(Received April 11, 1988)

DYEING RATE OF STRETCHED WOOL FIBER IV — THE EFFECT OF THE MODIFICATION OF CELL MEMBRANE COMPLEX —

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ABSTRACT

The dyeing rate of stretched wool fibers pretreated with polar organic solvents which modify the cell membrane complex (CMC) was investigated in order to elucidate the structural effect in the individual histological components of the intact wool fibers on the dyeing rate of the stretched wool fibers.

By comparing the relationships between the relative dye uptake (C_t/C_∞) and the square root of the dyeing time ($t^{1/2}$) for the different stretched wool fibers, considerable differences were found in the initial dyeing behavior between the stretched wool fibers pretreated with the different solvents. On the other hand, there was little difference in the slope of the linear line. These changes of initial dyeing behavior by stretching were attributed not only to the changes into the rough and porous nature of the surface layer, but also to the difference in the modified structure of CMC in the cuticle layer caused by the solvent treatment. The rate of dye penetration within the bulk phase of fibers was nearly the same for all of the stretched wools. A suggestion was made that the structural modification of the cortical-cortical CMC by the solvent treatment was offset by some structural modification in the cortical cells caused by stretching.

1. INTRODUCTION

Wool is a composite material containing minor histological components that behave differently from the bulk of the fiber; for example forming regions of low mechanical and chemical stability. One of these weak regions is the intercellular regions so-called "cell membrane complex" (CMC) that exist between all cells in assemblies of keratinized tissues¹⁾. This intercellular region has recently become a subject of interest following suggestions that this region exerts considerable influence on mechanical properties²⁻⁵⁾ and diffusion behavior^{2,5,6)}. In our previous papers^{7,8)}, effects of the pretreatment of wool fibers with organic solvents on the dyeing rate of acid dyes were investigated in connection with the structural

changes in the CMC and it was shown that the pretreatment with the solvents leads to an increase in the apparent dyeing rate of acid dyes. This result indicates that the intercellular regions exert considerable influence on the dyeing behavior of acid dyes for wool.

In our other papers^{9,10)}, we studied the dyeing rate of dyes for wool fibers of which the surface and bulk structures had been modified by stretching, and found that the apparent dyeing rate increased with increase in the extent of stretching. It was concluded that the increase in apparent dyeing rate was due to the morphological changes of the cuticle layer and to the fine structural changes of the cortex entity. However, we could not elucidate the structural effect of the individual histological components in the intact wool on the

dyeing behavior of the stretched wool.

It is of interest to elucidate how the structural modification in the individual histological components of the intact wool affect the dyeing behavior of stretched wool. Such a study is important in understanding the characteristics of the dyeing properties of wool. In this paper, we deal with the dyeing rate of C. I. Acid Orange 7 for the stretched wool fibers pretreated with the polar organic solvents and discuss the dyeing behavior of the stretched wool fibers with relation to the structural changes of the intercellular regions caused by stretching.

2. EXPERIMENTAL

2.1 MATERIALS

WOOL SAMPLES: A sample of Australian Merino 64's wool in the form of dry-combed top was supplied by the IWS, Japan; it has been washed with detergent, dried and combed.

"Cleaned" wool¹¹⁾: The wool extracted under strictly anhydrous conditions successively with *t*-butanol (30°C, 3 day) and *n*-heptane (20°C, 1 day) and *t*-butanol (30°C, 1 day). The wool was then washed in several changes of deionized-distilled water over 24hr at 20°C, dried under vacuum, and conditioned in a silica-gel desiccator at room temperature.

"Formic acid", "chloroform/methanol" and "*n*-propanol" extracted wools¹¹⁾: The cleaned wool was extracted at 50:1 liquor ratio, with slow agitation in 98–100% formic acid (20°C, 1hr), 2:1 (v/v) chloroform/methanol (70°C, 4hr) or 50% aqueous *n*-propanol (70°C, 4hr) respectively. The wools were then washed in several changes of deionized-distilled water for 3 days. It was then air-dried and conditioned as above.

DYESTUFF AND REAGENTS: The dye, C. I. Acid Orange 7 (A. Orange 7) was purified by recrystallizing three times from deionized-distilled water and then dried in a vacuum oven at 60°C for 10hr. The other reagents of analytical grade were used without further purification.

2.2 STRETCHING PROCEDURE OF WOOL FIBERS

After the fibers were well combed, both ends of the fiber bundle were fixed with collodion, and the bundle was set on a hand-stretching apparatus and stretched in steam. The specimens stretched

at various extension ratios were dried on the apparatus with cold air and stored at room temperature.

2.3 DYEING METHOD

The dyeing experiments were performed in the same manner as previously described¹⁰⁾. The wool samples which were attached to stainless-steel holders were immersed in an acetate buffer solution of pH 4.2 for overnight at the dyeing temperature before the dyeing experiments. Dyeing was carried out in a well-stirred dyebath with very large liquor to sample ratios. After a desired time, the sample was removed quickly, rinsed thoroughly with distilled water at room temperature and air dried. Dye on the fiber was extracted with 25% aqueous pyridine solution and the dye concentration was determined spectrophotometrically.

3. RESULTS AND DISCUSSION

In the case of acid dye, it is well known that when the dyeing rate curve is represented by a relationship between relative dye uptake and square root of dyeing time, the curve for the intact wool shows the upward curvature at the initial stage of dyeing, followed by a linear line¹²⁾. We have previously shown that not only is the apparent dyeing rate increased with increasing the extension ratio, but the initial upward curvature for the unstretched wool fibers is altered to the downward curvature by 50% extension⁹⁾. The wool fiber used in the previous studies^{9,10)} was purified by the Soxhlet extraction with ethyl ether, followed by ethanol, each for 20 hours. This cleaning procedure may modify the CMC, since ethanol extraction removes some portion of lipids, proteins and inorganic materials from the CMC^{13–15)}.

On the other hand, the cleaning procedure in the present study, employing nonswelling condition with anhydrous *t*-butanol and *n*-heptane, removes surface lipids and contaminants without affecting the internal structure of the fiber including CMC.

The effect of stretching on the dyeing rate of A. Orange 7 for the cleaned wool fibers is shown in Figure 1, which illustrates the relation between the relative dye uptake C_t/C_∞ and the square root of dyeing time, where C_t and C_∞ represent

Fig. 1. Rate of dye uptake by the unstretched (—●—) and the stretched (—○—) wool fibers pretreated with *t*-butanol and heptane for A. Orange 7 at 50°C, pH 4.2.

the dye uptake at the dyeing time t and infinity, respectively.

It is noted from Figure 1 that there is little difference in the negative intercept of the extrapolated straight line at $t=0$ between the unstretched and the stretched wools, but the stretching gives rise to an increment of the line slope, and hence a diminution of concavity. Regarding the initial dyeing behavior, this result is not in accord with the change in the initial curvature caused by stretching for the ether-ethanol extracted wool fibers reported in the previous papers^{9,10}. Contrary to this, the scanning electron microscope image of the morphological structure of cuticle layer after stretching was similar to that obtained with the ether-ethanol extracted wool¹⁰. This result indicates, therefore, that the change of initial dye uptake can not be satisfactorily explained by only the morphological changes of cuticle layer which is accompanied by the changes into the rough and porous nature of the surface layer. This suggests, further, that the difference in the initial dyeing behavior between the cleaned and the ether-ethanol extracted wool is closely related to the CMC structure in the cuticle layer.

To make sure this, we investigated the dyeing rate for the stretched wool fibers pretreated with the solvents such as formic acid, chloroform/methanol and 50% aqueous *n*-propanol. These organic solvents are known to remove lipid and

protein material from the interior of the wool fiber^{11,17}. There seems to be little doubt that the action of these solvents occurs preferentially at or within the CMC, as evidenced with a change in the transmission electron microscope image¹⁷ and the ease of breakdown of the wool into their constituent cuticle and cortical cells in the presence of the swelling reagent^{4,5}. However, the microfibril-matrix texture appears to have been unaffected by treatment with these solvents¹⁶⁻¹⁸. Figure 2 gives the plots of C_t/C_∞ against $(\text{time})^{1/2}$ ("the $t^{1/2}$ plots") for the stretched wool fibers pretreated with formic acid, chloroform/methanol and 50% aqueous *n*-propanol.

It can be seen from the initial curvature that the treatments with chloroform/methanol and 50% aqueous *n*-propanol, except for formic acid, makes remarkable changes in the initial dyeing behavior as compared with the result for the cleaned wool; the intercept at $t=0$ for the chloroform/methanol and 50% aqueous *n*-propanol extracted wool becomes zero and a positive value, respectively. This result seems to give support to the assumption that the difference in the modified CMC structure before stretching is responsible for the difference in the initial dyeing behavior between the solvent-extracted wools after stretching. This assumption, however, is insufficient to explain the experimental result that the intercept for the formic acid-extracted wool agrees with that for the cleaned wool.

Nakamura et al.¹⁶ found that from histochemical staining, the intercellular cement has different chemical compositions in cuticle-cuticle and cortex-cortex cell membrane complexes. Holms¹⁹ and other workers²⁰ found differences in reactivity of the CMC associated with cuticle and cortical cells by electron microscope studies on keratin fibers after the combined action of reducing agents and enzymes. These electron microscopical studies suggest that there are differences in response to chemical reagents and organic solvents on the CMC between cuticle cells and between cortical cells. In fact, Peters and Bradbury²¹ have observed a difference in electron staining behavior of the cuticle-cuticle and cortical-cortical CMC after immersion in formic acid. Leeder et al.¹⁷ have also observed that formic acid gives rise to some kind of modifications in

the CMC between adjacent cortical cells but not between cortical and cuticle cells, whereas chloroform/methanol and 50% aqueous n-propanol modify the structure of the whole CMC, including mainly the intercellular cement (δ -layer) but occasionally the β -layers.

According to these observations, it is reasonable to consider that the difference in the initial dyeing behavior between the stretched wools pretreated with different solvents is dependent on the difference in the structure of cuticle-cuticle CMC modified by solvent, and furthermore, that the initial dye uptake for the stretched wool pretreated with chloroform/methanol and 50% aqueous n-propanol occur preferentially into the endocuticle region, which is composed of similar structural components to the δ -layer in the CMC of cuticle-cuticle layer¹⁶), via the cuticle-cuticle CMC modified by these solvents.

Another noticeable fact in Figure 2 is that "the $t^{1/2}$ plots" for the formic acid-extracted wool overlap with that of the cleaned wool, though there is an apparent difference in the line slope of "the $t^{1/2}$ plots" between these unstretched wools as reported in the previous paper⁸). This suggests that the structural modification of the cortical-cortical CMC by formic acid is offset by the structural modification of the cortical cells caused

by 50% extension. From these discussions, it is likely that the difference in the slope of the line between the unstretched and the stretched wool shown in Figure 1 is attributable to an increase of dye penetration accompanying not only the structural changes in the microfibril/matrix texture, but the modification of the CMC structure by stretching; particularly the structural changes of the β -layer in the CMC that is mechanically weaker than the δ -layer, since the β -layer is preferentially disrupted under mechanical stress^{16,22}). However, Figure 2 shows that there is little difference in the slope of the linear line for all of the solvent-extracted wools. This fact suggests that the structural modifications of the cortical-cortical CMC by pretreatments with chloroform/methanol and 50% aqueous n-propanol, as well as formic acid, are offset by the structural modifications of the cortical cells caused by 50% extension, since the microfibril/matrix texture in three solvent-extracted wools is considered to be substantially similar to that in the cleaned wool^{17,18}). Thus, for each stretched wool, similar structural alterations are considered to have occurred in other regions of the wool fiber, as well as the region of cuticle-cuticle CMC, during the extension.

From the facts described above, we concluded that the initial dyeing behavior of the stretched wool is attributed not only to the changes into the rough and porous nature of the surface layer by stretching, but also to the difference in the modified structure of CMC in the cuticle layer caused by the solvent treatment, and that the rate of dye penetration within the bulk phase is governed by the structural modification of the cortical cells caused by stretching.

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Fig. 2. Rate of dye uptake by the stretched wool fibers pretreated with t-butanol and heptane ($\circ$), 98–100% formic acid ($\square$), 2:1(v/v)chloroform/methanol ($+$) and 50% aqueous n-propanol ($\triangle$) for A. Orange 7 at 50°C, pH 4.2.

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延伸羊毛繊維の染色速度 IV —細胞膜錯合体の改質の影響—

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延伸前の羊毛繊維の各構成成分の構造が延伸後の羊毛繊維の染色速度にどのように影響をおよぼすかを明らかにするため、有機溶剤処理により細胞膜錯合体(CMC)を改質した羊毛繊維の延伸後の染色速度について検討した。

種々の溶剤で前処理した羊毛繊維の延伸後における相対染色量と時間の平方根で表した染色速度を比較したところ、初期染色挙動に著しい違いが見られたが、その後の直線部分の傾きにはほとんど違いは見られなかった。

このことから、延伸羊毛繊維の初期吸着は延伸処理による表面層の性状変化に依存するだけでなく、延伸前のクチクルークチクルCMCの構造に依存することが明らかになった。また、繊維内部での染料のみかけの浸透速度は、溶剤処理の種類にかかわらずほぼ同じであるとみなされ、溶剤前処理によるコルテックス-コルテックスCMC構造変化が延伸処理によるコルテックス細胞の構造変化により相殺されるものと考えられた。