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The Coloristic Properties of Biodegradable Fibers

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Abstract: This work aims to present the results of evaluating the coloristic properties of polylactic acid (PLA) fibers. PLA is common nowadays in much research, as it is a biodegradable plastic from renewable sources. However, little research is devoted to PLA fibers, and even less to applied research of colored fibers. The prepared color masterbatches, created using inorganic pigments, such as titanium dioxide and carbon black, were subsequently used to prepare dyed PLA fibers in mass. The fibers were drawn to the maximum drawn ratio. The properties of the pure and dyed fibers were investigated before and after accelerated light aging using Q-SUN equipment. The changes were recorded by Fourier Transform Infrared (FTIR) spectroscopy and colorimetric properties were recorded using a device spectrometer from TECHKON SpectroDens. We also evaluated thermal properties from the first heating via differential scanning calorimetry (DSC). The measurements were taken before and after the aging of the PLA fibers, in order to see the effect of aging on the supermolecular structure, excluding the influence of the preparation process and the influence of the kind of PLA. Using inorganic pigments showed sufficient color stability even after accelerated light aging, which is beneficial for using colored fibers in practice.

Keywords: polylactic acid; inorganic pigments; dyeing; coloristic properties

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1. Introduction

Nowadays, it is possible to perceive the search for ecological solutions in all areas of our life. Therefore, research in the field of fibers and textiles is also looking for the possibility of replacing synthetic fibers with fibers that will not burden our planet so much. Investigating the possibilities of textile and fiber recycling also has its place. The recovery of textiles can result in either materials or composting. This is where biodegradable materials and materials from renewable sources come into play. The major ecological benefit of bioplastics lies in their biodegradability. Biodegradable plastics are intended to play a key role in creating a low-carbon, circular economy and improving recycling efficiency [1–5].

Among them, we also recommend polylactic acid (PLA). PLA is a linear aliphatic thermoplastic polyester that is biodegradable. Biodegradation mainly occurs in industrial compost, under precisely defined conditions, the material decomposes into low-molecular-weight products—carbon dioxide, water, and/or methane and biomass—through the biological activity of microorganisms. Lactide dimer occurs in three different optical isomers: L-lactide, D-lactide, and DL-lactide. The proportion of these in the PLA polymer can lead to different polymer properties [6–8].

A study on the dyeability of PLA fabrics with varied proportions of the D- and L-isomers showed that D forms in fibers exhibit more significant dye exhaustion and color strength due to more amorphous and less crystalline areas in the polymer. Very little difference was found between low-content D and high-content D fibers regarding wash fastness [9]. One area of research has been looking at PLA filaments colored in the bath. Chen et al. investigated the synthesis and dyeing performance of new heterocyclic azo disperse dyes for polylactic acid fibers, where they concluded that the substituents in the dye molecules affect the dye–fiber interaction. They also evaluated its exhaustion on

PLA fibers [10]. Several scientific works have been devoted to the coloring and properties of PLA masterbatches for 3D printing. Some have evaluated prepared filaments, while others have already focused on the properties of print products. The data obtained in this area serve to optimize the printing process itself, but also to improve the properties of the acquired product. Mikołajczyk et al. monitored thermal and optical properties of color PLA filament for 3D print. The divergencies in thermal and optical properties of the different colors of filaments were noticeable but not significant [11]. Hrabovská et al. prepared dyed PLA fibers for intelligent textiles, using fluorescent pigments. The specially modified halloysite with fluorescent pigment, which protects the pigment from change due to sunlight, was used during the preparation of PLA fibers. In this work, different properties were evaluated, but what were important for us were coloristic properties and the effect of light aging [12].

Since it is a biodegradable material, it is necessary to monitor the various effects of processing on the degradation of the material, but also, the effect of aging on the rate of biodegradation. Several scientific works have described the degradation of PLA material. In their review, Zaaba and Jaafar described the degradation mechanisms of PLA. These mechanisms include hydrolytic, photodegradation, microbial, and enzymatic degradation [13]. Egan and Salmon also presented an interesting work, which dealt with various forms of degradation of biopolymers. This work schematically depicted (Figure 1) the possibilities of the recovery of textiles [14].

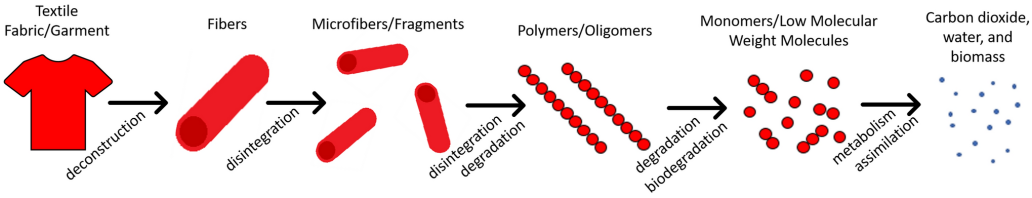


Figure 1. Schematic pathway of deconstruction, disintegration, and degradation outcomes [14].

Podkoscielna et al. focused in their work on the degradation and flammability of bioplastics based on PLA and lignin. They described the degradation of these materials very well and followed the changes in attenuated total reflectance—Fourier Transform Infrared Spectroscopy (ATR—FTIR) and differential scanning calorimetry (DSC) measurements, just like us. Based on the combustibility and thermal stability tests, they concluded that the selected additives can be successfully used as biomodifiers for increasing the thermal resistance of PLA, reducing its flammability [15]. Virág et al.'s study investigated the effects of long-term exposure to UV-C irradiation on the properties of PLA as it goes about the photodegradation of polylactic acid [16]. Effects of ultraviolet light (315 nm), temperature, and relative humidity during degradation of polylactic acid plastic films were studied by Copinet et al. The difference between virgin PLA and the prepared samples in the -C-O- and -C-C- linkage was found. The crystallinity degree of PLA material showed different properties and the course of degradation. Also, if the average molecular weight of the polymer decreased, the glass temperature (T_g) decreased [17].

So, the objective of the studies was to evaluate the coloristic properties of the prepared pure PLA and color fibers and to evaluate the total color difference after the aging of the fibers. Also, changes in ATR-FTIR spectra were evaluated due to the light aging of PLA fibers. We also evaluated the effect of aging, kinds of PLA (PLA L175 has a higher content of crystallinity, while PLA I6100D is more amorphous), and various kinds of pigments (TiO_2 and PXA) on the supermolecular structure, because the crystallinity is one of the indicators of supermolecular structure. All these measurements led to evaluating the color stability of the dyeing of the PLA fibers in mass.

2. Materials and Methods

2.1. Materials

2.1.1. Polymer

Two kinds of PLA polymers with different crystallinities and amorphous shares in polymers were used.

Polylactic acid LUMINY L175 (PLA L175) is a thermoplastic polymer in crystalline white pellet form, MFI (the melt flow index) = 3 g/10 min at 190 °C, glass temperature T_g = 60 °C, melting temperature T_m = 175 °C (produced by Total Corbion PLA B.V., NS Gorinchem, The Netherlands).

Polylactic acid INGEO I6100D (PLA I6100D) is a thermoplastic polymer in pellet form, MFI = 8 g/10 min at 190 °C, glass temperature T_g = 55–60 °C, melting temperature T_m = 165–180 °C (produced by NatureWorks LLC, Blair, NE, USA).

2.1.2. Inorganic Pigments

The choice of pigments was related to the fact that PLA is polyester and TiO_2 and PXA are often used for synthetic fibers colored in mass. It is also necessary to comply with the European Standard EN 13,432 for polymer blends (including dyes) of biodegradable polymers to maintain their biodegradable state.

1. Titanium dioxide Pretiox AV01SF (Ti) is ultrafine milled TiO_2 with a particle size of 20 nm, T_m = 1850 °C (produced by Precheza a.s., Přerov, Czech Republic).
2. Carbon black Printex Alpha (PXA) is a fine black powder with a high specific area, with an average particle size of 20 nm, T_m > 3000 °C (produced by Orion Engineered Carbons GmbH, Cologne, Germany).

2.1.3. Dispersing Agent

Silicone oil V350 (V350) was used as a dispersing agent (produced by Azelis Slovakia, s.r.o., Bratislava, Slovakia).

2.2. Preparation in Two Steps

2.2.1. Preparation of Color Masterbatches

For the preparation of color PLA masterbatches, a laboratory line with a twin-screw extruder was used. Melting was performed on the screw extruder with a diameter of 28 mm, in the temperature range of 180–210 °C. The extruder string of PLA was cooled and pelletized. The concentration of inorganic pigments (Ti, PXA) in the masterbatches was 1 wt.%.

2.2.2. Preparation of Color Fibers

The pellets of pure PLA and color masterbatches were dried in a laboratory oven for 3 h at 60 °C before spinning. Subsequently, blends of pure PLA and a specified quantity of color masterbatches (with pigments TiO_2 and PXA) were mixed so that we obtained dyed fibers with 0.1 and 0.5 wt. % pigment in the fiber. The PLA fibers were spun using a laboratory spinning line at 190 °C, extruder speed 60 rpm, and number of nozzle openings 13, with the take-up speed of 150 $m \cdot min^{-1}$. The undrawn pure PLA and colored PLA fibers were prepared (Figure 2).

After spinning, the undrawn pure PLA and color PLA fibers were drawn using a laboratory drawing machine at maximal drawn ratio λ_{max} of 95, with 105 °C as drawing temperature. The principle of drawn fiber consists of obtaining an anisotropic system using a different speed of feeding and withdrawing the fiber on the drawing galettes (increasing the length of the fiber compared to the virgin length of the undrawn fiber after spinning).

(**a**) (**b**)

Figure 2. Prepared pure PLA and color PLA fibers. (**a**) PLA I6100D and (**b**) PLA L175.

2.2.3. Process of Aging

The accelerated light aging was performed with the intensity of radiation 300–800 nm approx. 494 W·m^{-2} in the Q-SUN Xe-1-S chamber (Q-LAB, Westlake, OH, USA), in which temperature was regulated at 65 °C (black panel). Measurement conditions were radiation intensity at 340 nm–0.68 W·m^{-2} and light intensity at 142,000 lx, too. The samples were evaluated before and after aging. For comparison, 48 h of accelerated light-heat aging corresponds to approximately 2.3 years of real external aging. The aging period corresponds to continuous exposure of fibers to conditions of increased temperature, intense UV radiation, and visible light (midday sunlight). Therefore, the real, total time of use of the textile exceeds this period of calculated laboratory aging.

2.3. Methods

2.3.1. Colorimetric Properties

System CIELAB was used to evaluate the color difference (ΔE) and difference in color shade (ΔH). The samples' colorimetric trichromatic coordinates (L, a, b) were obtained according to STN EN ISO 105-J01 [18] and STN EN ISO 105-B05 [19] by portable spectrophotometer SpectroDens (TECHKON GmbH, Kőnigstein, Germany). The data were acquired with the device setting of D65 for illumination and the observer angle of 10°, with calibration on an absolute white point and the polarization filter turned off. The measurements were replicated twenty times. The total color difference ΔE was calculated from Equation (1), and the difference in color shade ΔH was calculated from Equation (2).

$$\Delta E = (\Delta L)^2 + \Delta a^2 + \Delta b^2 \tag{1}$$

$$\Delta H = (\Delta a)^2 + (\Delta b)^2 - (\Delta C)^2 \tag{2}$$

where L is the lightness and it is the position between black and white on the axis of color space, a is the position between red and green on the axis of color space, b is the position between yellow and blue on the axis of color space, and C is chroma.

2.3.2. Attenuated Total Reflectance—Fourier Transform Infrared (ATR-FTIR) Spectroscopy

The ATR-FTIR spectra were measured using the FTIR spectrophotometer Nicolet iS20 (Thermo Fisher Scientific, Waltham, MA, USA), equipped with the ATR adapter with a single-reflection ZnSe crystal. The measurement range was from 3500 to 600 cm^{-1}; resolution 4 cm^{-1}; 30 scans. The measurements were replicated two times. The background was air. The FTIR spectra were evaluated using Origin Pro 8.5 software.

2.3.3. The Thermal Properties

Differential scanning calorimetric (DSC) measurement was evaluated by DSC 1/700 STAReSystem software 16.40 and DSC 1/750 equipment from Mettler Toledo (Greifensee, Switzerland). Non-isothermal analysis of evaluated PLA fibers was performed and used to evaluate the thermal properties of PLA fibers. Conditions for the first heating used in the measurement were the rate of heating of 10 °C/min and a temperature range of 20–190 °C. The measurements were taken in an inert nitrogen atmosphere. From the measured thermograms for the first heating, we obtained glass temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), enthalpy of melting (ΔH_m), and enthalpy of cold crystallization (ΔH_{cc}).

3. Results and Discussion

The fibers were prepared by spinning from the color masterbatches. So, the research was aimed at preparing fibers dyed in mass. Two different pigments were used, white TiO_2 and black PXA. The concentrations of pigments in the prepared fibers were either 0.1 or 0.5 wt. %. Two types of PLA were used. PLA L175 has a higher content of crystalline proportion, while PLA I6100D is more amorphous.

The prepared fibers were evaluated as non-aging and were subsequently inserted into Q-SUN. The effect of light aging was evaluated in a precisely determined schedule, after 1 h, 3 h, 6 h, 12 h, 24 h, and 48 h. Coloristic properties, specifically total color difference, were compared for a given type of pure PLA, and samples with pigment 0.1 and 0.5 wt. % of every kind of pigment. This comparison is depicted depending on the aging time.

3.1. Colorimetric Properties

The colorimetric coordinates of three-dimensional space define the relationships between colors. The CIELab color space is commonly used for color evaluation. With the help of coordinates, the color difference between two colors can be mathematically defined and characterized by evaluating the total color difference. The color difference is the measure of agreement or discrepancy between the two evaluated colors.

The evaluation of the color difference (Figure 3) from the point of view of the two types of PLA manifested itself differently. PLA L175 indicated that a greater increase in the color difference occurred after 3 h of aging and this difference did not significantly increase until the end of the observed aging (48 h). For PLA I6100D, there was an increase after only 1 h of aging ($\Delta E \approx 4$), which was the same until 6 h of aging. Then, there was a further increase in color difference after 12 h of aging ($\Delta E \approx 7$).

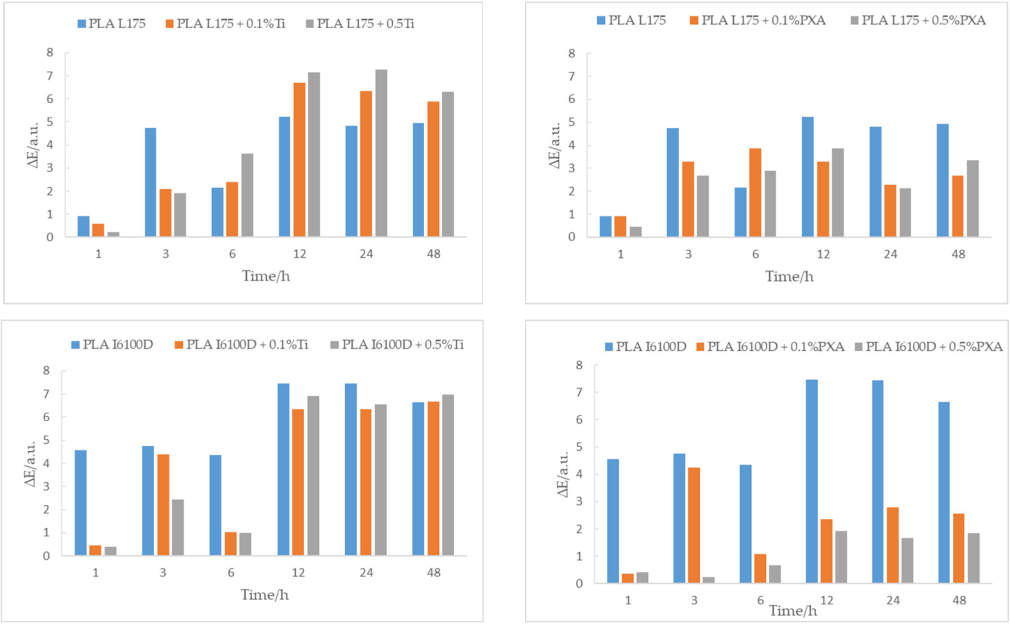


Figure 3. The total color difference of pure/color PLA fibers depending on the aging time.

For color PLA L175 fibers with Ti, a gradual increase in the color difference after individual hours of aging up to 12 h was evident, after which the value of the color difference was approximately the same.

For color PLA I6100D fibers with Ti, we saw a jump increase in the color difference after 3 h of aging, and after 12 h of aging, there was another larger increase in the color difference, which was preserved until the last measurement.

For PLA L175 with PXA, there was a gradual increase in color difference during aging, although the color difference did not reach the color difference of pure PLA fibers and was without a significant effect of time.

For colored PLA I6100D fibers with PXA, we saw only a slight increase in color difference during aging, and this was an even smaller change than for pure PLA fibers. In addition, a content of 0.5 wt. % PXA brought a smaller change in color difference than 0.1 wt. % of PXA.

A more significant color difference occurred with PLA I6100D compared to PLA L175. However, in both cases, the values of the total color difference were not higher than the value of 8. The values of the total color difference are generally considered significant if they exceed the value of 8 [20].

The difference in color shade (Figure 4) reflected the same trend as when comparing PLA fibers in the total color difference. The difference in color shade within 12 h from the start of aging reached minimum values for all samples. Its value increased after 12 h of sample aging. We observed this increase mainly in samples of pure PLA fibers and PLA fibers with TiO_2 pigment.

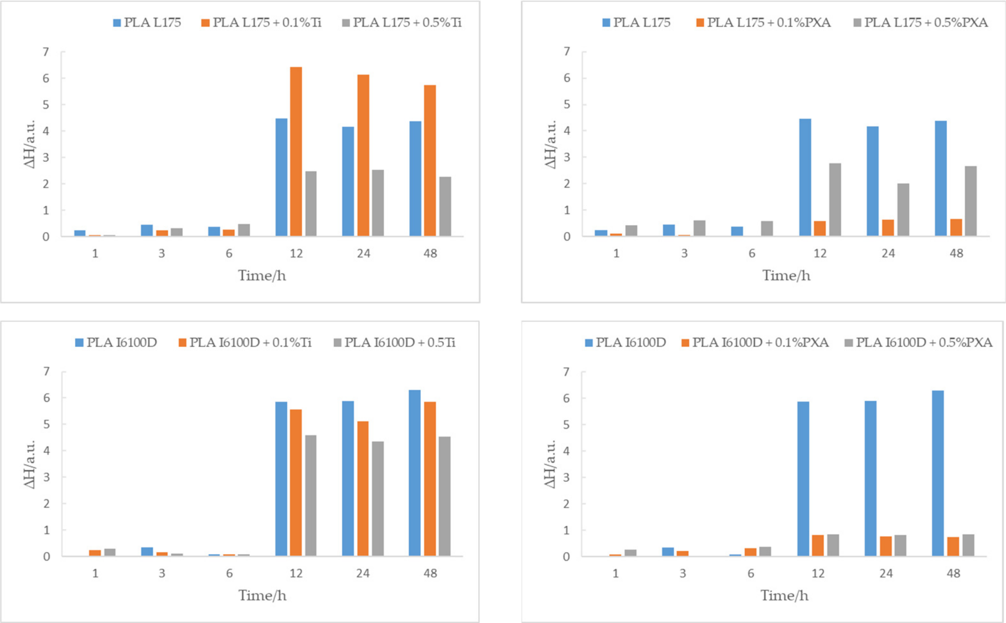


Figure 4. The difference in color shade of pure/color PLA fibers depends on the aging time.

PLA L175 saw a greater increase in the difference in the color shade than PLA I6100D. The PLA L175 sample containing 0.1 wt. % TiO_2 achieved a greater change in color shade difference than pure PLA fibers and color fibers with 0.5 wt. % TiO_2, too. Colored fibers with 0.5% wt. % TiO_2 PLA L175 were more color-stabilized. For PLA L175 with pigment PXA, there were smaller changes than pure PLA fibers and a higher content of PXA resulted in greater color fastness.

For color fibers from PLA I6100D, pigment TiO_2, there were smaller changes compared to pure PLA I6100D. For PLA I6100D with pigment PXA, there was a smaller change compared to all other samples—the difference in color shade is close to zero.

3.2. ATR-FTIR Spectroscopy

The PLA fibers were characterized by ATR-FTIR spectroscopy as well (Figure 5). In the spectra of PLA L175, the typical bands at 3250–3350 cm^{-1} (–OH), 2920–2850 cm^{-1} (-CH_2

and -CH_3), 1730 cm^{-1} (C=O), 1460 cm^{-1} (-CH_2 and -CH_3), 1115 cm^{-1} (C-O in alcohols or C-O-C in ethers), and 860 cm^{-1} (C-C) were detected [12]. Adding additives (Ti, PXA) did not cause significant changes in FTIR spectra (Figure 5). Similar results were obtained in FTIR spectra of another type of PLA I6100D.

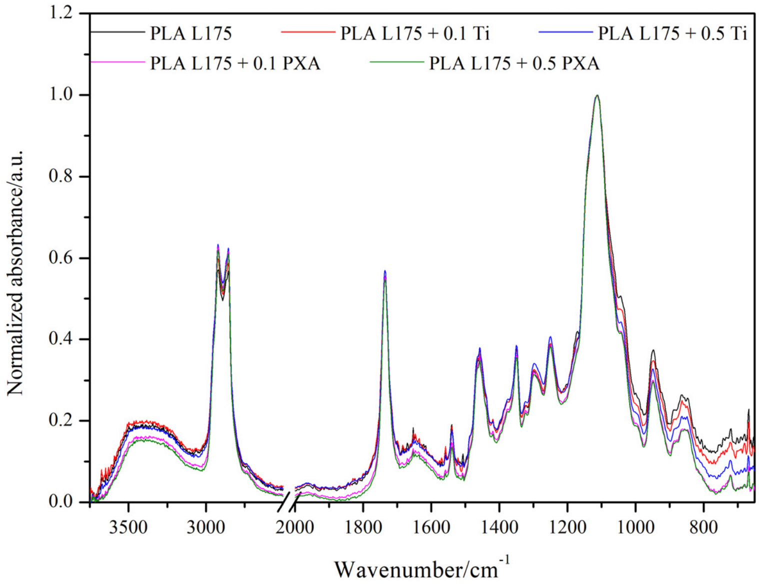


Figure 5. ATR-FTIR spectra of pure/color fibers before aging based on PLA L175.

During accelerated aging in the Q-sun chamber, there was an increase in the absorbance at 3500 cm^{-1} (OH) in the FTIR spectrum (Figure 6), as well as an increase in the absorbance of the bands at 1730 cm^{-1} (A_{1730}; C=O) compared to the absorbance of the bands at 1115 cm^{-1} (A_{1115}; C-O), indicating PLA degradation due to photoaging. The photodegradation of PLA was previously described in the literature by Ikada [21], proposing a Norrish II mechanism of carbonyl polyester (Figure 7) [22].

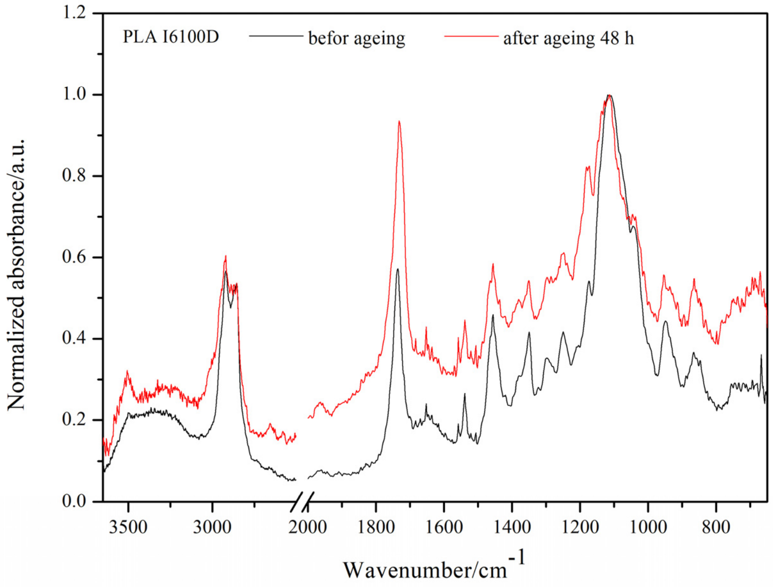


Figure 6. ATR-FTIR spectra of fibers based on PLA I6100D before and after 48 h accelerated aging in Q-sun chamber.

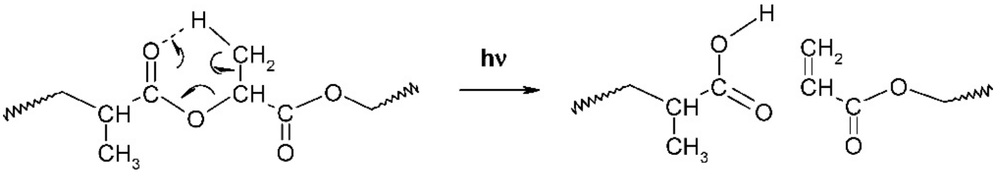


Figure 7. Norrish II reaction for PLA acid [22].

Observed changes in FTIR spectra corresponded to this reaction (Figure 7). Other authors also dealt with the degradation of PLA, while some of them attributed the increase in A_{1730} to the fact that the main products of thermal degradation of PLA are carboxylic acids and alcohol [15]. Other authors [17] explained the decrease of C-O-C bands at 1050–1150 cm^{-1} during light aging of PLA by the fact that the degradation mechanism was predominantly hydrolysis of ester linkage connected with breaking down macromolecular chains [23].

The ratios of the bands belonging to the C=O group at 1730 cm^{-1} (A_{1730}) and the C-O-C group at 1115 cm^{-1} (A_{1115}) are summarized in Table 1. The ratio A_{1730}/A_{1115} for unaged samples was only minimally affected by adding additives and ranged between 0.59–0.63. As a result of light aging, there was a change in this ratio, which may have been due to the cleavage of the C-O bonds associated with the increase in C=O, probably due to the Norrish II reaction.

Table 1. Absorbance ratio A_{1730}/A_{1115} (A_{1730} is absorbance at 1730 cm^{-1} and A_{1115} is absorbance at 1150 cm^{-1}).

Inorganic Pigment	$C_{pig.}$/wt. %	PLA I6100D		PLA L175	
		Before Aging	After Aging	Before Aging	After Aging
-	-	0.63	1.22	0.59	0.90
Ti	0.1	0.63	1.16	0.61	0.98
	0.5	0.62	1.22	0.62	1.20
PXA	0.1	0.61	1.35	0.61	1.04
	0.5	0.62	1.23	0.61	0.95

The addition of Ti in the case of PLA I6100D affected the course of degradation only minimally, in the case of PLA L175 it led to an acceleration of degradation. In contrast, the degradation increased with the increasing amount of pigment Ti. In the case of PXA, a higher degree of degradation was achieved with the addition of a smaller amount of PXA, but with the increasing amount of PXA, it decreased roughly to the level of samples without PXA, probably due to the effect of the internal filter.

3.3. The Thermal Properties

The thermogram from the first DSC heating carries the thermal history of the formation of the supermolecular structure due to the influence of the spinning and drawing process during fiber preparation. But also, it reflects the properties of the material used in connection with the preparation conditions (spinning and drawing). We mainly wanted to evaluate the resulting structure of anisotropic fibers after preparation, which forms due to the effect of the applied stress. We evaluated the effect of accelerated aging on the structure of the anisotropic system of fibers, from the first heating. The second heating reflects only the influence of the polymer and additives on the polymer crystallization at the cooling during DSC measurements. During DSC measurement at the cooling, an isotropic system occurs when it is not possible to ensure/model the effect of the applied stress as in the process of spinning and drawing. From the thermograms measured, thermal parameters, such as glass temperature (T_g), cold crystallization temperature (T_{cc}), enthalpy of cold crystallization (ΔH_{cc}), melting temperature (T_m), and enthalpy of melting (ΔH_m)

were determined. The endothermic peak with a maximum corresponds to the melting temperature, while the area under this peak corresponds to the melting enthalpy.

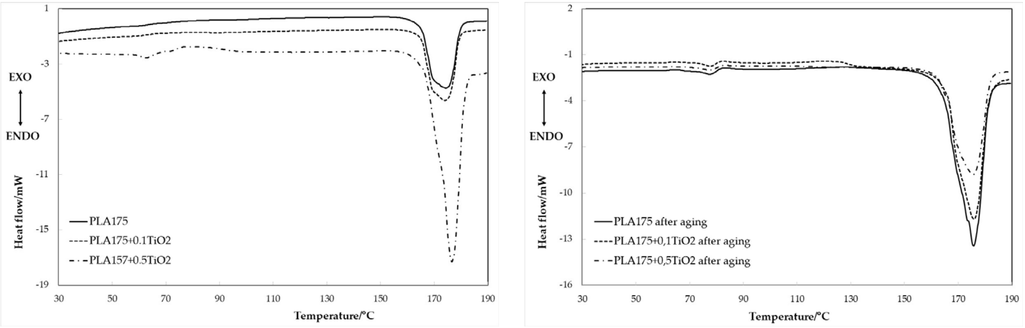
PLA L175 fibers are described in Tables 2 and 3 and Figures 8 and 9, with 0, 0.1, 0.5 wt. % of inorganic pigment TiO_2 (Table 2) and pigment PXA (Table 3). PLA I6100D fibers are described in Tables 4 and 5 and Figures 10 and 11, with 0.1, 0.5 wt. % of inorganic pigment Ti (Table 4) and pigment PXA (Table 5).

When we compared pure PLA L175 fiber with pigmented PLA L175 fibers with Ti (Table 2), the glass temperature (T_g) of pure PLA fiber was higher than color fibers. This indicates less mobility of macromolecular chains of pure PLA fibers. Meanwhile, in fibers with the addition of pigment, the crystalline structure could be different and, therefore, the glass temperature (T_g) dropped from 59 °C to 56 °C. The mobility of the chains can be affected by the crystallinity or possible reduction of the free volume due to aging conditions (T = 65 °C). The crystallinity better describes the melting enthalpy (ΔH_m).

The melting temperature (T_m), as well as cold crystallization temperature (T_{cc}), was approximately the same for all fibers, both pure PLA fiber and color fibers. However, the enthalpy of melting (ΔH_m) was higher for color fibers. We must also note the contribution of cold crystallization, where the enthalpy of cold crystallization (ΔH_{cc}) increased with the amount of added pigment.

Table 2. Glass temperature (T_g), cold crystallization temperature (T_{cc}), enthalpy of cold crystallization (ΔH_{cc}), melting temperature (T_m), and enthalpy of melting (ΔH_m) of PLA L175 and color PLA fibers with pigment Ti, before and after aging, obtained by DSC measurement during the 1st heating.

PLA L175 + Ti						
Aging	**$c_{pig.}$/wt.%**	**T_g/°C**	**T_{cc}/°C**	**ΔH_{cc}/J·g^{-1}**	**T_m/°C**	**ΔH_m/J·g^{-1}**
before	0	59.2	75.5	2.7	174.1	47.9
	0.1	56.1	73.1	2.9	173.7	53.8
	0.5	56.8	73.2	4.7	174.4	50.7
after 48 h	0	75.9	79.4	1.2	175.2	46.9
	0.1	46.0	-	-	175.5	48.7
	0.5	59.5	79.4	1.2	174.7	46.7



(**a**) (**b**)

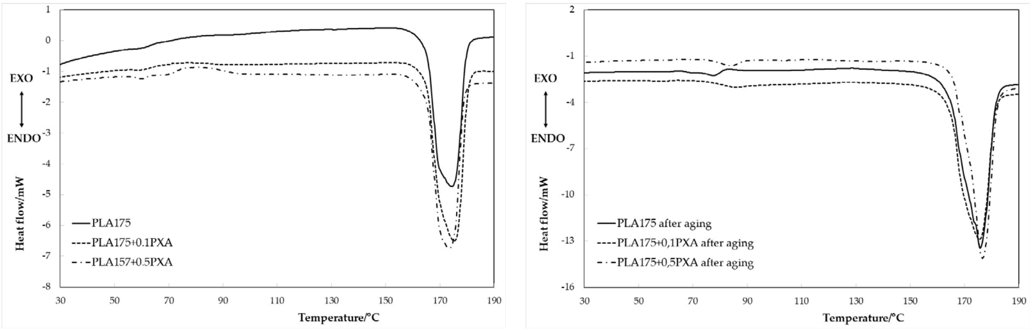
Figure 8. Thermograms of pure/color PLA L175 fibers with different concentrations of pigment Ti from the first heating: (**a**) before aging and (**b**) after aging.

The light aging, where we cannot forget the temperature conditions under which this aging took place, had different effects on individual fibers. While with pure PLA fiber, we noticed a significant increase in glass temperature (T_g) from 59 °C to 76 °C, color fibers behaved differently. At 0.1% wt. Ti, the glass temperature (T_g) was reduced from 56 °C to 46 °C, and no cold crystallization was noted. While at 0.5 wt. % Ti, the glass temperature (T_g) slightly increased from 56 °C to 59 °C, and other values, such as the contribution of cold crystallization (ΔH_{cc}) or melting enthalpy (ΔH_m), were very similar to pure PLA fibers.

Also, other researchers have followed the impact of aging on the PLA fiber and confirmed the same trend in increasing the glass temperatures (T_g) after the aging of PLA fibers [12].

Table 3. Glass temperature (T_g), cold crystallization temperature (T_{cc}), enthalpy of cold crystallization (ΔH_{cc}), melting temperature (T_m), and enthalpy of melting (ΔH_m) of PLA L175 and color PLA fibers with pigment PXA, before and after aging, obtained by DSC measurement during the 1st heating.

PLA L175 + PXA						
Aging	**$c_{pig.}$/wt. %**	**T_g/°C**	**T_{cc}/°C**	**ΔH_{cc}/J·g^{-1}**	**T_m/°C**	**ΔH_m/J·g^{-1}**
before	0	59.2	75.5	2.7	174.1	47.9
	0.1	57.3	71.3	2.5	175.0	49.0
	0.5	57.3	74.0	4.5	172.9	51.0
after 48 h	0	75.9	79.4	1.2	175.2	46.9
	0.1	54.7	73.1	1.5	174.9	51.5
	0.5	58.8	-	-	175.8	46.0



(**a**) (**b**)

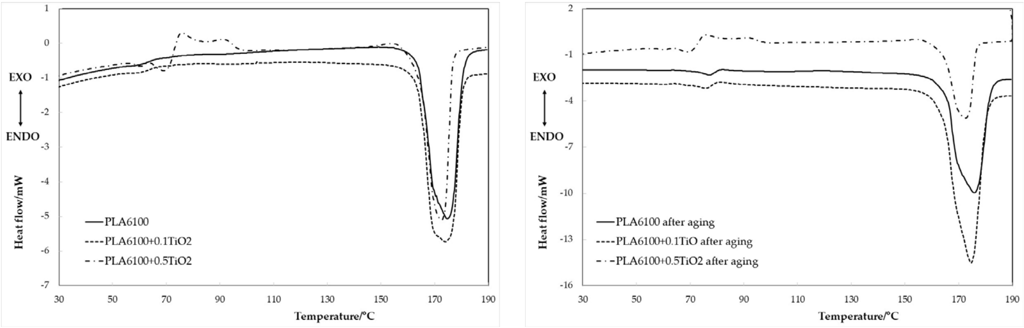
Figure 9. Thermograms of pure/color PLA L175 fibers with different concentrations of pigment PXA from the first heating: (**a**) before aging and (**b**) after aging.

The thermal behavior of PLA L175 fibers dyed with PXA pigment (Table 3) was very similar to that of fibers with Ti pigment (Table 2). Before aging the fibers, the glass temperature (T_g) recorded smaller differences. After aging, as with fibers containing Ti, we noticed a smaller change in glass temperature (T_g) with color fibers than with pure PLA L175 fiber. The other evaluated parameters were also very similar to the previous case, only cold crystallization was absent for fibers with a concentration of 0.5 wt.% and not 0.1 wt.%, after aging.

In Tables 4 and 5 and Figures 10 and 11, thermal parameters for PLA I6100D fibers are described. For the pigment Ti (Table 4), the glass temperatures (T_g) achieved very similar values as the samples from PLA L175. These temperatures (T_g) were from 56 °C to 58 °C before aging, and from 58 °C to 59 °C after aging. From this, it follows that the glass temperature (T_g) area does not change significantly with the use of different pigments. But different kinds of PLA have been manifested in different glass temperatures of fibers before aging—PLA L175 had T_g 59.2 °C, while PLA I6100D 56.3 °C. These differences are declared by the manufacturers, and further heat treatment (spinning and drawing) did not lead to significant changes in both polymers.

Table 4. Glass temperature (T_g), cold crystallization temperature (T_{cc}), enthalpy of cold crystallization (ΔH_{cc}), melting temperature (T_m), and enthalpy of melting (ΔH_m) of PLA I6100D and color PLA fibers with pigment Ti, before and after aging, obtained by DSC measurement during the 1st heating.

PLA I6100D + Ti						
Aging	**$c_{pig.}$/wt. %**	**T_g/°C**	**T_{cc}/°C**	**ΔH_{cc}/J·g^{-1}**	**T_m/°C**	**ΔH_m/J·g^{-1}**
before	0	56.3	74.7	2.3	174.4	41.9
	0.1	55.8	74.6	2.8	173.7	47.5
	0.5	58.9	75.7	16.6	172.4	32.5
after 48 h	0	58.1	-	-	175.4	50.7
	0.1	58.4	-	-	174.0	50.7
	0.5	59.1	79.4	1.2	174.7	46.7



(**a**) (**b**)

Figure 10. Thermograms of pure/color PLA I6100D fibers with different concentrations of pigment Ti from the first heating: (**a**) before aging and (**b**) after aging.

A significant increase in the enthalpy of cold crystallization (ΔH_{cc}) occurred at Ti pigment concentration of 0.5 wt. % compared to other PLA I6100D fibers. The enthalpy of cold crystallization (ΔH_{cc}) of PLA I6100D fibers with content 0.5 wt. % Ti pigment increased fourfold compared to PLA L175 with 0.5 wt. %.

On the contrary, we observed a significant decrease in the melting enthalpy (ΔH_m) of PLA I6100D and color PLA I6100D fibers compared to the first type of PLA. As we know from the supplier, PLA I6100D contains a higher amorphous content, which corresponded to the melting enthalpy (ΔH_m) values. The influence of different kinds of PLA was manifested in the melting enthalpy (ΔH_m), mainly before aging. But we cannot forget the addition of cold crystallization, which also contributed to the creation of a supermolecular structure, and the addition of pigment caused an increase in cold crystallization, especially for PLA I6100D.

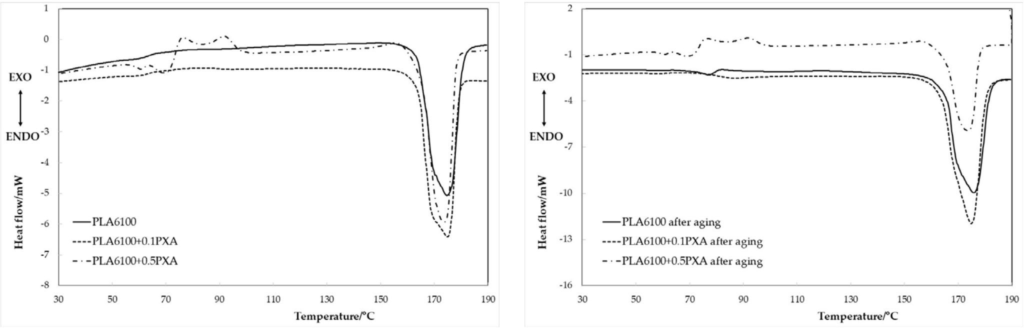
Table 5. Glass temperature (T_g), cold crystallization temperature (T_{cc}), enthalpy of cold crystallization (ΔH_{cc}), melting temperature (T_m), and enthalpy of melting (ΔH_m) of PLA I6100D and color PLA fibers with pigment PXA, before and after aging, obtained by DSC measurement during the 1st heating.

PLA I6100D + PXA						
Aging	**$c_{pig.}$/wt. %**	**T_g/°C**	**T_{cc}/°C**	**ΔH_{cc}/J·g^{-1}**	**T_m/°C**	**ΔH_m/J·g^{-1}**
before	0	56.3	74.7	2.3	174.4	41.9
	0.1	57.3	77.1	2.4	174.5	46.7
	0.5	59.1	76.2	15.8	173.4	32.0
after 48 h	0	58.1	-	-	175.4	50.7
	0.1	55.3	-	-	174.3	49.3
	0.5	51.8	-	-	172.6	48.1

After aging, there was a change in the melting enthalpy (ΔHm), mainly in pure PLA I6100D. The melting enthalpies (ΔHm) of colored PLA fibers were affected by the addition of pigments and the formation of a supramolecular structure before aging.

Another, more significant, change was that in PLA I6100D fibers, cold crystallization disappeared in all cases after aging. The conditions during aging allowed recrystallization and, upon subsequent heating during DSC measurements, cold crystallization was no longer noted.

The enthalpy of melting (ΔHm) of PLA fibers with PXA pigment reached very similar values to the Ti pigment, for the same kind of PLA, so it can be said that the influence of pigments manifested itself at the creation of a crystalline structure during the preparation of fibers. Exposure of the samples to accelerated aging led to possible recrystallization and subsequent formation of very similar structures of supermolecular crystallinity. Although a higher content of PXA already led to a significant increase in the enthalpy of melting (ΔH_m), the enthalpy of melting (ΔH_m) reached very similar values to the Ti pigment, for the same kind of PLA, so it can be said that the influence of pigments manifested itself in the creation of crystalline structure during the preparation of fibers.



(**a**) (**b**)

Figure 11. Thermograms of pure/color PLA I6100D fibers with different concentrations of pigment PXA from the first heating: (**a**) before aging and (**b**) after aging.

4. Conclusions

In this work, we evaluated the color properties of the prepared fibers and the effect of accelerated aging on the color changes of the resulting products—dyed fibers. We used the CIELab system to evaluate the color difference (ΔE) and difference in color shade (ΔH). It is a mathematical system for the expression of color change. It is very important to know the mechanisms that would occur in the resulting products from biodegradable materials due to aging and would lead to a change in the properties of the resulting product. One of the important properties is color fastness. This work brought very interesting results. We can say that the color change, even in aging fibers, was small enough that we can say that the use of inorganic pigments was able to maintain color constancy.

We also monitored the effect of accelerated aging on the internal change in the chemical nature of the polymer material (ATRE-FTIR), as well as on the change in the structure of macromolecular chains (DSC measurement).

Based on Fourier Transform Infrared Spectroscopy (FTIR), a change in the chemical structure of PLA fibers was recorded. The change was mainly reflected in the decrease of C-O-C bands and the increase in C=O, probably due to the Norrish II reaction.

From the results of the evaluation of the supramolecular structure of the fibers, where the effects of two kinds of PLA and two kinds of inorganic pigments were evaluated, we can say that the influence of different kinds of PLA was much smaller than the influence of accelerated light aging. However, it was noted that the pigment concentration also led to different structural changes in the prepared fibers.

The knowledge gained shows that it is possible to prepare PLA fibers with inorganic pigments, which would not be subject to significant changes in properties due to light aging. These results can be a good basis for the development of PLA fibers dyed in mass with a larger color range while maintaining the degradability of PLA fibers. However, these findings can also be applied to other products dyed in biodegradable PLA.

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