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Analysis of Darkening Shampoos:Chemical and Physical Properties and Their Impact on Hair Color Change and Cuticle Damage Evaluation

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ABSTRACT: This study comprehensively analyzes the characteristics and effects of various darkening shampoos available in the market on hair. The shampoos under studywere observed to have different effects on hair based on their ingredients and manufacturing principles. This was confirmed by measuring the pH, electrical conductivity, and particle size of the shampoosamong other characteristics.Coal tar dye-containing, coating-based shampoos S_B and S_C showed higher darkening effects and dyeing properties than oxidation-based shampoos S_A and S_D containing 1,2,4-Trihydroxybenzene (1,2,4-THB). Additionally, the extent of hair damage caused by the darkening shampoos was evaluated, and some shampoos causedmore significant damage to the cuticle. These results may enhance our understanding of darkening shampoos, enabling consumers to select products more cautiously, thereby improving consumer satisfaction and contributing to improvement inquality by manufacturers.

KEYWORDS: Darkening Shampoo, Dye Shampoo, Coloring Shampoo, Darkening Effect, Dyeability, Hair Dye, 1,2,4-THB, Hair Damage

I. INTRODUCTION

The popularity of darkening shampoos is driving market expansion, offering a significant divergence in composition compared to traditional hair dyes. Generally, hair dyes contain oxidants and pigments that destroy melanin pigments and penetrate hair shafts to alter the color of hair. However, these traditional methods of using oxidants often cause unavoidable hair and scalp damage. In contrast, darkening shampoos do not contain oxidants, thus possessing a major advantage in preventing such damage.

In the domestic market, 14 hair dye shampoos have been identified as containing substances that may pose genotoxic risks [1]. According to data provided by the Ministry of Food and Drug Safety, some of these products contain 1,2,4-Trihydroxybenzene(1,2,4-THB), a component that is a subject of controversy. The use of products containing this ingredient is banned in the European Union and ASEAN countries, raising concerns about the safety of shampoos commonly used in daily routines.

Furthermore, some cosmetic manufacturers are developing products that produce temporary dyeing effects using ingredients extracted from plants without inclusion of oxidants or 1,2,4-THB. However, these products are not entirely free from controversies associated with harmful effects of tar dyes. The fact that numerous companies and pharmaceutical firms continue to manufacture and sell darkening shampoos despite these controversies highlights the importance of using appropriate substances and product development for safe use of hair products by consumers [2].Emphasis on the safety of hair products underlines the need for more refined development of products tailored to different scalp types and hair conditions to ensure safe usage by consumers.

Recent research trends in hair dyeing include studies that have investigated the dyeing properties of synthetic and human hair,compared their differences [3], and analyzed changes in white and dark brown hair before and after dyeing with permanent hair dyes [4,5]. Direct studies on darkening shampoos include research that compares the effects of hair-oxidation and hair coating-based hair color shampoos,analyzes the functionality of hair color shampoos [6], and investigates harmful

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effects of color shampoos on the scalp-skin barrier [7]. Such studies have contributed to the expansion of knowledge in the field of hair dyeing.

Furthermore, the development of darkening shampoos with various ingredients and mechanisms of action has prompted the Ministry of Food and Drug Safety to provide consumer usage guidelines. A study conducted by Future Consumer Behavior on the ingredients and labeling status of darkening shampoos currently available in the market has revealed that these products can be categorized into four distinct types based on their principles and components.

The first type of darkening shampoo contains 1,2,4-Trihydroxybenzene (1,2,4-THB). These shampoos include polyphenols, which, according to manufacturers, change color upon being oxidized through binding with oxygen. In this process, 1,2,4-THB does not act as a dye but assists in converting insoluble polyphenols into soluble forms, ensuring maximum retention of the dye on the hair. The second type contains coal tar dyes, which are derived from coal tar or its by-products, or are synthetically obtained [8].According to the administrative regulations of the Cosmetic Act, 'Types and Standards of Cosmetic Colorants and Their Testing Methods', 31 types of tar dyes are permitted to be used for hair coloring. These dyes, which are typically used in temporary hair tints and treatments, coat hair to alter its color. Their safe use in daily-use hair dye shampoos requires assessment by the Food and Drug Administration, along with guidelines for safe use and cautionary labeling. The third type includes shampoos that containnotified functional hair dye ingredients.These products have separate compartments for the dye (component 1) and oxidant (component 2) within the same container, which have shampoo functionality but essentially mirror the principles and composition of conventional hair dyes. The fourth type of shampoo achieves darkening effects solely through polyphenols without using 1,2,4-THB, coal tar dyes, or notified functional hair dye ingredients. The polyphenols used include plant extracts such as tannic acid, gallic acid, black bean extract, black sesame extract, and caffeine. Manufacturers claim to have developed technologies that attach polyphenols to hair using ion binding, hair fixatives, or mordants without using 1,2,4-THB. The efficacy of these shampoos in providing such advertised hair dyeing function needs to be verified [7].When combining shampoos and hair dyes, it is crucial to determine whether they are harmless to the human body while effectively performing their intended functions. It is essential to consider potential harmful effects of shampoos and hair dyes, especially because their long-term use is inevitable until alternatives are developed. Consequently, it is important for consumers to understand the improvements in harmful ingredients and product verification processes in different countries, thereby enabling them to choose safe and effective products.

In this context, we selected two types of darkening shampoos containing 1,2,4-THB and two types containing coal tar dyes, and meticulously examined their physical and chemical properties. This study aims to conduct a relatively precise analysis of color changes and damage levels in gray hair washed with these shampoos to evaluate the impact of each shampoo on hair. Through this study, we seek to gain a deeper understanding of how various components and mechanisms of action of darkening shampoos affect hair health and color retention.

II. MATERIALS AND METHODS

2.1 Materials

The four types of darkening shampoos (S_A, S_B, S_C, and S_D) used in this study were purchased from official online stores of each manufacturer. Table 1 shows classification of the shampoos into four types based on categorization by Future Consumer Behavior (2022), indicating the type to which each sample belongs. As the shampoos are highly concentrated formulations, they were diluted 1,000 times with distilled water for accurate analysis of their physical properties. The samples were sonicated to disintegrate any clumps and subsequently stored at room temperature.

Hair samples used in the experiments were hairpieces for dye testing, purchased from a color research institute, consisting of a mix of 100% gray hair and virgin hair of Asian origin that were not chemically bleached. After cleansing the hair samples with a neutral shampoo and air-drying, they were washed 28 times with each of the four shampoos. The shampoo-washing procedure was as follows:

a. A weighing dish was placed on a scale, brought to zero, and 1 g of shampoo was weighed.

b. Lukewarm water (0.8 L) was added to a one-liter beaker, the hair was rinsed, and then the shampoo prepared in step 'a' was manually applied. The hair was then placed on aluminum foil and left for 3 min.

c. The hair was rinsed in three separate beakers, each containing 0.8 Lof pre-prepared lukewarm water.

d. The rinsing method involved immersing the hair in water, removing it ten times, and then pressing it between the thumb and forefinger to extract the liquid.

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e. After rinsing, the hair was dried with a Kimwipe and then with a hair dryer.

f. This process was repeated 28 times for each hair sample under identical conditions.

Table 1. Four types of darkening shampoos

Type	Dyeing principle	Samples used in experiment
Contains 1,2,4-THB	1,2,4-THB plays a role in converting insoluble polyphenols into soluble forms, aiding in maximizing their retention on hair.	S_A, S_D
Contains coal tar dye	Coats the hair to temporarily change its color.	S_B, S_C
Contains ingredients notified in functional hair dyes	Products features a two-component system, with hair dye in one compartment and oxidant in another within the same container, thereby enhancing the functionality of a shampoo.	-
Contains only polyphenols	Implements a technology that utilizes ion binding, hair fixatives, or mordants to attach polyphenols to hairwithout the use of 1,2,4-THB.	-

2-2. Measurement of pH &conductivity of Darkening Shampoo

To measure pH of the four darkening shampoos, the glass electrode of a pH meter was cleaned meticulously with distilled water. Calibration was then performed twice using buffer solutions at pH 4.01, 7.00, and 9.21. Additionally, electrical conductivity of the shampoos was measured by first cleaning the electrode of a conductivity meter with distilled water and then performing a two-time calibration using a buffer solution of 1.413 µS/cm. The pH and electrical conductivity measurements were repeated three times for each sample.

2-3. Measurement of particle size of darkening shampoos

Dynamic Light Scattering (DLS, ELSZ-2000ZS, Japan) was used to evaluate the particle sizes of the four darkened shampoos. Measurements for each sample were repeated three times. Data obtained from the cumulative results, particularly the diameter and Polydispersity Index (PDI), were analyzed. The diameter primarily indicates the average size of the particles, whereas PDI reflects diversity of the particle size distribution. A low PDI value denotes a narrow and uniform distribution of particle sizes, whereas a high PDI value indicates a diverse and broad range of particle sizes. Hence, PDI is used as an important indicator for assessing the breadth and diversity of particle size distribution.

2-4. Color analysis of hair washed with darkening shampoos

To evaluate the effectiveness of darkening shampoos, hair samples were colorimetrically analyzed .After washing the hair samples 28 times, a colorimeter (Konica Minolta, CHROMA METER CR-400, Japan) was used to perform three colorimetric measurements. The measured values quantitatively represented the color of the hair samples, encompassing various elements such as color intensity, saturation, and brightness. Color changes were analyzed based on standardized color coordinates L*, a*, b*, as defined by the International Commission on Illumination (CIE). This study particularly observed the darkening effect through changes in the L* value and evaluated the dyeing effect by calculating the color difference (ΔE). The calculation of ΔE was based on the differences in L*, a*, b* values, using the following equation:

$$\Delta E^*_{ab} = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

The color differences were assessed according to a six-level color difference standard, [9] referenced from the American standard for color differences

2-5. Scanning electron microscopic observations of hair washed with darkening shampoo

Morphological changes occurring in the cuticle of hair washed with darkening shampooswere observed usinga Scanning Electron Microscope (SEM, JSM-7001F, JEOL, Japan). After washing the hair samples 28 times with each

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of the four darkening shampoos, three strands per hairpiece were selected to compare and analyze the extent of cuticle damage.

2-6. Energy Dispersive Spectroscopy (EDS) analysis of hair washed with darkening shampoos

EDS was used to analyze the chemical composition of hair washed with darkening shampoos. After preparing hair samples using identical conditions as those for SEM a, the content and distribution patterns of key elements in hair fibers, such as carbon (C), oxygen (O), nitrogen (N), sulfur (S), and other elements, were analyzed.**(till here)**

Ⅲ. RESULTS AND DISCUSSION

Results for darkening shampoos available in the domestic market and for hair washed with these shampoos are as follows:

3-1. pH &conductivity measurement results of darkening shampoos

According to the pH measurement results, darkening shampoo S_D exhibited the lowest pH value at 5.85, whereas S_A showed a pH of 6.61, S_B 6.56, and S_C 6.24. These results indicate little variation in pH values among the darkening shampoos, reflecting a product design that minimizes loss in color of the darkened hair. Additionally, this slightly acidic pH range of the shampoos supports the findings of previous studies [10], suggesting that unlike alkaline hair dyes, these shampoos do not cause cuticle swelling, thereby leading to a relative reduction of hair damage. Thus, the pH range of these darkening shampoos can be interpreted as aligning with product designs that are focused on minimizing hair damage while maintaining color. In terms of electrical conductivity, S_A registered 65.38μS/cm, S_B 106.1μS/cm, S_C 82.47μS/cm, and S_D 70.97μS/cm, indicating that most of the darkening shampoos exhibited conductivity below 100μS/cm. Notably, the darkening shampoos containing coal tar dyes showed slightly higher conductivity values than those containing 1,2,4-THB, with the highest conductivity observed for S_B, which was likely due to the high content of ionic surfactants in the dye. These characteristics related to pH and electrical conductivity are thought to be important factors affecting the cleaning efficacy and darkening effects of the shampoos.

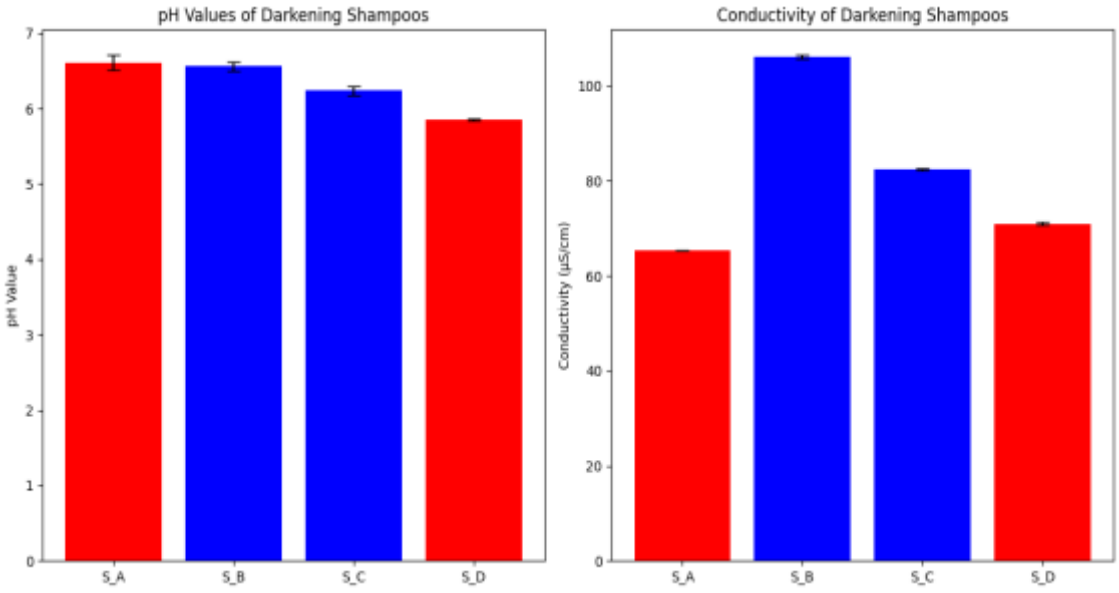

Fig.1. Comparison of pH & electrical conductivity of different darkening shampoos.

3-2. Results of particle size analysis of darkening shampoos

According to the DLS measurements of particle size ofthe darkening shampoos, the average particle size ofS_A was 639.6 nm with aPDI of 0.394, S_B had an average particle size of 8,969 nm with PDI of 2.594, S_C showed an average particle size of 257.0 nm with PDI of 0.177, and S_D had an average particle size of 1,192 nm with PDI of 0.679. Such diverse DLS measurement values can be interpreted as being influenced by the various ingredients and complex molecular structures of the darkening shampoos, which may have affected the particle size and distribution.

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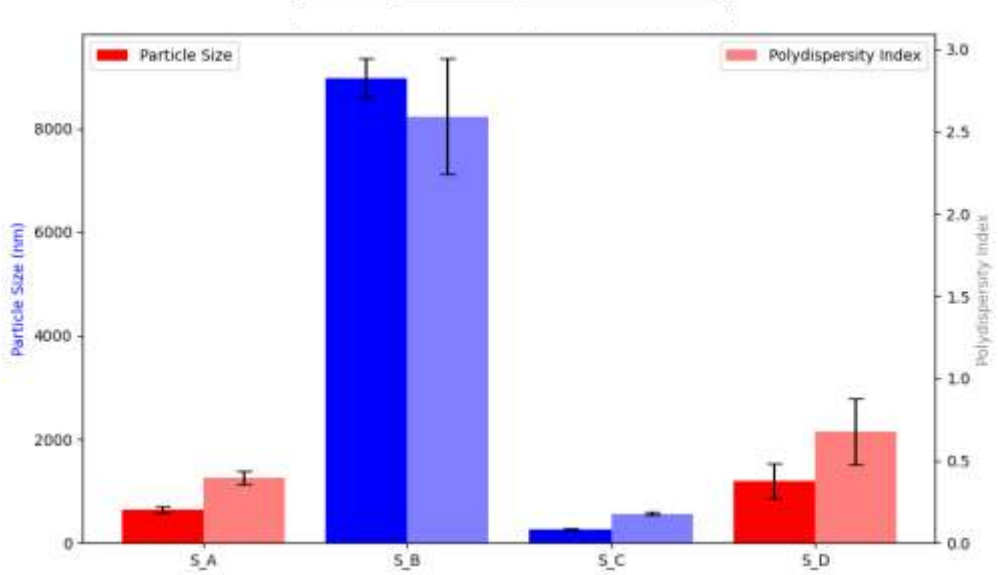

Fig.2. Comparison of particle size and PDI of different shampoos.

3-3. Results of colorimetric analysis of hair washed with darkening shampoo

The fourtypes of shampoos revealed a visuallyobservable darkening effect as demonstrated by colorimetric analysis(Figure.3). The shampoos showed a tendency to darken the color of gray hair even after just one wash, and this effect became more pronounced with an increasing number of washes.

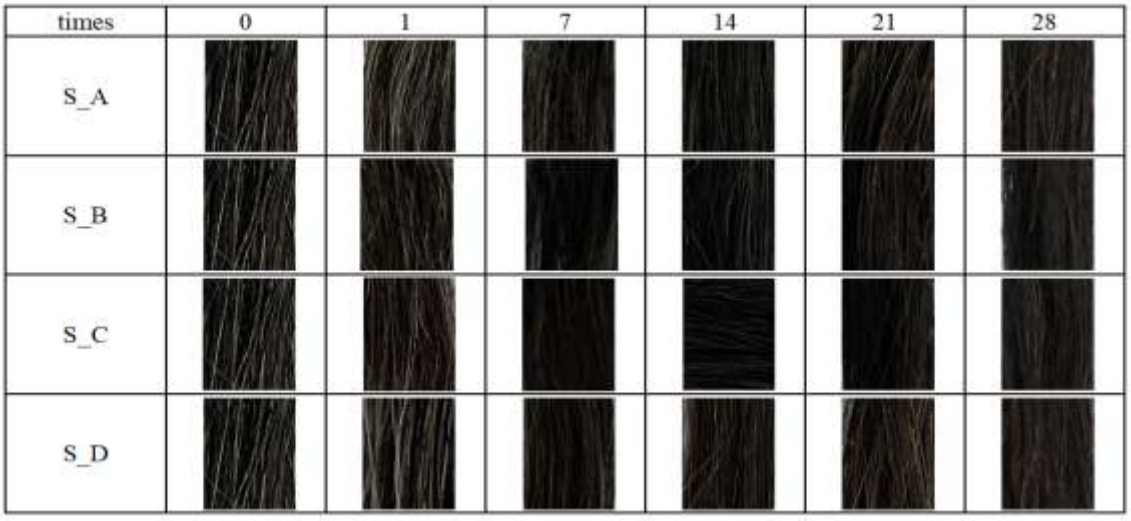

Fig 3. Images of changes in hair color corresponding to the number of washes.

As depicted in Figure.4., the darkening effect of each shampoo was evaluated based on the changes in L* values measured using a colorimeter. Shampoos S_B and S_C, which contained coal tar dyes, showed a greater decrease in L* values than shampoos S_A and S_D, which contained 1,2,4-THB, indicating a higher darkening effect of S_A and S_D.

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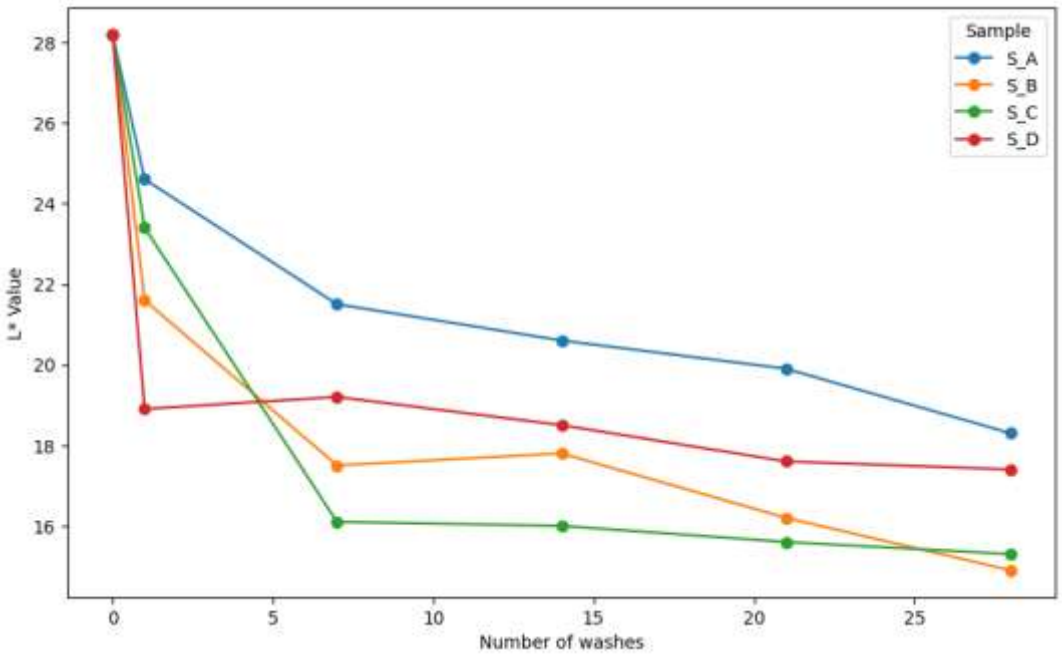

Fig.4. Changes in L* value corresponding to thenumber of washes.

For the evaluation of dyeability, the color changes in hair washed 28 times with darkening shampoos were quantified using the color difference (ΔE) values calculated from the differences in L*, a*, b* values. The ΔE values for hair washed with S_A, S_B, S_C, and S_D were 9.85, 13.4, 13.0, and 11.0, respectively, indicating a distinct dyeing effect of these shampoos on gray hair. These results confirmed that the darkening shampoos possess high dyeing properties for gray hair.

In addition, the ΔE values of hair samples before and after washing with the four types of darkening shampoos were compared (Figure. 5). The darkening shampoos containing coal tar dyes S_B and S_C, categorized as having similar darkening mechanisms, exhibited relatively higher dyeing properties than those containing 1,2,4-THB, namely S_A and S_ D.

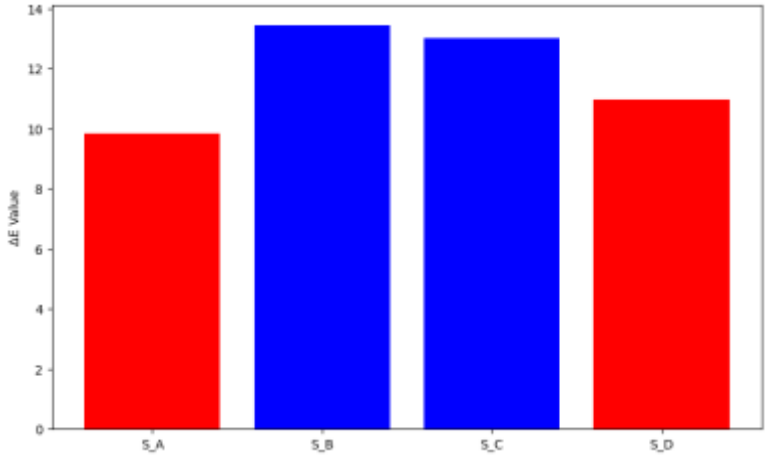

Fig.5. ΔE values indicating differencein color between different shampoos .

3-4. Analysis of hair cuticle washed with darkening shampoos

Morphological changes in hair samples washed with darkening shampoos, as analyzed by SEM, are illustrated in Figure.6. Varying degrees of damage were observed in most of the hair samples. For hair washed with S_A, irregular patterns and a small number of particles distributed

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on the surface were observed, with localized protrusions, indicative of the chemical components of the shampoos affecting the hair surface. Additionally, the hair surface exhibited several small uneven bumps, suggesting physical and chemical damage during the washing process. The surface of hair washed with S_B was generally smoother, with a few microparticles and irregularities observed. Minor cracks or cuticle damage that may have occurred during the washing process were visible on the surface; however, such damage was relatively limited. A reduced amount of clarity of the image compared to that of the other samples may have been due to the coating effect of the coal tar dye on the hair surface. Tar dye forms a thin layer on the hair surface to impart color, which can obscure or complicate the analysis of fine details on hair surface in SEM images. The properties of the coated dye that reflect or absorb light may result in less distinct surface textures, when observed using SEM. This makes it more challenging to accurately discern natural-scale patterns or other morphological features of hair in SEM images. The surface of hair washed with S_C showed clear scale patterns;however, partial lifting and cracking of cuticles were observed, indicating chemical damage. The surface of hair washed with S_D generally maintained its smoothness, showing a uniform texture without significant damage or cracks. Although minor particles and small cracks were detected, they appeared to be within the expected range of changes caused due to the washing process.

Overall, hair washed with S_A exhibited the highest degree of damage, whereas hair washed with S_D showed the least damage. Hair washed with S_B, although challenging to assess owing to the tar dye coating, appeared to have the smoothest surface, indicating less damage. Hair washed with S_C showed a moderate level of damage with a cuticle-lifting pattern. These results partially differ from those of studies comparing the effects of oxidative- and coating-based shampoos, suggesting that the impact on hair varies depending on the composition of shampoos and dyeing principles.

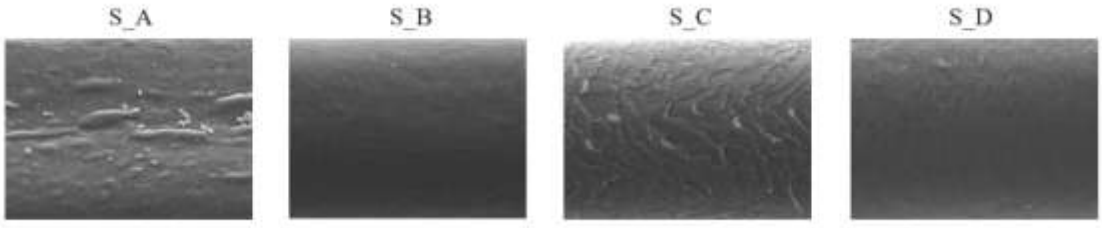

Fig. 6. Images of the hair cuticle after washing with darkening shampoos.

3-5. Results of analysis of morphological changes in hair washed with darkening shampoo

EDS analysis of hair after washing with darkening shampoos is shown in Figure.7. The shampoos containing 1,2,4-THB, S_A, and S_D showed different chemical changes in hair after washing. Although S_A showed a decrease in the content of carbon (C), sulfur (S), and nitrogen (N), and an increase in oxygen (O), S_D exhibited a decrease in all these major elements. This suggests that despite containing the same ingredient 1,2,4-THB, different types of interactions with hair can occur owing to a combination withother components and their concentrations.

The coal tar dye-containing shampoos, S_B and S_C, showed a decrease in carbon and sulfur content, and an increase in nitrogen and oxygen in the hair. This can be interpreted as the chemical properties of the coal tar dye reacting with other chemical components in hair, thereby causing such changes.

Overall, the different types of darkening shampoos induced unique chemical reactions during their interaction with hair, which is clearly reflected in the changes in the proportions of constituent elements of hair. This provides important information for understanding the chemical characteristics as well as cleansing and dyeing effects of these products.

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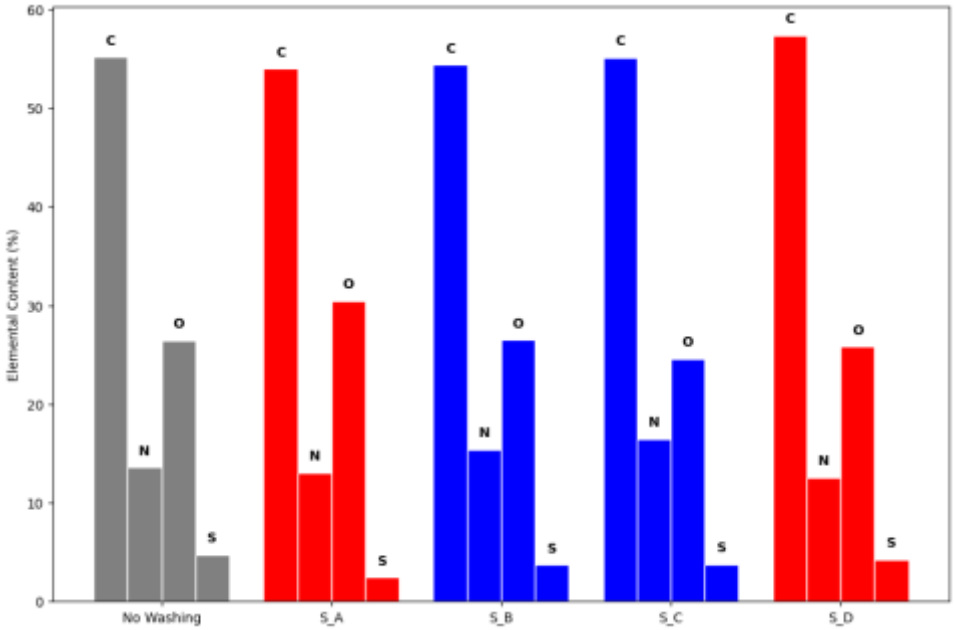

Fig.7. Comparison of changes in composition ofelements present in hair before and after washing with darkening shampoos.

III. CONCLUSION

This study provides valuable information to consumers and foundational data for industrial research and product development by analyzing the effects of various darkening shampoos and their impact on hair. The experiments demonstrated that darkening shampoos substantially darkened hair color, with certain shampoos imparting relatively higher dyeing properties to the hair. Additionally, the extent of hair damage caused by darkening shampoos was evaluated, and some shampoos were found to cause significant damage, particularly to hair cuticles. These findings offer crucial criteria for consumers to select darkening shampoos suitable for their hair type and condition.

As the hair darkening shampoo market is expected to see a diverse range of colors and brands , there is a need to provide detailed product information and clear criteria for product selection to enable consumers to choose safe and effective products. This study is expected to enhance the comprehensive understanding of darkening shampoos to enable consumers to adopt a more cautious approach towards product selection, thereby increasing consumer satisfaction and contributing to improvement in quality by manufacturers.

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