In hair beauty treatments such as permanent waving and hair coloring, and in daily treatments using shampoo and hair conditioner, most of the hair care products are used under wet conditions. Therefore, it is important to understand how water-soluble products penetrate into hair. The structural information of hair in aqueous solutions seems essential for understanding the penetration mechanism. However, conventional methods such as electron microscopy are not suitable for hair structural analysis in aqueous solutions. Because X-ray has a characteristic of high transmittance to materials, we have performed small angle X-ray diffraction (SAXD) experiments of hair cuticle in aqueous solutions. From the diffraction patterns, we have estimated the structure of the cell membrane complex (CMC) in the cuticle. The cuticle is the outermost layer of a hair fiber and is composed of a stack of several sheet-like cells. CMC is a substructure of the cuticle composed of three layers; a proteinous layer (δ-layer) is sandwiched between two lipid layers (β-layer), and considered to be an important penetration pathway. We have investigated the effects of penetration enhancers on the CMC structure in aqueous solutions. Penetration enhancers such as benzyl alcohol are used in hair coloring products to enhance coloring ability.

Using a 5 μm high flux beam (λ = 0.083 nm), SAXD experiments were carried out at beamline BL40XU (Fig. 1). Hair samples were obtained from Japanese women who had not undergone any chemical treatments. After cutting to a length of 8 cm, each hair fiber was fixed on a hair holder and dipped into aqueous solutions of alcohols. The SAXD patterns from hair cuticle in aqueous solutions were recorded using an imaging intensifier and a charge coupled device detector. The thickness of the β-layer and δ-layer was estimated from X-ray scattering patterns using an electron density model [1,2]. Some alcohols, such as benzyl alcohol, increase the dyeing extent of acidic hair dye. The effects of benzyl alcohol on the CMC structure were estimated by comparison between the structure of hair dipped in 4% benzyl alcohol solution and that in distilled water. The obvious increase in thickness by benzyl alcohol was detected both in the β-layer and δ-layer, indicating that the structural change of CMC induced the penetration-enhancing effect. We compared the effects of alcoholic compounds on the CMC structure. The CMC structure was measured in aqueous solutions of 2% or 4% ethanol, n-propanol, n-butanol, cyclohexanol, benzyl alcohol and cyclohexanediol. The thicknesses of the β-layer and δ-layer are shown in Fig 2. The thickness of the β-layer increased in alcohol solutions except cyclohexanediol. The comparison of structures in 2% and 4% solutions showed that a higher concentration of alcohols
produced a larger thickness of the β-layer in each alcohol. The swelling effect was detected in a dose-dependent manner and was marked in cyclohexanol and benzyl alcohol. These circular alcohols also induced significant swelling of the δ-layer at 4% concentration. Figure 3 shows the β-layer and the dyeing extent: a larger increase in β-layer thickness resulted in a greater increase in dyeing extent. Similarly, the thickness of the δ-layer shows a correlation with dyeing extent. These correlations agree with the penetration-enhancing mechanism, that is, a penetration enhancer affects directly the penetration pathway to promote mobilization of substances.

Microbeam SAXD provided other structural information regarding CMC. The β-layer is a lipid layer in CMC, and the structural conformation is different from that of ordinary plasma membrane. It is suggested that the β-layer is composed of covalently linked fatty acids and loosely bound lipids [3]. It is unclarified whether the lipids in individual β-layers of CMC are monolayers or bilayers [3,4]. Our analysis showed that the thickness of the β-layer is 3.4 nm in pure water (Fig. 2). The thickness of the β-layer seems too large for a monolayer model. We also detected obvious swelling of the β-layer induced by benzyl alcohol. This observation indicates that the thickness of the β-layer changes in response to the environment the hair fiber is placed. These lines of evidence agree with the bilayer model: that is, the β-layer consists of a bilayer of lipids with a partially interdigitated structure as shown by Robbins et al. [4].

Microbeam SAXD is useful for hair structural research. We found changes in the thickness of the β-layer indicating that the β-layer was composed of a partially interdigitated bilayer structure. The structural changes of both the β-layer and δ-layer induced by alcohols correlated with the changes in dyeing extent. This correlation indicates a new penetration enhancing mechanism, that is, alcohols induce structural changes of the penetration pathway.

Takafumi Inoue a,*, Noboru Ohta b and Naoto Yagi b

a Basic Research Laboratory, Kanebo Cosmetics
b SPring-8 / JASRI

* E-mail: inoue.takafumi@kanebocos.co.jp

References