Vat dyeing of Wool and Cotton fabrics with Sepia Melanin

Su-jin Kim and Jinho Jang†

Dept. of Nano-Bio Textile Engineering, Kumoh National Institute of Technology, Gumi, Korea

(Received: May 14, 2010/Revised: June 11, 2010/Accepted: June 15, 2010)

Abstract— Using extracted sepia melanin powder by repeated treatments with aqueous sodium hydroxide and acetic acid solutions, vat dyeing of wool and cotton fabrics was carried out under various dyeing conditions including concentration of melanin, alkali, reducing agent and salt, as well as dyeing time and temperature. A K/S of 25.3 for wool fabrics was obtained at the optimal dyeing condition with 9% owf melanin, 0.5g/L NaOH and 56g/L $Na_2S_2O_4$ without salt at 80°C for 90minutes. The vat dyeing of sepia melanin was applicable to both cotton and wool fabrics but the wool showed higher dyeability. The color fastness properties of the dyed wool and cotton fabrics were excellent to washing, rubbing and light irradiation.

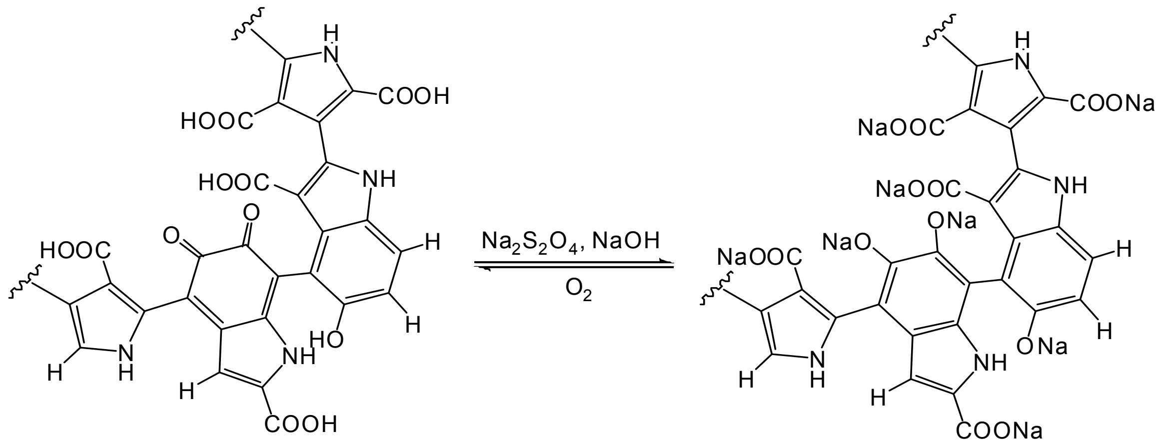
Keywords: *squid ink, sepia melanin, polymeric dye, vat dyeing, color fastness*

1. Introduction

Sepia melanin is a natural pigment derived from the ink sack of various species of cephalopoda, more commonly from cuttlefish. The study on application of melanin has been carried out in various fields such as textile coloration, food and cosmetics[1-3]. The most widely accepted function of melanin is the photoprotection of an animal body. And several other functions have been proposed including free radical scavenging, photosensitizing, thermoregulation, metal-ion chelation, drug binding which may prevent cancer generation and block the reproduction of *penicillium* and *staphylococcus*[4-7]. With tyrosinase containing Cu secreted from ink sack of squid, tyrosine was oxidized to DOPA (3,4-Dihydroxyphenylalanine) and subsequently DOPA-quinine and DOPA-chrome were derived. Finally melanin is biosynthesized with DHI(Dihydroxyindole) and DHICA(Dihydroxyindole carboxylic acid)[2,8]. Sepia melanin is insoluble in neutral water or organic solvents but it can be dispersed in alkalis[9,10].

Vat dyeing is traditionally carried out for natural dyes such as indigo or Tyrian purple[11,12]. Melanin, a natural animal pigment, has similar carbonyl chromophores like synthetic vat dyes (Scheme 1)[13]. Most synthetic vat dyes contain two or more carbonyl groups separated by a conjugated system of double bonds such as indigo or anthraquinone. The chemical constitution of the dye influences the dyeing properties of the leuco form such as chemical stability during vatting, absorption rate and leveling properties. It is also a key factor in determining the resultant dyeing characteristics including color and fastness properties. Dyeing with vat dyes is based on the conversion of a water-insoluble colorant to a water-soluble leuco form by alkaline reduction, which can penetrate into the fiber. Subsequently the original form can be regenerated by oxidation. Close control of vatting process requires because several undesirable effects can be occurred. If there is insufficient alkali, the dyes may form the practically insoluble leuco compound. And the leuco form of indigo has been reported to exist in nonionic at pH 7, univalent ion at pH 10.8~11, or bivalent ion above pH 11[14-16]. Higher reducing agent concentration than optimum can cause over-reduction while low reduction results in poor adsorption due to insufficient formation of leuco compound. Careful control of temperature is also important; if the temperature is too low reduction may be incomplete, and if too high the reducing agent may react with the dye in other

†Corresponding author. Tel.: +82-54-478-7715; Fax.: +82-54-478-7710; e-mail: jh.jang@kumoh.ac.kr



Scheme 1. Formation of leuco melanin

ways to produce undesirable products. The leuco dyes can have good substantivity for wool and nylon as well as cotton[14,17,18).

Acid dyeing of wool and cotton with sepia melanin has been previously investigated[3)]. However in this study, the extracted melanin powder from squid ink was used to dye wool and cotton fabrics by vat dyeing technique under optimum dyeing conditions and the dyeability of melanin to both fabrics were also compared.

2. Experimental

2.1 Materials and chemicals

Sepia melanin was prepared by extracting raw squid (*Todarodes pacificus*) inks. Wool (65g/m^2) and cotton (98g/m^2) fabrics, supplied by Sombe, were used for the study. Sodium hydroxide (NaOH) and acetic acid (CH_3COOH) were used for melanin preparation and dyeing.

Sodium hydrosulfite ($Na_2S_2O_4$), hydrogen peroxide (H_2O_2) and sodium sulfate (Na_2SO_4) were used as reducing agent, oxidizing agent and neutral salt respectively.

2.2 Extraction of melanin powder

Squid inks were extracted from squid's ink sacs and 1% sodium hydroxide was added for dispersion with respect to the inks.

And squid ink was precipitated at pH 3 with 10% acetic acid solution. After washing with distilled water three times the melanin powder was extracted with acetone and subsequently was dried for 24 hours under vacuum.

2.3 Dyeing process

Optimal dyeing condition of melanin to wool and cotton were investigated in relation with melanin, alkali, reducing agent and salt concentrations, dyeing time and temperature. The fabrics were dyed at a liquor ratio of 25:1 using an IR dyeing testing machine (Daelim Engineering, Korea), and the dyeing liquor was oxidized by 1% aqueous H_2O_2 solution. K/S values were calculated from reflectance at λ_{max}(wool: 360nm, cotton: 440nm) measured with a reflectance spectrophotometer (Gretag Macbeth, Canada) and percent exhaustion of the remaining liquor was evaluated at 360nm with a UV/VIS spectrophotometer (Daelim Engineering).

2.4 Color fastness test

The colorfastness to laundering, rubbing and light irradiation of dyed fabrics were carried out with a Launder-O-meter (Daelim Engineering, Korea), crock meter (Heungshin Engineering, Korea), and Fade-O-meter (Korea Science, Korea) according to KS K ISO 105-C01, KS K 0650 and KS K 0700 respectively.

3. Results and Discussion

3.1 Reducing agent concentration

The optimum concentrations of alkali and reduction agent should be obtained for vat dyeing. Wool and cotton fabrics were dyed with 1% owf melanin, 8g/L $Na_2S_2O_4$, 15g/L Na_2SO_4 at 50°C for 50min. The effect of alkali addition on the melanin dyeing was shown in Fig. 1. Higher alkali concentration than 0.5g/L NaOH decreased the dyeability of both fabrics. Thus, 0.5g/L was chosen as optimum alkali concentration. The addition of NaOH is required not only to disperse the extracted sepia melanin in water but also to enhance water solubility of the leuco form of melanin.

Fig. 2 showed the effect of reducing agent concentration on the coloration under 0.5g/L NaOH addition. The K/S of both fabrics increased with increasing reducing agent up to 8g/L, but it decreased above 8g/L of reducing agent. The amount of reducing agent more than optimum condition resulted in poor coloration and leveling. The decreased dyeability of both fabrics may be due to over-reduction of the sepia melanin.

3.2 Salt concentration

Fig. 3 showed the K/S of both fabrics dyeing with 1% owf melanin, 0.5g/L NaOH, 8g/L $Na_2S_2O_4$ at 50°C for 50min. Dyeabiliy of cotton increased with increasing salt concentration up to 15g/L, but it decreased above 15g/L. However wool showed negative effect on the dyeability. Melanin has a low affinity to cotton fabrics because of charge repulsion between leuco form of melanin and negative charge on cotton under alkaline condition. The repulsion may be reduced by neutral salt addition, where the optimum salt concentration was 15g/L.

Wool has positive charge at lower pH than isoelectric point(pH 4.9) and has negative charge above the pH 4.9. However because partial positive charge still exists under high pH condition, the partial positive charge of wool can exhaust the negative leuco form without neutral salt.

Also it is expected that the added salt up to 10g/L may interfere the ionic interaction between dyes and fiber.

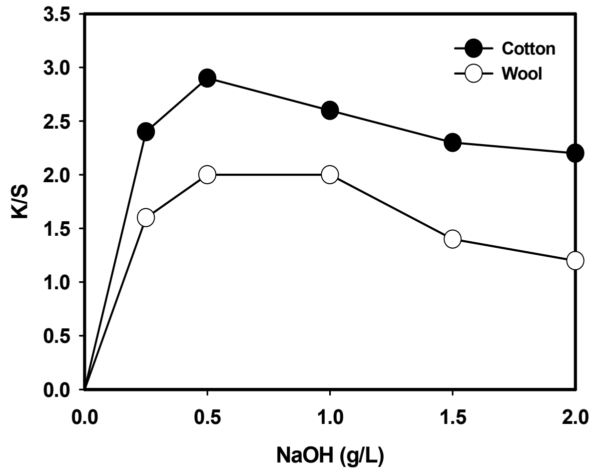


Fig. 1. Effect of alkali concentration on K/S.

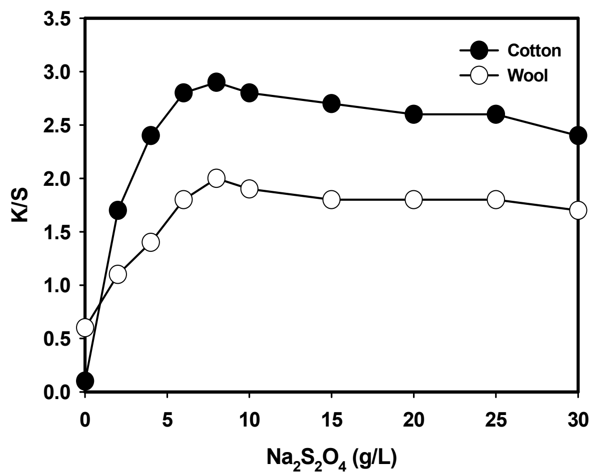


Fig. 2. Effect of reducing agent concentration on K/S.

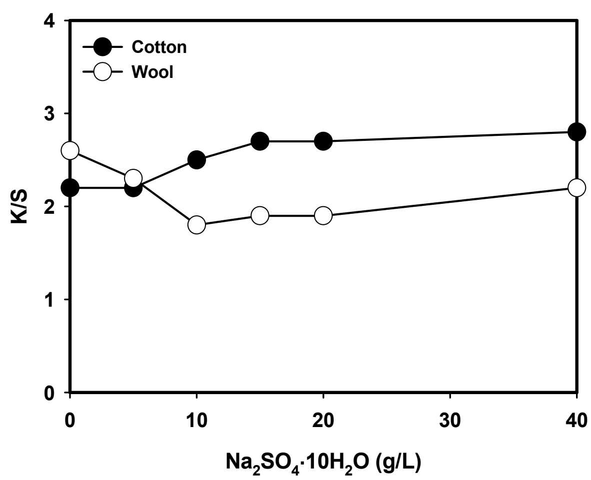


Fig. 3. Effect of salt concentration on K/S.

3.3 Dyeing temperature and time

Wool and cotton fabrics were dyed for 50min at different dyeing temperatures with 1% owf melanin, 0.5g/L NaOH, 8g/L $Na_2S_2O_4$, 15g/L of Na_2SO_4 was added in case of cotton fabrics. The K/S of wool increased with increasing temperature up to 100°C, whereas that of cotton decreased above 50°C as shown in Fig. 4. It is expected that dyeability of cotton decreased above 50°C due to over-reduction of the sepia melanins. However wool may be capable of adsorbing the melanin in spite of over-reduction.

The optimum dyeing temperatures of cotton and wool were chosen to 50°C and 80°C respectively due to substantial felting shrinkage of the wool fabrics at the elevated temperature.

The effects of dyeing time was studied on 1% owf melanin, 0.5g/L NaOH and 8g/L $Na_2S_2O_4$. Cotton fabrics were dyed with 15g/L of Na_2SO_4 at 50°C and wool fabrics were dyed at 80°C without salt. The optimum time of wool and cotton was obtained at 90min and 50min respectively as shown in Fig. 5. The dyeing times higher than the optimum dyeing times substantially decreased the dyeability of cotton due to over-reduction of the melanin or poor exhaustion.

3.4 Melanin concentration

The effect of melanin concentration was studied at 0.5g/L of NaOH, where the hydrosulfite concentration was adjusted to twice of the melanin concentration. Cotton was dyed with 15g/L of Na_2SO_4 at 50°C for 50min and wool was dyed without salt at 80°C for 90min. With increasing melanin concentration, the K/S values of wool increased proportionally but cotton did not change substantially as indicated in Table 1. Wool has larger adsorption capability of the dyes because of the relaxed molecular structure, while cotton is

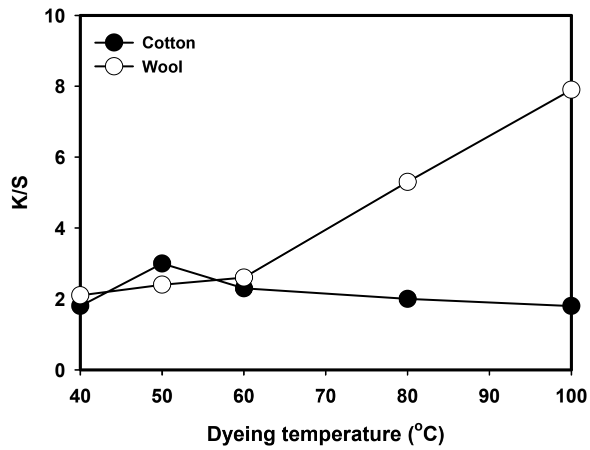


Fig. 4. Effect of dyeing temperature on K/S.

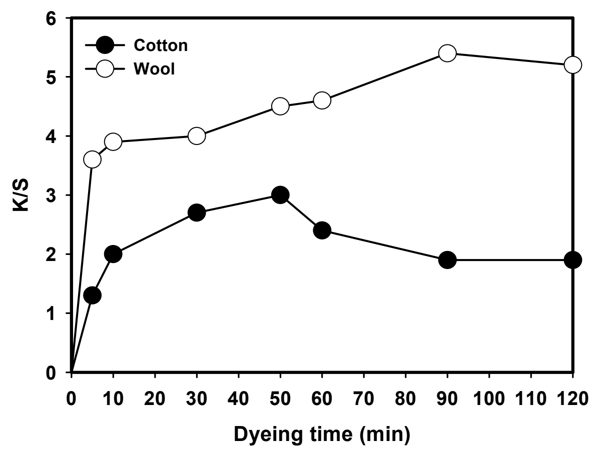


Fig. 5. Effect of dyeing time on K/S.

Table 1. Effect of dye concentration on color characteristics

	Dye conc.(% owf)	K/S	%E	L*	a*	b*	ΔE
Wool	1	5.0	53.8	49.5	5.1	15.9	40.8
	3	10.0	51.6	40.4	5.9	18.0	50.1
	5	18.5	42.3	29.0	6.8	15.6	61.3
	7	21.6	34.4	24.5	6.5	12.1	65.6
	9	25.3	20.2	22.0	6.6	9.8	68.1
Cotton	1	2.8	40.1	58.3	5.8	15.8	41.0
	3	2.8	37.0	58.3	5.1	16.3	41.0
	5	3.0	35.9	56.4	4.3	15.9	42.5
	7	3.5	33.7	55.1	4.3	15.4	43.5
	9	3.3	12.2	52.7	4.7	17.1	46.4

Table 2. Color fastness of melanin-dyed fabrics

Fabrics	K/S	Laundering								Rubbing		Light
		Shade	Stain							Dry	Wet	
			Wool	Acrylic	PET	Nylon	Cotton	Acetate				
Wool	5.0	4-5	5	5	4-5	4-5	4-5	4-5		5	5	6
	11.5	5	4-5	5	4	4	3-4	5		5	4-5	6
	14.3	4-5	4	4-5	4-5	3-4	3	4-5		5	4-5	6
Cotton	2.8	1	4	5	5	5	4	5		4-5	4-5	4
	3.0	3	4-5	5	5	5	3-4	4-5		5	4-5	6
	3.3	2	4-5	5	4-5	5	3	4-5		4-5	4	6

difficult to adsorb large amount of melanin molecules due to relatively higher crystallnity compared to wool, possibly resulting in the adhered melanin on the surface of cotton. The dyeability of cotton did not increase with increasing melanin concentration.

However the wool was degraded at the melanin concentration of 9% or more, it is expected that the large amount of reducing agent may degrade the wool fabrics themselves in addition to the desirable melanin reduction.

3.5 Color fastness

The color fastness of the dyed fabrics to washing, rubbing and light were shown in Table 2. The washing and rubbing fastness properties of the dyed wool fabrics were excellent and surprisingly light fastness was also very good. In the case of cotton, the rubbing and light fastness as well as staining fastness were also very good except for the poor shade rating.

The color fastness of wool was excellent because the melanin may have various intermolecular interactions with wool. The melanin, originally derived from tyrosine, has similar polarity to wool protein and accordingly strong molecular interaction with wool can be formed. However cotton seemingly has relatively weak interactions with the melanin, which can be removed easily from fabric under the laundering condition.

4. Conclusions

Sepia melanin powders are extracted from squid ink with repeated treatments of sodium hydroxide and acetic acid solutions. Vat dyeing of melanin to wool and cotton fabrics was investigated.

Optimum vatting condition of both fabrics was obtained at 0.5g/L NaOH and 8g/L $Na_2S_2O_4$ at 1% owf melanin concentration. The optimum salt concentration, dyeing temperature and time were at 80°C for 90min without salt for wool. And optimal dyeing condition of 50°C for 50min with 15g/L of Na_2SO_4 was required for cotton. At the optimum condition using 1% owf melanin, the K/S value of 5.0 for wool was obtained that higher than cotton. And dyeability of melanin to wool increased upto a K/S of 25.3 at 9% owf melanin concentration. Color fastness of the dyed wool fabrics to washing, rubbing and light was excellent because of the polymeric nature of the extracted sepia melanin. The color fastness of the dyed cotton to stain, rubbing and light irradiation were also very good. However the shade rating of cotton fabrics was poor which maybe due to the relatively weak interactions between melanin and cotton.

Acknowledgment

This work was supported by the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning(KETEP) grant funded by the Korea government ministry of Knowledge Economy(*No.2007EID11p043010*).

References

1. H. J. Lee, S. Y. Ban and H. J. Yoo, Fabrics Dyeing using Natural Dyestuff Manufactured from Squid Ink, *J. Korean Soc. Clothing Textiles*, **22**(8), 1011-1019(1998).
2. M. H. Yoon, "An Investigation of the Antitumor Substance Isolation and Characteristic from Squid

Ink", Master thesis, Hanseo University, pp.1-27, 2001.

3. S. J. Kim, H. R. Kwon, J. H. Yoo, and J. Jang, Wool Dyeing with Sepia Melanin, *Textile Coloration and Finishing(J. Korean Soc. Dyers & Finishers)*, **22**(1), 14-20(2010).
4. F. Delgado-Vargas, A. R. Jimeney, and O. Paredes-Lopez, Natural Pigments: Carotenoids, Anthocyanins, and Betalains-Characteristics, Biosynthesis, Processing, and Stability, *Critical Review in Food Science and Nutrition*, **40**(3), 173-289 (2000).
5. J. P. Ortonne, Photoprotective Properties of Skin Melanin, *Br. J. Dermatol.*, **146**, 7-10(2002).
6. H. Z. Hill, The Function of Melanin or 6 Blind People Examine an Elephant, *Bioessays*, **14**, 49-56(1992).
7. W. L. Morison, What is the Function of Melanin?, *Arch. Dermatol*, **121**, 1160-1163(1985).
8. E. J. Ryu, "Clinical Hair Coloring", Chung- Ku Publishing, Korea, pp.55-58, 2001.
9. A. Katritzky, N. Akhmedov, S. Denisenko, and O. Denisko, ^{1}H NMR Spectroscopic Characterization of Solutions of Sepia Melanin, Sepia Melanin Free Acid and Human Hair Melanin, *Pigment Cell Res.*, **15**, 93-97(2002).
10. Z. Matuszak and M. Wasilewska-Radwanska, "Proc. 7th Sympo. Optical Properties of Melanin Solutions. Estimation of Polymer Particles Size", Wroclaw, Vol.12-14, pp.533-537, 2006.
11. P. Westbroek, G. Priniotakis and P. Kiekens, "Analytical Electrochemistry in Textiles", Woodhead Publishing, U.K., pp.161-197, 2005.
12. S. Bruni, V. Guglielmi and F. Pozzi, Surface-enhanced Raman Spectroscopy (SERS) on Silver Colloids for the Identification of Ancient Textile Dyes: Tyrian purple and Madder, *J. Raman Spectrosc.*, **2010**(41), 175-180(2009).
13. S. A. Centeno and J. Shamir, Surface Enhanced Raman Scattering (SERS) and FTIR Characterization of the Sepia Melanin Pigment used in Work of Art, *J. Mol. Struct*, **873**(1-3), 149-159(2008).
14. J. Shore, "Cellulosics Dyeing", Society of Dyers and Colourists, U.K., pp.246-279, 1995.
15. R. M. Christie, R. R. Mather, and R. H. Wardman, "The Chemistry of Colour Application", Blackwell Science Publishing, U.K., pp.88-90, 2000.
16. I. M. Jung and S. O. Woo, Effect of Reducing Agent, Sodium Hydrosulfite on the Natural Indigo Dyeing of Silk Fabirc, *Korean J. Sericult. Sci.*, **44**(2), 93-98(2002).
17. E. K. Hwang, M. S. Kim, D. S. Lee and S. Y. Choi, Dyeing on Silk with Vat Dye, *Korean J. Sericult. Sci.*, **38**(2), 168-174(1996).
18. W. K. Jeong, "Practical Dyeing", Hyung Seol Publishing, Korea, pp.42-43, 2000.