Application of Wide Angle X-ray Diffraction to Hair Conditioners

Consumer products from diapers to laundry detergents to cosmetics to toothpastes are all indispensable for maintaining our health and comfort in daily life. These commodities are consistently expected by consumers to be better than previous products, and therefore relentlessly developed by manufactures towards superior performance. A high-tech trend of consumer products requires top-notch methodologies to analyze and evaluate product performance, structure, and composition. The needs for unique and powerful analytical and evaluation tools lead us to the application of synchrotron radiation-sourced techniques in order to utilize excellent features of SR's, e.g., super brilliance and directionality. These features are favorable for microscopic understanding and elucidation of product efficacies and performance, specifically, of beauty care products based on the interaction of ingredients with the skin and hair at the molecular level. This article reports two examples of the application of an SR-sourced X-ray analytical technique to the development of hair conditioners.

X-ray diffraction (XRD) analysis of single hair fibers was carried out to evaluate hair conditioning products, which were supposed to affect the internal structure and mechanical response of hair fibers. The human hair shaft is composed of keratin protein, which has the basic structure of three α-helices wrapped around one another to form a protofibril, then the assemblance of eleven protofibrils to form a microfibril. Bundles of these microfibrils pass through and around hair cells. XRD data were collected at Hutch A of beamline **BL24XU** (Hyogo ID), using a monochromatic (15 keV, 0.08266 nm) and collimated incident beam (80 × 80 μm^2). An IP Laue camera (camera length at 500 mm) was used with a sample holder, in which a single hair fiber is oriented perpendicular to the incident beam. SR-XRD of single hair fibers shows diffraction patterns of hard α-keratin, which have two major characteristic features in the wide angle X-ray diffraction (WAXD) region [1]: (1) a broad equatorial spot centered at 0.97 nm, corresponding to the mean distance, or spacing, between α-helical axes, and (2) a fine meridian arc at 0.517 nm, which is related to the projection of the α-helix pitch along the coiled-coil axis, above a broader arc around 0.5 nm of less ordered coiled coils.

First, changes in the XRD pattern of hair fibers after a chemical treatment indicate the microscopic effect of the treatment on the hair structure. We observed changes in the WAXD pattern of identical single fibers of Asian virgin hair over sequential bleaching and conditioning on site to eliminate variations among fibers. We found that the degree of crystallinity across the hair fiber axis could be an illustrative parameter to describe the mechanism underlying the repair of damaged hair using hair conditioning products. Three key findings follow: (1) The degree of crystallinity across the hair axis was increased by 28±6% at 95% confidence level by the

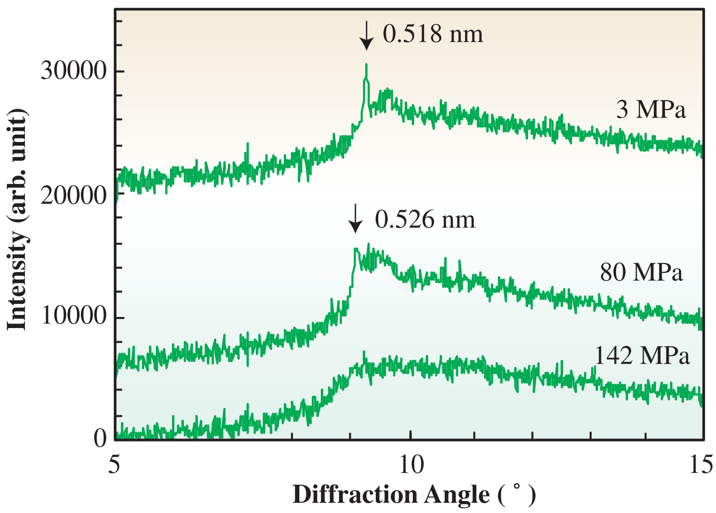

Fig. 1. Shift of diffraction peak of helical pitch after stress application. Sample: human hair treated with dilute hydrochloric acid at pH = 4.5.

bleaching condition we applied in the series of XRD studies. (2) Treatment with an aqueous solution of key ingredients of a candidate conditioning formulation (T-1, hereafter) demonstrated a consistent decrease in diffraction intensity after the treatment. The intensity change *versus* bleaching was calculated at 13±5% at 95% confidence level. (3) The ratio of diffraction intensity changes over treatment *versus* bleaching, i.e., $(I_B-I_T)/(I_B-I_V)$, where I_V, I_B, and I_T are intensities of the "spacing" diffraction of virgin, bleached, and treated hair fibers, respectively, was chosen as a measure of the "recovery" of crystallinity, and was defined as "recovery rate" in this study. Thus, we concluded that the T-1 solution recovered the crystallinity, which was increased by the bleaching, at 68±43% back to the virgin state at 95% confidence level.

Second, the XRD pattern of human hair under mechanical stress provides us with information on the microscopic deformation of the constituent keratin protein. The pitch elongation of α-keratin contributes 50% of the macroscopic strain [2]. Bundles of healthy hair fibers of an Asian female were damaged by a standard damaging treatment, shampooed, and then treated with a conditioning formulation (T-2, hereafter), while a control sample was prepared by treating with water after the shampooing. Mechanical stress was applied by hanging weights down on a sample. The stretching speed of α-keratin was measured at about 1%/h. The helical pitch of the α-keratin molecule for each stress was determined from the diffraction pattern (Fig. 1). Thus, a stress-strain, or crystal deformation, curve of the α-keratin pitch of the hair sample was obtained, as shown in Fig. 2, in which the stress-crystal deformation data points were collected from three hair fibers taken from an identical hair bundle. The longitudinal crystal modulus of elasticity, or spring constant, of α-keratin in the hair fibers was calculated as a slope in the Hookean region of the stress-crystal deformation curve. A duplicate measurement confirmed that the crystal modulus of elasticity of α-keratin in hair fibers treated with the T-2 formulation was 5.1 GPa *versus* 6.5 GPa of the control. The spring constants demonstrated that the T-2 formulation softened the damaged hair fibers.

We could develop and launch successfully the following two hair care products on the basis of the above-mentioned two research outcomes, respectively: a conditioner with hair breakage defense efficacy launched in September 2004 (the former), and a conditioner for unruly or naturally wavy hair launched in April 2007 (the latter).

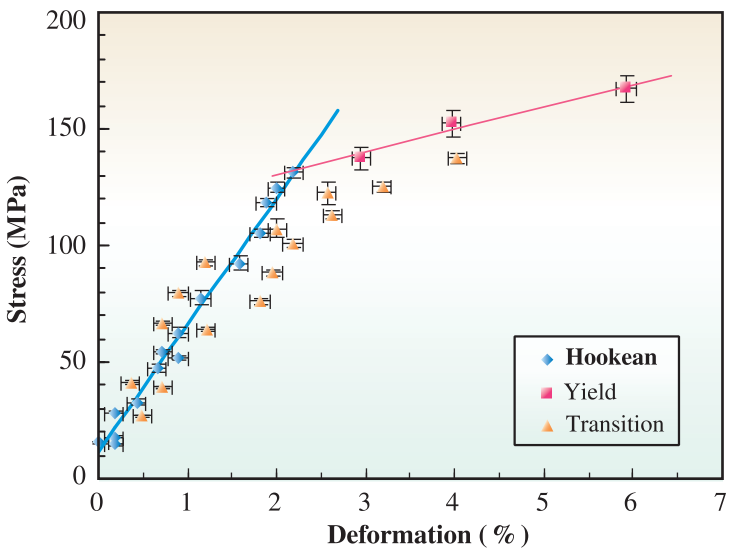

Fig. 2. Stress-crystal deformation curve of α-keratin in hair fibers. Sample: human hair damaged, shampooed, then conditioned with T-2 formulation.

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