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Color stability of polylactic acid pigmented with natural indigo of *Isatis Tinctoria* in artificial weathering

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Abstract

Our study presents lightfastness properties of polylactic acid colored with plant-based natural indigo. Indigo is a blue colorant which is widely used in textile industry as a vat dye in coloration of jeans. Problematically, it is most commonly synthesized from petroleum-based sources. However, indigo can also be extracted from various plants, for example woad (*Isatis tinctoria*), thus offering a natural alternative for synthetic indigo. Woad is a biperennial plant, which produces extractable precursors of indigo in its leaves. It grows especially well in the harsh Northern European climate, making it a desirable plant-based source of indigo in Finland. Even though woad indigo is well known in the textile coloration field, little research has been done to determine lightfastness performance of woad indigo in non-textile applications. Thus, for our lightfastness study, natural indigo from woad was obtained and added to plastic matrices via extrusion. The extruded plastic filaments were injection molded into sample rods suitable for artificial weathering. After that, all the indigo-colored plastics and uncolored reference plastics were subjected to the artificial weathering test (ISO 4892-3:2016). Appearance and color fastness of the sample rods were assessed with visual inspection, reflectance spectrophotometry and hyperspectral imaging before and after the artificial weathering test. Hitherto, our results have showed that the natural indigo pigment produces a uniform color comparable to that obtained with synthetic indigo pigment, but the color fastness properties of the natural indigo samples are substantially worse than those of synthetic indigo samples.

Keywords: Natural indigo, accelerated weathering, woad, polylactic acid, hyperspectral imaging, reflectance spectroscopy

INTRODUCTION

Annually, over 700000 tons of synthetic dyes are produced mainly from petrochemical sources (Chequer, 2013). An example of the commonly used synthetic colorants is indigo, which is produced approximately 50000 tons every year (Blackburn et al., 2009; Clark et al., 1993; Towns, 2019). It is mainly used as a vat dye for textile coloration, but it can also be used as a pigment (Melo, 2009). As a natural alternative, indigo can also be extracted from various plants such as *Isatis Tinctoria*, commonly known as woad (Orsini et al., 2012). Woad is a biperennial plant, which survives well in northern European climate (John and Angelini, 2009). The indigo dye is produced in the leaves of the plant, which can be harvested already on the first year after sowing (Hartl et al., 2015). After harvesting, precursors of the indigo dye are extracted from the leaves via hot water extraction and then further processed depending on the application (John, 2009).

Currently, one of the main uses for colorants is plastic coloration (Towns, 2019). Like colorants themselves, thermoplastics are most often manufactured from non-renewable raw materials, which poses problems for sustainable lifestyle due to limited amount of non-renewable resources (Biron, 2007). Some bio-based plastics have attempted to tackle this issue, for example polylactic acid (PLA). PLA a widely available bio-based thermoplastic material which is commonly used for agriculture, automotive, and packaging purposes (Helanto et al., 2019; Taib et al., 2022). So far however, there is little published research about combining PLA with natural colorants.

The objective of this study was to determine the artificial weathering stability of natural indigo pigmented PLA and to compare it to synthetic indigo pigmented PLA. The pigmented PLA samples were prepared via filament extrusion and injection molding. Artificial weathering was done in UVA test chambers with periodic cycles of UVA radiation and water condensation. Effects of the artificial weathering were assessed by visual inspection, reflectance spectrophotometry and hyperspectral imaging.

MATERIALS AND METHODS

Materials

Natural indigo pigment was provided by Natural Indigo Finland Ltd and synthetic indigo powder manufactured by Sigma-Aldrich Ltd was obtained from VWR International Ltd. Polylactic acid (PLA) granulate was obtained from Resinex Nordic AB.

Sample preparation and testing

Natural and synthetic indigo pigments were ground to fine powder with a planetary ball mill (Fritsch Pulverisette 6 with zirconium oxide grinding balls). Grinding was done in ten one-minute periods with rotational speed of 550 rpm. Pigmented filaments of five different compositions were formed by extrusion of PLA granules in 200 °C with a twin-screw extruder. During the extrusion, indigo pigment was gradually applied to molten plastic to ensure even mixing in the twin-screw system. The molten pigmented PLA was cooled in a water bath and collected as a continuous monofilament. Compositions of the filaments are presented in Table 1 below.

Table 1. Compositions of the sample plastics.

Sample name	Pigment type	Pigment (wt-%)	PLA (wt-%)
Nat 0,5	Natural indigo	0,5	99,5
Nat 1	Natural indigo	1,0	99,0
Nat 2	Natural indigo	2,0	98,0
Synt 0,5	Synthetic indigo	0,5	99,5
Ref	-	-	100

The sample filaments were cut to small granules and injection molded into sample rods. After that, the sample rods were exposed to artificial weathering in UVA test chamber (QUV Accelerated Weathering Tester, Q-Lab Corporation). The exposure was conducted according to standard ISO 4892-3:2016, method A, cycle 1 except that temperature of UVA exposure phase was lowered from 60 °C to 50 °C due to heat sensitivity of PLA. One exposure cycle consisted of 8 h of UVA radiation in 50 °C followed by 4 h of water condensation without UVA radiation in 50 °C. This cycle was repeated for 9 weeks in total. Every 7 days, reflectance spectra and CIELAB color values of the pigmented plastic rods was measured with Datacolor 600 reflectance spectrophotometer. Moreover, hyperspectral images of the samples in wavelength range of 400 – 1000 nm were obtained with Specim IQ portable hyperspectral camera before and after the artificial weathering.

RESULTS AND DISCUSSION

Photographs of the samples after 0, 3 and 6 weeks of artificial weathering are shown in Figure 1. As can be seen from the images, samples with natural indigo became much lighter during the exposure. The samples with synthetic indigo showed almost no visual changes, whereas the unpigmented sample changed from translucent to opaque white color.

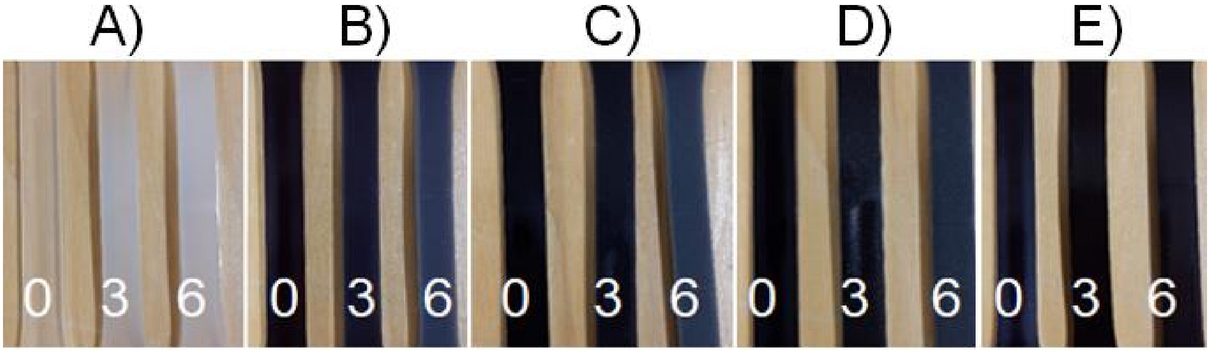

Figure 1. Photographs of the samples 0, 3 and 6 weeks after artificial weathering. Samples in the figure: A = unpigmented sample, B = 0,5 % of natural indigo, C = 1,0 % of natural indigo, D = 2,0 % of natural indigo and E = 0,5 % of synthetic indigo.

Colors of the samples were measured with Datacolor 600 reflectance spectrophotometer to quantify visual changes in the samples during artificial weathering period. CIELAB lightness (L^*) and CIELAB color parameters a^* and b^* during the exposure testing are shown in Figure 2A. As seen from the Figure 2A, lightness of the natural indigo pigmented samples increased steadily over time. Particularly, lightness of the samples with less indigo pigment increased faster over exposure time than lightness of the samples with more natural indigo pigment. Unlike the natural indigo pigmented samples, synthetic indigo pigmented sample showed almost no change in lightness during the exposure period.

In Figure 2B, color parameters a^* and b^* show that the natural indigo samples changed substantially from green to red and slightly from yellow to blue over the exposure time. The sample pigmented with synthetic indigo showed nearly no changes in color parameters a^* and b^* during the exposure time. Of all samples, color parameters of the unpigmented sample changed the most, changing its color substantially from yellowish to bluish and from reddish to greenish.

In addition to basic CIELAB values L*, a* and b*, total color change over time (ΔE*) of the samples was calculated with the following formula:

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

CIELAB total color change over exposure time is presented at Figure 2C. The sample pigmented with 0,5 % of natural indigo showed almost no color change in first 2 weeks and the samples pigmented with 1,0 % and 2,0 % of natural indigo showed almost no color change in first 3 weeks. After that, the total color change of natural indigo pigmented samples increased linearly over exposure time. The increasing rate of color change was lower for samples with more natural indigo and higher for samples with less natural indigo. Unlike all other samples, color of the sample with synthetic indigo showed almost no color change during the exposure. The total color change of the unpigmented sample increased almost linearly for the first 6 weeks of the testing period and after that settled between natural indigo pigmented samples with 1,0 % and 2,0 % of pigment.

As the visual and colorimetric examinations showed, increased amount of natural indigo pigment in the samples resulted to better resistance against color change in artificial weathering. However, samples with synthetic indigo pigment had substantially better color fastness than any of the samples with natural indigo pigment. As synthetic and natural indigo are ideally the same compound obtained from different sources, the differences between the two pigments might be caused by impurities in the natural indigo.

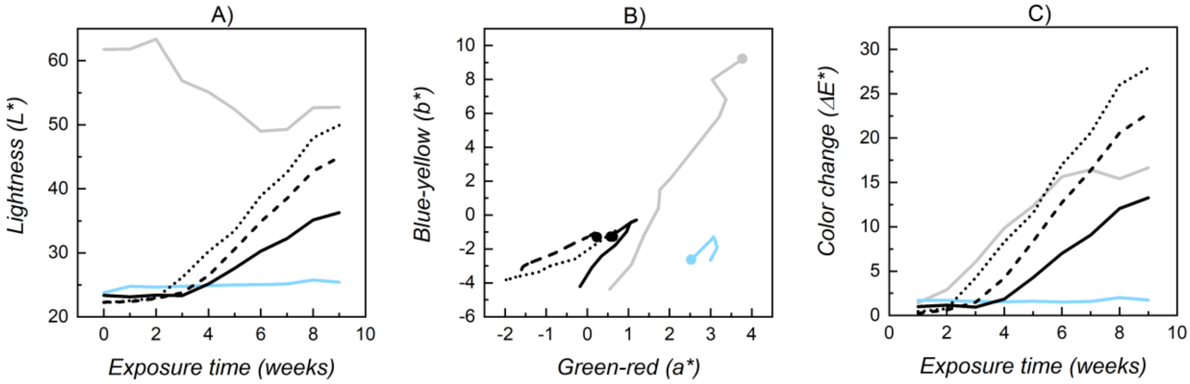

Figure 2. A) Development of CIELAB lightness of the samples during the exposure period, B) CIELAB color parameter $b*$ as a function of color parameter $a*$ over time and C) development of CIELAB total color change of the samples during the exposure period. In B) the first time point is indicated by larger marker. Samples in the figure: black dot = 0,5 % natural indigo, black dash = 1,0 % natural indigo, black solid = 2,0 % natural indigo, blue = 0,5 % synthetic indigo and grey = unpigmented sample.

To further examine the visual changes in the samples during the exposure period, visible reflectance spectra of the samples was measured after 0, 2, 4, 6 and 8 weeks of exposure. Development of visible reflectance spectra of the samples during the exposure period is presented in Figure 3. As seen from the figure, reflectance of all indigo pigmented samples increased over the exposure time, especially in 400 – 450 nm region. Moreover, reflectance curve of the natural indigo pigmented samples was originally flat in the 400 – 450 nm region but started developing a peak over exposure time. Reflectance of the natural indigo pigmented samples with lower percentage of pigment increased more over time than reflectance of those with higher percentage of pigment.

Reflectance of the sample pigmented with synthetic indigo increased substantially less than reflectance of the samples pigmented with natural indigo. Furthermore, the reflectance curve of synthetic indigo pigmented samples had a distinctive peak around 400 – 450 nm already at the beginning of the exposure and the shape of the peak did not change during the exposure. In the 500 – 650 nm range however, reflectance of the synthetic indigo pigmented sample increases substantially during the first two weeks of exposure.

Because the reflectance spectra of synthetic and natural indigo samples are substantially different, it is probable that the natural indigo pigment contains some impurities that do not exist in synthetic indigo pigment. Moreover, the impurities seem to substantially lower the lightfastness stability of the natural indigo samples. However, in samples with more natural indigo pigment, the differences between synthetic indigo pigment are less distinct and the overall reflectance of the sample changed less over time. Additionally, reflectance properties of the natural indigo samples changed substantially less over time than reflectance properties of the unpigmented PLA sample. So, from the reflectance data it can be deduced that both synthetic and natural indigo pigment have protective abilities against lightfastness in the PLA despite of the probable impurities hindering the lightfastness of the natural indigo pigment.

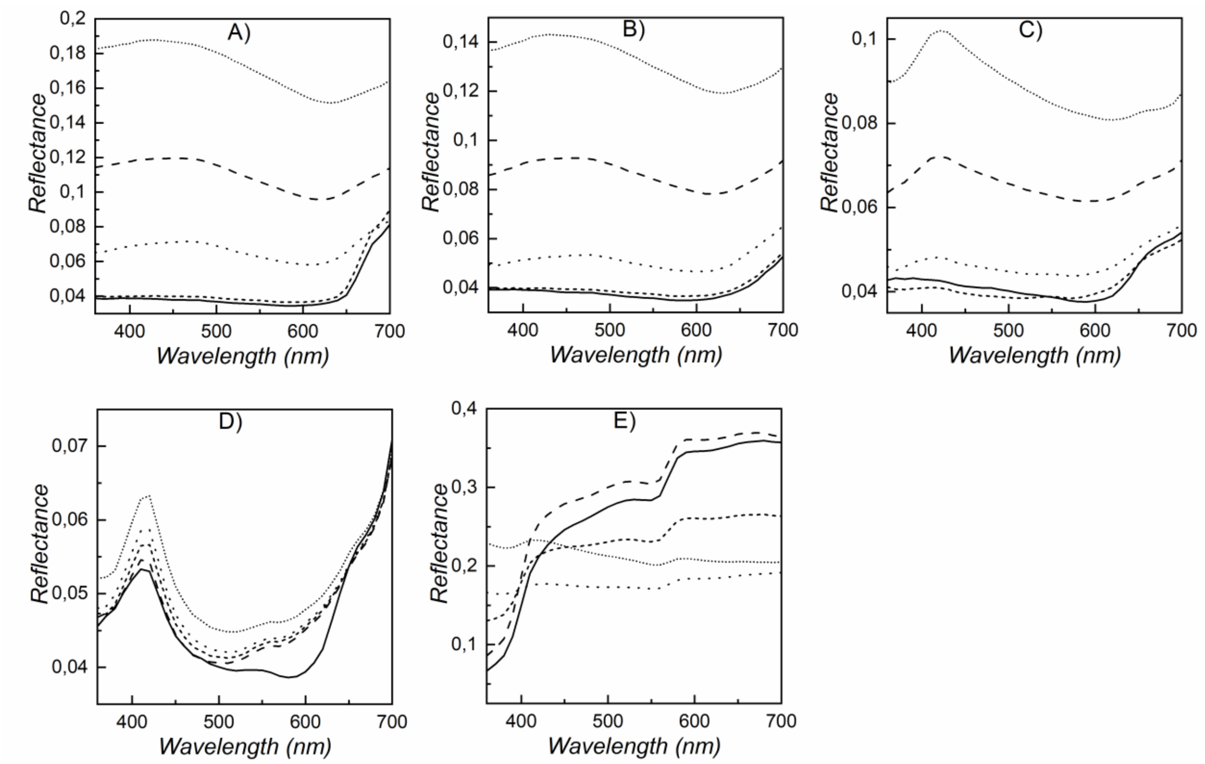

Figure 3. Development of visible reflectance spectrum of the samples during the exposure period. Samples in the figure: A = 0,5 % of natural indigo, B = 1,0 % of natural indigo, C = 2,0 % of natural indigo, D = 0,5 % of synthetic indigo and E = unpigmented sample. The spectra were measured before exposure (solid line) and after 2 weeks (long dashed line), 4 weeks (dashed line), 6 weeks (tightly dotted line) and 8 weeks (dotted line) of exposure.

Hyperspectral reflectance of the samples after 0, 3 and 6 weeks of exposure was measured in the wavelength range of 400 – 1000 nm to detect possible non-visible changes in the samples caused by the artificial weathering. Average spectra between 400 and 1000 nm of natural indigo pigmented (0,5 % of pigment), synthetic indigo pigmented (0,5 % of pigment) and unpigmented sample are shown in Figure 4. It can be seen from Figure 4 that meanwhile reflectance of the natural indigo pigmented sample increases over time in all wavelengths, reflectance of the synthetic indigo sample increases only between 750 nm and 1000 nm. Also, the reflectance spectra of natural indigo pigmented sample resemble more the spectra of the unpigmented sample than the synthetic indigo pigmented sample.

The hyperspectral data shows that even though synthetic indigo pigment substantially slowed down aging of the plastic in the 400-700 nm region, the synthetic indigo pigment did not have considerable effect against surface aging in the 700-1000 nm region. Moreover, shapes of the reflectance curves from natural indigo samples are closer to unpigmented samples than the synthetic indigo samples. It is thus likely that the impurities in the natural indigo sample are not only hindering the lightfastness performance of the samples but also substantially hindering the coloring capability of the natural indigo pigment.

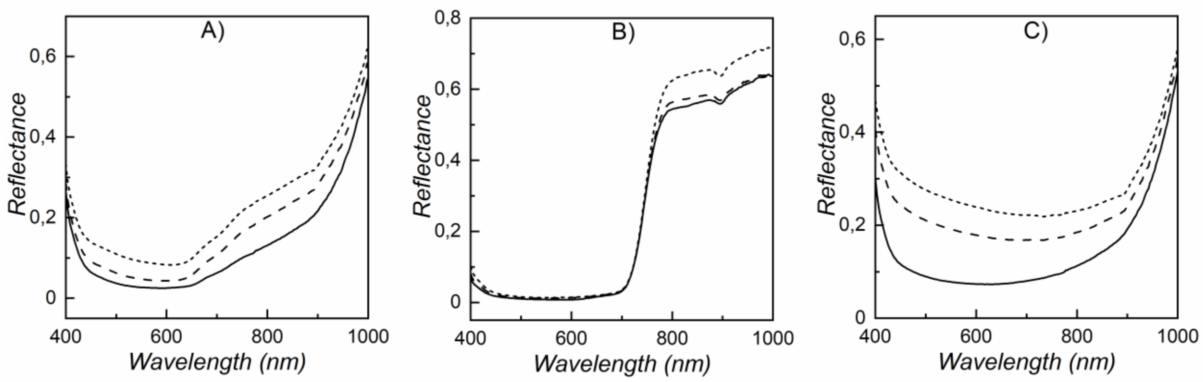

Figure 4. Development of reflectance spectrum of the samples between 400 and 1000 nm during the exposure period measured with SPECIM portable hyperspectral camera. Samples in the figure: A = 0,5 % of natural indigo, B = 0,5 % of synthetic indigo and C = unpigmented sample. The spectra were measured before exposure (solid line), after 3 weeks of exposure (long dashed line) and after 6 weeks of exposure (dashed line).

CONCLUSIONS

The results in this study show that natural indigo colored PLA somewhat resisted color change in relatively harsh artificial weathering conditions. The more natural indigo pigment was used in PLA coloration, the better resistance PLA had to color change during artificial weathering. However, weathering resistance of natural indigo pigment in PLA was substantially outclassed by its synthetic counterpart. We believe that weaker weathering performance of the natural indigo pigment is a concerning issue hindering the usefulness of natural indigo in otherwise promising applications. Thus, its cause must be thoroughly investigated in the future.

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