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Permanent Waves

By Roberta Baxter

Since ancient times, people have experimented with many ways to change their hair. The Assyrians favored curly hair, the Egyptians wore wigs, and the Romans used curling irons. Today, it seems that people with straight hair want curls and the curly-haired people covet straight hair. Now, we can change the shape of our hair with permanent waving or hair-straightening products. How do these products work and what do they do to the hair?

Hair structure

The part of hair that protrudes above the skin line—the part we see—is called the hair shaft. It looks simple to the naked eye but, when magnified, it shows a complex structure. The outer layer, the cuticle, consists of dead epithelial cells that overlap each other like the shingles of a roof, as shown in Figure 1. Inside the cuticle is the cortex, which contains the protein that gives hair its strength and determines its shape, and the pigment that determines its color. Proteins are large molecules that are assembled from small amino acids (see Figure 2). Your hair contains a class of protein known as keratin. As the shaft emerges from the follicle, the keratin hardens as chemical bonds form that cross-link one protein backbone to another. Three types of chemical bonds are at work: ionic, covalent, and hydrogen.

The zipper

Under the conditions usually found in the hair, the amine group and acid group on the ends of a protein molecule are ionized. The -COOH group has lost a hydrogen ion, H^+, to become $-COO^-$, and the $-NH_2$ has gained a hydrogen ion to become NH_3^+ (see Figure 3). The attraction between the positive and negative charges pulls these ions together and forms an ionic bond. (Typically, ionic bonds are found in salts, such as sodium chloride, and involve many more ions. When single + and - ions join organic molecules the bond is sometimes called a salt bridge.)

Hydrogen bonds consist of attractions between weaker + and - charges, in which the weak positive charge is always found on a hydrogen atom. The weak negative charge may be on any of a variety of atoms, including nitrogen and oxygen. Hydrogen bonds are weak, but there are millions of them in your hair. Hydrogen bonds form attractions within protein molecules as well as between different molecules.

In contrast to the ubiquitous hydrogen bonds, cross-linking covalent bonds form only at special locations—where the sulfur-containing amino acid named cysteine is present in both molecules. Cysteine contains an -SH group that projects out from the protein backbone. Under proper conditions, two neighboring -SH groups can lose their hydrogen atoms and form a covalent bond between the sulfurs, thereby forming a crosslink between two proteins. This type of cross-link is called a disulfide bond and is very important for hair waving.

Unzipping the bonds

Hair waving changes the shape of the cortex by breaking and reforming the bonds that cross-link proteins. (The bonds within protein molecules are little affected by waving.) The hydrogen bonds are broken with water. Your hair may be 30% H_2O by weight, but when you stand under the shower it absorbs more water, which begins to break hydrogen bonds.

Because water contains both weakly charged hydrogen and weakly charged oxygen, water molecules are attracted to the charged locations in the protein that have formed hydrogen bonds. When water penetrates the hair shaft, the negatively charged nitrogen that originally was attracted to a hydrogen in a solid protein molecule may find itself attracted to the hydrogen in a water molecule. The nitrogen loses its grip because it is attached to a liquid instead of a solid. This is why hair is dampened before it is set. Wet hair swells as the hydrogen bonds are broken, and this makes it easier for other chemicals to penetrate the shaft.

The ionic bonds are easily broken by acids or bases, though most waving solutions are basic. In a basic solution, the hydroxide ion, OH-, is attracted to and reacts with the $-NH_3^+$ group. During the reaction, the positive group loses its charge:

$$NH_3^+ + OH^- \Rightarrow NH_2 + H_2O$$

Without a positive charge to attract the negative charge, the ionic bond collapses.

The remaining bonds, which give chemists problems, are the covalent disulfide bonds. Long-lasting permanent waves didn't exist until chemists synthesized a suitable reagent for breaking disulfide bonds. That reagent is ammonium thioglycolate, the active component in most waving solutions (see Figure 4).

The alkalinity of the permanentwave solution breaks the ionic bonds but has little effect on the disulfide bonds, which require a redox reaction. The reducing agent, ammonium thioglycolate, adds hydrogen (a reducing reaction) to the sulfur atoms, breaking the disulfide bonds. This breaks the main cross-links of the hair protein. Once the disulfide bonds have been broken, the molecules of the keratin can be pulled past each other (see Figure 5). This allows the hair to be reshaped.

The pH of the waving solutions is 8.0 to 9.5. The alkalinity causes the cuticle of the hair to open and allows the solution to penetrate more rapidly than acid perms. Unfortunately, the solution of ammonium thioglycolate and ammonium hydroxide combines the acrid scent of ammonia and the "rotten egg" smell of sulfur compounds.

It's enough to curl your hair

After the chemical action of the waving solutions, physical action changes the hair shape. The hair is smoothly wrapped around curlers. Because the cross-links between protein chains have been broken, the hair assumes the shape of the curler. Now it is time to reverse the chemical reaction.

The rest of the process is the other half of a redox reaction. First, all the ammonium thioglycolate solution is washed out of the hair with warm water. A so-called neutralizing agent, usually hydrogen peroxide, is applied. The oxygen atoms go to the S-H bonds and pull the hydrogen atoms away to form water (an oxidation reaction).

$$2e^- + H_2O_2 + 2H^+ + 2H_2O$$

The sulfur atoms re-form bonds with other sulfur atoms, and the structure of the protein is restored (see Figure 5).

Zipping up

The neutralizing agent is then washed out of the hair. As the hair dries, the hydrogen bonds and ionic bonds re-form. The hair is strong again, but with a different shape imposed on it because of bonds in different places. The protein chains are extremely small in comparison to the size of a single hair. Therefore, a slight change in the disulfide bonds of the protein results in a big difference in the curve of the hair.

This chemical reaction of thioglycolate on the disulfide bonds of hair, followed by the neutralizing action of hydrogen peroxide, is carried out thousands of times a day across the country. It is an important set of reactions; it is enough to curl your hair.

CAPTIONS

Figure 1. Each strand of your hair contains thousands of protein fibrils, which are surrounded by a mass of globular proteins called the matrix. If the matrix proteins were free to slide past each other, your hair would be limp and shapeless. The fibrils cannot slide because chemical bonds link them to the matrix and to neighboring fibrils, which locks the hair into a particular shape. The minute fibrils are impenetrable by water. In waving, the most important chemical reactions affect the matrix and the matrix/fibril boundary.

Figure 2. Amino acids (top) contain an amine group, $-NH_2$, and an acid group, -COOH. When they join to make proteins, the amine group of one molecule reacts with the acid group of another and, even though the reacting groups are gone, the final molecule still has an amine end and an acid end. These can react with more amino acids to form a longer molecule. Proteins resemble chains of beads with the carbon and nitrogen atoms forming a backbone.

Figure 3. The protein molecules in your hair link to neighboring protein molecules via all the major types of bonds. In this illustration, ionic bonds are represented by the + and - at top; hydrogen bonds are represented by the row of dots, middle; and covalent bonds are represented by solid lines, at bottom.

Figure 4. A typical waving solution contains 7% ammonium thioglycolate, 3% ammonium hydroxide, and water. The thioglycolate is the reducing agent that breaks the disulfide bonds. The net reaction below shows that the -SH groups from two thioglycolate ions are exchanged for the -S-S- group of the protein. If ammonium is replaced with calcium, the resulting solution has a higher pH and dissolves hair completely. It is used in commercial hair removers.

Figure 5. This simplified illustration of the waving process shows portions of two globular proteins (A). When moist hair is wound around a roller (B), the hair becomes stressed because the outer protein stretches more than the protein next to the roller. When the waving solution (usually alkaline thioglycolate) is applied, the disulfide bonds are broken (C), and the protein molecules slide past each other, relieving the stress. After the waving solution is rinsed from the hair with water, the neutralizing solution is applied. This causes disulfide bonds to re-form, but in new locations (D). In a typical waving, 20% to 30% of the disulfide bonds are broken.

The non-permanent permanent wave. Would you like to liven up your naturally straight hair (top), but are afraid of a permanent commitment? What if you hate the way the perm looks and are stuck with it for three months? The new Try-On Perm by Toni addresses this problem. It lets you “road test” a new style (middle), but during the next couple of weeks the curls gradually fade away and leave your hair with just a little more body (bottom).

BIOGRAPHY

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REFERENCES

Handbook of Cosmetic Science: An Introduction to Principles and Applications; Hibbott, H.W., Ed.; Pergamon Press Books, the Macmillan Company: New York, 1963.

Cosmetics: Science and Technology, 2nd ed.; Balsam, M.S.; Sagarin, Edward, Eds.; Wiley-Interscience: New York; 1972; Chapter 21, pp. 167-250.

Kibbe, Constance V. *Standard Textbook of Cosmetology*; Milady Publishing: New York, 1982.