

# Functions of the disulphide bond on Dyeing of Keratin Fiber with Oxidation Dyes

Kyohei Joko , Yumi Yoshikatsu and Keiko Sakata

Kyoto Women's University, Kita-hiyoshi, Imakumano, Higashiyama-ku, Kyoto 605-8501, Japan  
E-mail: [joko@kyoto-wu.ac.jp](mailto:joko@kyoto-wu.ac.jp)

## 1. INTRODUCTION

We have reported that the color depth of samples which modified the cell membrane complex (CMC) in wool fibers decreased apparently compared to that of the intact wool sample on the dyeing with oxidative dyeing system [1]. The decrease extent of their color depth was dependent on the modification extent of CMC. It was concluded that not only the CMC regions play an important role as accumulation regions of the finished dye, but also the components of CMC contribute directly to the oxidizing reactions for the formation of oxidation dye.

Furthermore, in our previous paper [2], we have also found that the dye uptake of the wool samples pretreated with ethylenediaminetetraacetic acid (EDTA), solutions decreased compared to that of the intact wool sample, and that on the contrary, the wool samples pretreated with copper, iron and nickel salts allowed the dye uptake of oxidation dye inside wool fiber to increase. These findings indicate that the metal ions presented primarily within the intercellular materials play an important role in developing the colored oxidation dye in the fiber. The presence of transition metal ions in the intercuticular material causes hydrogen peroxide to undergo radical decomposition, leading to active radical species that take part as initiator of oxidation reaction in where the dye precursor is oxidized to its corresponding iminium ion.

In keratin materials such as wool and hair, there are disulphide and thiol groups which chemically react with oxidizing and reducing agents. In particular, thiol groups is known to neutralize the hydrogen peroxide and superoxide radicals formed on exposure to UV radiation [3]. Thus one might intrusively expect the thiol and disulphide groups to affect the oxidizing reactions for the formation of oxidation dye.

In this study, to clarify the effect of disulphide and thiol groups on the development of oxidation dye into wool fibers with oxidation-dye formation system, we have investigated the effects of disulphide bond scission induced by peracetic acid (PAA) and thioglycolic acid (TG) on the dye uptake of the oxidation dyes in wool fibers.

## 2. EXPERIMENTAL

### Materials

The wool fabric was treated with a solution containing 1g/l of sodium dodecyl sulphate. The dye precursors; p-phenylenediamines (pPDA), p-toluylenediamine chloride (pTA), p-aminophenol (pAP), the dye coupler; p-amino-o-cresol (pAOC), hydrogen peroxide and other reagents were all of laboratory grade.

### Pretreatment of wool fabric

Oxidized wool was prepared by treating wool fabric with 0.3% peracetic acid solution for desired periods of time at 30°C with shaking. Reduced wool fabric was made by treating wool with 10<sup>-1</sup>mol/L thioglycolic acid solution for desired periods of time at 30°C with shaking. The treated wool samples were then well rinsed with ion exchanged followed by immersing in 0.1mol/L (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution of pH 9.95.

### Dyeing of fabrics

The dye solution contains 10<sup>-3</sup>mol of pAP, pPDA or pTA and 10<sup>-3</sup>mol of pAOC with 10<sup>-3</sup>mol of EDTA and 2x10<sup>-3</sup>mol of ascorbic acid in 100ml of 10<sup>-1</sup>mol/L (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> aqueous solution, which was mixed with an equal volume of 4.5% hydrogen peroxide just before use. The pH of the dyeing solution was adjusted to 9.95 with ammonium hydroxide.

Dyeing were carried out in 100ml sealed flask without shaking at a liquor-to-wool ratio of range 40:1 and the temperature of 30°C for 30min.

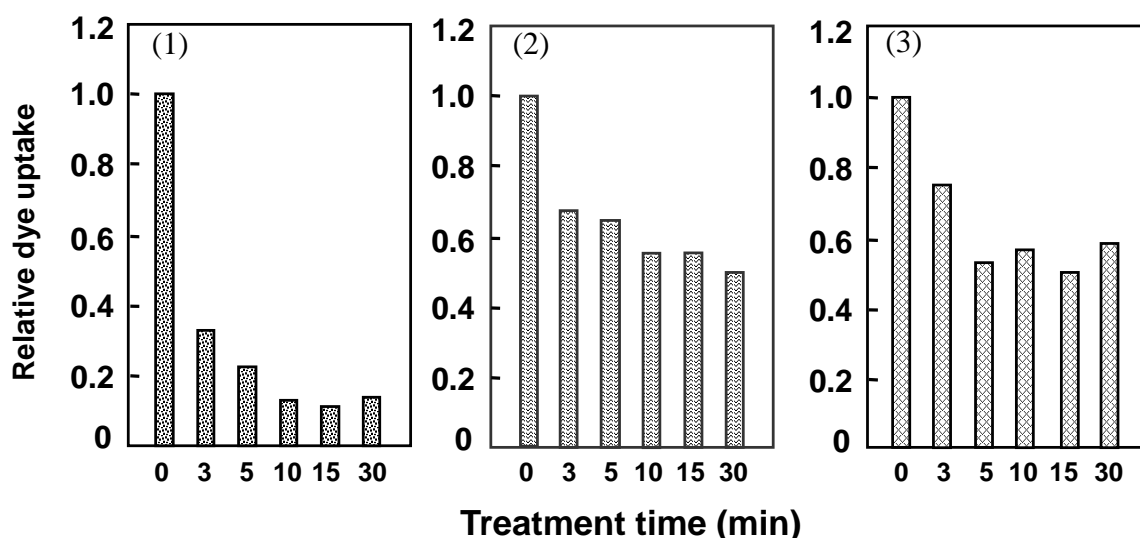
### Dye uptake measurements

The dye uptake of dyed fabrics was expressed as K/S values which were calculated using Kubelka-Munk function. The reflection index was measured with SQ2000 spectrophotometer (NIPPON DENSHOKU, Japan) at the wavelength of minimum reflection.

## 3. RESULTS AND DISCUSSION

### Oxidation dyeing of the oxidized wool fiber

Figure 1 shows how the values of dye uptakes, which were resulted from dyeing in pAP/pAOC, pPDA/pAOC, and pTA/pAOC system, change with the time of PAA treatment for oxidized samples.



**Fig. 1** The relative dye uptakes of wool samples oxidized with 0.3% peracetic acid solution for the different treatment times at 30°C. Dyeing carried out using pAP/pAOC couple system (1), pPDA/pAOC couple system (2) and pAT/pAOC couple system (3) with ascorbic acid and EDTA at 30°C for 30min. (Relative dye uptake =  $[K/S]_s / [K/S]_T$ ;  $[K/S]_s$ : K/S value of the untreated fabric,  $[K/S]_T$ : K/S value of the treated fabric.)

The K/S value of the oxidized wool illustrated as relative ones with that of the intact wool as reference. Although the effects of the disulphide bond scission on dye uptake among pPDA/pAOC, pTA/pAOC and pAP/pAOC couple system are different, as it appears in all cases, the value of relative dye uptake decreased with the time of treatment for oxidized samples. Particularly, these values are drastically lower with increasing the immersion time up to 10 minutes, and then after 10 minutes of treatment are almost unchanged. Although these treatments lead to a slight decrease in the metal ion content in the modified wool fibers, this decrease was ensured to have little effect on the dye uptakes.

#### **Oxidation dyeing of the reduced wool fiber**

The wool samples subjected to the different degree of thioglycolic acid treatment were dyed with pAP/pAOC, pPDA/pAOC, and pTA/pAOC system with ascorbic acid and EDTA at 30°C for 30min (no figure). The treatment of wool with reducing agents is believed to convert disulphide groups to thiol groups, each cystine residue giving two cysteine residues. As a result for each dyeing system, the disulphide scission induced by thioglycolic acid led to decrease markedly the dye uptake of all the reduced wool samples compared with that of the intact wool sample.

In conclusion, it is clear that the scission of disulphide bonds by oxidizing or reducing reaction have adverse effects on the oxidation dyeing behavior of wool fiber.

#### **4. COCLUSION**

On the results of dyeing in the presence of ascorbic acid and EDTA, the color depth of the wool samples pretreated with peracetic acid and thioglycolic acid solution decreased apparently compared to that of the intact wool sample. Further, the dye uptakes of reduced wool reoxidized with air were identical virtually with those of the intact wool samples in all oxidation dyeing system. Accordingly, these results implied that the disulphide bond could play an important role in developing the colored products in the fibers. From these finding, it was suggested that the disulphide bond in keratin components is attributed to the regeneration of catalytic ability of metal ions by conjugated redox reaction due to the disulphide exchange reaction. Consequently, we proposed the cyclically catalytic mechanism in which a conjugated redox reaction was carried out across the intercuticular material.

#### **5. REFERENCES**

- [1] K.Joko, Y.Yoshikatsu and K.Sakata, *Seni-gakkaishi*, **62**, 280-286(2006).
- [2] Y.Yoshikatsu, K.Sakata, J. Sugai and K. Joko, *Seni-gakkaishi*, **63**, 264-2270(2007).
- [3] K.R.Millington and L.J.Kischenbaum, *Color Technol.*, **118**, 6-14(2002).