreases in dispersion, gains in importance. I would conclude that this may be due to the migration of the extract from the interior of the material to the surface. For PLA samples with 3.0 phr of hemp-derived substances, there is a tendency for total surface energy to increase during weathering. As with the smaller amount, the dispersive component also decreases and the polar component increases with time, especially in the last stage of ageing.

5. Conclusions

Samples of aliphatic polyester-based composite materials in which the anti-ageing substance was hemp extract showed increased flexibility and gloss on the surface of the extrudates. In addition, the materials obtained as a result of the CBD addition were characterised by high smoothness and acquired a yellow-green colour. As a result of the introduction of the hemp-derived compound into the composite, the materials acquired a distinct, not very intense, but very characteristic aroma.

The peaks characteristic of the CBD phyto-additive are not visible in the PLA samples during both weathering and thermo-oxidative ageing. The spectra differ only in the intensity of the signals, which made direct analysis of the changes taking place difficult. However, the results obtained allowed the calculation of the carbonyl index, which made it possible to assess the ageing processes depending on the time and type of ageing simulation. In this case, it turned out that PLA samples with hemp extract as an antioxidant additive were stable and resistant to thermo-oxidative ageing, but the opposite effect was shown by the addition of cannabidiol, which catalysed the degradation of the composite during weathering.

All samples obtained of both composites containing the extract in their composition showed a colour change. There was a marked reduction in the brightness of the samples and an increase in colour saturation. As a result of both thermo-oxidative and weathering processes, the tested materials became partially discoloured. This is probably due to the occurrence of physicochemical transformations of the extract components during these processes. Likely, the hemp-derived additive was also partially degraded as a result of the environmental factors, resulting in reactions to other chemical compounds with different spectrophotometric properties, from which the changes taking place were visualised.

One of the first observations during the analyses was that the thermoplastic composite samples were plasticised when the phyto-additive was added to the mixtures. In all likelihood, it can be postulated that the addition of the phytosubstance resulted in a reduction in the number and weakening of inter-chain interactions, which was observed as lower stresses and elongations needed to fracture the tested materials. The CBD-rich extract as a natural antioxidant in the present study showed a dual action in the

tests performed, i.e. as an inhibitor of polymer degradation on thermo-oxidative ageing and as a catalyst for weathering. In the case of mechanical testing, this observation was most pronounced due to the significant degradation of the material as a result of the joint action of factors such as moisture, temperature, light and oxygen during weathering. As a result of these factors, the samples degraded significantly and could not be tested by static mechanical property methods.

The surface free energy test showed that SFE values decrease for CBD-reinforced samples mainly during thermo-oxidative ageing. In the case of weathering, the total surface energy values are higher on average to a slight but noticeable extent. Interestingly, the differences in the surface free energy components may be indicative of the different thermodynamic stability of the polymer-cannabidiol systems. This supposition is due to the holistic reason for the study. In the case of PLA-based samples, a trend towards a change in SFE values can be observed, where the polar component decreased with thermo-oxidative ageing and increased with degradation in simulated weathering. These observations suggest that the degradation of the added extract during these two types of ageing as a result of different environmental factors follows a different mechanism and yields a different product. However, further research is needed to analyse whether the presence of water and light during the ageing of hemp extract has a real and strong effect on changing the degradation mechanism of this phytochemical.

A reference was found in the literature to a further red-ox reaction of CBD itself, which converts to hydroxyquinone (CBD-HQ) and benzoquinone, which is itself a very good oxidant at a later time (hence the possible increase in degradation rate after 150 and 200h for samples in weathering) in particular when following the reaction of CBD itself and its oxidation to hydroxyquinone, followed by its reduction to the 1,4-p-benzoquinone derivative, resulting in an oxidation reaction of the polymer itself (hence the carbonyl index shows a strong increase in its value)[25]. Preliminary speculation requiring even more in-depth studies concerns the reaction of CBD during weathering, where the derivatives react with water at elevated temperatures and are irradiated (possible oxidation of water during the reduction of hydroxyquinone to quinone). In contrast, in the case of thermo-oxidative ageing, the resulting quinone-based CBD derivatives belong to the group of colour compounds and are used as good light absorbers, resulting in conversion to other structural forms and excited states with lower radiant emission energy. Which would explain the stabilising effect during this ageing. The colour change results also agree with this concept.

The most important aspect of this study was the identification of high cannabidiol cannabis extract as a compound with potential anti-ageing properties in the polymer industry. The research shows even more interesting results than the initial assumptions. CBD is antagonistic depending on the influence of environmental factors. Where it is a good stabilizer in the case of thermo-oxidative ageing, and becomes a catalyst for polymer degradation in the case of atmospheric ageing.

Declarations

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Figures

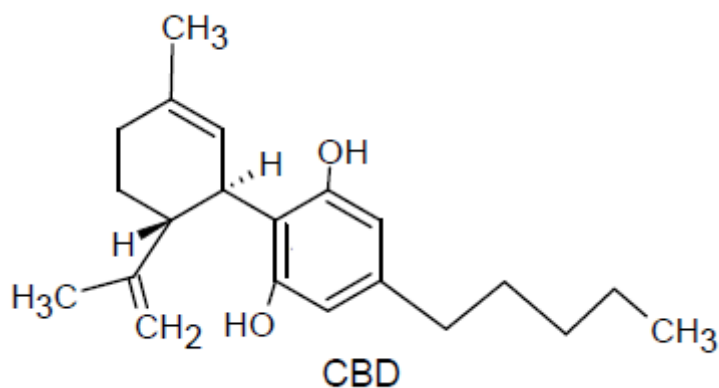


Figure 1

The structural pattern is one of the most important cannabinoid found in hemp[21].

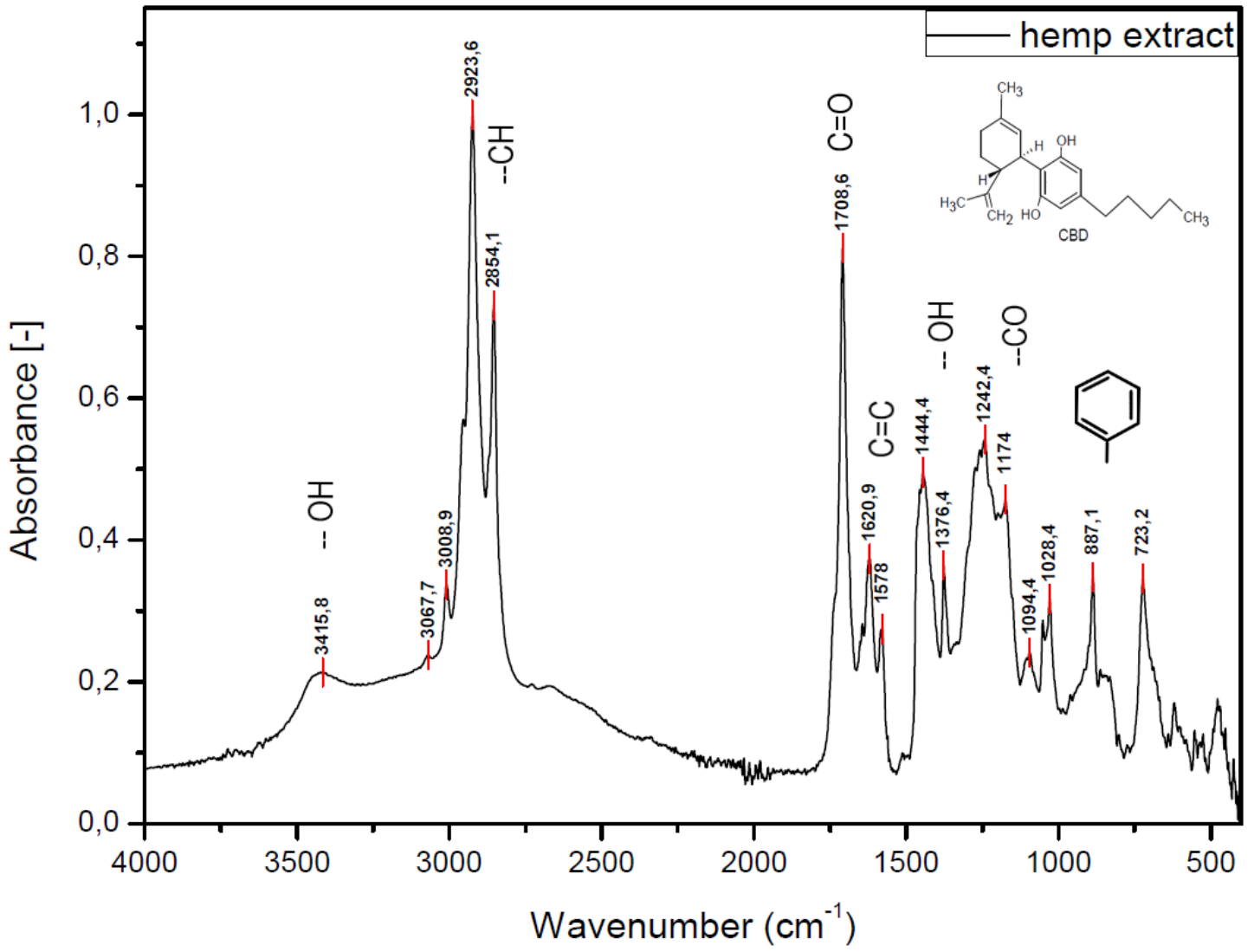


Figure 2

FTIR spectrum of hemp extract.

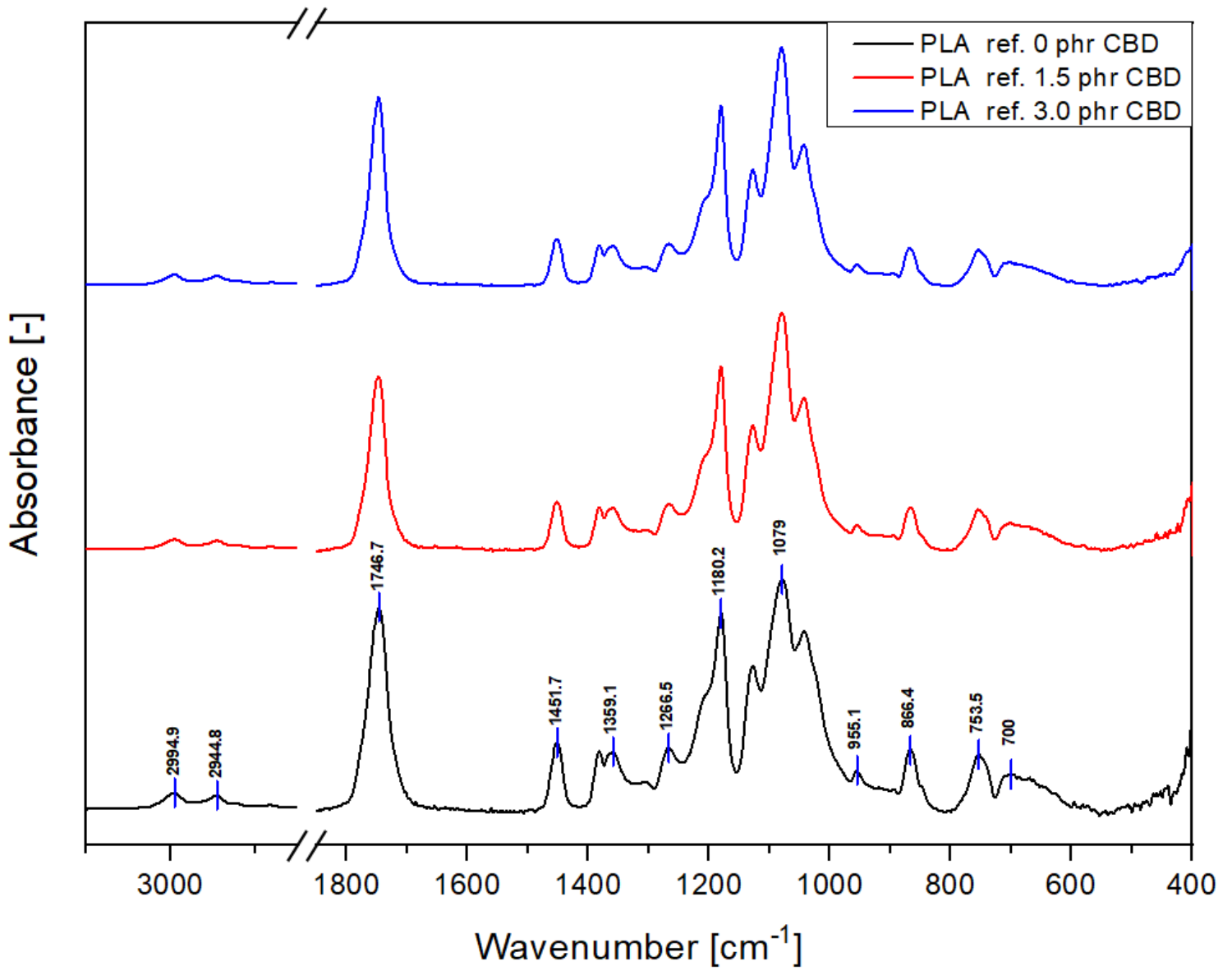


Figure 3

Comparative FTIR spectrum for reference (unaged) PLA samples with different hemp extract content.

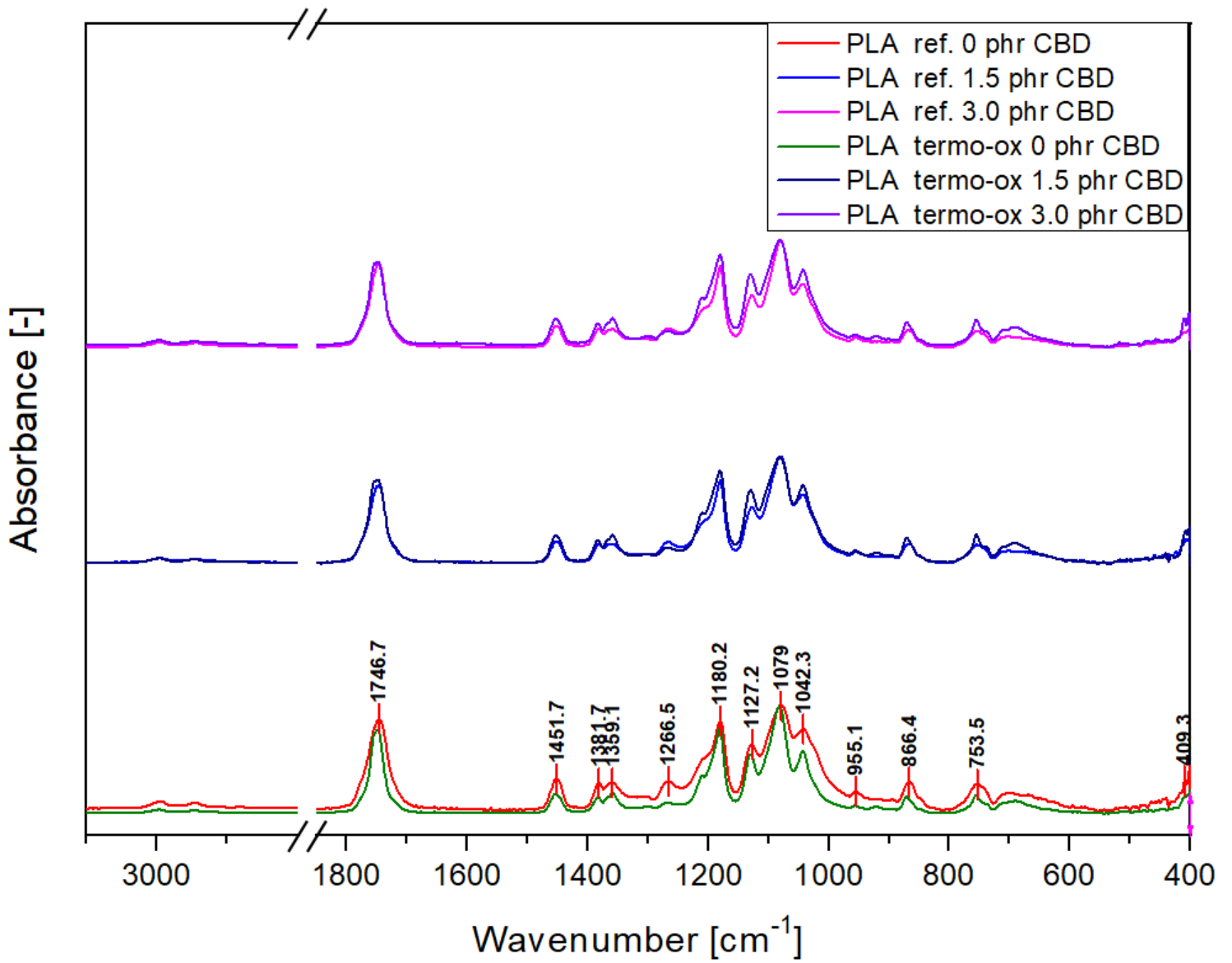


Figure 4

Comparative FTIR spectrum for PLA samples with different hemp extract content after 200h of thermo-oxidative ageing.

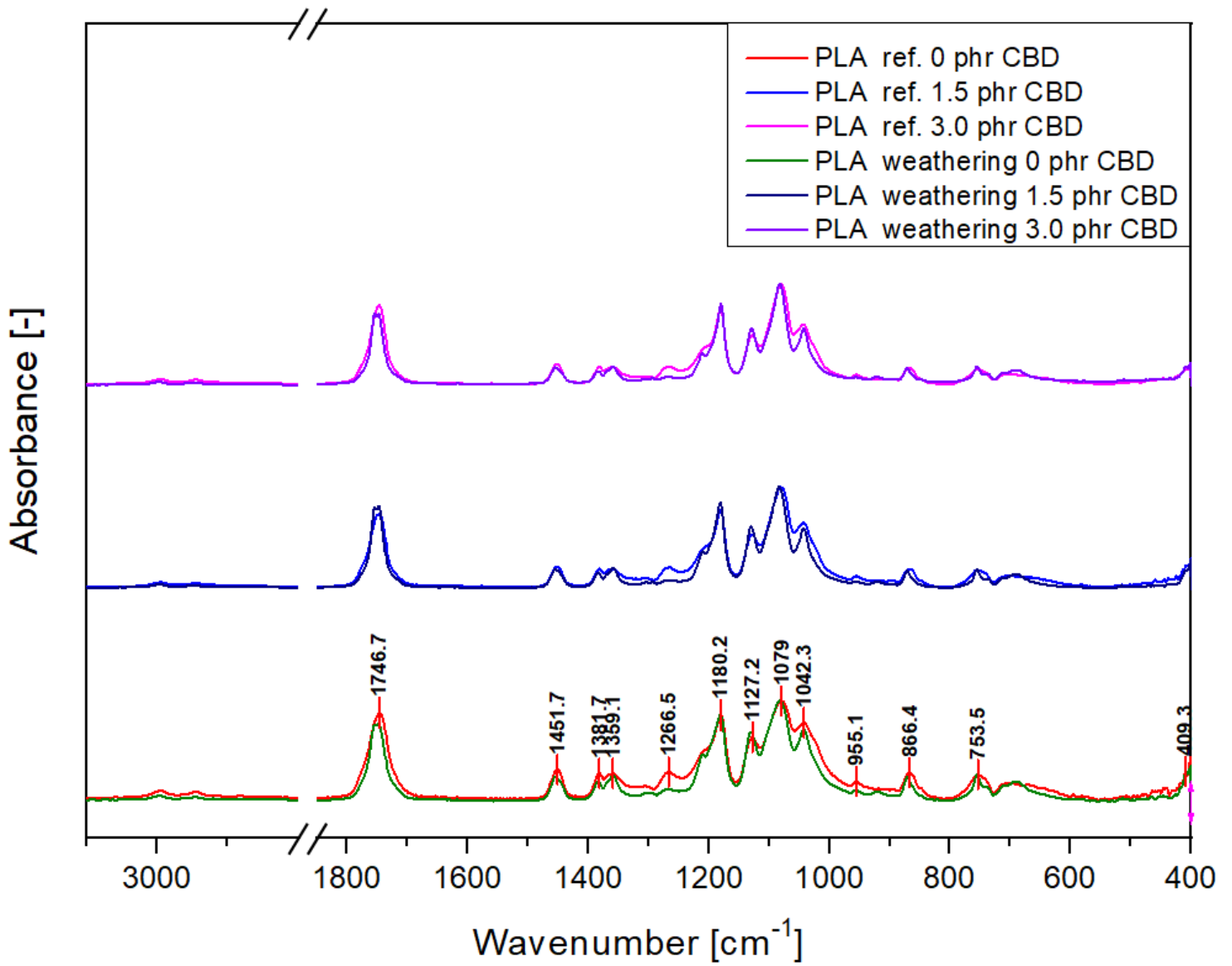


Figure 5

Comparative FTIR spectrum for PLA samples with different hemp extract content after 200h weathering ageing.

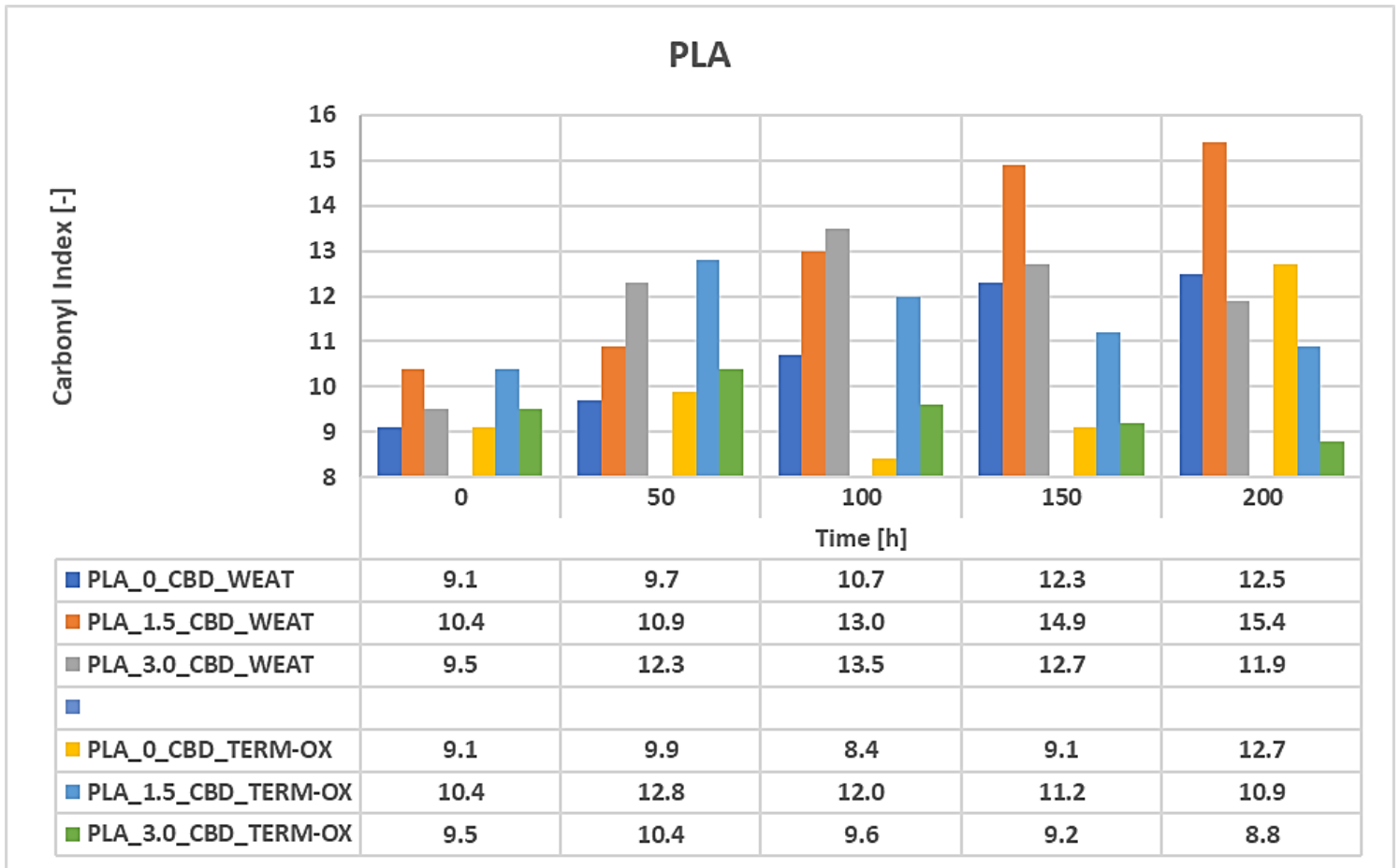


Figure 6

Graph of changes in the value of the carbonyl index for PLA samples as a function of ageing time and hemp extract concentration.

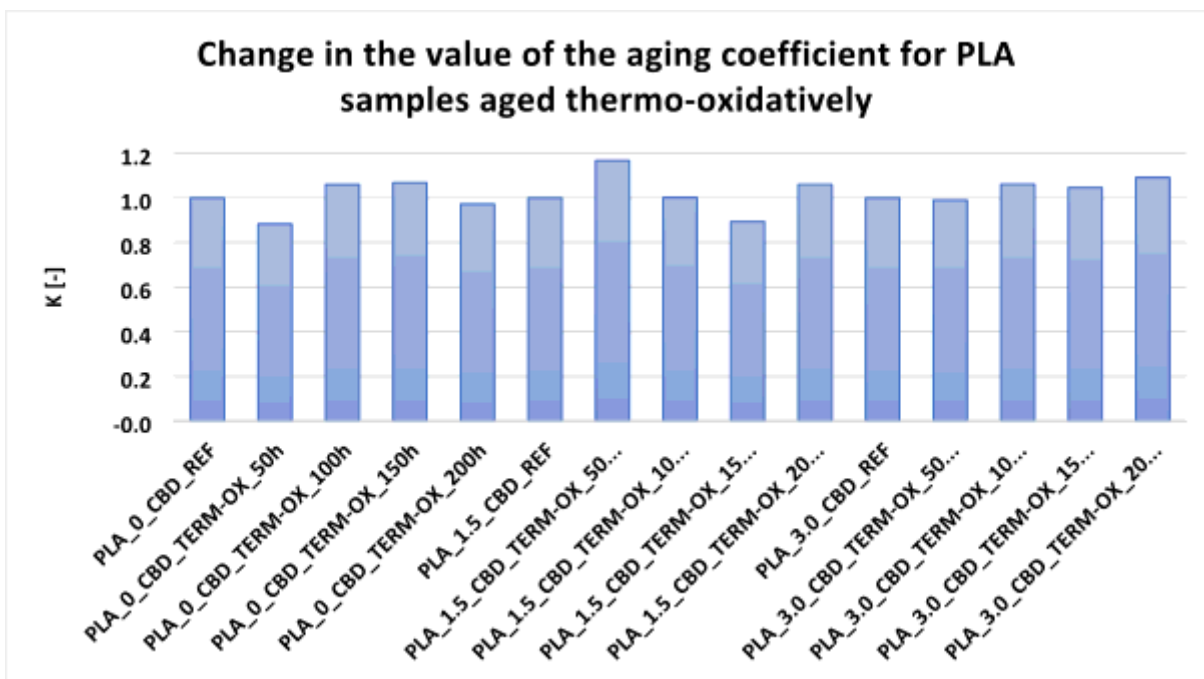


Figure 7

Change of the thermo-oxidative ageing coefficient for samples of PLA composites

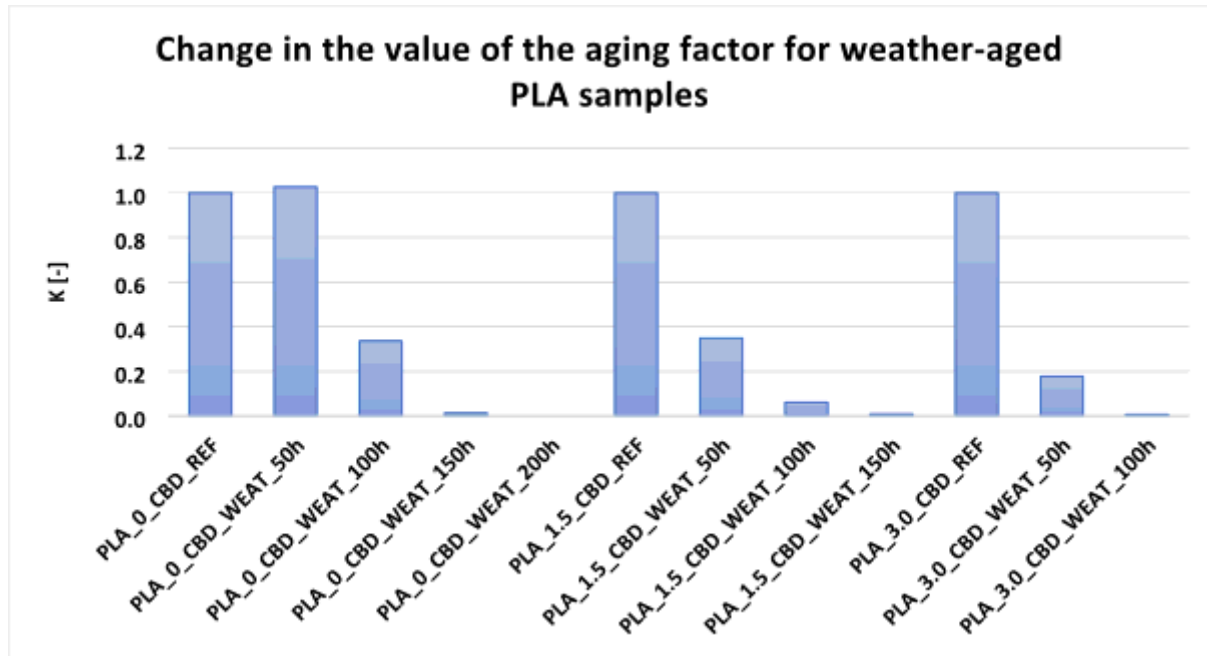
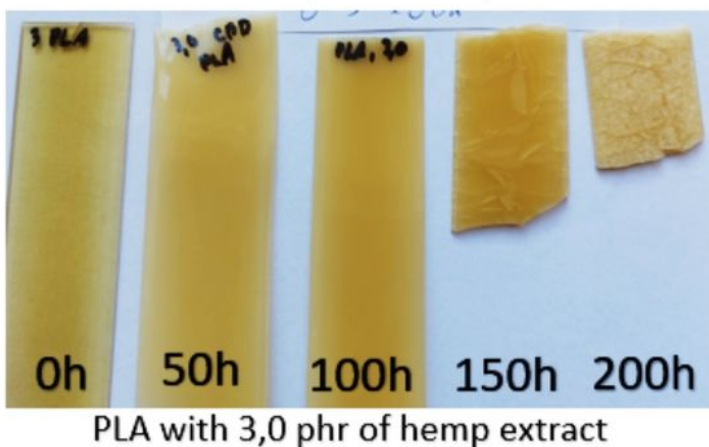
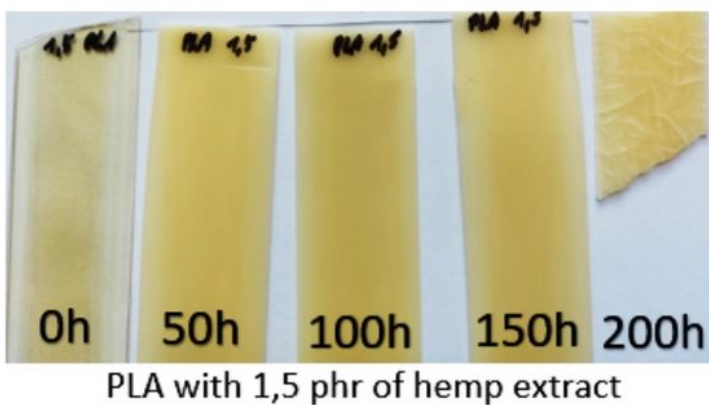
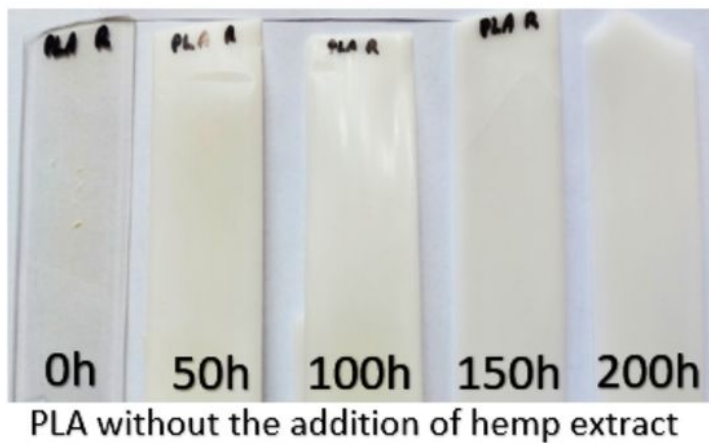


Figure 8

Graph of changes in the ageing factor for PLA composite samples subjected to weather ageing

Aging under weathering simulation conditions



Aging under thermo-oxidation simulation conditions

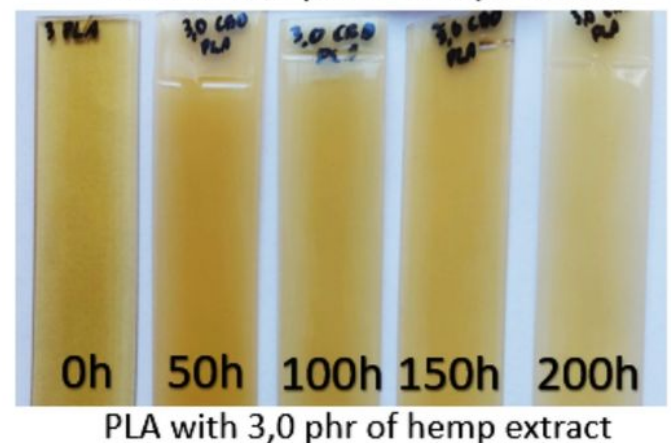
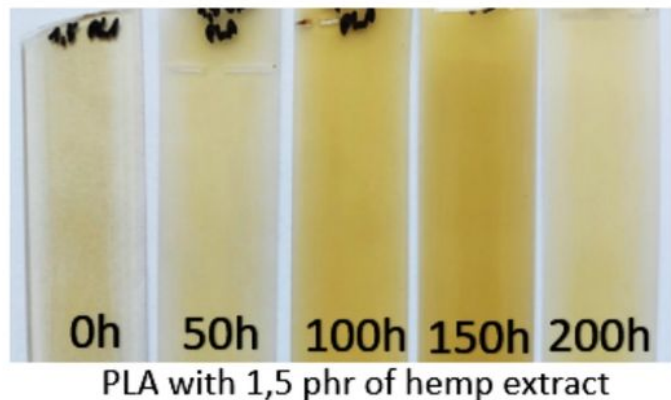
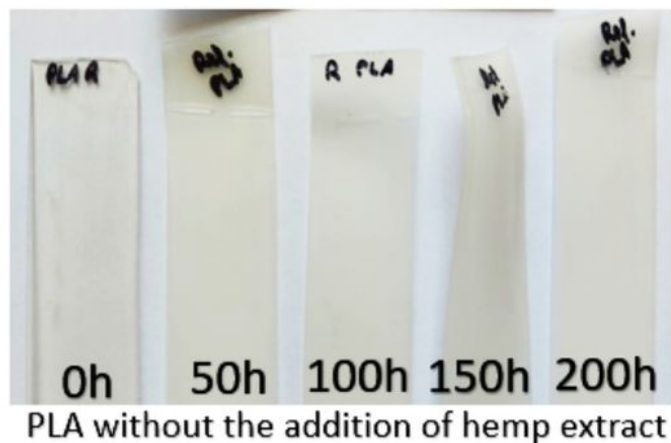


Figure 9

Photographs of composite samples with different hemp extract contents subjected to weathering and thermo-oxidative ageing at different time intervals

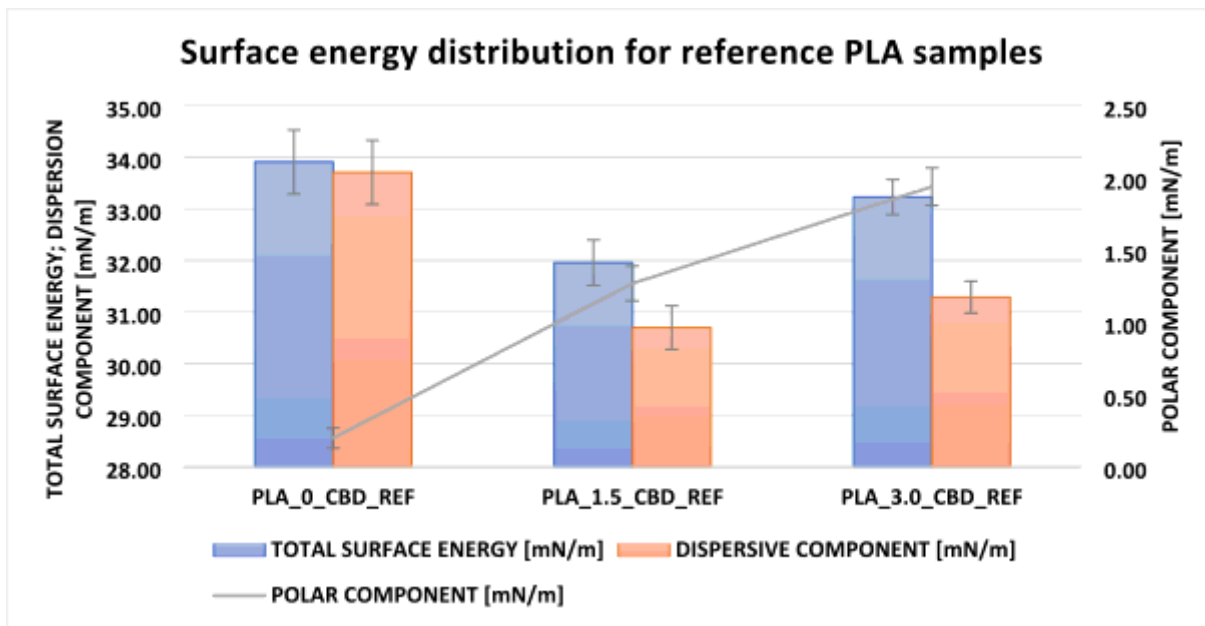


Figure 10

Surface energy distribution for reference PLA samples

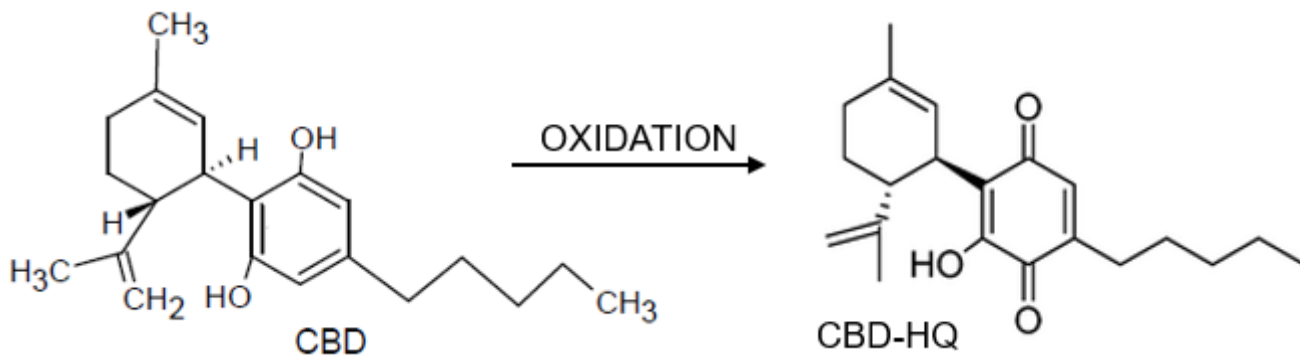


Figure 11

The potential oxidation reaction of CBD to CBD-HQ

Supplementary Files

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- [AbstraktgraficznyPLAekstraktkonopny1.pdf](#)