Surface activation of textile fibers by plasma DBD for dyeing with teak leaf

A J S Ferreira[1], M B Goede[1], N T Vila[2], M G Silva[2], S Fiori[2], T A Nascimento[2], M Fernandes[3] and A P Souto[3]

[1]*Departamento de Engenharias, Universidade Federal de Santa Catarina, Blumenau, Santa Catarina, Brasil*
[2]*Departamento de Engenharia Têxtil, Universidade Estadual de Maringá, Goioerê, Paraná, Brasil*
[3]*2C2T-Centro de Ciência e Tecnologia Têxtil, Universidade do Minho, Guimarães, Portugal*

Corresponding author: alexandre.ferreira@ufsc.br

Abstract The use of natural dyes is a field of great interest to solve the problems related to environment pollution and health risks. The objective of this research was to study the plasma discharge of double dielectric barrier (DDB) to modify the fabrics surfaces of polyamide 6.6 (PA66), silk (SK) and cotton (CO) dyed with leaf extract of teak (*Tectona grandis*). It was also aimed the improvement in the penetration and fixation properties to the natural dyes even without using metal mordants, which are toxic and usually used in this type of dyeing. The dye extract obtained from the teak leaves was chemically characterized by using UHPLC/QTOF-MS. The color parameters were calculated by means of spectroscopy to evaluate the color intensity (K/S) and its fastness was evaluated for washing, friction and perspiration.

Keywords— **Plasma DBD, *Tectona grandis*, Silk, Polyamide 6.6, Natural Dye, UHPLC/QTOF-MS.**

I. INTRODUCTION

THE extracts of organic dyes from animal, plants and fungus oriented to several industries are currently the focus of attention for several research groups. Unlike its alternative synthetic, the natural dye revealed a product with a reduced environmental impact. The natural dyes may be based on tannin, indigo, anthraquinone, naphthoquinone, benzoquinone, flavonoids, carotenoids and, with various applications in food, cosmetics, pharmaceuticals and textile industry. The natural dyes are emerging as novels agents to produce textiles with antimicrobial, insect repellent, fluorescent and UV protection properties [1-3]. The variety of natural dyes as well as the color palette is quite large. *Tectona grandis* is an Asian native plant known also as Teak. This plant can be also found in Brazil. Teak wood is widely used by the naval industry due to its durability, moreover which has beautiful texture and resistance to fungal and termite damage and, its dried leaves are used as natural dye. Phytochemical investigations on teak has revealed the presence of different classes of compounds, such as: tannin, coumarins and amino acids mostly [4]. Anthraquinone based coloring compounds can be found in leaves of Teak [5].

Dielectric Barrier Discharge (DBD) plasma is one of the most efficient atmospheric plasma. The DBD has aroused the interest of the textile industries due to their scalability for large systems [6-8]. Natural dyes are applied to substrates that have been subjected to plasma treatment [9] in a few studies. The low temperature plasma is characterized by being a dry process, eco-friendly, simple processing by changing the surfaces without modifying the intrinsic properties of the material [10]. In particular, in textile substrates, atmospheric plasma is particularly recommended due to its non-thermal characteristic, appearing as an advantage when limited to heat-sensitive polymer fibers [11]. It has already been showed that the creation of functional groups on the surface of the substrates, namely hydroxyl and carboxyl groups ensure effective covalent bonds, whose, are indispensable in order to create a covalent attachment of the natural precursors to the substrate and thus ensuring the color fastness [12,13].

II. EXPERIMENTAL SECTION

A. Materials

Commercial pre-washed pure PA66 woven fabric (warp 52 yarns cm^{-1}, weft 32 yarns cm^{-1}, 110 GSM), pure SK woven fabrics (warp 60 yarns cm^{-1}, weft 50 yarns cm^{-1}, 50 GSM) and CO bleached woven fabric (warp 58 yarns cm^{-1}, weft 22 yarns cm^{-1}, 160 GSM) were employed in this study.

B. Preparation of dye extract from teak

Dye extract from the teak was obtained by aqueous extraction, weighing 10 g of teak 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 to 3.0 with acetic acid for SK, 5.5 to PA66 and 10.5 to CO.

C. UHPLC/QTOF-MS analysis

Extracts were analysed by ultra high-performance liquid chromatography (Shimadzu, Nexera X2, Japan) coupled to high resolution mass spectrometry (Impact II, Bruker Daltonics Corporation, Germany) equipped with an electrospray ionization source. The capillary voltage was operated in negative ionization mode, set at 3000 V and with an end plate offset potential of -500 V. The dry gas parameters were set to 8 L min^{-1} at 180°C with a nebulization gas pressure of 4 bar. Data were collected from m/z 50-1300 with an acquisition rate of 5 spectrums per second, and the ions of interest were selected by auto MS/MS scan fragmentation. Chromatographic separation was performed with a gradient mixture of solvents A (H_2O 0.1% formic acid v/v) and B (acetonitrile 0.1% formic acid v/v) using a C18 column (Waters, ACQUITY UPLC®). The gradient system was structured as follows: 5% of B during 0-2 min, 50% of B through 2-10 min, 95% of B, through 10-18 min and maintained at 95% of B 18-20 min, 5% of B, during 20-22 min and maintained at 5% of B, during 22-25 min. Identification of the compounds was performed based on similarity of the high-resolution fragmentation spectra and exact mass information of the compounds, with literature spectra and public databases.

D. Plasma treatment

The DBD plasma treatment was conducted in a semi-industrial prototype machine (Softal Electronics GmbH/University of Minho) working at room temperature and atmospheric pressure, using a system of metal electrode coated with ceramic and counter electrodes coated with silicon with 50 cm effective width, gap distance fixed at 3 mm and producing the discharge at high voltage 10 kV and low frequency 40 kHz. The machine was operated at 1 W of power, velocity of 4 m min^{-1}. Plasmatic dosage was defined by the equation 1:

$$Dosage = \frac{N \times P}{v \times l} \qquad (1)$$

Where, N=number of passages, P=power (W), v = velocity (m min^{-1}), and l = width of treatment (0.5 m).

E. Dyeing

The samples were dyed for 60 minutes at 40 rpm on the Ahiba Texomat Turbo Color equipment, employing a bath ratio of 1: 100 and a temperature of 90 ºC. After dyeing the samples were rinsed with distilled water and dried at ambient conditions.

III. CHARACTERIZATION

A. Contact Angle

Contact angle measurement was carried out in a Dataphysics instrument (Filderstadt, Germany) using OCA20 software (Germany) with a video system for the caption of images in static and dynamic modes. A drop of 5µL of distilled water was placed on the composite surface with a microliter syringe and observed with a special CCD camera. At least five measurements at different places were taken for each fabric. The camera takes an image every 0.04 s.

B. Color parameters

The color strength of the dyed fabrics expressed as K/S value was calculated from the Kubelka–Munk equation (2) as given below [14]:

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

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 Spectraflash SF 600 Plus CT 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 (3), as described below [14].

$$I = \sum_{\lambda=400nm}^{\lambda=700nm} \frac{K}{S}(\lambda) \times \triangle \lambda \qquad \triangle \lambda = 10 \qquad (3)$$

where λ represents the wavelength.

C. Washing fastness test

For the washing fastness tests, the dyed fabrics were treated in a Linitest C1-20 Original Hanau, Germany, for 30 min at 40ºC in accordance with ISO Standard 105-C06 A1S. The solution of ECE detergent was replaced by a non-ionic detergent with a concentration of 4 g L^{-1} and volume of 150 mL. This replacement is justified in natural dye field research by a several number of research groups. They use this substitution due a color change when the ECE detergent is used. With this particular situation the measurement of color parameter was impracticable [15-17]. When the cycle was finished, the samples were washed with distilled water dried under ambient conditions.

D. 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.

E. Perspiration fastness test

For the 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 Spectraflash SF 600 Plus CT spectrophotometer.

IV. Results and Discussion

A. Chemical characterization of the extract by UHPLC/QTOF-MS

Figure 1 shows the base peak ion chromatogram of the teak leaf extract obtained in the negative ionization mode.
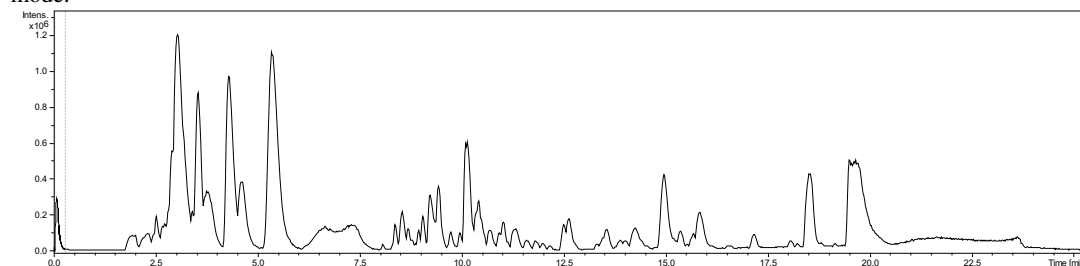

Fig. 1. Chromatogram of teak leaves extract, negative ionization mode

The mass spectra of teak leaf extract presented spectral match with ten characteristic ions of phenolic compounds. Their identities were confirmed by comparing mass accuracy and fragmentation behaviours with data available in the literature. The mass error for the molecular ions of all the compounds identified was within ± 8 ppm.

A list of compounds identified in the teak extract using UHPLC/QTOF-MS, retention time, experimental [M-H]⁻, ion fragmentation profile and the literature consulted are described in Table 1.

TABLE I.
CHEMICAL COMPOSITION OF TEAK LEAVES AND CORRESPONDING FRAGMENTATION PROFILE

No.	T_R (min)	Compound name	Formula	$[M-H]^-$ (m/z)	$[M-H]^-$ experimental (m/z)	Error (ppm)	Fragment ions (m/z)	Reference
1	2.97	Quinic acid	$C_7H_{12}O_6$	1,910,556	1910552	1.90	127.0391, 111.0449, 93.0336, 85.0285	(Abdel-Hameed et al. 2013)
2	7.84	Mesaconic acid	$C_5H_6O_4$	1,290,188	1290181	5.30	85.0283, 66.3217	HMDB ID: HMDB0000749
3	9.18	Chlorogenic acid	$C_{16}H_{18}O_9$	3,530,873	3530856	4.69	209.0286, 191.0549, 147.0291, 85.0288	(Santos et al. 2011)
4	9.90	Rutin	$C_{27}H_{30}O_{16}$	6,091,456	6091420	5.84	300.0254, 178.9973	(Wu et al. 2017)
5	9.93	Caffeic acid	$C_9H_8O_4$	1,790,344	1790337	4.10	135.0443, 107.0490	(Kivrak et al. 2017)
6	10.29	quercetin-3-glucoside	$C_{21}H_{20}O_{12}$	4,630,877	4630866	2.27	415.1589, 300.0257, 271.0217, 255.0304, 191.0557, 149.0445, 119.0344, 99.0081, 89.0234	(Abdel-Hameed et al. 2013)
7	10.30	Kaempferol 7-O-glucoside	$C_{21}H_{20}O_{11}$	4,470,927	4470901	5.90	327.0459, 285.0376, 269.1388, 225.1491, 209.1163	(Sánchez-Rabaneda et al. 2003)
8	11.26	Coumaric acid	$C_9H_8O_3$	1,630,395	1630387	5.02	119.0491	(Koley et al. 2017)
9	12.52	Luteolin	$C_{15}H_{10}O_6$	2,850,399	2850377	7.76	272.0303, 257.0440, 243.0659, 223.0331, 213.0555, 199.0379, 175.0373, 151.0020, 133.0282, 107.0119, 91.0371	(Santos et al. 2011)
10	12.65	Quercetin	$C_{15}H_{10}O_7$	3,010,348	3010328	6.74	273.0350, 255.0251, 189.0158, 178.9991, 161.0234, 151.0017, 121.0271, 107.0118	(Wang et al. 2015)

B. Plasma Treatment

The DBD plasma treatment was optimized for 5 passages on PA66, SK and CO at the power of 1 kW and velocity of 4 m/min. The Table 2 presents de results for contact angle in the silk fabric.

The plasma treatment has enabled an increase in hydrophilicity of fabric, which can be understood by the decrease of the static contact angle.

TABLE II.
STATIC CONTACT ANGLE IN THE SILK FABRIC

	Untreated	1500 W min m^{-2}	3000 W min m^{-2}
Static contact angle	132.53º	11.13º	6.06º

C. Color strength

It was possible to observe changes in the dyeing behaviour of silk and polyamide fibers after being submitted to plasma
treatment and dyed with the natural dyes. Silk was the fiber that presented a higher increase in dye yield after the plasma treatment as can be observed in the graph of K/S in Figure 2.
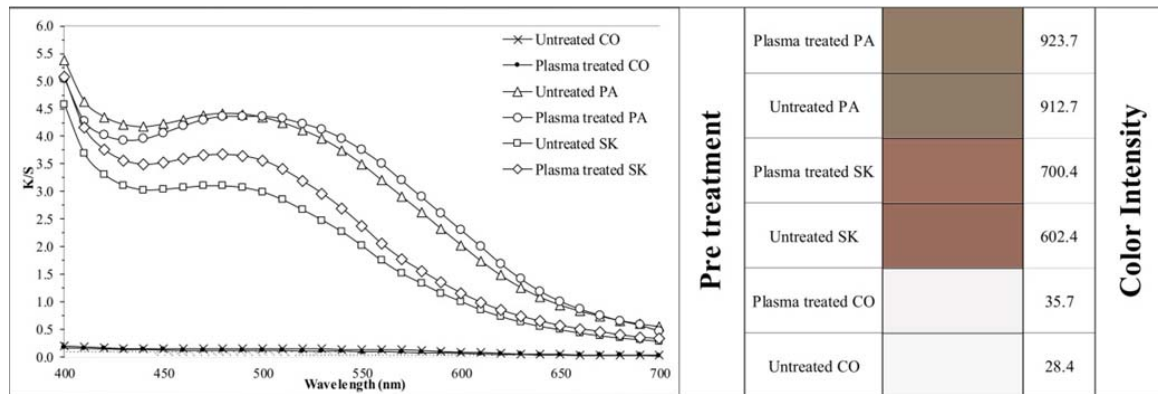
Fig. 2. Color strength of teak leaves and color intensity.

Indeed, plasma treatment may have potentiated the silk and polyamide dye sensitivity due to changes in chemical and possibility structural effect (increased chemical groups containing nitrogen and oxygen and creating microroughness) on the surface of that fibers.

On the other hand, the cotton fiber did not absorb the dye, which may indicate that there is no affinity between the dye and the fiber under the conditions tested. Thus, the strength tests were not performed on the cotton samples.

D. Washing and rubbing fastness

The results of the washing and rubbing fastness tests of the polyamide and silk samples dyed with teak leaves extracts are shown in Table 3. The wash fastness indices can generally be considered to be reasonable at very good, with the exception of the silk samples, which presented color change of grade 1-2 for sample without treatment and grade 2 for the sample treated with plasma. The colors change were lower with samples treated with plasma Furthermore, plasma treatment also showed no influence on color transfer indexes for adjacent fibers.

TABLE III.
WASHING AND RUBBING FASTNESS TEST RESULTS

| Sample | Color change | Washing Fastness | | | | | | Rubbing Fastness | |
| | | Staining on adjacent fibers | | | | | | Dry | Wet |
		WO	PAC	PES	PA	CO	AC		
Polyamide Untreated	4	4	5	5	3-4	4-5	4-5	4-5	4-5
Polyamide Plasma Treated	5	4	5	5	3-4	4-5	4-5	5	5
Silk Untreated	1-2	3-4	4-5	4-5	3-4	4	5	5	4-5
Silk Plasma Treated	2	3-4	4-5	4-5	3-4	4	5	5	5

E. Perspiration Fastness (acid and alkaline)

The acid and alkaline indexes may, in an overview, be considered reasonable to very good, with the exception of the untreated silk sample, which showed a color change specifically of grade 2-3 in the alkaline perspiration test, as shown in Table 4.

With polyamide fiber, plasma did not contribute to the improvement of perspiration indexes, and even influenced negatively in some cases. With silk, plasma treatment improved color change indexes for both acid and alkaline perspiration, however, it had no influence on transfer indexes, except for wool fiber in the acid and acetate fiber for alkaline perspiration, in which the indices were worse for treated samples.

Acid perspiration, in general, was better than alkaline perspiration for all samples tested. This behaviour is possibly related to the degradation suffered by the natural dye in basic conditions [18].

TABLE IV.
PERSPIRATION FASTNESS TEST 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
Polyamide Untreated	4	4	4-5	4-5	4-5	5	4	4	3-4	4-5	4-5	3	4	4
Polyamide Plasma Treated	4	4	4-5	4-5	3-4	4-5	4	3-4	3-4	4-5	4-5	3	4	4
Silk Untreated	3-4	4-5	5	5	4-5	4-5	4	2-3	3	4	4	3	3-4	4-5
Silk Plasma Treated	4-5	3-4	5	5	4-5	4-5	4	3	3	4	4	3	3-4	4

V. Conclusion

The results show that PA66 and SK fabrics are possible to dye with teak extract, being obtained the reddish brown and brown colors for PA66 and SK, respectively.

The chemical characterization showed that the aqueous extract of the teak leaves consists of several types of compounds from the flavonoid class. Plasma treatment promoted increased dye yield for silk and polyamide fibers. This was also detected washing and friction fastness indexes were improved with plasma treatment.

REFERENCES

[1] M. Shahid, I. Shahid ul, and F. Mohammad, "Recent advancements in natural dye applications: a review," Journal of Cleaner Production, vol. 53, no. 0. pp. 310–331, 2013.

[2] F. Mohammad, "Natural colorants in the presence of anchors so-called mordants as promising coloring and antimicrobial agents for textile materials," ACS Sustain. Chem. Eng., vol. 3, no. 10, pp. 2361–2375, 2015.

[3] M. Shahid and F. Mohammad, "Green chemistry approaches to develop antimicrobial textiles based on sustainable biopolymers⎯ A review," Ind. Eng. Chem. Res., vol. 52, no. 15, pp. 5245–5260, 2013.

[4] R. B. Nidavani and A. M. Mahalakshmi, "Teak (tectona grandis linn.): A renowned timber plant with potential medicinal values," Inter J Pharm Pharm Sci, vol. 6, no. 1, pp. 48–54, 2014.

[5] A. K. Prusty, T. Das, A. Nayak, and N. B. Das, "Colourimetric analysis and antimicrobial study of natural dyes and dyed silk," J. Clean. Prod., vol. 18, no. 16–17, pp. 1750–1756, Nov. 2010.

[6] G. Borcia, C. A. Anderson, and N. M. D. Brown, "Surface treatment of natural and synthetic textiles using a dielectric barrier discharge," Surf. Coatings Technol., vol. 201, no. 6, pp. 3074–3081, 2006.

[7] H. Zeng, C. Gao, Y. Wang, P. C. P. Watts, H. Kong, X. Cui, and D. Yan, "In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 1010 composites: Mechanical properties and crystallization behavior," Polymer (Guildf)., vol. 47, no. 1, pp. 113–122, 2006.

[8] U. Kogelschatz, "Dielectric-Barrier Discharges: Their History, Discharge Physics, and Industrial Applications," Plasma Chem. Plasma Process., vol. 23, no. 1, pp. 1–46, 2003.

[9] A. Zille, F. R. Oliveira, and A. P. Souto, "Plasma treatment in textile industry," Plasma Process. Polym., vol. 12, no. 2, pp. 98–131, 2015.

[10] F. S. Denes and S. Manolache, "Macromolecular plasma-chemistry: an emerging field of polymer science," Prog. Polym. Sci., vol. 29, no. 8, pp. 815–885, 2004.

[11] R. Morent, N. De Geyter, J. Verschuren, K. De Clerck, P. Kiekens, and C. Leys, "Non-thermal plasma treatment of textiles," Surf. Coatings Technol., vol. 202, no. 14, pp. 3427–3449, 2008.

[12] F. R. Oliveira, A. Zille, and A. P. Souto, "Dyeing mechanism and optimization of polyamide 6,6 functionalized with double barrier discharge (DBD) plasma in air," Appl. Surf. Sci., vol. 293, pp. 177–186, 2014.

[13] F. R. Oliveira, A. P. Souto, N. Carneiro, and J. H. O. Nascimento, "Surface modification on polyamide 6.6 with double barrier discharge (DBD) plasma to optimise dyeing process by direct dyes," in Materials Science Forum, 2010, vol. 636, pp. 846–852.

[14] M. Štěpánková, J. Wiener, and K. Rusinová, "Decolourization of vat dyes on cotton fabric with infrared laser light," Cellulose, vol. 18, no. 2, pp. 469–478, 2011.

[15] D. Jothi, "Extraction of natural dyes from African marigold flower (Tagetes ereectal) for textile coloration," Autex Res. J., vol. 8, no. 2, pp. 49–53, 2008.

[16] R. Räisänen, P. Nousiainen, and P. H. Hynninen, "Emodin and dermocybin natural anthraquinones as mordant dyes for wool and polyamide," Text. Res. J., vol. 71, no. 11, pp. 1016–1022, 2001.

[17] M. Montazer, M. Parvinzadeh, and A. Kiumarsi, "Colorimetric properties of wool dyed with natural dyes after treatment with ammonia Coloration Technology," Color. Technol., vol. 120, pp. 161–166, 2004.

[18] V. R. Giri Dev, J. Venugopal, S. Sudha, G. Deepika, and S. Ramakrishna, "Dyeing and antimicrobial characteristics of chitosan treated wool fabrics with henna dye," Carbohydr. Polym., vol. 75, no. 4, pp. 646–650, Feb. 2009.