New Method of Dyeing Keratin Fibers Using Poly(ethylene imine) and Its Coloring Mechanism

A. Kuzuhara,[1] T. Hori[2]

[1]*Central Research Laboratories, Mandom Corporation, Osaka, Japan*
[2]*Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Fukui University, Fukui, Japan*

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ABSTRACT: To improve the colorability of keratin fibers at lower temperatures, we developed a novel coloring method using poly(ethylene imine) (PEI) as a counterion reagent (human hair was treated beforehand with a PEI solution and then was colored with an acid dye). As a result of this new method, the coloring and color fastness to shampooing clearly improved with respect to the usual method. Next, to study the coloring mechanism with PEI, we investigated the penetration of PEI and Orange II into bleached human hair by optical microscopy. The results showed that the penetration of PEI and Orange II into bleached human hair increased with an increasing PEI treatment time and with a decreasing PEI molecular weight. With these experiments, we demonstrated that PEI, which penetrated the cortex region, exerted counterionization on Orange II, thereby increasing the penetration of Orange II into bleached human hair. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3806–3810, 2003

Key words: fibers; dyes/pigments; diffusion; adsorption

INTRODUCTION

Hair coloring with acid dyes is widely used because it is safe and does not damage hair, among other reasons. However, hair coloring with acid dyes does not produce good coloring and fastness to shampooing because it cannot be used at higher temperatures. For wool dyeing, solvent-assisted dyeing[1–3] and cold dyeing[4–8] have been proposed because wool fabrics are better dyed at low temperatures: this prevents damage to the texture of the wool caused by boiling water. In solvent-assisted dyeing, benzyl alcohol, *n*-butyl alcohol, and such are used as solvents, benzyl alcohol being the most commonly used solvent in hair coloring with acid dyes. Also, in cold dyeing, when urea[4–8] and phenol[4] are added, the rate of dyeing is improved.

In this study, to improve the ability of keratin fibers at lower temperatures, we developed a novel hair coloring method using poly(ethylene imine) (PEI) as a counterion reagent (human hair was treated beforehand with a PEI solution and then was colored with an acid dye). The coloring and color fastness to shampooing of hair treated with this new method were evaluated. Next, to study the coloring mechanism with PEI, we investigated the penetration of PEI and Orange II into bleached human hair with optical microscopy.

Correspondence to: A. Kuzuhara (kuzuhara-a@mandom.co.jp).

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EXPERIMENTAL

Materials

Virgin Chinese white hair as a keratin fiber was purchased from Staffs Co. (Tokyo, Japan) PEI (number-average molecular weight = 300, 600, 1200, or 1800) was supplied by Nippon Shokubai Co., Ltd. (Tokyo, Japan) Tissue-Tek OCT 4583 (Sakura Finetechnical Co., Tokyo, Japan) was used as an embedded resin to make up the fiber cross section. Also, Orange II as an acid dye, *N*-methyl-2-pyrrolidone, a 25 wt % ammonia solution, 35 wt % hydrogen peroxide, and citric acid were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Sodium poly(oxyethylene lauryl ether sulfate) (3EO; 25 wt %) was purchased from Kao Co. (Tokyo, Japan).

Preparation of bleached human hair

Bleached human hair was prepared according to Tate et al.'s method.[9] The virgin white hair was immersed in a solution of 6.0 wt % hydrogen peroxide (pH adjusted to 10.1 with ammonia water) at a hair/solution ratio of 1:50. The hair was soaked for 1 h at room temperature. After being sufficiently washed in distilled water, the bleached hair was dried at room temperature.

Preparation of hair treated with PEI and hair coloring

The aforementioned bleached human hair was immersed in a solution of 10 wt % PEI of various molecular weights (number-average molecular weight

= 300, 600, 1200, or 1800) and 5 wt % *N*-methyl-2-pyrrolidone at a hair/solution ratio of 1:15. The hair samples were soaked at 50°C and pH 11.1 for various durations (15, 30, or 60 min). After being washed in distilled water for 1 min, the colored hair samples were prepared with the following procedure. The hair samples were immersed in a solution of 0.1 wt % Orange II and 4.0 wt % citric acid at a hair/solution ratio of 1:15. The hair was soaked at 26°C and pH 2.53 for 20 min. After being washed in distilled water for 1 min, the hair samples were dried at room temperature (the coloring procedure).

Also, as a control, a sample not treated with PEI was prepared with the following procedure. The aforementioned bleached human hair was immersed in a solution of 5 wt % *N*-methyl-2-pyrrolidone at a hair/solution ratio of 1:15. The hair samples were soaked at 50°C and pH 11.1 for 15 min and then were washed in distilled water for 1 min. Finally, the coloring procedure was performed.

Evaluation of colorability

The difference of the lightness (ΔL^*; undyed and dyed) and the difference of the total color change (ΔE^*ab) for the colored hair samples were obtained with a Minolta CM-6310d spectrocolorimeter (Tokyo, Japan). The colored hair samples were immersed in a solution of 2.5 wt % 3EO at a hair/solution ratio of 1:15. The hair samples were soaked at 40°C for 3 h. After being washed in distilled water for 1 min, the hair samples were dried at room temperature. Finally, the coloring fastness to shampooing of the hair samples was evaluated by the measurement of ΔL^* and ΔE^*ab with the spectrocolorimeter. Next, the degree of elution of Orange II from the colored hair samples was evaluated by the measurement of the Orange II absorbancy at 487 nm of the eluate solution that was created by the immersion of the colored hair samples in the 3EO solution. This elute solution was diluted to a ratio of 1:30 (the elute was 2.5 wt % 3EO), before the absorbancy was measured with a Shimadzu UV-2200 spectrophotometer (Kyoto, Japan).

Evaluation of the penetration of Orange II and PEI

White human hair fibers dyed with Orange II, as described in the previous section, were embedded in a resin (Tissue-Tek OCT 4583) and frozen. The frozen blocks were microtomed on a Leica CM1800 (Heidelberg, Germany) to a 10-μm thickness, and the penetration of Orange II into the cross-sectional samples was examined by optical microscopy.

White hair fibers treated with PEI, as described in the previous section, were embedded in a resin (Tissue-Tek OCT 4583) and frozen. The frozen blocks were microtomed on a Leica CM1800 to a 10-μm thickness and mounted on a slide glass. Next, the PEI-penetrated parts of the cross-sectional samples were stained with a solution of 0.1 wt % Orange II at room temperature with a syringe. Finally, the penetration of PEI into the cross-sectional samples was examined by optical microscopy.

RESULTS AND DISCUSSION

Colorability

An acid dye does not, for the most part, penetrate into human hair to combine with the cationic ions of the hair surface. For that reason, the coloring and fastness are not good when an acid dye is used as a hair dye. Therefore, we devised a new coloring method in which the human hair was treated beforehand with a PEI solution and then was colored with an acid dye to improve the colorability of the hair. PEI has many cationic charges because of the large amount of nitrogen in the molecule.[10] Therefore, an improvement in the colorability could be expected by the introduction of PEI into the hair before ion-binding formation with an acid dye.

TABLE I
Coloring and Color Fastness to the Shampooing of the Colored Hair Under Different Conditions

10 wt % PEI treatment		Coloring		Fastness		Elution of Orange II (487 nm)
M_w	Time (min)	$\Delta E*ab$	(ΔL)	$\Delta E*ab$	(ΔL)	
None	None	55.7	(−19.3)	34.2	(−10.9)	0.14
300	15	68.0	(−22.9)	64.2	(−19.4)	0.122
600	15	62.4	(−20.2)	54.0	(−15.8)	0.155
1200	15	63.3	(−20.0)	53.1	(−15.5)	0.124
300	30	72.3	(−24.8)	69.9	(−21.5)	0.11
600	30	68.1	(−22.7)	63.8	(−18.5)	0.112
1200	30	65.9	(−21.0)	61.4	(−17.8)	0.134
1800	30	67.1	(−22.9)	59.6	(−17.9)	0.194
600	60	72.3	(−24.9)	70.2	(−21.6)	0.13
1200	60	70.5	(−23.6)	69.9	(−20.2)	0.151
1800	60	72.3	(−25.0)	71.0	(−21.7)	0.203

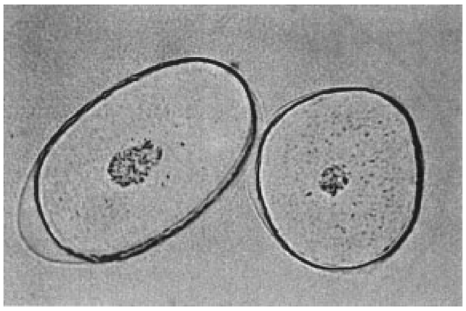

Figure 1 Cross-sectional photomicrograph of bleached-white human hair dyed with Orange II, which was not treated with PEI beforehand.

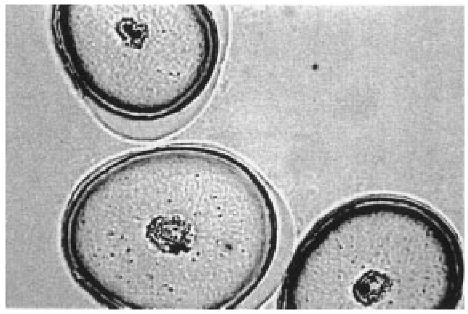

Figure 2 Cross-sectional photomicrograph of bleached-white human hair dyed with Orange II, which was treated with PEI (M_w = 600) beforehand at 50°C for 60 min.

The coloring and color fastness to shampooing of the bleached human hair dyed with Orange II, after being treated with PEI, which had various molecular weights, for various pretreatment times are reported in Table I. The colorability of the hair clearly improved by PEI treatment. The coloring and color fastness to shampooing of the colored hair samples improved as the number-average molecular weight of PEI decreased and as the pretreatment time of PEI increased. Also, the degree of elution of Orange II from the colored hair samples did not clearly change in comparison with that of the sample not treated with PEI, despite an improvement in the coloring and color fastness to shampooing.

This experiment showed that the coloring and color fastness to shampooing could be improved by the introduction of PEI as a counterion into hair.

Penetration of Orange II into bleached human hair

To study the coloring mechanism with PEI, we investigated the penetration of Orange II into bleached human hair by optical microscopy.

The bleached-white human hair was dyed with Orange II, after being treated with PEI, which had various molecular weights, for various pretreatment times. The penetration of Orange II was evaluated by the observation of the cross-sectional hair samples with an optical microscope. A cross-sectional photomicrograph of a bleached-white human hair dyed with Orange II, which was not treated with PEI beforehand, is shown in Figure 1. The cross-sectional photomicrograph of a bleached-white human hair dyed with Orange II, which was treated with PEI [weight-average molecular weight (M_w) = 600] beforehand at 50°C for 60 min, is shown in Figure 2. The penetration of Orange II into the bleached human hair clearly increased with the PEI treatment. Also, the penetration of Orange II into bleached human hair dyed with Orange II, which was treated with PEI beforehand, which had various molecular weights, for various pretreatment times, is shown in Table II. The penetration of Orange II into bleached human hair clearly increased as the number-average molecular weight of PEI decreased and the pretreatment times of PEI increased. Also, the diffusion coefficient (D) of Orange II was estimated by eq. (1),[11] under the assumption that the diffusion of Orange II was non-Fickian (Table II). L is the distance of penetration, and t is the diffusion time. The diffusion rate of Orange II into bleached human hair dyed with Orange II, after being treated with PEI, was improved 20–60 times in comparison with that of colored hair untreated with PEI:

$$L^2 = 2DT \tag{1}$$

This experiment showed that the coloring and color fastness to shampooing were improved by better Orange II penetration into human hair. That is, the coloring and color fastness to shampooing of a hair dye can be improved if the penetration of acid dyes into human hair is increased.

Penetration of PEI into bleached human hair

It has been suggested that PEI can increase the penetration of Orange II into bleached human hair. With

TABLE II
Penetration and the Diffusion Coefficient of Orange II Under Different Conditions

10 wt % PEI treatment			
M_w	t (s)	L (μm)	D(cm^2/s)
None	None	0.93	3.60×10^{-12}
300	15	4.6–7.4	8.82×10^{-11} to 2.28×10^{-10}
600	15	1.9–3.7	1.50×10^{-11} to 5.70×10^{-11}
1200	15	1.9–3.7	1.50×10^{-11} to 5.70×10^{-11}
300	30	4.6–9.3	8.82×10^{-11} to 3.60×10^{-10}
600	30	5.6–7.4	1.31×10^{-11} to 2.28×10^{-10}
1200	30	3.7–4.6	5.70×10^{-11} to 8.82×10^{-11}
1800	30	3.7–5.6	5.70×10^{-11} to 1.31×10^{-10}
600	60	6.5–9.3	1.76×10^{-10} to 3.60×10^{-10}
1200	60	3.7–5.6	5.70×10^{-11} to 1.31×10^{-10}
1800	60	3.7–6.5	5.70×10^{-11} to 1.76×10^{-10}

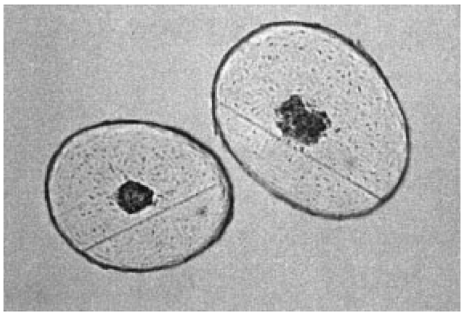

Figure 3 Photomicrograph of bleached-white human hair cross-sectioned and dyed with Orange II.

this relationship in mind, we investigated the penetration of PEI into bleached human hair. PEI is a branched polymer with many cationic charges due to the large amount of nitrogen in the molecules.[10] Therefore, the penetration of PEI into human hair could be observed by the dyeing of PEI-penetrated parts with Orange II. We prepared cross-sectional samples of bleached human hair treated with PEI. Next, the penetration of PEI for cross-sectional samples dyed with Orange II was estimated by optical microscopy.[12] A photomicrograph of bleached-white human hair cross-sectioned and dyed with Orange II is shown in Figure 3. A photomicrograph of bleached-white human hair treated with PEI (M_w = 600) at 50°C for 60 min, cross-sectioned, and dyed with Orange II is shown in Figure 4. The bleached-white human hair sample not treated with PEI adsorbed Orange II a little into the surface of the cuticle and did not adsorb Orange II into the cortex. However, bleached-white human hair treated with PEI (M_w = 600) at 50°C for 60 min adsorbed Orange II from the cuticle to the cortex. This suggests that the penetration of PEI can be observed with this method. The penetration of PEI under different conditions is shown in Table III. The penetration of PEI into bleached human hair clearly increased as the number-average molecular weight of PEI decreased and the pretreatment time of PEI increased.

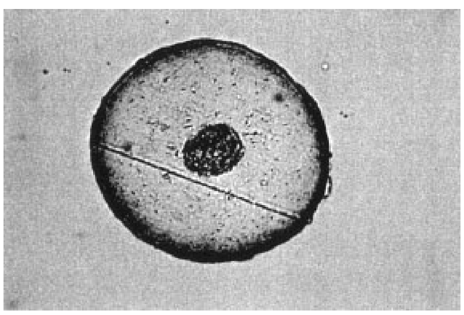

Figure 4 Photomicrograph of bleached-white human hair treated with PEI (M_w = 600) at 50°C for 60 min, cross-sectioned, and dyed with Orange II.

TABLE III
Penetration of PEI Estimated by Optical Microscopy for the Cross-Sectional Samples Dyed with Orange II

	Penetration (μm)		
M_w	15 min	30 min	60 min
300	8.35	23.2	—
600	6.95	9.3	10.2
1200	3.25	5.55	8.35
1800	—	3.25	4.65

Coloring mechanism of keratin fibers with PEI

The penetration of PEI into bleached-white human hair treated with 10% PEI, which had various molecular weights, at 50°C for 30 min is shown in Table IV. Also, the penetration of Orange II for bleached-white human hair dyed with 0.1% Orange II at 26°C for 20 min, after treatment with 10% PEI, which had various molecular weights, at 50°C for 30 min is shown in Table IV. The PEI molecular weight had a small influence on the penetration of Orange II in comparison to the great influence on the penetration of PEI. This suggests that the penetration of Orange II into human hair can be increased when PEI is first introduced into the cortex region of human hair.

With this experiment, we have demonstrated that PEI, which penetrates the cortex region, exerts counterionization on Orange II, thereby increasing the penetration of Orange II into bleached human hair. For the usual dyeing method, as the penetration of an acid dye into human hair is interrupted by the cuticle layer, the acid dye does not penetrate the cortex region. However, the acid dye penetrates the cortex region when PEI is introduced into human hair. As a result, the coloring and color fastness to shampooing of colored hair improve with respect to hair treated with the usual method.

CONCLUSIONS

When human hair was treated beforehand with a PEI solution and then colored with an acid dye, the color-

TABLE IV
Penetration of PEI and Orange II into Bleached Human Hair

	Penetration (μm)	
M_w	PEI[a]	Orange II[b]
300	23.2	6.95
600	9.30	6.50
1200	5.55	4.15
1800	3.25	4.65

[a] Treated with 10% PEI at 50°C for 30 min.
[b] Treated with 10% PEI at 50°C for 30 min and then 0.1% Orange II at 26°C for 20 min.

ing and color fastness to shampooing of the colored hair clearly improved with respect to those treated with the usual method. Also, the coloring and color fastness to shampooing of the colored hair clearly improved when the PEI treatment time increased and the PEI molecular weight decreased. To study the coloring mechanism with PEI, we investigated the penetration of PEI and Orange II into bleached human hair by optical microscopy. The results showed that the penetration of PEI and Orange II into bleached human hair clearly increased as the PEI treatment time increased and the PEI molecular weight decreased.

With these experiments, we have demonstrated that PEI, which penetrates the cortex region, exerts counterionization on Orange II, thereby increasing the penetration of Orange II into bleached human hair.

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