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Abstract The use of natural dyes for textile fibers has become an alternative to solve issues as environmental pollution and health risks caused by synthetic dyes. With this purpose, the use of silkworm excrement to dye textile fibers was targeted in silk (SK) and polyamide 6.6 (PA) weave fabric. This extract was characterized by spectroscopy to evaluate the color intensity and the color strength (K / S) and, finally, measured color fastness to wash, to friction and perspiration. The SK fiber as a better dye yield with silkworm excrement. Although the PA fiber shows also reasonable dye yield. With the results presented, it is possible to conclude that the SK and PA fabrics can be easily dyed with the natural dye extracted from the excrement of the silkworm, obtaining yellowish-brown colors.

***Keywords*—Silkworm Excrement, Silk, Polyamide 6.6, Natural Dye**

I. Introduction

WIyh the recent environmental policies and the introduction of more stringent legislation, the use of natural dyes in fiber dyeing tends to become a viable alternative, since this class of dyes show desirable characteristics such as: they do not cause allergies, they are not toxic and are eco-friendly.

The natural dyes are mostly derived from plant material and can be simultaneously renewable and biodegradable products. This range of dyes allows to dye a large part of natural and even some synthetic fibers. The dyes, such as those obtained from safflower flowers, onion peel and pomegranate peel are by-products of agricultural activity. The curcuma, safflower, marigold, and indigo are obtained from fruits, flowers and tree seeds that regenerate at least annually without compromising the potential for sustainability [1–3].

In this case, the present research intends to study the potential of using silkworm excrement as a natural dye alternative for dyeing fibers, especially silk (SK) and polyamide 6.6 (PA). It is a non-toxic and low-cost material, naturally generated in the SK production. Silkworm excrement is the result of feeding entirely based on mulberry leaves (*Morus*). When the silkworm ingests mulberry leaves, about 60% are excreted without being digested [4]. Therefore, this excreta are probably composed of leaves of mulberry and several constituents biotransformed by microbes or enzymes in the intestine of the beetle [5]. Constituents isolated from mulberry leaves include flavonoids, such as rutin, quercetin, quercitrin, isoquercitrin, steroids and triterphoids, substances present in various materials used as natural dyes [4], [6].

Thus, it is used widely, from healing iron-deficient research to its use in removing pesticides in activated carbon form [7], [8]. In dyeing context, the extract was used for dyeing cotton and wool. Wool fiber have better acceptance to this dye [9].

II. Procedures

A. *Materials and methods*

Commercial pre-washed pure PA (warp 52 yarns cm^{-1}, weft 32 yarns cm^{-1}, 110 GSM) and pure SK woven fabrics (warp 60 yarns cm^{-1}, weft 50 yarns cm^{-1}, 50 GSM) were employed in this study.

B. *Preparation of dye extract from silkworm excrement*

Dye extract from the silkworm excrement was obtained by aqueous extraction, scaling 10 g of silkworm excrement and mixing with 1 L of distilled water. The sample was then heated with stirring at 90 ° C in a thermostatic bath for 60 minutes. After heating, the contents were cooled to room temperature and filtered. Prior to dyeing, the pH of the extract was adjusted from 9.6 to 3.5 with acetic acid.

C. Pre-mordanting process

Potassium alum and tannic acid were used as mordants. The pre-mordanting procedure consisted of fabrics immersed in a mordant solution of 5g L^{-1} each at 90ºC for 45 min. The mordanting process was also conducted in the dyeing machine Kimak AT1-SW. After treatment, samples were dried at room temperature.

D. Dyeing

The samples were dyed for 60 minutes at 40 rpm on the Kimak AT1-SW equipment, employing a bath ratio of 1: 100 and a temperature of 90 ºC. Following, the dyed samples were rinsed with distilled water and dried at ambient conditions.

III. CHARACTERIZATION

A. Color parameters

The color strength of the dyed fabrics expressed as K/S value was calculated from the Kubelka–Munk [10] equation (1) as given below:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (1)$$

where K is the absorbance coefficient, S is the scattering coefficient, and R is the reflectance ratio measured at the maximum absorbance of dye using a Datacolor 550 reflectance spectrophotometer. Measurements were taken at five different positions on the fabric surface and averaged.

The color intensity (I) of the samples was also determined, using equation (2), as described below [10].

$$I = \sum_{\lambda=400nm}^{\lambda=700nm} \frac{K}{S}(\lambda) \times \triangle\lambda \qquad \triangle\lambda = 10 \qquad (2)$$

where $\boldsymbol{\lambda}$ represents the wavelength.

B. Washing fastness test

For the washing fastness tests, the dyed fabrics were treated in a Kimak AT1-SW, for 30 min at 40ºC in accordance with ISO Standard 105-C06 A1S-2010. A solution of ECE detergent type B was prepared with a concentration of 4 g L^{-1} and volume of 150 mL. When the cycle was finished, the samples were washed with distilled water dried under ambient conditions.

TABLE I
COLOR INTENSITY (I), CIELAB COLOR COORDINATES AND COLOR REPRESENTATION OBTAINED WITH THE MORDANTS

Fibre	Mordant	Intensity (I)	CIELAB Color Coordinates			Color
			L*	a*	b*	
Silk	Tannic acid	1080,33	43,20	8,52	21,14	
	Non-mordanted	933,15	49,20	6,59	25,75	
	Potassium alum	777,67	51,91	6,30	25,85	
PA 6.6	Tannic acid	515,30	54,84	6,27	20,01	
	Potassium alum	479,93	59,77	5,66	27,47	
	Non-mordanted	477,30	59,71	5,85	27,35	

C. Rubbing fastness test

Rubbing fastness tests were performed to analyse the resistance of the natural dyed fabrics to physical action, in accordance with ISO Standard 105-X12:2016. Each sample was abraded against cotton abrasive fabric for ten cycles in a dry and wet state.

D. Perspiration fastness test

For perspiration fastness tests each sample was tested in acid and alkaline form, in accordance with ISO Standard 105-E04:2013.

After the fastness tests, all staining and color change measurements were carried using a Datacolor 550 spectrophotometer. Results related to color strength (K/S) and wash fastness of non-mordanted and pre-mordanted fabrics were compared.

IV. Results and Discussion

The SK and PA samples dyed with silkworm excrement showed different color for each mordant used, however, all the samples were verified to be yellowish brown.

The K/S values as a function of the wavelength were plotted for the dyed SK without mordant, SK mordanted with tannic acid and for SK mordanted with potassium alum, shown in figure 1. The color intensity and the respective coordinates for the samples are presented in table I.

The results show a better color intensity for SK treated with tannic acid, as well as a higher K/S, restating the dye uptake. Following, the SK non-mordanted showed a relevant K/S curve when compared to the SK treated with potassium alum.

A better yield was noticed for the PA pre-mordanted with tannic acid, as it can be seen in the figure 2 and the table I. The pre-mordanted PA with potassium alum did not show any significant influence on the PA that did not go through the pre-mordanting process.

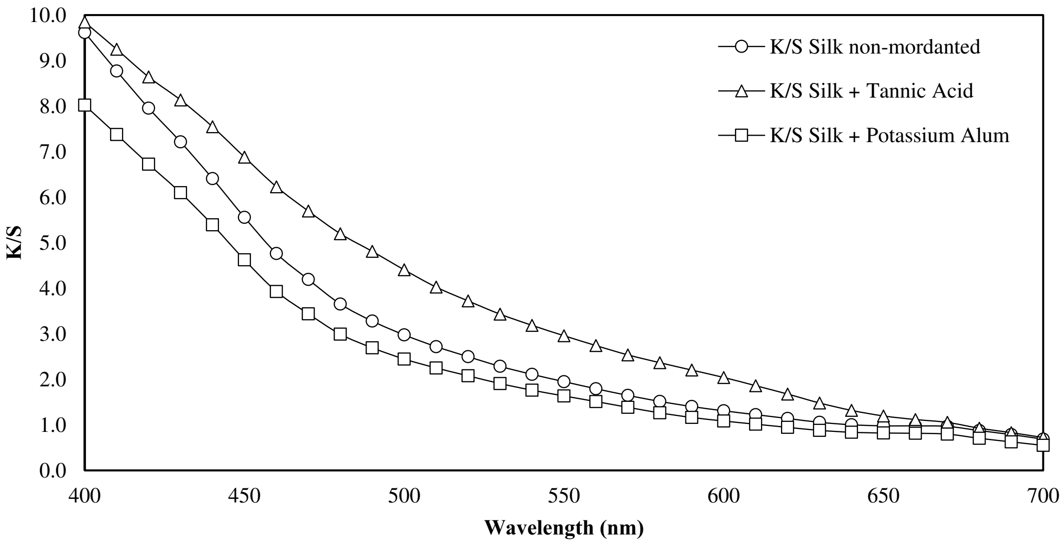

Fig. 1. Color strength of silk with different mordants.

The analysis of the samples dyed in the different conditions tested also allows to verify that the obtained shades have changed as a function of the mordant used before the dyeing, a situation that is confirmed by the existence of crossings in the curves of K/S of the dyed samples, as evidenced into variations in the respective chromatic coordinates, as shown in figure 2.

From the analysis of the color intensity (I) values of SK and PA samples dyed with silkworm excrement (table I), it is possible to analyse that the dye uptake was higher in SK for all conditions tested. This behaviour is possibly related to the greater number of functional groups present in the SK fibers, available to bond with the dye molecules as it is possible to see in Wei [11].

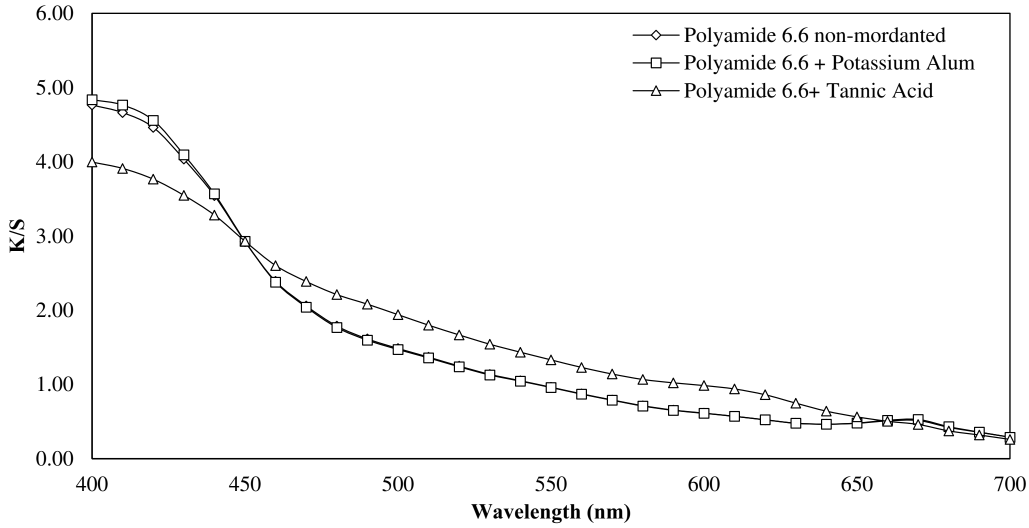

Fig. 2. Color strength of polyamide 6.6 with different mordants.

By analysing the chromatic coordinates of dyed SK and PA samples, the pre-mordanting process with tannic acid, followed by dyeing, produced darker shades (lower luminosity L *), more reddish (a* coordinate increase), and less yellowing (decrease of the b * coordinate) in relation to the other samples. The SK samples pre-mordanted with potassium alum, however, presented lighter, less reddish and more yellowish than the samples without pre-treatment with mordant. In the case of PA dyeing, pre-treatment with alum did not significantly influence L * luminosity, providing less reddish and more yellowish tones compared to the sample without mordant pre-treatment.

The results for washing fastness, as well as the results for rubbing fastness are presented in table II for SK and PA samples.

TABLE II
WASHING AND RUBBING FASTNESS TEST RESULTS

Sample	Washing Fastness							Rubbing Fastness	
	Color Change	*Staining on adjacent fibers*						Dry	Wet
		WO	PAC	PES	PA	CO	AC		
SK	4-5	5	5	5	4-5	4-5	5	3	3
SK/Tannic	4-5	4-5	5	5	4-5	5	5	4-5	4
SK/Alum	4-5	4-5	5	5	4-5	5	5	4	4
PA	3-4	5	5	5	5	5	5	5	5
PA/Tannic	3-4	5	5	5	5	5	5	5	5
PA/Alum	3-4	5	5	5	5	5	5	5	4-5

SK – Silk non-mordanted, **SK/Tannic** – Silk pre-mordanted with tannic acid, **SK/Alum** - Silk pre-mordanted with Potassium alum, **PA** – Polyamide non-mordanted, **PA/Tannic** – Polyamide pre-mordanted with tannic acid, **PA/Alum** - Polyamide pre-mordanted with Potassium alum, **AC**- Acetate, **CO**- Cotton, **PA**- Polyamide, **PES**- Polyester, **PAC**- Acrylic, **WO**- Wool, **CC**- Color change.

The washing and rubbing fastness index were classified as good (3) to excellent (5). Comparing the SK samples to the PA samples for washing fastness, it is explicit that the PA had a greater color change, due to a worse fastness property for this dyeing.

The results or rubbing fastness for SK indicated a benefit when using the mordants. However, for the PA, the addition of the pre-mordanting with Potassium Alum presented worse fastness to rubbing than without mordant.

In table III, the results for the perspiration fastness tests are presented.

TABLE III
PERSPIRATION FASTNESS RESULTS

Sample	Perspiration Fastness													
	Acid							Alkaline						
	Color change	*Staining on adjacent fibers*						*Color change*	*Staining on adjacent fibers*					
		WO	PAC	PES	PA	CO	AC		WO	PAC	PES	PA	CO	AC
SK	4-5	4-5	4-5	4-5	3-4	4	4-5	4	4	4-5	4-5	4	4-5	4-5
SK/Tannic	4-5	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4	4-5	4-5
SK/Alum	4	4-5	4-5	4-5	4	4-5	4-5	4	4-5	5	4-5	4	4-5	4-5
PA	3	4-5	5	5	4-5	5	5	3-4	5	5	5	4-5	4-5	5
PA/Tannic	2-3	4-5	5	5	4-5	5	5	3	4-5	5	5	4-5	5	4-5
PA/Alum	3-4	4-5	5	5	4-5	5	5	3	4-5	5	5	4-5	4-5	5

It is possible to verify that the silk samples presented good perspiration fastness indexes, both regarding the color change and the staining of the samples, from grade 3-4 to 5. In the case of polyamide samples, the fastness indexes were slightly lower, ranging from 2-3 to 5.

The use of the mordants generally did not significantly improve the perspiration fastness indexes of the samples, and it has even worsened in some cases.

The PA samples, either the PA non-mordanted, the PA+Tannic and the PA+Alum showed a more relevant change in color, stating a worse fastness compared to SK. For the multifiber fabric tested in acidic and alkaline solutions, there were no relevant improvement using mordants. Nevertheless, it can be observed a decrease in fastness in alkaline solution to PA using PA/Alum and PA/Tannic, what invalidates the use of mordants when in an alkaline solution.

V. CONCLUSION

According to the results presented, it is possible to conclude that the SK and PA fabrics can be easily dyed with the natural dye extracted from the excrement of the silkworm, obtaining yellowish-brown colors. Nevertheless, more work will be done, namely with fluorescence microscope technique to confirm the degree of the dye penetration in PA fiber.

For both fibers, the best dye yield was obtained using tannic acid as a mordant. Potassium alum, however, negatively influenced the color intensity of the SK samples and showed no significant influence on the dye yield of the PA samples. The colors obtained were more intense for the SK samples, due to the greater dye uptake as a consequence of the greater number of groups functioning in the chemical structure of the fiber. For the wash fastness tests, it does not influence the addition of mordants. In the friction tests, tannic acid showed a positive influence. In this way, we can conclude that for both fibers (SK and PA), the pre-mordanting process with tannic acid was the best regarding dye uptake, but none of the pre-mordanting processes are significantly effective for the fastness properties.

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