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The effect of cationic polymer treatment on adhesion of iron oxide to eyelashes

S. KO, Y. H. ROH, J. H. CHOO, S. H. JANG, S. H. HAN, and
H. G. JANG, *Korea University, Seoul 136-701 (S.K., H.G.J), and AMOREPACIFIC R&D Center, Yongin 446-729 (S.K., Y.H.R., J.H.C., S.H.J., S.H.H.), Republic of Korea.*

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Synopsis

The aim of this study was to investigate the effect of iron oxide application on improving the volume of eyelashes. Iron oxide, having a negative surface charge in its natural form, was coated with commercial cationic polymers to increase its adhesion. The iron oxides coated with different types and concentrations of these polymers were incorporated into a basic mascara formula to test their volume effects by means of the weight difference of eyelashes.

The results indicated that the type and concentration of coating materials affect the surface zeta potential and particle cluster size of iron oxides. The type of cationic polymer, especially, was shown to modify both factors of iron oxide. The obtained results also suggested that the volume effect of mascara increases with a higher positive surface zeta potential and a smaller particle cluster size of the coated iron oxides.

INTRODUCTION

Iron oxides are a class of coloring matter used in cosmetics for application on skin or keratin fibers. In the past few decades, they have become an increasingly important component of color cosmetics, especially as a primary ingredient in eye makeup. Much research on iron oxides, in surface treatment, material hybridization, and morphology control, has been conducted to improve the long-lasting effect, skin adhesiveness, and smooth texture of the final cosmetic product (1).

Pigments treated with methicone, dimethicone, or alkyl silane are known to present waterproof effects due to the hydrophobicity of these silicone materials. Perfluoro compounds, especially polytetrafluoroethylene (PTFE), have a lower surface energy than any oil, thus granting stronger long-lasting effects against hydrophobic solvents.

Skin adhesion can be improved by coating pigments with keratin or silanyl glutamate. Keratin, being the basic component of skin, demonstrates higher affinity, and silanyl

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Address all correspondence to H. G. Jang.

glutamate, acquired by an esterification reaction between silanol and L-glutamic acid, causes the surface charge of pigments to turn positive, producing stronger attraction to the negative-charged keratinous surface (2).

Although the interaction of such treated pigments on skin has been described in previous studies (3–6), little is known regarding their adhesion to keratin fibers. Therefore, in this study, we evaluated the influence of variously coated iron oxides, using the surface charge characteristics of human hair keratin that are known to be most similar to those of eyelashes (7).

The isoelectric point of human hair is known to be pH 3.7, at which functional groups of the 18 constitutive amino acids remain electrically neutral. Application of mascara (pH 7–8) would cause the eyelash fibers to become negatively charged, resulting in a favorable surface potential for cationic polymer adhesion (8). We, therefore, examined the effect of cationic polymer treatment of iron oxide on adhesion to eyelashes by evaluating mascara formulae consisting of such coated pigments (Figure 1).

EXPERIMENTAL

MATERIALS

The black iron oxide used in this study was Tarox® BL-100 supplied by Titan Kogyo Kabushiki Kaisha (Japan). The cationic polymers used to treat the iron oxide were polyquaternium-6 (PQ-6) (Salcare® SC30; Ciba, Switzerland), guar hydroxypropyl trimonium chloride (GHC) (Jaguar® C 17; Rhodia Novecare, New Jersey), and polyquaternium-10 (PQ-10) (UCARE™ Polymer JR 400; Amerchol, New Jersey).

The GHC and PQ-10 used in this experiment had an average molecular weight, degree of substitution, and charge density, respectively, of 2,200,000 g/mol, 0.2, 1.1 meq/g (GHC) and 600,000 g/mol, 0.4, 1.57 meq/g (PQ-10). PQ-6, with an average molecular weight

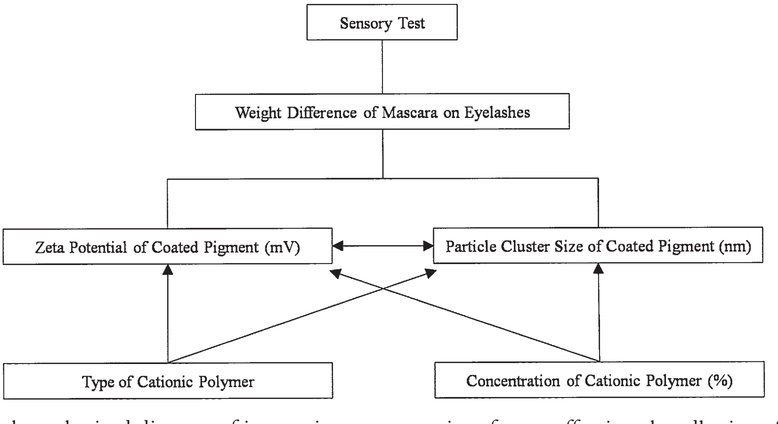

Figure 1. A hypothesized diagram of interaction among various factors affecting the adhesion of iron oxide treated with cationic polymers to eyelashes.

of 240,000 g/mol and a charge density of 6.2, had one cationic group in each monomer unit.

Artificial eyelashes (Echo's Eyelash®; Taeil, Republic of Korea) were manufactured, using untreated human hair, to measure the volume effects by mascara application. The eyelashes were designed to achieve an average length of 7.0 mm and a thickness of 72.0 μm by referring to the results of a previous study (9).

SURFACE TREATMENT

The surface of iron oxide was treated with cationic polymers by a wet process well known to those in the industry (2). This method has been used to treat pigments with a hydrophilic surface (such as clay minerals), inorganic materials (such as silica or titanium dioxide), and polymeric materials (such as polymethyl methacrylate).

Iron oxide was dispersed in deionized water in a ratio of 1:2. The cationic polymers were agitated in a separate tank to reach transparency in deionized water at 50°C. The aqueous polymer slurry was added to the pigment to form a colloidal dispersion of the coating materials. Following agitation for 1 hr, the mixture was filtered to form a paste and dried under heat. The pigment was then ground using an atomizer (BRA-15; Baro Engineering, Republic of Korea) and finally screened with a polarizer (CSTS-601; Chang Sung Hitech, Republic of Korea).

MEASUREMENT OF ZETA POTENTIAL AND PARTICLE CLUSTER SIZE

The zeta potential values and particle cluster sizes of the coated pigments were measured using a zeta potential spectrophotometer (ELS-8000; Otsuka Electronics Co. Ltd., Japan). All measurements were made at pH 7 to simulate mascara application. The samples were diluted 1,000-fold in 0.1 M NaCl solution or deionized water for zeta potential or particle cluster size, respectively, and sonicated 5 min prior to measurement. The measurements were repeated three times.

MASCARA FORMULATION

Mascara bulks were prepared employing a basic mascara formula using coated and uncoated iron oxides. The formula included: water (to 100%), acrylates copolymer (20%), paraffin (10%), iron oxides (10%), beeswax (5.0%), carnauba wax (3.0%), stearic acid (3.5%), palmitic acid (1.5%), polybutene (1.0%), triethanolamine (1.0%), butylene glycol (1.0%), and hydroxyethylcellulose (0.2%) with necessary chelating agents and preservatives.

Mascara weight measurement. Mascara weight was defined as the weight difference of artificial eyelashes before and after twelve mascara applications. Twelve applications is defined as dividing the eyelashes into three sections (i.e., left, middle, right) and applying mascara in each section twice from the top and twice from the bottom. The experiments were repeated three times.

Sensory test. Sensory tests were conducted by a trained panel of thirty Korean women in the age range of 20-35 regularly using mascara every day. Volume and spreadability scores were marked in the range of 0-14.

DATA ANALYSIS

Data were presented as mean ± SD, and all statistical analyses were performed using MINITAB 15 software (Minitab Inc., Pennsylvania).

RESULTS AND DISCUSSION

EFFECT OF TYPE AND CONCENTRATION OF CATIONIC POLYMERS ON ZETA POTENTIAL AND PARTICLE CLUSTER SIZE OF TREATED IRON OXIDES

Iron oxide, naturally having a negative surface charge, was coated with cationic polymers in an effort to improve its adhesion to the eyelashes. The type and concentration of the coating polymers were shown to significantly modify the zeta potential and particle cluster size of the treated iron oxides by using two-way ANOVA ($p < 0.05$).

The zeta potential of iron oxide was relatively affected more by the type of polymer used than its concentration. PQ-6 and GHC especially resulted in a higher positive zeta potential value than PQ-10 treatment. The concentration of coating polymers was in direct proportion to the surface zeta potential in all three types.

The type of cationic polymer also showed a stronger effect on the particle cluster size compared to its coating concentration. The data indicated that treatment by any of the three polymers tested resulted in a smaller-sized particle cluster of iron oxide. The relatively low difference in particle cluster size by means of GHC concentration strongly suggests that cationic treatment itself has more influence than the concentration of the polymers (Table I).

RELATIONSHIP BETWEEN SURFACE ZETA POTENTIAL AND PARTICLE CLUSTER SIZE OF TREATED IRON OXIDES

The relationship between the surface zeta potential and particle cluster size of treated iron oxides was evaluated by general linear model (GLM) analysis. Figure 2 describes

Table I
Effect of Cationic Polymer Treatment on Particle Cluster Size and Zeta Potential of Iron Oxides

Coating material		Particle cluster size	Zeta potential	Weight difference
Type	Concentration (%)	(nm)	(mV)	(mg)
None	0	4396.7 ± 74.6	-12.033 ± 0.605	7.673 ± 0.111
PQ-6	3	2934.0 ± 74.1	25.273 ± 1.222	8.973 ± 0.068
	5	1562.4 ± 29.3	52.483 ± 0.468	15.123 ± 0.136
	10	1099.3 ± 84.6	63.437 ± 1.217	15.843 ± 0.060
GHC	3	1514.3 ± 41.2	43.927 ± 0.612	11.350 ± 0.461
	5	1290.6 ± 8.54	45.677 ± 0.389	11.913 ± 0.178
	10	1215.0 ± 36.7	47.693 ± 0.441	12.517 ± 0.333
PQ-10	3	3579.8 ± 21.0	28.080 ± 0.896	9.090 ± 0.187
	5	2372.2 ± 10.5	33.763 ± 1.293	10.573 ± 0.095
	10	2057.4 ± 29.9	40.553 ± 0.338	11.230 ± 0.099

Data presented as mean ± SD (n = 3). PQ-6: polyquaternium-6. GHC: guar hydroxypropyl trimonium chloride. PQ-10: polyquaterium-10.

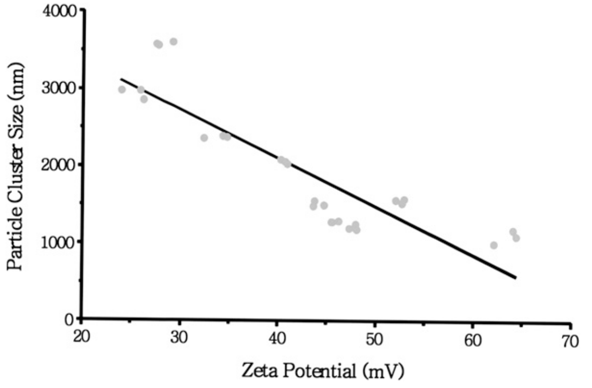

Figure 2. Correlation between zeta potential vs particle cluster size of treated iron oxides (n = 27).

the significant correlation between the two factors, and the equation was determined as P = –35.293Z + 3451.9 (P: particle cluster size (nm); Z: zeta potential (mV); $p = 0.000$; $R^2 = 0.951$). It is evident from the data that cationic polymer treatment results in a stronger particle–particle interaction due to the positive surface charge of the coated pigments, producing an even dispersion and a smaller particle cluster size.

EFFECT OF ZETA POTENTIAL AND PARTICLE CLUSTER SIZE OF TREATED IRON OXIDES ON WEIGHT DIFFERENCE BY MASCARA APPLICATION

Factor analysis was performed, at 5% significance level, to verify whether the surface zeta potential and particle cluster size of treated iron oxides affect weight difference by mascara application, and the results showed that both factors have a significant effect ($p = 0.000$).

Figure 3 shows the correlation between the zeta potential of treated iron oxides and the weight difference. It was shown that a bigger weight difference is achieved by a stronger zeta potential, which in turn is caused by a higher concentration of coating cationic polymers. The results suggest that cationic-treated pigments are more strongly attracted to

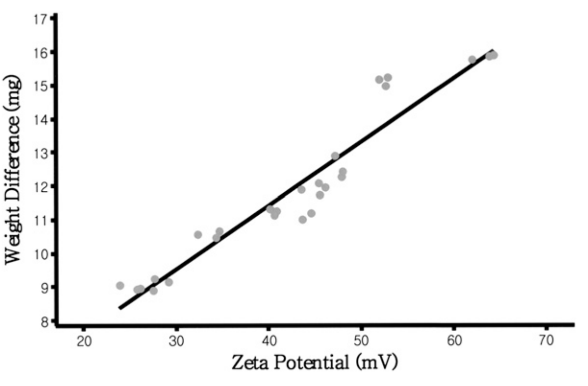

Figure 3. Correlation between zeta potential of treated iron oxides and weight difference by mascara application on eyelashes (n = 27).

eyelashes, which are naturally negatively charged, and this is consistent with Coulomb's law in that the electrostatic force is directly proportional to the magnitude (10). Since uncoated iron oxide has a negative charge, as shown in Table I, much less weight difference is observed by mascara application, presumably due to the repulsive force against the eyelashes. The particle cluster size of treated iron oxides, on the other hand, shows an inverse proportion to weight difference by mascara application, as presented in Figure 4. This result implies that the smaller coated particles are arranged in a uniform and dense pattern, building up a gradual volume on the eyelashes.

Figure 5 displays a logistic regression plot of the effect of the zeta potential and particle cluster size of the treated iron oxides on weight difference by mascara application on eyelashes. The equation determined was $W = 0.0443Z - 0.000932P + 11.2$ (W: weight difference (mg); Z: zeta potential (mV); P: particle cluster size (nm); $p = 0.000$; $R^2 = 0.913$), and the zeta potential was shown to be relatively more significant compared to the particle cluster size. From the data of Figure 5 and Table I, we can conclude that the biggest weight

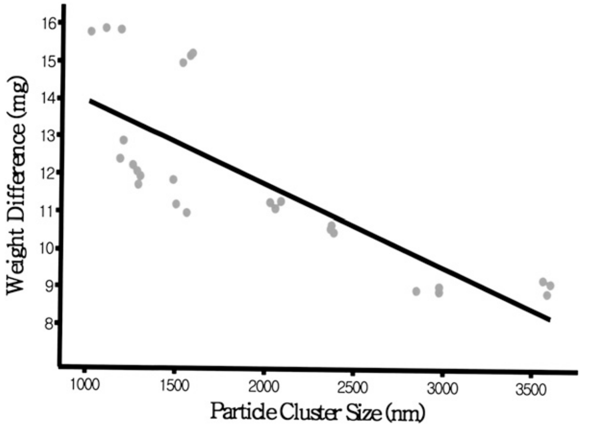

Figure 4. Correlation between particle cluster size of iron oxide and weight difference by mascara application on eyelashes (n = 27).

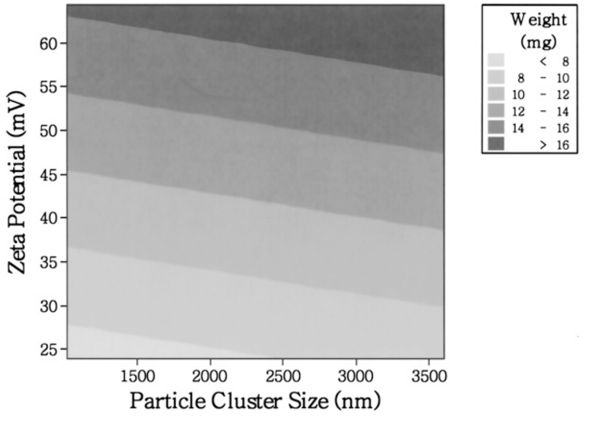

Figure 5. A logistic fitting graph of the effect of zeta potential and particle cluster size of treated iron oxides on weight difference by mascara application on eyelashes (n = 27).

difference is achieved by treating iron oxide with 10% PQ-6, with the strongest zeta potential (63.437 ± 1.217 mV) and smallest particle cluster size (1099.3 ± 84.6 nm).

RELATIONSHIP BETWEEN WEIGHT DIFFERENCE BY MASCARA APPLICATION AND SENSORY TEST SCORES

A sensory test by a panel of thirty Korean women was performed to determine the optimum volume effect of mascara, including the treated iron oxides, and the results are shown in Table II. The scores were marked in the range of 0–14, score 0 implying no volume and bad texture, score 14 indicating maximum volume and great texture, and score 7 being the average. The texture was also considered in the panel test, since undesirable effects such as clumping could result from volume alone.

The response surface regression method was used to analyze the relationship between weight difference by mascara application and sensory test scores, and the equation was determined as $S = -0.3353W^2 + 8.396W - 40.48$ (S: score; W: weight difference (mg); $p = 0.001$; $R^2 = 0.873$) (Figure 6). Contrary to the weight data in the previous result, the mascara including iron oxide treated with 10% GHC received the highest panel score due to the texture factor. Using the panel data and response optimization method, we predicted the conditions for a perfect sensory score, which was estimated to be a weight difference of 12.34 mg, a zeta potential of 48.01 mV, and a particle cluster size of 1186.3 nm.

CONCLUSIONS

In this research, we studied the effect of coating iron oxide with cationic polymers to increase the weight of mascara application on eyelashes. The results suggest that the adhesion of iron oxide to eyelashes was increased significantly by cationic polymer treatment. The

Table II
Effect of Cationic Polymer Treatment on Weight Difference and Sensory Test Scores by Mascara Application

Coating material			
Type	Concentration (%)	Weight difference (mg)	Sensory test scores
None	0	7.673 ± 0.111	5.667 ± 0.884
PQ-6	3	8.973 ± 0.068	6.333 ± 0.758
	5	15.123 ± 0.136	9.333 ± 0.802
	10	15.843 ± 0.060	8.333 ± 0.480
GHC	3	11.350 ± 0.461	12.333 ± 0.711
	5	11.913 ± 0.178	12.667 ± 0.661
	10	12.517 ± 0.333	13.333 ± 0.607
PQ-10	3	9.090 ± 0.187	7.333 ± 0.547
	5	10.573 ± 0.095	9.667 ± 0.844
	10	11.230 ± 0.099	12.000 ± 0.743

Data presented as mean ± SD (n = 3 for weight difference and n = 30 for sensory test scores). PQ-6: polyquaternium-6. GHC: guar hydroxypropyl trimonium chloride. PQ-10: polyquaterium-10.

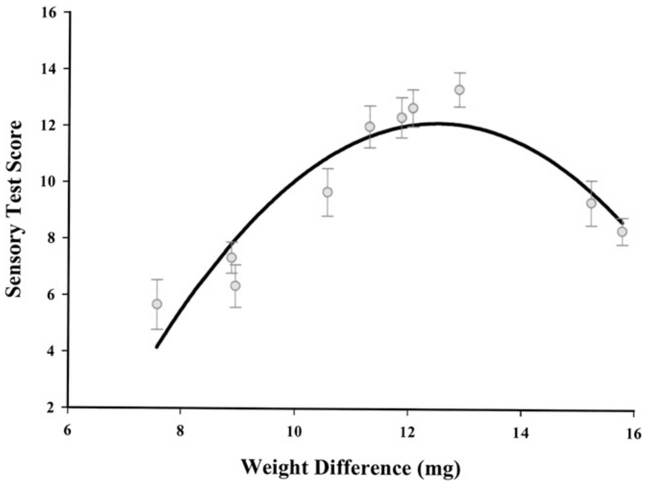

Figure 6. Correlation between weight difference by mascara application on eyelashes and sensory test score (n = 10).

type of polymer coating was shown to have more influence than its concentration, and the weight difference by mascara application increased, as cationic treatment resulted in a lower particle cluster size and surface charge modification of the pigments.

The biggest difference in weight on artificial eyelashes was obtained from treatment with 10% PQ-6, whereas 10% GHC coating showed the best texture and volume effects from the panel sensory test. From the findings of this study, we can conclude that treating the surface of iron oxides with cationic polymers is an attractive approach in increasing the volume effect of eyelashes by mascara application.

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