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Thermal styling: Efficacy, convenience, damage tradeoffs

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Synopsis

We introduce a simple method to explore the efficacy of thermal styling, By using a temperature gradient curling iron we rapidly explore a range of thermal treatment conditions. The thermodynamic literature on the glass transition in keratin fibers explains the surprisingly limited role of elevated temperature in improvements in the efficacy of holding the styled curvature of the fibers. The onset of damage, however, is strongly temperature dependent. This combination of measurements of damage and efficacy shows the range of conditions over which thermal protection products must be functional.

INTRODUCTION

The age-old practice of using heat to style hair has been growing in popularity and, with this growth, the interest in protecting hair from heat damage has risen. Of course, the easiest way to avoid heat damage is to minimize heat. But how much efficacy, and how much convenience is sacrificed when a style is set without heat? There is little literature on the efficacy of heat in setting and holding hairstyle. To understand the need for heat-protection from cosmetic products, we undertook the project described in this paper to better document the tradeoffs between convenience, efficacy and damage in heat styling.

Efficacy has at least three distinct, measurable attributes. First is the initial set $S_{0,}$ the degree to which the hair attains the desired shape. Second is the hold time describing the initial fading of style. This is a fairly rapid process typically taking one to two hours. After the initial fade time, the rate of fading slows dramatically and remains fairly constant approaching a final value of the retained shape R_f, which can hold all day at constant humidity.

Convenience, in these laboratory tests, refers simply to the duration of heat treatment. Consumer convenience, of course, also includes other factors such as ease of use, packaging and storage; these are beyond our scope.

There are many measures of damage caused by heat, and a good literature describing them (1–3). We will focus on single fiber tensile properties including break stress σ_b, elastic modulus E, and shear modulus $G = G' + iG''$ and loss tangent $\tan(\delta) = G''/G'$. We describe one measures of chemical damage, the contact angle, which quantifies oxidative damage to the surface of the fiber.

METHODS

HAIR

The hair used in the thermal studies was from a stock of virgin European medium brown 4-inch wide tresses supplied by De Meo Brothers, Inc. Bleached hair was prepared from these tresses soaking in pH of 10.2, 6% hydrogen peroxide solution for 40 minutes at 40°C. Smaller and thinner tresses were made from these stock tresses. They are approximately one fiber layer thick, 10 cm wide, and 8 cm long below the tape securing the tress. The 8-cm length wrapped exactly once around our 1 inch diameter curling rod without overlap ($2.54\pi = 8.01$ cm).

The tresses are prepared in one of three states. Wet, is soaked in water for at least 10 minutes. Dry is made wet and then equilibrated for at least 24 hours at either 20% or 65% relative humidity.

THERMAL TREATMENT, IMAGING, AND EFFICACY MEASUREMENT

To increase the throughput in the screening of curling conditions, we constructed a temperature gradient curling iron (Figure 1), which holds a fixed temperature at each end and has a linear temperature gradient along the iron. The linearity of the gradient was checked using thermocouples along the length of the iron. The iron was allowed to equilibrate for at least 20 minutes prior to use.

After curling, hair was quickly transferred to a chamber set to 50% RH and imaged using a computer controlled digital camera (Fuji S5 pro). The camera field of view is large enough to image multiple tresses simultaneously.

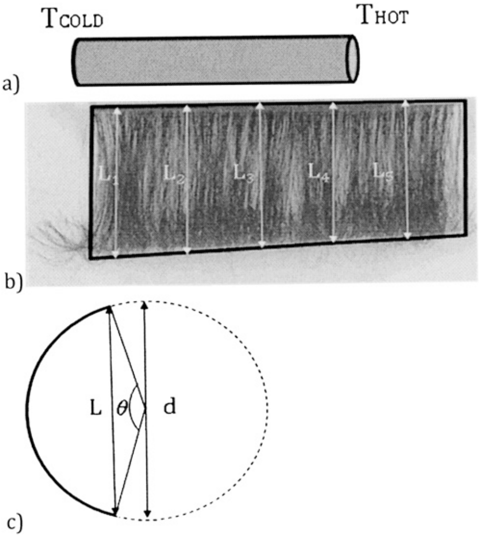

Figure 1. Temperature gradient curling iron. (a) Schematic. (b) Sample image of hair some time after curling. (c) Geometric construction relating the visible curl length to the diameter of curvature.

In the context of studying water-set, Wortmann and collaborators connected this experimental geometry (a single loop curl) to quantities that can be connected to a thermodynamic description of the problem (4). In Figure 1, the curl geometry and the relation of the evolving curl shape to the set and fade time are illustrated.

The images are analyzed using software written by the authors in three stages. First, each image is sectioned to produce a single, time-stamped frame for each tress. Second, each tress image is further sectioned into five slices of varying temperatures. Third, the diameter of the tress' single curl is computed using the visible height of the tress (Figure 1b-c). When the fiber tips are not visible, the diameter of curvature is simply the tress height. When the tress opens far enough that the bottom of the tress is the tip of the fiber, we use the geometry shown in Figure 1c, which leads to the relation $L/d = \sin(L_m/\pi d)$ where L_m is the length of the straightened hair to determine the curl diameter d.

The diameter data are converted to thermodynamically relevant quantities using the procedure of Wortmann *et al*. (4,5). The set S is the diameter of the rod (1 inch) divided by the diameter of the curl. The initial set S_0 is measured from the first image after removal of the hair from the rod. Recovery is described by $R = 1 - S = 1 - d_{\text{rod}}/d$.

DAMAGE ASSESSMENTS

Damage is assessed by several methods including mechanical and chemical assessments.

Tensile properties of the fibers are measured using the Diastron MTT-675 Fibers are clamped between brass ferules, which are used by the robot to handle the fiber. The fiber cross section is measured using a laser scanning micrometer (Mitutoyo LSM 6100. The fibers are extended to breaking and each force extension curve is analyzed to extract the elastic (Young's) modulus, the post-yield modulus and the break stress.

The complex shear modulus is determined using a torsional pendulum. An L = 3 cm length of fiber with a 5 g weight of moment M = 8.85119e-8 kg-m^2 is held in the automated pendulum. First the fiber dimensions are scanned using a Mitutoyo LSM6100, then the pendulum is wound 360° and released. The major and minor axes are a and b. The period of the pendulum's motion T is used to extract the shear modulus $G = 16\pi LM/T^2(a^3b + ab^3)$ The speed of the pendulum is measured by the time it takes for a white stripe on the weight to pass in front of a photodetector. On each oscillation, the pendulum slows and the ratio of the velocity on one cycle to the next is used to extract tanδ.

EXPERIMENTAL DESIGN

Bleached and Virgin hair prepared in each of three moisture conditions (wet, 65% and 20% RH) are curled for 15, 30, or 60 seconds on the gradient iron. All temperatures between 100°C and 225°C were tested. From these tresses, single fibers were selected for damage assessment.

RESULTS

The temperature gradient curling iron was used to collect efficacy data for bleached and virgin hair over a wide range of conditions. We see the overall effects and the range in

Figure 2 where recovery is plotted as a function of time after 60 second treatments for a variety of initial conditions and temperatures. A few trends are immediately obvious. First, every curve shows the same qualitative behavior - an initial rapid relaxation followed by a very slow, stable phase in which curl can hold essentially all day. Initial water content is a critical factor, especially for bleached hair. But for treatments above 180°C initial conditions matter less. Also, irons are far more effective at lower temperatures on wet than dry hair and there is very little temperature dependence for wet heating in either bleached or unbleached hair.

Turning in Figure 3 to a more detailed look at the initial set, we see that heating is detrimental for bleach-damaged hair. For the dry hair, or any hair, higher temperatures provide little improvement in initial set. Above 200°C, there is no benefit and in some cases the added heat actually produces worse results.

Duration of hold is the one quantity that consistently improves with increasing temperature (Figure 4). This effect is clear and also large, producing factors of two difference in hold time between 200°C and 100°C as hold times vary from fractions of an hour to nearly two hours.

The final hold (Figure 5) shows the most compelling result on efficacy. There is little temperature dependence. Again wet, bleached hair is an exception. But even in this case, heating to just 150°C seems sufficient. Heating above 200°C seems counterproductive.

We also investigated the effects of treatment time on efficacy, but found little of note and do not display these data here.

Turning to the measurement of damage we detect this damage from a single treatment. In other papers on hair damage it is common to perform multiple cycles of damage representing the accumulated effects over time (1–3,6). Extensional stiffening coupled with a drop in break stress is observed for bleached hair, but not for virgin hair. The loss of plasticity seen through the decrease in log-decrement in Figure 6 is a sign that bound

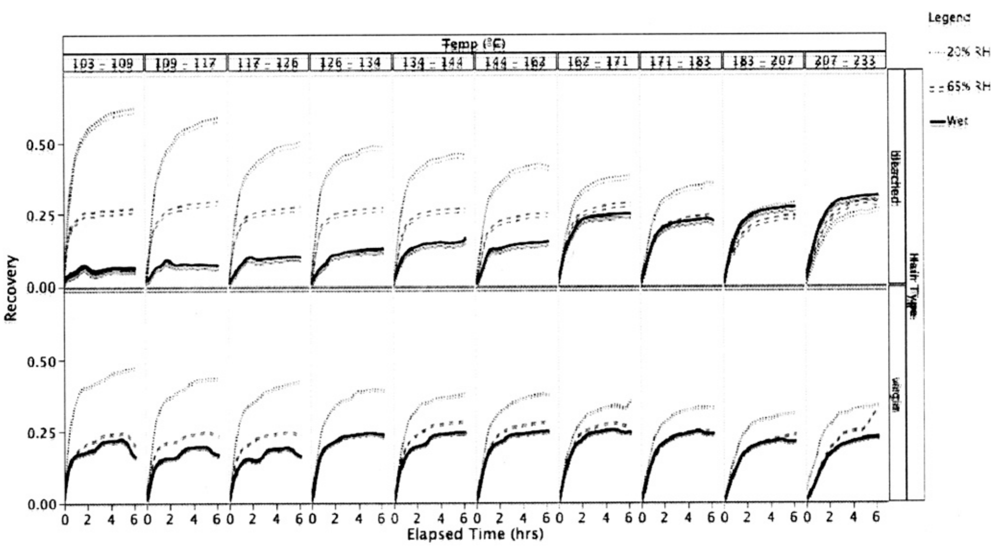

Figure 2. Efficacy results showing recovery vs. time for many combinations of temperature and initial moisture for bleached and virgin hair.

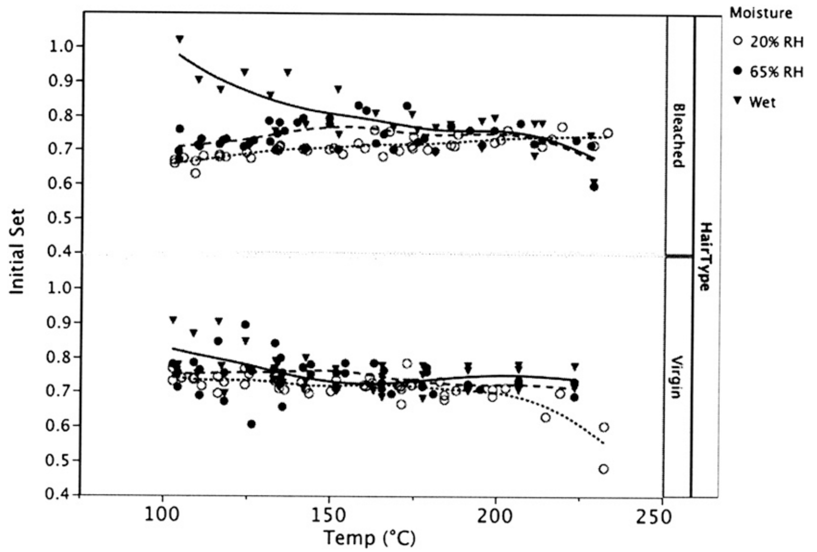

Figure 3. Efficacy: Initial set vs. temperature (1 - perfect set; 0 - no set).

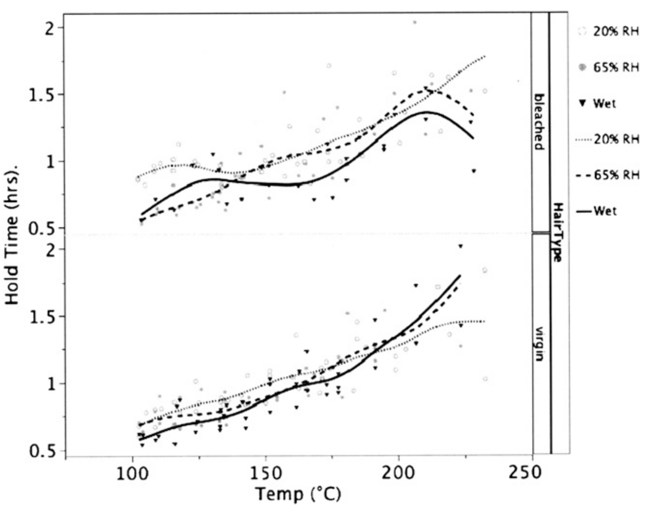

Figure 4. Efficacy: Duration of initial hold vs. temperature.

water plays a larger role in bleached than virgin hair. Looking simply at extensional properties, we see stiffening with heat for bleached hair (Figure 7) as well as a steady decrease in break stress with heat (Figure 8). All these results show that the oxidative damage makes the fiber less resilient to heat treatments.

One can also monitor chemical effects, in particular we have tracked changes in surface chemistry through contact angle measurement (7). We plot the cosine of the contact angle, which is negative for hydrophobic surfaces and positive for hydrophilic ones. We see the loss of resiliency for oxidatively damaged hair in Figure 9. But with or without prior

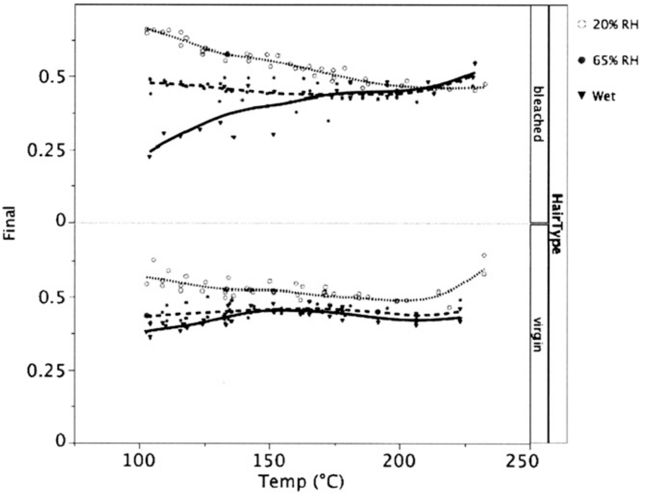

Figure 5. Efficacy: Final recovery vs. temperature (0 - perfect hold; 1 - no remaining hold).

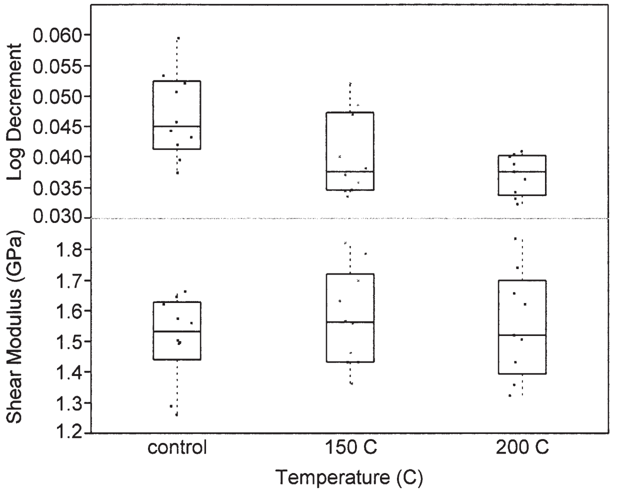

Figure 6. Torsional changes from heat damage (bleached hair, 60 sec. treatment).

damage, this is suggestive of damage to the hydrophobic 18-MEA coating on the fiber surface after exposure to high temperatures.

DISCUSSION AND CONCLUSION

The thermodynamics of water set have been well explained in terms of the glass transition and the process of aging (4,5,8–10). Water set is performed by shaping wet hair into the desired shape and holding it for some time after the water evaporates. We understand why this works by examining how the glass transition temperature depends on water in

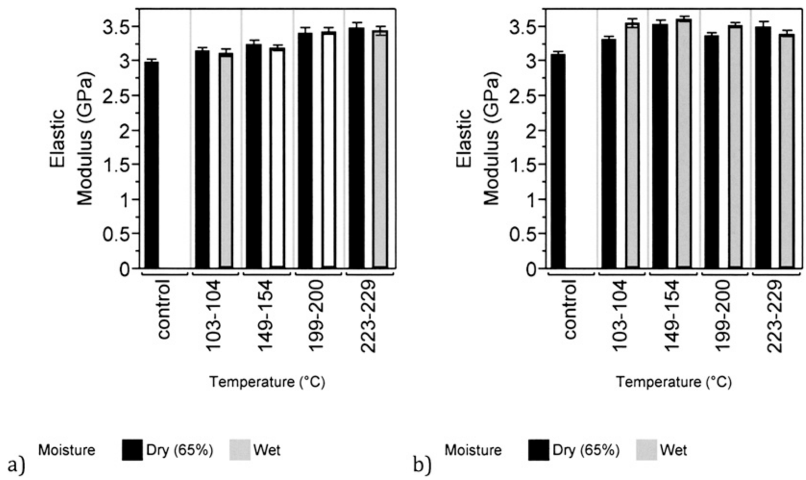

Figure 7. Elastic modulus after heat treatment. (a) Virgin. (b) Bleached.

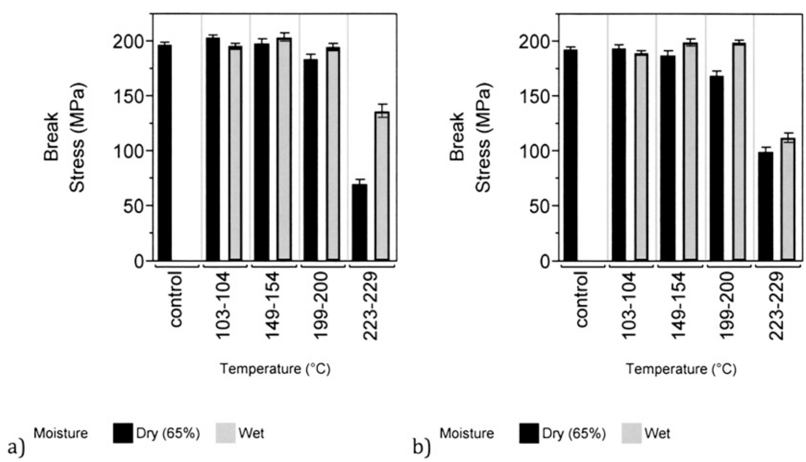

Figure 8. Break stress following heat treatment. (a) Virgin. (b) Bleached.

the hair. The T_g of keratin fibers has been well characterized using differential scanning calorimetry (11). When wet, the glass transition temperature is below 0°C, and so the fiber acts like a viscoelastic fluid. As the fiber dries, the transition temperature increases, passing through room temperature and slowly rising to 50° or even 100°C, depending on the relative humidity. As an aid to understanding this effect, we have replotted the results of reference (11) which expresses T_g vs. the amount of water in the hair as T_g vs. relative humidity, assuming the fiber has acquired an equilibrium amount of water at 24°C (Figure 10). To associate regain with relative humidity we use dynamic vapor sorption results taken on virgin hair in our laboratory, these agree quantitatively with classical values found in the literature (12).

The longer the hair is held after it quenches during drying, the slower its relaxation and the less it recovers. The dependence of curl retention on hold time is an example of the

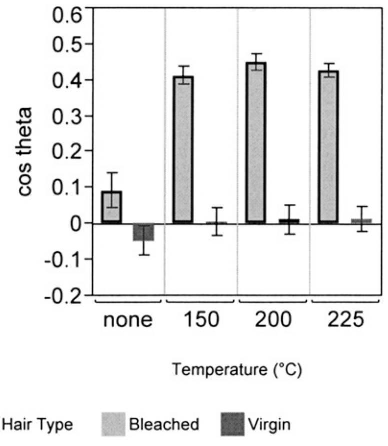

Figure 9. Contact angle following heat treatment.

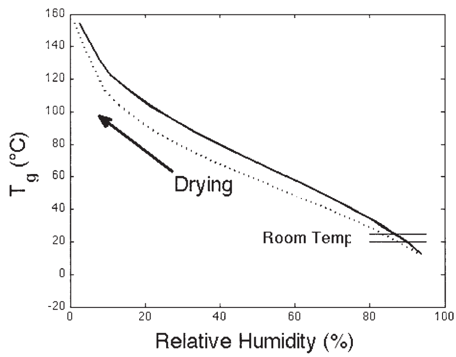

Figure 10. T_g vs. RH at 24°C.

phenomenon known as aging in the study of glassy systems (13). For heat styling, we know that considerable thermal work must be done to rapidly remove water and that the amount of this work is proportional to the amount of water in the fiber (14). In heat styling, the hair is driven towards T_g in two ways: by driving off the plasticizing water, raising T_g and by heating the hair towards the elevated T_g. Once the hair is removed from the iron, its temperature plunges, quenching the fiber. In this description, it matters not at all how long the hair is held far above the melting temperature. Rather it is the time spent near and below T_g under mechanical force that determines efficacy. The quenching process will proceed in almost the same way for any iron temperature far above 150°C.

Having understood that temperatures above 150°C play little role in improving performance, we now turn to the role of heat and water in producing damage. The evidence from a single cycle of heating in this work shows little damage from heating wet fibers. This should not be taken as an endorsement of the practice of heating wet fibers as considerable literature has shown this to be quite damaging after multiple treatments (1,6). The use of multiple rounds of treatment prior to testing for mechanical damage will be an important follow up to this report.

Chemically damaged hair, however, shows significant effects from a single heat treatments. And these effects are dramatic at temperatures above 200°C. At these temperatures there is further oxidation of the fibers, degradation of the 18-MEA layer, a loss of plasticity and a drop in break stress.

Generally accepted wisdom is that heat is damaging but also effective and allows for faster, more convenient styling. The results in this paper suggest that, for most hair, temperatures above 100°C do not provide greater benefits, but do produce greater damage. For chemically treated hair, in particular, there may be efficacy gains for going to 150°C, but not higher. The water present in the hair before treatment is important. As there is considerable evidence that rapidly heating wet fibers produces damage, the limited benefits gained from fibers beings preconditioned in water compared to equilibrating at 65%RH.

The window of opportunity for technologies to protect against relevant heat damage is also clear in examination of these data. As consumers choose to use irons at temperatures above 200°C there is a need for products that protect from these treatments.

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