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論 文 内 容 の 要 旨

Influence of the disulfide (SS) cross-linked structure of keratin fiber on its mechanical property was investigated in this dissertation. Relevance of microstructure of keratin fibers to its mechanical behavior has been unclear. Since mechanical degradation of the keratin fiber is the problem related to hair damage by hair-coloring, permanent waving and hair straightening and so on, this study is also very interesting in the view of cosmetic technology. We attempted to clarify the number, type, and location of SS cross-links and identify the cross-links related to its mechanical properties. The contents in this dissertation are summarized below:

In chapter 1, the background and the aim of this study are introduced. In keratin, there are a lot of cystine residues that exist as inter- or intramolecular SS cross-links, that is, keratin has huge polymeric network structure composed of a large number of SS cross-links. Keratin fibers from mammal such as wool and human hair constitute a complicated hierarchical structure composed of many cells, and shows characteristic mechanical properties. Since SS cross-linked structure of the keratin fiber seems to be related to its various mechanical behavior, understanding the SS cross-link structure in more detail and clarifying the relationship to its mechanical properties are very important in the view of not only protein chemistry but cosmetic industry.

In chapter 2, the SS cross-linked structure of hair and wool keratin fibers is discussed. Rubber elasticity theory was applied to the force–extension curves of swollen fibers in a diluent mixture of concentrated aqueous lithium bromide and diethylene glycol mono-n-butyl ether. On the basis of a two-phase structural model for the globular matrix keratin-associated protein (KAP) dispersed in the swollen network of intermediate filament (IF) proteins, structural parameters were obtained by fitting the force–extension curve to theoretically derived relations between elastic forces originating from nonuniform network and the extension ratios. The parameters extracted are the number of intermolecular SS bonds in the IF, the volume fraction of matrix proteins in the fiber, and the shape of the matrix domain. The number, type, and location of SS cross-linkages in the IF proteins were estimated using the difference in the conversion rate from disulfide to lanthionine and lysinoalanine induced by the treatment with boiling water, because it depends on the location of the SS cross-links in IF and KAP structure. The total number of SS cross-linking sites in the IF chain of an average molecular mass of 50000 is determined to be twenty-one moles. The twenty-one moles are divided into thirteen moles comprising intermolecular cross-linkages, which are subdivided to three moles between rod domains, eight moles between terminal domains and two moles between terminal and KAP domain, and eight moles comprising intramolecular cross-linkages, which are subdivided into four moles in the terminals and four moles at the interface region between rod and terminal domains. It was also found that a KAP molecule with an assumed molecular mass of 20000 involves seventeen moles of intramolecular SS bonds and 4–5 sites on the surface of the KAP molecule of hair keratin. These sites are linked to adjacent KAP molecules and form an aggregate of about six KAP molecules against the IF molecule. Finally, we proposed a network model for an IF–KAP structural unit in the hair and wool fiber cortex.

In chapter 3, the SS cross-linked structural change by permanent wave treatment for hair and the structure and mechanical property relationships are investigated using the network structural model proposed in chapter 2. Scission and reformation mechanisms of SS cross-links by the treatments with a reducing agent of thioglycolic acid (TGA) and an oxidizing agent of sodium bromate were demonstrated. It was found that cleavage of the SS cross-links between KAP molecules by preferential attack with TGA leads to the shape change from ellipsoidal form of globular aggregates to near spherical one, and these cross-links and shape are not recovered perfectly by subsequent oxidation. On the other hand, it was also found that nearly complete reformation of SS cross-links occurs between IF proteins through oxidation even when a large number of SS bonds break under strong reducing conditions. An important suggestion was obtained that the extension modulus of the hair fiber in water is highly dependent on the number of intermolecular SS cross-links between KAP molecules around the IF.

In chapter 4, recovery behavior of mechanical property during washing after reduction with TGA is studied. It is well-known that the reduction of SS bonds with thiol is equilibrium reaction. In a permanent waving system consisting of three step processes of reduction with TGA, washing with water and oxidation by sodium bromate, it was found that the extension modulus and breaking stress of the treated hair fibers in water were increased with increase of washing time. Analysis of the SS cross-linked structure by applying a rubber elasticity theory showed that the integrity of SS cross-linked structure of IF is retained, while the intermolecular SS cross-links between KAP molecules cleaved by reduction are regenerated by reverse reaction of the equilibrium reactions occurring during washing. Hence, it is concluded that the mechanical properties for hair fibers are controlled by the intermolecular SS cross-links between the KAP molecules.

In chapter 5, the conclusions of this dissertation are summarized. The mechanical importance of the intermolecular cross-links between the KAP molecules is clarified, but theoretical interpretation for mechanical behavior of keratin fibers seems not to be quite simple. It is important that the contribution and mechanism of the SH/SS interchange reaction will be understood in the future.