## Mechanism of frizz phenomenon occurring in bleached hair

Owing to the spread of social networking service (SNS), bleached hair has become popular, especially among young people. Bleaching can lighten hair compared to coloring alone. However, bleaching causes serious problems that differ from those occurring during the coloring process.

The cortex cells, which are hierarchical structures that make up hair, are composed of intermediate filaments (IFs) with  $\alpha\text{-crystals}$  embedded in amorphous intermediate filament-associated proteins (IFAPs) [1]. In hair and wool, IFAPs suppress the hydration swelling of IFs and play a crucial role in maintaining their elastic modulus and strength in water [2]. Therefore, it is hypothesized that the oxidative decomposition of IFAP caused by bleaching reduces hair strength. However, hair oxidized with bleaching agents becomes frizzy and spreads out when washed and dried, and measures to prevent frizzing have become important (Fig. 1). To elucidate the mechanism underlying the frizz phenomenon caused by bleaching, we reproduced frizzy-bleached hair and analyzed its internal structure.

Bleached hair becomes frizzy through the process of forcible tangling during washing, and subsequently untangled during drying with a hair dryer. It was found that this frizziness could be eliminated by soaking the hair in water and air-drying it. Next, small-angle X-ray scattering measurements were performed at SPring-8 **BL24XU** on untreated hair (UT), thrice-bleached hair (BL3), "frizzy portion of BL3" produced by forcibly tangling and untangling BL3, and "unraveled frizzy

## Untreated hair bundle Thrice-bleached hair bundle

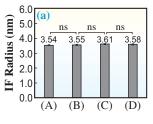


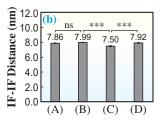


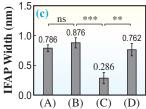
Fig. 1. Effect of shampooing and drying on hair bundle shape. Hair bundle shape: (1) dry state before washing, (2) wet state after washing, and (3) dry state after drying with a hair dryer.

portion of BL3," which was the frizzy portion of BL3 soaked in water and air-dried [3,4].

The results of the small-angle X-ray scattering measurements (Fig. 2) suggested that the bleaching treatment tended to increase the thickness of the IFAP and decrease the IF orientation. It is believed that the physical load that occurs during the untangling process compresses the IFAP, resulting in thinner and improved IF orientation. When the frizzy hair is immersed in water, the accumulated strain in the IFAP of the frizz part is relieved, and the IFAP is restored to its original thickness. In addition, the orientation of the IF returns to its original state before the physical load is applied. (See details in [4].)







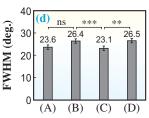


Fig. 2. Structural parameters on the aggregate structure of IF and IFAP characterized by small-angle X-ray scattering profile for (A) UT, (B) BL3, (C) frizzy portion of BL3, and (D) unraveled frizzy portion of BL3. Parameter: (a) IF radius, (b) IF-IF distance, (c) IFAP width and (d) Full width at half maximum (FWHM). Data are represented as means  $\pm$  SE, n = 10, ns: not significant, \*\*: p < 0.01, \*\*\*: p < 0.001 (Tukey–Kramer multiple comparison test)

Based on the above results, Fig. 3 summarizes the mechanism of the frizz phenomenon occurring in bleached hair during the hair-washing process. Untreated hair had a straight shape, as shown in Fig. 3(A). As shown in Fig. 3(a), the IF/IFAP molecular chains were cross-linked by disulfide bonds, and IF was oriented along the fiber axis. Similarly, the bleached hair exhibited a straight shape, as shown in Fig. 3(B). However, as shown in Fig. 3(b), some

disulfide bonds between the IF/IFAP molecular chains were oxidatively cleaved. This tends to reduce the orientation of the IF. In the wet state, water penetrates the space between the IF and IFAP, where disulfide bonds are broken, resulting in swelling of the IF and reduction in its elasticity and strength in water. The surface of bleached hair is highly hydrophilic; therefore, water easily spreads between the hairs. Therefore, during shampoo and water washing, the bleached hairs adhered to each other in a curved state and became tangled. The appearance of hair in this state is shown in Fig. 3(C). Furthermore, when the tangled bleached hair, as shown in Fig. 3(D), dried while being untangled, the tangled intersections moved and stretched, causing the frizz phenomenon, as shown in Fig. 3(E). In this case, when the crosssection of the hair shrinks as it is stretched, the IFAP is compressed, and its thickness decreases without inducing denaturation of the secondary structure of IF or cleavage of disulfide bonds, as shown in Fig. 3(c). When the frizzy-bleached hair was immersed in water, the frizz portion was eliminated. In the airdrying process, the hydrogen bonds broken by water recombined, straightening the hair shape, as shown in Fig. 3(F). When the frizzy-bleached hair was immersed in water, the water penetrated between the IF/IFAP molecular chains and facilitated their movement. The accumulated strain in the IFAP was relieved, its thickness, which had been compressed and thinned, returned to its original thickness, and the orientation of the IF returned to the state before the cross-stretching sliding treatment (Fig. 3(d)).

In this study, we investigated the mechanism of the frizz phenomenon in bleached hair, which is a serious concern for hair-bleaching customers. We found that the bleached hair became frizzy during the drying process and tangled after washing. Furthermore, small-angle X-ray scattering measurements revealed that the tangled intersections moved and stretched, resulting in a thinner, compressed IFAP. This revealed that the frizz phenomenon caused by the washing and drying of bleached hair led to the discovery of a method for dealing with frizzy-bleached hair. This result has been applied to products such as Mizulisse and Elujuda Bleach Care Serum, which are sold not only in Japan, but also in many other countries.

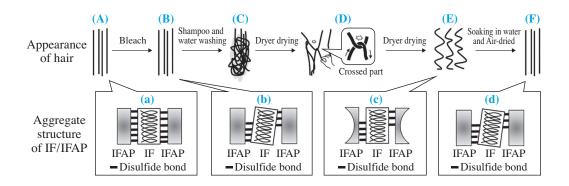


Fig. 3. Mechanism of the frizz phenomenon occurring in bleached hair. Hair appearance: (A) untreated hair, (B) bleached hair, (C) tangled bleached hair after washing, (D) bleached hair in the dry step, (E) frizzy-bleached hair, (F) bleached hair removed frizz by soaking in water.

Structure of IF/IFAP: (a) untreated hair; (b) bleached hair: decrease in disulfide bonds and reduction in IF orientation; (c) frizzy-bleached hair: improvement in IF orientation and compression of the IFAP; (d) bleached hair removed frizz: reduction of IF orientation, recovery from compression of IFAP.

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## References

[1] K. Arai: J. Soc. Cosmet. Chem. Jpn. 49 (2015) 2.

[2] D. S. Fudge and J. M. Gosline: Proc. R. Soc. Lond. B **271** (2004) 291.

[3] Y. Kajiura et al.: J. Struct. Biol. 155 (2006) 438.

[4] J. Kamikado, Y. Toyota, N. Fujiwara, K. Kobayashi, K. Suzuta and K. Joko: J. Soc. Cosmet. Chem. Jpn. 57 (2023) 251.