J. Cosmet. Sci., **72,** 99–133 (January/February 2021)

A Review of Permanent Waving and Perm Chemistry

TREFOR EVANS, *TRI-Princeton, Princeton, NJ*

Accepted for publication August 31, 2020.

Synopsis

Although traditional perm chemistry has been around for over 70 years, it still arguably remains our best means of permanently altering the shape of hair. The hullabaloo created by the so-called Brazilian keratin treatments has led to resurgence in research activities in this area—and so an overview of the incumbent technology would seem pertinent. This review highlights underlying chemistry responsible for the success of traditional thioglycolate solutions but makes the case that our knowledge gap lies with the kinetics of the process. To this end, the merits and limitations of the single-fiber tensile kinetic approach are addressed—where, despite seemingly questionable assumptions, logical outcomes are obtained from systematic experiments intended to probe the validity of this method. Furthermore, results demonstrate how considerably different rates can arise between a common perm solution and hair from different sources. It is therefore proposed that "resistant" hair is a consequence of slow reaction rates which lead to an insufficient number of cystine disulfide bonds being broken during the processing time. Additional analysis of these kinetic data suggests the presence of different mathematical models that describe the progression of the process with varying experimental conditions. The reproducibility of results and the frequency with which models arise add confidence to findings.

INTRODUCTION

To product developers, hair stylists, and consumers alike, the word *perm* conjures up images of noxious chemical treatments that impart a degree of wave or curl to otherwise straight hair. The chemistry behind this transformation is the primary focus of this review article, yet it is worth remembering that the word itself is a truncation of the term *permanent wave*, and whereas thiol chemistry is the most common means of achieving this end; in theory, it could apply to any process that promotes an enduring makeover.

By means of illustration, the origin of the expression is often traced back to the late 19th century and the use of extreme heat to change the shape of hair. Marcel Grateau is generally credited with the introduction of hot curling tongs in 1872 that produced what became known as a *Marcel wave*. The introduction of *chemical reagents* is usually attributed to the work of Charles Nessler who in 1905 used a combination of borax (sodium borate) and heat to produce curls in hair. However, this procedure took many hours to perform and necessitated the use of hot, heavy metal curling rods. Accordingly, complex chandelier-like devices were needed to deliver the heat, support the weight, and keep the burning

Address all correspondence to tevans@triprinceton.org.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

rollers from contacting the scalp. The later development of the so-called *machineless waving* primarily involved the elimination of electric heaters and the subsequent use of reagents that induced exothermic chemical reactions to provide thermal stimulus (1). It can therefore be seen why the next advancement in the area (and indeed the technology that still exists today) became known as a *cold wave*.

It perhaps should go without saying that permanently changing the shape of hair requires a significant rearrangement of its internal assembly. Hair predominantly comprises keratin protein, and long-lasting reshaping necessitates the use of chemical reagents that can deconstruct and subsequently reform this structure. Specifically, it is cross-linking cystine disulfide moieties within protein chains that are targeted during this process. The reason for the two-step nature of the current technology becomes evident. First, these structure-supporting bonds are attacked while the hair is anchored in a desired conformation. A subsequent second step then reforms these bonds to lock in the new shape. This review shows that the perm process involves rather straightforward textbook chemistry, but a sizable complicating factor involves the ability for reactants to come together. Equations in textbooks generally involve homogeneous gaseous- or liquid-state reactions where molecules readily collide and react. However, here, an extra level of complexity occurs as the aqueous perm active must first diffuse into the hair and encounter appropriate chemical bonds in pertinent structural regions. This critical first step is often glossed over when discussing the chemistry of the perm process. Perhaps, this arises because of the ease by which liquid water penetrates into hair, and it may therefore be presumed that dissolved species do likewise. Yet, as will be outlined, this seems to be an oversimplification.

To illustrate this point, it is well-recognized within the industry that chemical treatments can produce a markedly different performance when used on hair from the heads of different individuals. In many instances, a given perm treatment will effectively produce the desired transformation, but in others, a considerably less successful outcome is attained. To an extent, this represents the "art" of the perming process as stylists attempt to judge and adjust application conditions to provide their client with the desired outcome. This occurrence is frustrating for all involved, but it also highlights a more fundamental issue, namely, there is nothing in our current understanding of the hair structure to explain this behavior. One hypothesis may involve some difference in the chemical composition of hair dictating variance in reactivity. This suggestion is not totally ruled out, but the current mindset within the industry is generally that the chemical makeup of hair of all shapes, sizes, and ethnicity is relatively constant (2). A resistance to chemical bleaching can also be encountered in certain individuals, and so emphasis seems to shift from any specific reaction chemistry to hair itself. This introduces a second postulate, wherein it is theorized that variability occurs because of a differing ability for materials to diffuse into and through the hair. This topic will be given particular attention over the cause of this study. Specifically, it will be demonstrated that distinctly different kinetic behaviors are encountered when applying a given perm formulation to hair procured from a selection of individuals.

The most widely used active ingredient in today's perms continues to be salts of thioglycolic acid, whose usage dates back in origin to the early 1940s. Alternative actives also tend to fall within the general *thiol* classification, as characterized by the presence of a sulfhydryl functional group. Figure 1 shows the chemical structure of a selection of thiols that have been used commercially in the perm industry. The scientific literature describes investigations involving a considerably wider range of such molecules, yet very few have

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 1. Structure of some common perm ingredients.

demonstrated commercially viability. This presumably has some relationship to the high cost associated with addressing toxicological issues. The main exception to the thiol category of actives involves the use of sodium sulfite and bisulfite, which can be found in weaker, so-called *body waves* or *demi-perms*.

Although considerable effort has been dedicated to studying the cleavage of cystine disulfide bonds, relatively little has been published on their restoration. It is possible that this second step in the transformation is seen as somewhat trivial because bonds can be reformed by air oxidation. Nonetheless, there is an obvious desire to properly perform this important function, and consequently, treatment with a "neutralizing agent" is prudent. With this said, it is generally not possible to completely rebuild all disulfide bonds, and consequently, the hair is somewhat depleted in cystine content and therefore left in a compromised state.

The variety of shapes and styles that can be created by this process is predominantly related to the accessories used to support the hair during this chemical process. It will be shown that a variety of formulation parameters are available for controlling the strength of these treatments, but tight curls are generally produced by wrapping the hair around rollers with a small diameter, whereas softer, looser curls are formed using larger curling rods.

At the time of writing, the permanent wave market has been soft for many years because straight hair styles remain popular, yet this exact same chemistry is commonly used to flatten curly hair. A survey of the beauty aisle will show several relaxer-type products that use conventional "perm chemistry." These treatments can be effective on most hair types, although they are generally not strong enough to adequately straighten highly curly African hair. Before the advent of "*Brazilian straightening*," the market was already familiar with "*Japanese straightening*," which comprises traditional perm chemistry in combination with heat (presumably to drive kinetics). The hullabaloo created by Brazilian straightening products has led to renewed interest in the development of new and improved approaches to straighten hair. This has resulted in some novel product forms reaching the shelves, for example, *smoothing creams* incorporate conventional perm chemistry into a white opaque, conditioner-like base. In short, there is still considerable interest in this chemistry, even if it does not specifically relate to traditional perm products. To this end, it is further recognized that depilatory products often use this exact same chemistry, but in this instance, the intent is to produce more aggressive conditions that completely disintegrate the hair structure.

As with many fundamental aspects of hair structure and chemistry, it is evident that considerable learning comes from the related wool industry. Hair and wool possess very similar structures and chemistry, and much can be learned from the literature pertaining to this commercially important relation. Therefore, in certain instances, references from this related field will be used to illustrate points.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

AN OVERVIEW OF THE STRUCTURE OF HAIR RELATING TO THE PERM PROCESS

A comprehensive review of the complex structure of hair is outside the scope of this article, and accordingly, the reader is referred to excellent texts in this area (3,4). Nonetheless, it is impossible to discuss the chemistry of the perming process without a brief overview.

The tensile strength of a hair fiber is widely believed to be dictated by the inner cortex structure, with no appreciable contribution from the outer protective cuticle. More specifically, it is the crystalline, alpha helical keratin protein contained within the intermediate filaments (sometimes called *microfibrils*) that support the permanent mechanical integrity. Therefore, this region of the hair structure becomes the target for reagents in terms of both diffusion and reaction. More specifically, it is the disulfide cross-links associated with the amino acid cystine within the keratin protein that needs to be broken down and subsequently reformed. To his point, the first part of the process involves incursion through the hair's outer protective layer, the cuticle. This cumulative structure consists of overlapping tile-like scales which have further substructures as shown in Figure 2.

This laminate structure consists of (from bottom to top) an endocuticle, exocuticle, A-layer, and epicuticle, with the degree of cross-linking increasing in this same order. Furthermore, the very outer layer of healthy hair consists of a lipid assembly (the f-layer) that provides an additional hydrophobic outer barrier. In short, water is unlikely to penetrate through the cuticle face in a top-to-bottom manner, except for when occasional advantageous cracks are present. The nature of this penetration pathway represents a topic of debate. Brady (5) advocated a "cell membrane complex diffusion" model where infiltration occurs through the cell membrane complex "gaps" between the cuticle cells. This same idea has also been promoted by Leeder (6). However, Wortmann et al. (7) question this being the primary pathway because of the low level of this "extracellular" material in the hair. Accordingly, an alternative theory was promoted which involved diffusion through all nonkeratinous components of the fiber—most predominantly, the endocuticle. This same idea has also been advocated by Swift (8), although Gummer (9) suggests that all structures within hair should be considered as penetration routes for the delivery of materials.

With all this said, liquid water rapidly penetrates into the hair's inner structure, and it may therefore be presumed that dissolved species would similarly diffuse readily. However, it is becoming evident that water-soluble materials do take some time to permeate the structure. An analogy is drawn to the principles associated with liquid chromatography, whereby the mobile phase readily traverses the stationary phase and dissolved species progress at different rates depending on their size and interaction with the column. The reason for belaboring this point relates to the well-known occurrence that hair from

Figure 2. Schematic of cuticle substructure.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

different individuals can respond very differently to a given perm treatment. One hypothesis to explain this occurrence involves diffusion rates representing a rate-limiting step.

REDOX CHEMISTRY OF THE PERM PROCESS

The most common chemical species used for attacking cystine disulfide bonds in the perm process are organic thiols, which are characterized by the presence of a sulfhydryl functional group. The cleaving of keratin disulfide bonds by a thiol is typically represented by the reaction scheme given as follows:

$$\text{K-S-S-K} + \text{RSH} \leftrightarrow \text{K-S-S-R} + \text{HS-K}, \tag{1}$$

that is, the thiol (RSH) attacks cystine disulfide bonds within the keratin (K-S-S-K) and itself becomes attached to form a mixed disulfide (K-S-S-R) and cysteine (sometimes called ½ cystine, HS-K). In addition, it is also possible for continued reaction of the thiol with the mixed disulfide (Reaction 2) with the production of another mole of cysteine and the dimer of the original thiol (R-S-S-R).

$$\text{K-S-S-R} + \text{RSH} \leftrightarrow 2\text{K-SH} + \text{RSSR} \tag{2}$$

In actuality, it is widely acknowledged that the active species in the perm reaction is the thiolate ion, as opposed to the thiol itself. Therefore, the first step in the previous reaction scheme involves deprotonation of the thiol, as illustrated in step 3. As will be shown momentarily, the presence of a proton in this equilibrium represents the origin of the pH dependence in the perm reaction.

$$\text{RSH} \leftrightarrow \text{RS}^- + \text{H}^+ \tag{3}$$

The equilibrium constant for any reaction is given as the concentration of products divided by the concentration of reactants, that is:

$$\text{K} = \frac{[\text{RS}^-][\text{H}^+]}{[\text{RSH}]} \tag{4}$$

Taking negative $\log_{10}$ of each side of the equation leads to the following equation:

$$-\log_{10}\text{K} = -\log_{10}[\text{H}^+] - \log_{10}\frac{[\text{RS}^-]}{[\text{RSH}]} \tag{5}$$

It is recognized that $-\log_{10}[\text{H}^+]$ is the pH, whereas $-\log_{10}\text{K}$ is the pK_a. Therefore, equation (5) can be rearranged to give the following equation:

$$\text{pH} = \text{pK}_a + \log_{10}\frac{[\text{RS}^-]}{[\text{RSH}]} \tag{6}$$

In short, equation (6) shows how knowledge of pKa for a given thiol allows for calculating the relative proportions of the active thiolate ion, $[\text{RS}^-]$ versus the inactive fully protonated species [RSH] as a function of pH. By means of illustration, Figure 3 shows

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 3. Calculations for the relative abundance of thiolate ion as a function of pH for two common perm actives.

the result of performing this exercise for two commonly used perm actives, cysteamine and ammonium thioglycolate (ATG). That is, the concentration of the active thiolate ion [RS−] is seen to increase dramatically when the pH is raised through the pK_a. It is common practice to formulate chemical treatments, such as bleaches or permanent color products, at elevated pH because these conditions cause increased swelling and facilitate penetration into the hair. The same is likely true for permanent wave actives, but at the same time, Figure 3 shows that there is also a more fundamental chemical reason for using an elevated pH in these formulations. It is recalled that depilatory products also use this same underlying chemistry, but these products are formulated at considerably higher pH. These conditions produce still higher concentrations of the active thiolate ion, which compromise the hair structure to the point of disintegration. Figure 3 also illustrates why cysteamine-based perms can be formulated at lower pH than traditional thioglycolate formulas, namely, a lower pKa means that the pH does not need to be raised to such high levels to produce a suitable quantity of the thiolate ion.

Returning to the chemical equations for cleaving the cystine disulfide bond, it now becomes evident that there is the need to also balance electronic charge in addition to the atoms. It is necessary to add electrons to the left-hand side of the equation for disulfide bond cleavage equation (7) and to the right-hand side for the conversion of the thiol to its dimer equation (8).

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

$$\text{K-S-S-K} + 2e^- \leftrightarrow 2\text{KS}^- \tag{7}$$

$$2\text{RS}^- \leftrightarrow \text{R-S-S-R} + 2e^- \tag{8}$$

$$\text{K-S-S-K} + 2\text{RS}^- \leftrightarrow 2\text{KS}^- + \text{R-S-S-R} \tag{9}$$

In accordance with standard textbook chemistry, the acquisition of electrons represents a *reduction* reaction, whereas loss of electrons is *oxidation*. Cleavage of disulfide bonds within the hair therefore represents a *redox reaction*: the cystine bonds are reduced and the thiol is the reducing agent which itself becomes oxidized in the process. The two half equations are combined (with cancelation of the electrons) to produce the total ionic equation shown in equation (9).

The thermodynamic driving force for a redox reaction is given by the following equation:

$$\Delta G = -nFE, \tag{10}$$

where ΔG is the Gibbs free Energy, n is the number electrons involved, F is the Faraday constant, and E is the difference between the reduction and oxidation potentials of the species involved. Therefore, the driving force for the perm reaction is directly proportional to the oxidation potential of the reducing agent.

An oxidation potential of +1.06 volts can be measured for thioglycolate, whereas a value of +0.56 volts results for cysteamine. This shows how thioglycolate is a significantly stronger reducing agent and explains the superior results associated with this active in producing tighter, true to rod-shaped curls.

In summary, we learn that cystine disulfide bonds can theoretically be cleaved by treatment with any reducing agent, with the effectiveness being related to the oxidation potential of the active. The most common means of achieving this end involves the use of thiols, with the level of activity being further controlled by manipulation of the solution pH. The scientific literature describes the use of numerous thiols (and other reducing agents) for cleaving disulfide bonds in wool and hair. However, virtually none of these have received commercial attention. Clearly, any reagent must be proven to be safe for use on consumers, and such testing is generally costly (and unpopular).

One additional benefit associated with the use of thiols involves an ability to minimize the likelihood of overprocessing hair. The reaction schemes shown previously all represent equilibrium processes, and so a buildup of the oxidized thiol (i.e., R-S-S-R) within the hair would be expected to progressively retard forward progress of equation (2) in a fortuitous manifestation of Le Chatelier's principle. The work of Salce et al. (10) appears to confirm this supposition, and consequently, it is relatively common to find dithioglycolate (DTG) being included in thioglycolate-based perms to help control the extent of reaction.

The previous discussion predominantly deals with chemical and thermodynamic aspects of the perm process, but as hinted previously, there is also the need to consider kinetic aspects. A comprehensive discussion of this topic is given in the following section.

THE RATE OF DISULFIDE BOND CLEAVAGE

Early efforts to follow the rate of the perming process involved chemical analysis of cystine content after exposing hair to reagents for differing periods of time (11–13). This is

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

a rather slow and tedious approach, and moreover, yields an overall change in total cystine content (it will be recalled that specifically we are interested in cystine contained within the alpha-helical keratin protein that makes up the microfibrils within the hair cortex). An interesting proposition for a potentially more useful method involves monitoring the tensile properties of hair while immersed in the perm solution. The crystalline protein that comprises the microfibrils is responsible for the wet-state tensile strength of hair, and so breakage of cystine bonds in this structure would be expected to produce a progressive decrease in mechanical properties. In short, the change in tensile properties is used as a proxy for the reaction progression. The inception of this idea dates back to the 1950s and the work of Reese and Eyring (14). A similar approach was used by Kubu (15,16) in the textile industry, although the method was subsequently popularized in perm research by the work of Wickett (17–22) during the 1980s and 1990s, who also coined the phrase *single-fiber tensile kinetics* (SFTK).

There are a number of assumptions that must be made in directly equating changes in tensile properties to the reaction progression, and in actuality, many of these appear distinctly dubious. However, the results shown herein will demonstrate that the method nevertheless yields predicted outcomes in validation studies while producing remarkably reproducible results. However, before discussing these assumptions, there is the need for a brief overview of the relationship between hair structure and the tensile properties.

The acquisition of mechanical data necessitates some form of sample perturbation. This is generally performed by one of two different approaches—either one precisely applies a given deformation (i.e., strain) to the test specimen and measures the generated force (i.e., a *strain-controlled experiment*) or conversely, one applies a force/stress and measures the concomitant deformation (i.e., a *stress-controlled experiment*). Figure 4 shows a *stress–strain curve* that was generated by stretching dry hair at a constant extension rate using a strain-controlled instrument.

When viewing these curves, it is convenient to consider the mechanical properties of hair in terms of deforming a spring (i.e., the alpha-helical keratin structure). A spring can be stretched within a given range whereupon removal of the applied deformation allows for complete recovery of the initial structure. This is termed *elastic* or *Hookean behavior* and is represented by a linear relationship between the stress and the strain. From Figure 4, it is seen that hair fibers approximate this behavior up to around 2% extension. The slope of this portion of the curve represents an indication of the spring strength and is termed *Young's modulus*. The application of deformations above this point causes the spring-like structure to unfurl, and in doing so, internal forces are dissipated via molecular motion. This threshold condition is termed the *yield point*, and extension beyond this limit distorts the spring to a point where it no longer returns to its original conformation on removal of the stimulus. The stress–strain curve remains relatively flat during extension through the *yield region*, but ultimately, at still greater extensions, the protein chains themselves become strained and internal forces again build until breakage eventually occurs.

The objective of SFTK experiments is to monitor the tensile properties of hair as a function of time while the test specimen undergoes reaction with a perm solution. Accordingly, it is imperative that experiments be carried out under deformation conditions that reside within the linear-like region. That is, under these conditions, the decrease in tensile properties is representative of cleaving strength-supporting disulfide bonds and

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 4. Typical stress–strain curve for hair.

not simply the result of molecular relaxation (plastic flow) within the fiber structure. The yield point for healthy hair is typically found to occur at around 2% extension, which subsequently led Wickett to initially perform his experiments using a 2% static strain.

The measurement of a progressively lower stress within the hair as a function of exposure time to a perm solution has led some to describe these as s*tress relaxation experiments*. However, this can be a source of confusion because this terminology is generally used in the mechanical testing world to describe an approach for separating the elastic and viscous components of viscoelastic materials. In principle at least, the measurement of a force at a consistent extension, which is itself within the "Hookean region," equates to the evaluation of Young's modulus. Therefore, strictly speaking, the SFTK approach evaluates a progressive decrease in this parameter as a function of time while the hair structure is attacked by a reducing solution.

This introduces a major assumption of the method and indeed possibly one of the main contentions, namely, it is recognized that hair is not a truly elastic material but is instead viscoelastic in nature (23). Therefore, application of a strain below the "yield point" will still result in some decrease in stress over time due to relaxation associated with the viscous portion of the hair structure. In an attempt to circumvent this issue, Wickett used a "preconditioning step" where the hair was first cycled through a strain regimen in water with the intention of inducing (and consequently eliminating) this viscous relaxation before

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

beginning the experiment. To this same end, Evans et al. (24) advocated using an intermittent strain profile (see later) that minimizes the time a hair fiber spends in an extended state during the experiment.

However, with all this said, the 2% yield extension limit that is frequently quoted in the literature specifically relates to pristine, healthy hair; and it appears likely that the elastic-like region would shrink because the internal structure of the hair is progressively broken down by the action of a perm solution. Therefore, even if experiments begin with an applied deformation within this range, it is questionable as to whether this condition is maintained as the process proceeds.

Perhaps, an even more fundamental condition of the method involves an assumption that each disulfide bond contributes equally to the overall tensile properties of the hair fiber, that is, cleavage of the first disulfide bond yields an equivalent decrease in tensile properties as that obtained by breaking the last. This is not easy to prove or disprove, but instinctively, it appears somewhat dubious. By means of illustration, an analogy for the complex internal structure of hair may be a length of rope, which itself is made of many intertwined smaller strands. Cleaving a small number of these filaments would likely have relatively little effect on overall strength, but eventually, with progressive breaking of additional strands, a diminution in strength would ultimately manifest. It may even be speculated that the tensile properties of such a fiber would degrade in a cascading manner as the strength is progressively distributed over fewer and fewer strands.

Despite apprehension over all these assumptions, the work shown in the following will illustrate how validation experiments do indeed yield predicted outcomes to systematic alteration of experimental variables. However, care is needed in not overinterpreting results in terms of extrapolating transition rates to real-life usage conditions. For example, SFTK experiments are often performed using an unrealistically high solution-to-hair ratio, where the perm solution is greatly in excess. Moreover, it has been suggested that straining of fibers places disulfide bonds in a higher energetic state, whereby there is enhanced reactivity (11,13). Results will be shown at the end of this section which appear to lend support to this hypothesis. Yet, with all this said, it will be shown that the SFTK approach appears to yield an effective relative comparison of transformation rates as a function of the numerous experimental variables.

SFTK

In theory, SFTK experiments can be performed on any suitable tensile tester, albeit with fabrication of an appropriate test cell. Most of the work described herein was performed using Instron® (Norwood, MA) tensile testers, but experiments have also been carried out using a Perkin Elmer Series 7 Dynamic Mechanical Analyzer (Waltham, MA). Figure 5 shows a custom-built test cell that attaches to the base of an Instron tensile tester.

It consists of a double-walled tube, where the inner portion contains the test solution and the outer cell can be attached to a circulating water bath that allows for temperature control. Individual hair fibers were carefully glued between plastic tabs such that the test specimen measured 2 inches in length. Before gluing, a punch was used to produce a precisely placed hole at the center of each plastic tab, and thus provided a reproducible means of anchoring the test sample. The fiber is initially hung from an upper hook and carefully lowered by hand into the empty cell. The hole in the lower tab is engaged in a

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 5. Custom-designed SFTK cell.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

hook located in the base of the cell. The upper hook is then attached to the Instron load cell by means of pneumatic jaws. The cell is filled to a mark with deionized water, and the fiber is allowed to sit for 5 min. Using a fine adjust dial, the Instron cross-head is raised to take up the slack in the hair fiber until a very slight static force is recorded by the load cell. At this point, the load cell and the gauge length of the device are tarred. Unless otherwise stated, experiments were performed by cycling a 2% intermittent strain at 30-s intervals. Initially, this strain profile is imposed on fibers suspended in deionized water and, as described earlier, is intended to remove/minimize viscous relaxation. An exponential decrease in stress occurs during this cycling in water, with a stable baseline typically being obtained within around 10 min. At this point, the water is rapidly drained from the cell via the tap shown on the front of the cell. The test chamber is quickly refilled to the same level with the test solution, and the experiment is ready to begin. The strain profile is restarted, and tensile properties of the hair are recorded as a function of time. Figure 6 gives an example of a typical experimental output which shows the progressive decrease in tensile properties over time on exposure to a perm solution.

In actuality, the previous graph shows a normalized decrease in force in which the scale has been adjusted such that the initial force becomes unity and the decrease in tensile properties can then be equated to a percentage. Therefore, if we accept all the assumptions described earlier, this *y* axis is taken to represent the progression of the perm reaction.

Figure 6. Typical output from an SFTK experiment.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

A quick indication of the reaction rate can be obtained by borrowing a concept from the field of heterogeneous reaction kinetics (25), that is, we evaluate a *halftime* ($t_{0.5}$) which equates to the period during which the initial stress is reduced by 50%. Figure 6 illustrates a halftime of around 3 min for this specific sample under these particular conditions. Figure 7 shows a Box and Whisker plot for halftimes associated with the reaction of single-source hair fibers with 0.42 M, pH 9.2 solutions of both ATG and cysteamine. Results indicate the presence of significantly faster reaction rates (i.e., shorter halftimes) for reduction with thioglycolate. This outcome is consistent with the aforementioned theory (and indeed real-life observations), whereby thioglycolate is recognized to be a stronger reducing agent.

Continuing with the theories outlined earlier, manipulating the pH of a perm solution changes the concentration of the active thiolate ion species [RS^-] and would therefore also be expected to influence the rate of transformation. Figure 8 shows SFTK results for single-source hair in contact with 0.42 M cysteamine solutions of varying pH and indicates the presence of faster rates with increasing solution pH. These findings are again in line with expectations and consequently help build confidence in the method. Similar experiments involving changes in the thiol concentration also gave rise to predicted responses. As such, despite various concerns outlined earlier pertaining to questionable underlying assumptions, the SFTK method does indeed hold up to validation studies, in that predicted outcomes are obtained from systematic variations in perm solution properties.

Figure 7. Halftimes for hair exposed to 0.42 M, pH 9.2 ATG and cysteamine.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 8. Effect of pH on the reaction rates of a 0.42 M cysteamine solution with hair.

SIGNIFICANCE OF HAIR TYPE

Hair samples and tresses provided by various suppliers for use in *in vitro* experiments usually consist of blended hair that is obtained from a selection of individuals. Initial SFTK testing using this hair source yielded a high standard deviation and poor reproducibility. However, this issue was overcome by switching to single-source hair. Specifically, the results shown earlier were obtained using hair donated by an Asian female who cut off a relatively long ponytail.

In retrospect, this finding is not necessarily surprising because differences in perming ability as a function of hair type have been noted since the advent of the so-called cold wave process (26). Initially, these differences were speculated to be a function of hair dimensions (i.e., fine, medium, and course); however, this appears to be an oversimplification. Nonetheless, Table I shows comparisons involving this Asian hair and a second single source of fine Caucasian hair on reaction with comparable thioglycolate and cysteamine solutions. Clearly, the fine hair (which traditionally might be expected to be more resistant)

Table I
Halftimes for Two Single-Source Hair Types Tested with 0.42 M, pH 9.2
Ammonium Thioglycolate and Cysteamine

	ATG (min)	Cysteamine (min)
Asian hair	3.3	5.4
Fine Caucasian hair	8.3	16.8

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

gives rise to considerably slower reaction rates with both solutions. Similar differences in SFTK rates as a function of hair type were also noted by Wickett (17). These findings suggest a hypothesis whereby the poor response of "resistant hair" to the perming process is a consequence of slower transformation rates which result in an insufficient number of disulfide bonds being cleaved during a given exposure time to the thiol solution.

Figure 9 shows the result of further investigation into the influence of hair type on the rate of transformation with a common perm treatment. Hair was procured from nine different donors, and SFTK experiments were performed using a 0.42 M, pH 9 cysteamine solution. Clearly, there are significant (and sizable) differences in reaction rates associated with these women's hair. The donors were asked to fill out a questionnaire documenting typical habits and practices, and some basic laboratory characterization measurements were also performed (e.g., fiber dimensions). However, no simple correlations were seen between the hair properties and transformation rates.

The one exception to this statement seems to involve the initial "health" of the hair. The donors in the previous experiment had not used any chemical treatments, and consequently, their hair was considered in relatively good condition. An additional experiment involved comparing the reaction rates for single-source virgin hair with a subbatch of the same hair that was exposed to a standard bleaching treatment. Results showed considerably faster reaction rates associated with the chemically damaged hair. This finding is in line with the popular opinion that extreme care is needed in attempting to perm, especially damaged hair, because of the danger of overprocessing. Again, this highlights the "art" of the perm process because stylists attempt to judge the reactivity of hair and obtain the desired result.

Figure 9. Halftimes for panelists' hair when exposed to 0.42 M, pH 9 cysteamine.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

ADDITIONAL ANALYSIS OF SFTK DATA

Further analysis of SFTK data can be performed to examine the mechanism (i.e., the mathematical expression or model) that describes the progression of the process. When performing this modeling, it is again recalled that progress is dependent on two distinctly different steps: the first involves the rate of the chemical reaction between the reactants, but the second comprises the readiness by which the perm active can diffuse throughout the hair and allow the reactants to come together. The slower of these two processes will become a bottleneck to the overall transformation, which can only proceed at a rate commensurate with this limiting condition. If the reaction rate is fast, but diffusion is slow (i.e., diffusion-limited conditions), an advancing reaction "front" would be anticipated within hair fibers, whereupon unreacted cystine bonds lie ahead of the interface, although reduced bonds would be present behind. Conversely, fast diffusion and slow reaction (i.e., reaction-limited conditions) allow the active to readily penetrate throughout the hair before appreciable reaction occurs. In this case, there would be no well-defined interface. Visualization of these behaviors can be attained through microscopic means in combination with staining techniques, that is, freshly permed hair is treated with reagents that specifically adhere to free thiol sites (27,28) and indicate where the disulfide bonds have been broken. Figures 10 and 11 show examples of these two occurrences as identified by fluorescence microscopy (24). In these specific experiments, treatment with a 0.42 M, pH 9.2 ATG solution resulted in an advancing front (i.e., diffusion-controlled behavior), whereas treatment with a cysteamine solution under the same conditions did not (i.e., reaction-controlled behavior).

These two conditions become central in deriving mathematical expressions for describing the progression of the perm reaction. Reese and Eyring (14) proposed a pseudo–first-order mechanism to describe the reaction-controlled condition see equation (11), and Wickett (17) later derived a diffusion-based expression that describes a moving boundary advancing through a cylinder see equation (12).

$$F(t) = F(0)\exp(-kC_o t) \tag{11}$$

$$F(t) = F(0)\exp\left(\frac{-2KC_0}{3T}\right)t^{3/2} \tag{12}$$

It is again noted that chapters on reaction kinetics in chemistry textbooks tend to deal with homogeneous gaseous and liquid systems, but there is a less well-known literature dealing with the rates of heterogeneous reactions (25) (i.e., solid–solid, solid–gas, and solid–liquid interactions). In this section, we borrow well-established ideas from this field and adapt them to studying the perm process.

The rate of a heterogeneous process is given by the following equation:

$$\frac{d\alpha}{dt} = k(T).f(\alpha), \tag{13}$$

where α is the fraction of transformation (in our case, the percentage of bonds broken at any time, t), k (T) is the temperature-dependent specific reaction rate constant, and f (α) is the mathematical expression that describes the overall progression. The simplest reaction mechanism is a conventional first order equation, where the rate is

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 10. Identification of reaction front in hair treated with 0.42M, pH 9.2 ATG.

proportional to the amount of the process still remaining, that is, $(1-\alpha)$. As such, our basic kinetic equation becomes as follows:

$$\frac{d\alpha}{dt} = k(1-\alpha) \tag{14}$$

It is desirable to eliminate the differential term; hence, the previous expression is integrated:

$$\int_{\alpha=0}^{\alpha=1} \frac{d\alpha}{(1-\alpha)} = k\int_{t=0}^{t=t} dt \tag{15}$$

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 11. Absence of reaction front in hair treated with 0.42M, pH 9.2 cysteamine.

and yields the following equation:

$$-\mathrm{In}\left(1-\alpha\right)=kt \tag{16}$$

In identifying the applicability of various mechanisms, we borrow from the reduced time method of Sharp et al. (29). In this particular instance, we again use the aforementioned

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

halftime ($t_{0.5}$) as a normalizing condition, that is, at $\alpha = 0.5$, the previous equation reduces to the following equation:

$$0.693 = kt_{0.5}. \tag{17}$$

Normalization then involves dividing the integral equation by this specific condition:

$$\frac{-\text{In}(1-\alpha)}{0.693} = \frac{kt}{kt_{0.5}}, \tag{18}$$

which reduces to the following form:

$$-\text{In}(1-\alpha) = 0.693\frac{t}{t_{0.5}}. \tag{19}$$

In short, time units cancel out (i.e., $t/t_{0.5}$) and we are left with a means of creating a time-independent, theoretical master plot of α versus $t/t_{0.5}$ for this first-order expression. Figure 12 shows master plots for both the first-order mechanism and Wickett's moving boundary model. Therefore, the applicability of a given model can be identified by treating experimental data in this same manner and comparing the shape of the resulting plots with those for theoretical models.

To illustrate this process, Figure 13 shows experimental data from eight separate SFTK experiments involving the interaction of single-source Asian hair with a 0.42 M,

Figure 12. Reduced time plots for the theoretical first-order and moving boundary models.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

pH 9.3 cysteamine solution. The reduced time approach involves evaluating the half-time for each individual experiment and then creating a new x axis by dividing the experiment time by the halftime for each test (i.e., $t/t_{0.5}$). Figure 14 shows the result of performing this same analysis on the data from all eight individual experiments. Despite some experimental variability in Figure 13, once the normalization step renders the x axis independent of time unit, all data reduce to a single curve that indicates the applicability of the same kinetic mechanism. However, Figure 15 shows these experimental data do not superimpose over either curve for the two theoretical models described earlier. It is therefore concluded that neither model applies in this case.

Figure 16 shows the result of performing this same reduced time analysis on SFTK experimental data for the interaction of this single-source Asian hair with both cysteamine and ATG solutions under identical conditions. Clearly, both data sets reduce down to differently shaped curves. In short, these two solutions not only do produce markedly different reaction rates (see Figure 7) but also two distinctly different kinetic mechanisms also appear to be present. (It will be recalled from the fluorescence microscopy images shown in Figures 10 and 11 that these two treatments also gave rise to different behaviors during dye staining experiments.) This said neither of the two theoretical models described earlier match the experimental data and the need for further mathematical modeling is needed in an attempt to

Figure 13. Raw SFTK data for reaction of single source Asian hair with 0.42M, pH 9.3 cysteamine.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 14. SFTK data for reaction of single source Asian hair with 0.42M, pH 9.3 cysteamine after reduced time analysis.

Figure 15. Comparing experimental reduced time data for single-source Asian hair reacting with 0.42 M, pH 9.3 cysteamine to theoretical models.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 16. Reduced time plots for single-source Asian hair reacting with 0.42 M, pH 9.3 cysteamine and ATG solutions.

derive expressions that better describe the progression of the perm reaction with time. Until then, curve-fitting software (TableCurve® by Systat Software, Inc., San Jose, CA) has been used to record shapes of experimental reduced time plots in Figure 16.

Confidence in these experimentally observed relationships (and indeed the SFTK approach itself) is strengthened by both the reproducibility of the data and the frequency with which they are found. To further illustrate this point, Figure 17 shows the result of performing reduced time analyses on the previously mentioned experimental data for 0.42 M cysteamine solutions as a function of pH (see Figure 8). In Figure 17, the solid and dashed lines represent the two experimental behaviors described earlier. Accordingly, it is seen how experiments involving cysteamine solutions with pH 6–9 all appear to abide by the same mechanism identified earlier; however, a change is evident when the pH is raised to 10. Moreover, this new behavior corresponds exactly to that identified previously for the 0.42 M, pH 9 ATG solution. Therefore, the reduced time method provides a simple and useful means for identifying these different mechanisms, and without this approach, the previously mentioned conclusions would not be evident.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 17. Reduced time plots for single-source Asian hair reacting with 0.42 M cysteamine as a function of pH.

DISCUSSION

The previously mentioned findings clearly lead to more questions than answers. Wickett frequently referred to "reaction-controlled" and "diffusion-controlled" conditions—with this designation primarily relating to the linear response of plots involving experimental data to the two mathematical mechanisms. Staining experiments apparently provide a clearer designation based on the presence (or absence) of reaction "fronts" within fibers as a function of different treatment conditions. Yet, our reduced time analysis of data from an experimental situation that did not yield such a front (and therefore indicates "reaction-controlled" conditions) did not abide by the first-order mechanism. Similarly, data from circumstances that yielded a reaction front (and therefore suggest "diffusion-controlled" conditions) did not abide by Wickett's moving boundary model. It is theorized that rather than being specific mechanisms, the descriptors "diffusion controlled" and "reaction controlled" represent a first line of classification for a variety of mathematical models that fall under each category. Again, there is clearly the need for additional mathematical modeling work to derive new mechanisms that adequately describe the experimental data.

It should be noted that other curve shapes have been obtained during performing this reduced time analysis on experimental SFTK data. The behaviors outlined earlier

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

(experimental and theoretical) all have their highest rate of transformation (at or near to) to the beginning of the process. In solid-state kinetics, these are termed deceleration mechanisms because the rate decreases over most of the process. However, it is not uncommon to find experimental reduced time curves with a distinctly sigmoidal behavior (see Figure 18). This implies that there is some induction period during which the rate of transformation progressively builds, but then another factor would appear to gradually dominate and the rate subsequently decreases.

It is again noted that the analysis approach described herein is commonly used in the field of heterogeneous kinetics, where a variety of mathematical models have already been derived based on underlying conditions such as diffusion, order, and/or geometric constraints (25,29). Some examples of reduced time curves derived from diffusion- and geometry-based equations are shown in Figures 19 and 20. As an aside, this author has also used the same kinetic approach in modeling the rate of water adsorption by hair as a function of changing humidity conditions, wherein the applicability of these same first-order and diffusion-based models has been identified (30).

ADDITIONAL VARIABLES IN SFTK EXPERIMENTS

This section began by highlighting a number of concerns and seemingly questionable assumptions pertaining to the SFTK approach. Despite these issues, it is observed that

Figure 18. Example of experimentally derived sigmoidal reduced time plot.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

Figure 19. Reduced time plots for theoretical mechanisms derived from diffusion based assumptions.

the method holds up to validation studies by producing expected results for systematic changes in conditions. However, with this said, there are several method-related variables that can influence the absolute value of the rate.

Figure 20. Reduced time plots for theoretical mechanisms derived from geometric based assumptions.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

As mentioned earlier, it has been suggested that there is enhanced reactivity associated with strained disulfide bonds. Table II shows results from a systematic set of experiments that were intended to investigate this idea. Intermittent stress relaxation experiments were performed as a function of the applied strain increment using single-source hair in combination with a 0.42 M, pH 9 ATG solution. Clearly, faster overall transformation results are obtained when using higher strain increments.

Further to this point, an additional set of experiments were performed wherein both the rate and period of this deformation were altered. The use of a slower sample deformation rate (i.e., 0.25 inches/min vs. 0.5 inches/min) was observed to yield significantly faster transformation rates. Similarly, repeated application of the strain every 15 s, rather than every 30 s, also led to faster rates. Both of these experimental conditions result in the hair being in a strained state for longer durations and may then be considered in line with the presumed proposition. Conversely, it could be argued that in spending more time in a strained state, there is greater opportunity for viscous relaxation, or indeed a yielding of the structure (if the stress begins to exceed the yield point). Further to this same point, static stress relaxation experiments were found to yield faster rates than the corresponding intermittent method.

In short, although these findings are in line with the premise, there may be other explanations for these outcomes. However, they do highlight the significant contribution of these variables to the magnitude of the rates that result. As such, it is again emphasized that the SFTK approach appears to provide a convenient means of comparing *relative* transformation rates that arise as a function of solution chemistry variables and/or hair type. However, these same rates should not be expected under real-life usage conditions.

From the previous results, it is hypothesized that poor perm performance in resistant hair is a consequence of slow transformation rates that do not induce sufficient bond breakage during treatment time. Accordingly, the SFTK approach would seem ideally suited for studying factors that may positively influence this state. For example, it would be anticipated that elevated temperatures could induce faster perming rates. Indeed, in real-life salon conditions, it is common practice for the client to sit under an upright hair drier that provides this extra stimulus. It is noted that Wickett performed some preliminary experiments to illustrate this expected influence of temperature. One may also conceive of experiments to investigate the effect of swelling agents in formulations or perhaps various prewraps or other pretreatments that could alter diffusion.

OXIDATION STEP

After concentrating so much time on the breaking of disulfide bonds, it now becomes necessary to consider their reformation. Following from the earlier chemistry discussion, if these bonds are cleaved by reduction, their restoration relies on oxidation. Whereas much has

Table II
SFTK Results as a Function of the Strain Increment

Strain increment (%)	Halftime (min)
0.5	20.4
1	17.0
1.5	11.6
2	4.7

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

been published on bond breaking, relatively little is written on this reformation process. It is again suggested that this step may be seen as somewhat trivial because bond reformation is recognized to occur to some extent by the so-called *air oxidation*, namely, this process appears to begin during rinsing of the perm solution from the head, wherein the hair becomes saturated with large amounts of aerated water. Nonetheless, there is obviously the desire to perform this important function properly, and consequently, treatment with an oxidizing agent is prudent. Most often this is accomplished using hydrogen peroxide.

$$2K\text{-}SH + H_2O_2 \leftrightarrow K\text{-}S\text{-}S\text{-}K + 2H_2O \tag{20}$$

Wortmann and Souren (31) used a method somewhat analogous to the SFTK approach to observe the recovery in mechanical properties of reduced hair on rinsing with water and treatment with hydrogen peroxide.

In performing this more thorough "neutralization" treatment, there is increased likelihood for a degree of "overoxidation" whereby cysteine is converted to the corresponding sulfonic acid (i.e., cysteic acid). In short, there is a reduction in the number of strength-supporting cystine disulfide bonds and a concomitant decrease in tensile properties. This topic of hair damage resulting from perm treatments will be discussed shortly.

REVERSION DUE TO SULFIDE–DISULFIDE BOND INTERCHANGE

The permanency of permanent waves merits some discussion, that is, it is well-recognized and relatively commonplace for the induced curls to relax somewhat from the initial freshly permed state. The culprit for this occurrence is generally considered to be *sulfide–disulfide bond interchange*, through which a rearrangement of the newly formed internal bonds takes place to release stress within the S-S bond network. A schematic of this process is given in Figure 21.

This occurrence is sometimes speculated as a reason why thiol-based relaxers are not especially effective on Afro hair, namely, a more dramatic change in conformation results in additional internal stress and an increased tendency for this interchange. The creation of more permanent lanthionine bonds under highly basic conditions may therefore represent more enduring chemistry for this challenging hair type.

HAIR DAMAGE ASSOCIATED WITH THE PERMING PROCESS

As documented throughout this article, the perm process involves the rather drastic process of breaking down a significant portion of hair's internal structure, followed by subsequent

Figure 21. Schematic representation of sulfide–disulfide bond interchange.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

reformation with fibers anchored in a new conformation. However, perhaps not surprisingly, it is not possible to put everything back exactly the way it was. Specifically, there will be some depletion in disulfide cystine content, a commensurate increase in cysteic acid, and a subsequent decrease in tensile properties. It has been shown how the aggressiveness of the perm process can be altered by many formulation variables, for example, concentration of the reducing agent, oxidation potential of the reducing agent, pH of the formulation, the presence of the oxidized form of the reducing agent, and also possibly the ability for the active to diffuse into the hair. The capability to cleave and reform a higher number of disulfide bonds would instinctively be expected to yield a stronger perm (at least perhaps up to some upper limit). However, the ability to effectively reform all these bonds would also seem to become more difficult as the extent of reaction progresses, and the hair is broken down further.

These ideas are realized in practice, where, for example, thioglycolate-based perms generally yield tighter, true to rod-shaped curls than a cysteamine-based perm, but at the same time, the hair is left in a more compromised state. This leads to the concept of a *damage–efficacy trade-off curve* whereby more aggressive, more efficacious treatments and conditions are obtained at the expense of higher damage (see Figure 22). Manufacturers will often offer different variants under a given product line that provide levels of activity commensurate with the end goals of consumers. In marketing such treatments, it is not uncom-

Figure 22. Schematic representation of a damage–efficacy curve.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

mon to encounter claims pertaining to an active or formula being "less damaging"; but these treatments are also milder and consequently also less effective. By means of illustration and continuing with the earlier example, the positioning of a cysteamine-based product as a "less-damaging" perm may be technically correct, but at the same time, it is not a true comparison as levels of transformation are unlikely to be equivalent.

It should be remembered that one can also move up and down this damage-efficacy trade-off curve by the way these products are used, namely, increased efficacy, but also greater damage, can result from higher product dosages and longer exposure times. With all this said, there are other means by which the hair structure can be damaged that lead to other consumer-related issues. A few articles describe extreme levels of swelling when treating hair with thioglycolate and other reducing agents. Valko and Barnett (32) and Powers and Barnett (33) reported swelling of up to 300% after prolonged soaking in a thioglycolate solution. This occurrence reverses during the oxidation process as bonds are reformed (34); although Shansky (35) noted additional swelling during the rinsing step between the reduction and oxidation steps which he attributed to osmotic forces. This ballooning of dimensions would seem to impose considerable strain on the outer structure of hair, whereby uplifting, cracking, and general deterioration of cuticle scales may be anticipated. The condition of this outer surface is the major contributor to the tactile properties of the hair, and its deterioration will be reflected in a variety of consumer-related terms. Perhaps most notably, a rough, course hair feel is often described by consumers as "dryness," although technical measures indicate no decrease in water content (30,36).

The aforementioned swelling properties of hair are permanently altered by these treatments whereby increased dimension changes arise during immersion in water. This has led some to suggest that this property can also be used as one measure of damage (37,38), but the consequences of this altered state are perhaps more interesting and important. One of the most notable repercussions of these treatments involves the considerable increase in wet-state grooming forces. The popular explanation for this occurrence generally involves a degrading cuticle structure; but in this author's experience, scanning electron microscopy images do not usually show an especially damaged surface in freshly permed hair. Instead, it is believed that enhanced swelling produces a marked increase in the wet hair volume which subsequently results in higher grooming forces. An increased predilection for swelling is also widely believed to impact diffusion rates for materials both in and out of the hair. This represents a likely explanation for the especially fast transformation rates that arose during SFTK experiments on bleached hair.

ADAPTATIONS WITHIN THE PERM PROCESS

Several perm variants can be found on the beauty aisle shelves. Most fall within a classification termed *alkali waves* because of their basic pH (generally 8–9.5) for the reasons described earlier. There is also an *acid perm* category, although technically the name is a misnomer as these products are also basic in composition (generally pH 7.5–8.5), but not as alkaline as the previous category. This positioning generally equates to propositions involving reduced hair damage, where more caustic conditions may be anticipated to compromise hair to a greater extent.

There is some truth to this idea, although there are complicating factors that preclude such a simple statement. High-pH conditions can lead to increased fiber swelling and

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

hydrolysis of the hair protein, although the literature suggests that these occurrences predominantly occur under more extreme conditions than those used in perms. However, as described previously, the concentration of the active thiolate ion is dictated by the value of the pH relative to the pKa of the thiol. Therefore, acid perms use less aggressive reaction concentrations and therefore sit toward the lower end of a damage–efficacy trade-off curve. In addition, acid perms often use glycerol monothioglycolate as an active, and it can be further speculated that reduced efficacy may also be a consequence of this larger molecule diffusing more slowly into the hair.

As described earlier, it is common to see DTG being added to thioglycolate-based perms to limit the progression of the second equilibrium reaction see equation (9). To chemists, this represents a fortuitous practical demonstration of Le Chatelier's principle; however, in the creative minds of product marketers, these formulations become *self-timing perms*. Salce et al. (10) generated results that showed this expected behavior on introducing the oxidized dimer into formulations, but Manuszak et al. (21) were not able to observe any effect in SFTK experiments. It is possible that the high solution-to-hair ratio in SFTK experiments prevents the buildup of sufficient concentrations of this reaction product.

Yet another variant involves *exothermic perms* which represent a modern adaption of the machineless waves that were described in the Introduction section. These treatments involve mixing two solutions before application. The first generally contains a somewhat higher concentration of thioglycolate, and the second has a relatively low level of hydrogen peroxide. Therefore, on mixing, the two reagents undergo reaction with a significant release of heat, while still providing sufficient thioglycolate concentration for reaction with the hair. In addition, this reaction produces DTG whose significance has been highlighted.

Outside of damage, the other major issue with conventional perm products involves the smell. There are two primary contributors to this issue: (i) the odorous nature of thiols themselves and (ii) the smell of ammonia, which is commonly used as a pH adjustor. Although unpleasant, these smells will only persist for a short time after treatment and will gradually dissipate after a few days. However, a curious alternative issue can arise when using cysteamine-based perms. These products were introduced into the U.S. market as low-odor perms because of the less noxious smell of the active relative to thioglycolate. However, an unexpected occurrence involved the development of a new odor, often likened to "wet dogs," that arose within a few days to a week of usage. It has been suggested that this new smell is due to the formation of alkyl thiazolidines (39) which are produced when residual cysteamine (tied up within the hair as mixed disulfide) is gradually released and reacts with sebaceous components.

The only commercial exception to the thiol classification of perm actives involves sulfites, SO_3^{2-} (or at low pH, bisulfites, HSO_3^-). These too are reducing agents, and equation (21) shows the half equation for the oxidation of sulphite to sulphate under alkali conditions.

$$SO_3^{2-} + 2OH^- \leftrightarrow SO_4^{2-} + H_2O + 2e^- \tag{21}$$

Meanwhile, equation (22) shows the reaction scheme for sodium sulfite attacking the keratin disulfide bond with the formation of the so-called bunte salt (i.e., K-S-SO_3Na).

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

$$K\text{-}S\text{-}S\text{-}K + Na_2SO_3 \leftrightarrow K\text{-}S\text{-}SO_3Na + NaS\text{-}K \tag{22}$$

The attraction of sulfite/bisulfite as an active relates to the ability to reverse the aforementioned reaction by rinsing with water and therefore essentially making it a one-step treatment. However, these treatments are not able to create tight well-defined curls and are mostly found as weak *body waves*. Sensitization issues associated with sulfites may also be a concern.

EVALUATION OF WAVE EFFICACY

In the salon, the efficacy of a perm treatment is judged by a visual assessment of the curl shape relative to the size of the waving rods. A close relationship between the resulting curl and the rod diameter is often termed "true to rod" performance. However, based on previous discussions, it is evident that any evaluation of perming performance should also involve some durability assessment, possibly after exposing the hair to adverse conditions that are nonetheless in line with everyday occurrences (e.g., repeated shampooing and/or exposure to elevated humidity).

A more precise method is often desired in the laboratory that allows for quantification of both the initial and long-lasting efficacy. A method that remains popular involves adaptations of an approach first described by Kirby (40). The testing process involved setting the hair shape by wrapping tresses or bundles of fibers around the pins on a pegboard. Figure 23 shows an example of such a utensil. (Note: a modification of this approach has been adopted in the hair spray category, where it is also used to quantify style retention and longevity.) Once anchored, the hair can then be treated with an appropriate dosage of

Figure 23. Pegboard for use in Kirby wave efficiency testing.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

perm solution, which is left on the hair for a suitable duration. The hair can then be rinsed and towel blotted before application of the neutralizing solution. The process finishes with one last rinse and drying of the hair. All manipulation can be performed with the hair anchored on the pegboards.

The waving efficiency can be expressed as percentage by comparing the length of the treated hair (L_{treated}) with the initial tress length (L_0) and that of the "perfect wave" as dictated by the dimension of the pegboard (L_∞), that is,

$$\text{Percentage waving efficiency} = \left[1 - \left(L_{\text{treated}} - L_\infty\right) / \left(L_0 - L_\infty\right)\right] \times 100 \tag{23}$$

Similarly, the longevity of the treatment can be assessed as a function of time (or other external stimuli) by equation (24), that is,

$$\text{Percentage waving efficiency} = \left[1 - \left(L_{\text{treated}} - L_\infty\right) / \left(L_0 - L_\infty\right)\right] \times 100, \tag{24}$$

where L_t is the tress length after the appropriate stimuli.

SUMMARY

It is possible to find reviews and summaries pertaining to the topic of perm chemistry, which perhaps presents the impression that this area is well-understood. Accordingly, this overview attempts to take a somewhat different stance, by dedicating a significant portion to what we still do not know about the process (perhaps in the hope that others will take up the cause). It is suggested that the underlying chemistry is relatively straightforward and can be found in any elementary textbook. But, before reactions can occur, it is necessary for reactants to come together, and to this end, it is surprising that so little is known about penetration routes and rates of diffusion into hair. It has been hypothesized that variability in diffusion rates could be a cause of differing activity between a common perm solution and hair obtained from a diverse population. Results shown herein indicate significant differences in both rates and kinetic mechanisms as a function of hair type, and it appears reasonable to suppose that "perm-resistant hair" is a consequence of relatively slow bond cleavage that produces an insufficient degree of transformation during treatment time. However, an explanation for these differences in diffusion rates (and indeed a means of measuring this property) requires further work. Addressing this point seems crucial in producing any enduring makeover (perm chemistry or not) because transformation will likely require penetration of "actives" into the hair.

After all this time, it is rather remarkable that perm chemistry still likely represents the best available means for permanently changing the shape of hair. The hullaballoo created by the so-called Brazilian keratin treatments in recent years has reignited research interest in this area, but there is no immediate indication of a safe, effective substitute for perm chemistry. Although not wanting to stifle new ideas, it is obviously prudent to ensure that everything has been squeezed out of existing technologies before moving on to new areas, and it is again noted that perm products have changed very little since their inception in the 1940s. Research efforts since this time have primarily focused on alternative actives (although still predominantly thiols), yet incumbent thioglycolate-based products still overwhelmingly dominate the shelves. It is worth re-examining why this material has been so difficult to

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

displace. Thioglycolate is a small reducing agent with a relatively high oxidation potential that seemingly diffuses into hair reasonably well. As with all thiols, the activity can be fine-tuned through a combination of the solution concentration and pH. In addition, the extent of reaction can seemingly be curbed by the buildup (or presence) of exogenous DTG which limits the chance of overprocessing. On the negative side, a certain amount of structural damage is produced within the hair, although the extent is still considerably less than other shape-shifting alternatives (i.e., caustic relaxers and formaldehyde cross-linking). The two-step nature of the perm process and the odor are considered inconveniences, although the outcome of the process can be somewhat unreliable.

The aforementioned summary creates a checklist when considering the resumes of new candidate molecules, but there is still the need for better understanding the role of hair itself. Wortmann and Kure (41) ascribe significance to the cuticle structure and suggest it acts as a barrier to penetration, while also providing resistance to fiber bending. The existence of different cortical cell types is recognized in the wool literature, where markedly different responses in alkali swelling have been reported (42). To date, only a few studies have extended these ideas into the hair literature (43–45).

Finally, the potential for formulation-related innovations should not be overlooked, wherein there is the possibility for alternative ways of applying the actives to hair and for manipulating penetration through formulation variables, or possibly prewraps; there is even the potential for packaging-related innovation to simplify the procedure. To this end, the appearance of the so-called smoothening creams on shelves, essentially representing a conditioner–perm hybrid, is noteworthy. These products are likely to be less aggressive than true perms and are intended to produce their effect progressively with repeated treatments, rather than one single application.

Hair fashions change over time, but there is a constant desire for those with straight hair to create curls, and those with curly hair to go straight. At the time of writing, straight hair styles have dominated for the past couple of decades, but the cycle that led to "big hair" styles in the 1970s and 80s seems destined to return at some time in the future. In the absence of new technologies, perm chemistry will continue to be how these looks are achieved.

ACKNOWLEDGMENTS

In undertaking this review, it is impossible to not become nostalgic and recall working relationships and friendships that were encountered during employment at Helene Curtis in the early to mid-1990s. I learned so much from the likes of Craig Herb, Kate Martin, Bruce Solka, Bin Chen, Min Liu, Paul Neill, and many others. It was also a delight to work with such skilled and innovative engineers as Steve Dokoupil and Saul Llamas. But most of all, I remember Priscilla Walling who gave me my start in this industry and who contributed immensely to shaping me as an industrial scientist, by providing the perfect mix of encouragement, independence, and sage advice. I also recognize the contributions of Tom Ventura, Pawel Milczarek and Daniel Kung to the SFTK data generation process. Similarly, Figures 10 and 11 were originally generated by Amy Qualls. I thank TRI-Princeton for access to their library of historical journals and acknowledge many hours of discussion with Randy Wickett on the topic of single-fiber tensile kinetics. Finally, I thank Rushi Tasker for discussions pertaining to the current status of the perm industry.

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

REFERENCES

(1) E. G. McDonough, The development of machineless permanent waving, *J. Soc. Cosmet. Chem.*, **1**(3), 183–189 (1948).
(2) C. R. Robbins, "Chemical composition of different hair types," in Chemical and Physical Behavior of Human Hair, 5th Ed. (Springer-Verlag, New York, 2012).
(3) J. A. Swift, "The structure and chemistry of human hair," in Practical Modern Hair Science (Allured Books, Carol Stream, IL, 2012).
(4) C. R. Robbins, "Morphological, macromolecular structure and hair growth," in Chemical and Physical Behavior of Human Hair, 5th Ed. (Springer, 2012).
(5) P. R. Brady, Diffusion of dyes into natural fibers, *Rev. Progr. Color.*, **22**, 58–78, 1992.
(6) J. D. Leeder, Comments on "pathways for aqueous diffusion in keratin fibers", *Tex. Res. J.*, **69**, 229 (1999).
(7) F. J. Wortmann, G. Wortmann, and H. Zahn, Pathways for dye diffusion in wool fibers, *Tex. Res. J.*, **67**, 720–724 (1997).
(8) J. A. Swift, Further comments on "pathways for aqueous diffusion in keratin fibers", *Tex. Res. J.*, **70**, 277–278 (2000).
(9) C. Gummer, Elucidating penetration pathways into the hair fiber using novel microscopic techniques, *J. Cosmet. Sci.*, **52**, 265–280 (2001).
(10) L. Salce, J. J. Cincotta, S. Barlow, A. Rubinstein, and E. J. Klemm, Reduction of hair in the presence of exogenous disulfide, *J. Soc. Cosmet. Chem.*, **38**, 99–107 (1987).
(11) J. B. Speakman, The reactivity of the sulphur linkage in animal fibers – part 1. The chemical mechanism of permanent set, *J. Soc. Dyers Col.*, **52**, 335–346 (1936).
(12) J. P. E. Human and H. Lindley, The reactivity of the disulfide bonds of stretched wool fibers, *Tex. Res. J.*, **27**, 917 (1957).
(13) L. J. Wolfram, Reactivity of disulphide bonds in strained keratin, *Nature*, **206**, 304–305 (1965).
(14) C. E. Reese and H. Eyring, Mechanical properties and the structure of hair, *Tex. Res. J.*, **20**, 743–750 (1950).
(15) E. T. Kubu, The stress relaxation of fibrous materials. I. instrumentation and preliminary results, *Tex. Res. J.*, **22**, 765–777 (1952).
(16) E. T. Kubu and D. J. Montgomery, II Kinetics of the reduction of wool keratin by cysteine, *Tex. Res. J.*, **22**, 778–782 (1952).
(17) R. R. Wickett, Kinetic studies of hair reduction using a single fiber techniques, *J. Soc. Cosmet. Chem.*, **34**, 301–316 (1983).
(18) R. R. Wickett and B. G. Barman, Factors affecting the kinetics of disulphide reduction in hair, *J. Soc. Cosmet. Chem.*, **36**, 75–86 (1985).
(19) R. R. Wickett and R. Mermelstein, Single fiber stress decay studies of hair reduction and depilation, *J. Soc. Cosmet. Chem.*, **37**, 461–473 (1986).
(20) R. R. Wickett, Disulfide bond reduction in permanent waving, *Cosmet. Toilet.*, **106**, 37–47 (1991).
(21) M. A. Manuszak, E. T. Borish, and R. R. Wickett, The kinetics of disulfide bond reduction in hair by ammonium thioglycolate and dithioglycolic acid, *J. Soc. Cosmet. Chem.*, **47**, 49–58 (1996).
(22) M. A. Manuszak, E. T. Borish, and R. R. Wickett, Reduction of human hair by cysteamine and ammonium thioglycolate: a correlation of amino acid analysis and single fiber tensile kinetic data, *J. Soc. Cosmet. Chem.*, **47**, 213–227 (1996).
(23) E. G. Bendit, There is no Hookean region in the stress-strain curve of keratin, *J. Macromol. Sci. Phys.*, **B17**(1), 129–140 (1980).
(24) T. A. Evans, T. N. Ventura, and A. B. Wayne, The kinetics of hair reduction, *J. Soc. Cosmet. Chem.*, **45**, 279–298 (1994).
(25) C. M. Bamford and C. F. H. Tipper. Eds., Comprehensive Chemical Kinetics, Vol. **22** (Elsevier, Amsterdam, Oxford, New York, NY, 1980).
(26) M. J. Suter, Chemistry in permanent waving – past, present and future, *J. Soc. Cosmet. Chem.*, **1**(2), 103–108 (1948).
(27) T. Toy'oka and I. Kazuhiro, New fluorgenic reagent having halogenbenzofurazan structure for thiols: 4-(aminosulfonyl)-7-fluoro-2,1,3-benzoxadiazole, *Anal. Chem.*, **56**, 2461–2464 (1984).
(28) D. J. Evans, A method for determining the penetration of reducing agents into wool using fluorescent microscopy, *Tex. Res. J.*, **59**, 569–576 (1989).
(29) J. H. Sharp, C. W. Brindley, and B. N. N. Achar, Numerical data for some commonly used solid state reaction equations, *J. Am. Ceram. Soc.*, **49**, 379–382 (1966).

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)

(30) T. A. Evans, "Adsorption properties of hair," in Practical Modern Hair Science, T. A. Evans and R. R. Wickett. Eds. (Allured Books, Carol Stream, IL, 2012).
(31) F. J. Wortmann and I. Souren, Extensional properties of human hair and permanent waving, *J. Soc. Cosmet. Chem.*, **38**, 125–140 (1987).
(32) E. I. Valko and G. Barnett, A study of the swelling of hair in mixed aqueous solvents, *J. Soc. Cosmet. Chem.*, **3**, 108–117 (1952).
(33) D. H. Powers and G. Barnett, A study of the swelling of hair in thioglycolate solutions and its reswelling, *J. Soc. Cosmet. Chem.*, **4**, 92–100 (1953).
(34) M. E. Eckstrom, Swelling studies of single hair fibers, *J. Soc. Cosmet. Chem.*, **2**, 4 (1951).
(35) A. Shansky, The osmotic behaviour of hair during the permanent waving process as explained by swelling experiments, *J. Soc. Cosmet. Chem.*, **14**, 427–432 (1963).
(36) F. J. Wortmann, A. Hullmann, and C. Popescu, Water management of human hair, *IFSCC Mag.*, **10**(4), 317–320 (2007).
(37) J. C. Brown, The determination of damage to wool fibers, *J. Soc. Dyers. Col.*, **75**, 11–21 (1959).
(38) E. J. Klemm, J. W. Haefele, and A. R. Thomas, The swelling behavior of hair fibers in lithium bromide, *Toilet Goods Assoc.*, **43**, 7–13 (1965).
(39) A. Nandagiri, B. Solka, and J. Kocis, Method of Reducing Malodor in Permanent Waving, US Patent #5,554,363.
(40) D. H. Kirby, The waving efficiency of cold permanent wave lotion, *Drug Cosmet. Indus.*, **80**(3), 314–400 (1957).
(41) F. J. Wortmann and N. Kure, Effects of the cuticle of the permanent wave set of human hair, *J. Soc. Cosmet. Chem.*, **45**, 149–158 (1994).
(42) R. D. B. Fraser and G. E. Rodgers, The bilateral structure of wool cortex and its relation to crimp, *Aust. J. Biol. Sci.*, **8**, 288–299 (1955).
(43) J. A. Swift, "The histology of keratin fibers," in The Chemistry of Natural Protein Fibers, R. S. Asquith. Ed. (Plenum Press, New York, NY, 1977), pp. 81–146.
(44) S. Thibaut, P. Barbarat, F. Leroy, and B. A. Bernard, Human hair keratin network and curvature, *Int. J. Dermatol.*, **46**(Suppl. 1), 7–10 (2007).
(45) W. G. Bryson, D. P. Harland, J. P. Caldwell, J. A. Vernon, R. J. Walls, J. L. Woods, S. Nagase, T. Itou, and K. Koike, Cortical cell types and intermediate filament arrangements correlate with fiber curvature in Japanese human hair, *J. Struct. Biol.*, **166**, 46–58 (2009).

Purchased for the exclusive use of nofirst nolast (unknown)
From: SCC Media Library & Resource Center (library.scconline.org)