Alignment control and softness creation in hair with glycylglycine

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Synopsis

Thick and coarse hair, as typically found among the Japanese population, frequently lacks softness that consumers are acutely aware of. Such poor feeling is accentuated by daily grooming, weathering, and chemical treatments, in particular, which can cause changes in the hair shape and the creation of frizzy or irregularly shaped hair. Existing technologies to improve the soft feel of hair, though effective, usually concentrate on the surface of the fiber and often leave the hair feeling either overconditioned or sometimes even sticky from product buildup.

Hair softness is said to be governed by a number of factors, but primarily hair diameter and surface condition. In this study, we have also identified hair alignment as playing a critical role in hair softness. In addition, by studying how Japanese women perceive hair softness when touching their hair, we have identified that the strain on the hair fiber associated with these manipulations is far smaller than previously considered. With these factors in mind, we have studied the mechanisms behind a new softening technology containing gly-cylglycine (GG). It has been found that treatment with GG can give a tangible feeling of hair softness by dramatically improving alignment in unruly hair and by lowering the modulus of the fiber. Moreover, using the atomic force microscope, it has been revealed that the properties of the cell membrane complex of the hair cortex may be modified after GG treatment; the role of this additive in modifying the internal properties of the hair to create softness will thus be discussed.

INTRODUCTION

Little information has been published about the softness of human hair fibers. Instead, research has focused on a close cousin to the human hair fiber: wool. Stevens (1) defines softness purely as (i) having a smooth surface or fine texture and (ii) yielding to pressure or easily deformed. Both of these characteristics may equally apply to a bulk of fibers or

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to a single fiber. Using subjective assessments of wool softness, i.e., the feeling when touched with fingers, the softest wool was that which had the smallest diameter and lower degree of crimp (i.e., straighter). Most importantly, Stevens found that it was the unique combination of both diameter and crimp that determined softness. Independently, it has also been concluded that Merino wool is softer if it has a lower mean fiber diameter, a lower crimp frequency, or a combination of both factors (2).

Yu and Liu (3) sampled and compared silk, wool, and alpaca in terms of equivalent bending modulus and rigidity, along with fiber diameter and fiber friction coefficient. Although alpaca fibers have an intermediate value of equivalent bending modulus, a high rigidity, and a large diameter, the soft feel of these fibers was assigned to the low friction coefficient. Contrastingly, silk fiber has a high equivalent bending modulus and a friction coefficient similar to that for alpaca, but is very thin. This feature was thus responsible for the soft touch of silk when compared with wool, which has a mean diameter between those of silk and alpaca fibers, an equivalent bending modulus close to, but slightly lower than, that of alpaca fiber, an intermediate rigidity, and a high fiber friction coefficient, which significantly worsens handling.

The most significant work on human hair fibers, in terms of softness, was reported by Wortmann and Schwan-Jonczyk (4). By investigating the diameter and cross-sectional geometry of hair from selected tresses, the sensory feeling of those tresses, and the physical attributes of the fibers, such as bending properties and friction, this work arrived at some key conclusions relating to handling of human hair. Lower diameters and higher ellipticities were considered to play dominant effects on fiber handle because these properties give low bending stiffness. It was suggested that friction played a much lower part for thin fibers but was important for thicker and stiffer hair.

Stress relaxation is a technique most commonly used to measure the way in which viscoelastic materials relieve stress under a constant strain. Human hair and other keratin fibers show viscoelastic properties (5,6), rendering stress relaxation measurements applicable to these bodies. The origin of hair's viscoelastic behavior lies in the fact that the hydrogen bonds within the fiber are easily broken by stretching or bending, whereas the disulfide bonds of hair remain unbroken (7). In the case of hair setting, a hair fiber is forced into a desired shape, and due to the continuous breaking and building of hydrogen bond cross-links (arising from the abundant CO- and NH- groups present in neighboring chains), the internal stresses in the molecular assembly are relieved, leading to the lowering of the tension within the hair fiber. Thus, some level of setting is achieved, such that the remaining deformation (set) is strongly determined by the amount of relaxation. As described by Zuidema et al. (7), the higher the relaxation, the better a curl can be maintained. In the literature, however, little information is available that connects physical property changes with particular regions of the hair. Feughelman and Irani (8) specify that the internal stresses during setting of wool fibers in the so-called Hookean region (described as <2% strain) are mainly carried by the undamaged microfibrils, with no unfolding of the α -helices. On release of the applied stress, the fiber tends to return to its native length. The authors also state that the setting of fibers in this region is more difficult than at higher strains. In their earlier work on the stress relaxation of wool fibers, however, Feughelman et al. (9) also described a change in behavior of wool fibers at strains of <1% such that wool behaves as a linear viscoelastic body and relaxation rate becomes independent of strain. It becomes evident, therefore, that the regions of keratin fibers that undergo stress relaxation differ at different strain levels.

In this study, we have investigated the effect of fiber alignment on the perception of human hair softness, together with a study of the role of a new softening agent, glycylglycine (GG), and attempted to connect consumer perception with tangible measurements of fiber properties. Stress relaxation, assessment of hair initial elastic modulus, and atomic force microscope (AFM) force measurements have been performed to evaluate the changes in hair fibers after treatment with GG.

EXPERIMENTAL

HAIR SAMPLES

In this study, hair samples for the physical measurements were obtained from a tress of heavily damaged (by bleaching) curly hair provided by a Japanese female volunteer, aged 32 years. For perception tests, hair samples were obtained from a virgin straight tress, collected from a Japanese female volunteer, aged 35 years, and a virgin naturally curly tress, collected from a Japanese female volunteer, aged 32 years. All hair samples were initially around 30 cm in length. For AFM force measurements on hair cross sections, 15-mm length samples from both the roots of the naturally curly Japanese hair fibers and the tips of the damaged curly Japanese hair fibers were then selected.

For the model damage experiment to show the effect that damage has on the alignment and shape of an otherwise healthy hair bundle, a virgin straight hair tress (approximately 8 g) was subjected to a chemical treatment comprising of permanent waving, followed by 15 cycles of shampooing, conditioning, and blow drying. The tress was then bleached and followed by another 15 cycles of shampooing, conditioning, and blow drying. The bleaching and washing process was repeated five times, in total. The permanent waving treatment was carried out using a commercially available permanent wave/straightening product containing approximately 4.7% thioglycolic acid (liquid 1) and approximately 8.7% sodium bromate (liquid 2). Liquid 1 was applied for 10 min at room temperature, in a ratio of 1:2 (hair/bath). After rinsing for 30 s under warm running tap water, liquid 2 was applied to the tress for 10 min at room temperature, also in the ratio 1:2 (hair/ bath). The tress was then shampooed, using a plain shampoo formulation, for 30 s, before rinsing for 30 s under warm running tap water. The tress was then blow dried. The bleaching treatment was also carried out using a commercially available product, containing approximately 1.3% ammonia, 1.0% monoethanolamine, and 3.4% hydrogen peroxide. The processing conditions were 30 min and 30°C, at a hair/bath ratio of 1:1. After processing, the tress was rinsed under warm running tap water for 30 s, shampooed for 15 s, rinsed and shampooed again, and then rinsed for 15 s and blow dried. The washing cycle applied between each treatment consisted of shampooing, with the plain formulation, for 30 s, followed by the application of a simple conditioner for 30 s, and then rinsing under warm running tap water for 30 s. Finally, the tress was blow dried.

TREATMENT CONDITIONS

The treatments used throughout this study are given in Table I. The level of GG used for these experiments was 2%. Prepared solutions were equilibrated at 40°C in a water bath

	Compositio	on/wt (%)					
Ingredient	Control formulation	GG formulation					
Lactic acid	4	4					
Benzyl alcohol	1	1					
GG	0	2					
Deionized water pH	Balance To 3.7	Balance To 3.7					

Table I Treatment Compositions

for several hours before use. All samples were individually tagged with small pieces of electrical insulation tape and numbered with waterproof marker pen before being treated by placing the samples of each set (untreated control, control treatment, GG treatment; N = 10 per set) in a shallow glass dish and covering with 20 ml of the relevant solution. After treatment for 30 min at 40°C, the samples were rinsed with deionized water for 30 s and air dried at 20°C/20% RH for at least 36 h.

Before the perception evaluation, the tress was treated by immersion in an excess of the GG treatment for 30 min at 40°C, rinsed with deionized water for 30 s, and then air dried at $20^{\circ}C/20\%$ RH for at least 36 h.

SOFTNESS PERCEPTION EVALUATIONS

Fifteen experienced researchers were chosen as panelists for evaluating the softness of six tresses containing samples of the virgin straight and naturally curly Japanese hair. Mean curl radii of both types of hair were estimated by measurements on 100 randomly drawn fibers from each initial tress. Curl radius was measured by placing the hair on a template of accurately drawn concentric circles of known radii. The straight hair showed a mean curl radius of 56.6 ± 22.0 mm, whereas for the curly hair the mean radius was 21.7 ± 17.9 mm, a statistically meaningful difference at the 99% confidence level (as determined by the Student's *t*-test).

For the perception test, the curly hair content of each tress was 0%, 2%, 5%, 10%, and 20%, by weight. A second tress containing 20% curly hair, by weight, was prepared and treated with an excess of the GG treatment as described earlier. Each tress weighed 5 g. The panelists were blindfolded and were asked to handle each tress and arrange in order in terms of softness. The order provided by each panelist was recorded and converted into a six-point scale, according to the frequency with which each tress was positioned. Each panelist was individually interviewed and asked to describe how they felt softness when touching their hair. Their comments were recorded, and then frequently occurring key points were extracted.

EVALUATION OF THE STRESS REQUIRED TO STRAIGHTEN UNRULY HAIR

The maximum load required to straighten an unruly tress during typical finger combing and teasing motions, such as would be performed by consumers when assessing the state of their hair, was estimated. Several small unruly tresses, consisting of 150 hair fibers each, collected from the virgin curly tress of a Japanese female, were attached to a force meter and the maximum loads achieved during finger combing and bunching of the tresses were measured; these loads corresponded to the points where the tresses were just straightened and aligned. The maximum loads achieved were then converted to approximate values of load per fiber.

STRESS RELAXATION MEASUREMENTS

Stress relaxation measurements were carried out on a KES-G1-SH tensile tester (Kato Tech Co. Ltd., Kyoto, Japan) in the stress relaxation mode. Damaged curly hair samples of 60 mm in length were taken from the tip part and set individually in the removable clips of the instrument to give a test length of 50 mm. The test apparatus consisted of a 1000-ml glass beaker lined with two overlapping 150-mm-diameter filter papers (Whatman International Ltd., Maidstone, England). These papers were thoroughly wetted with deionized water dispensed from a squeezy bottle 30 min before the experiment was started. Deionized water (200 ml) was then maintained in the beaker at all times to ensure that the filter papers remained damp and to maintain a relative humidity of above 95% within the beaker. A two-piece lid was fabricated from thin plastic sheet so as to form a tight fit around the arms of the tensile tester when in place. The beaker was raised around the sample area and the lid was carefully placed so as to form a tight fit around the arms of the tensile tester, but without touching the moving sample arm. This arrangement kept the mounted fiber centered in the beaker. The relative humidity conditions within the beaker apparatus were monitored with a Testo 635 handheld digital temperature and humidity probe (Testo AG, Lenzkirch, Germany).

After an equilibration time of 5 min, a slight strain (typically <5% of the final extended load) was applied to remove the crimp and straighten the sample. This equilibration time was also observed after the fibers were treated with the relevant solutions. A strain of 0.5% was then applied to the sample at a rate of 0.01 mm s⁻¹, and the stress relaxation was measured over a 20-min period. Data were collected via a personal computer and exported as a comma separated values (.csv) file that could be opened by any common spreadsheet and graphing software.

Due to the small extensions used in these experiments, it was possible to test each sample before and after treatment, thereby lowering uncertainty and minimizing the sample numbers. It also negated the need to measure the fiber diameters because the same fiber could be followed throughout. It was assumed that the swelling of the fiber due to the treatment was negligible.

ASSESSMENT OF INITIAL MODULUS

To obtain the initial modulus of hair in the low strain regions, stress versus strain measurements were carried out on a KES-G1-SH tensile tester (Kato Tech. Ltd., Kyoto, Japan) in the stress–strain mode. Measurements were performed on 50-mm-long hair under 20% relative humidity conditions, using a strain of 0.25% and a strain rate of 0.01 mm s⁻¹. The same fibers were tested before and after treatment for consistency. Data were exported in the .csv format for analysis in spreadsheet and graphing software.

NANOINDENTATION AND FORCE MAPPING BY AFM

Untreated virgin root, untreated damaged curly, control treatment-treated damaged curly, and GG treatment-treated damaged curly hair were set in parallel, at approximately 1-mm spacing from each other, in a mold and embedded in Epon 812 resin. Five samples of each type were embedded. After curing, the blocks were removed from the mold, trimmed, and cut with a diamond knife to reveal mirror-finish cross sections of the hair.

The parameters used for these measurements are given in Table II. The instruments used were Nanoscope V and Dimension 3100 (both Veeco Instruments Ltd., Santa Barbara, CA). Areas exhibiting components of the hair fiber of interest [exocuticle, endocuticle, bulk cortex, and cortex cell membrane complex (CMC)] were selected, and measurements were performed on $4 \times 4 \,\mu$ m regions (at 64×64 pixels). The number of fiber samples tested was between three and five and, typically, around 20 force curves were obtained for each fiber component (>300 in the case of the bulk cortex). Values of the reduced Young's modulus were then calculated using a simulation (10) adapted from the Hertz Model. All AFM measurements were performed under approximately constant conditions of 24° C and 50% RH.

RESULTS AND DISCUSSION

EFFECT OF DAMAGE ON ALIGNMENT AND SOFTNESS PERCEPTION

The generation of unruly and irregular hair samples through common hair treatments is shown in Figure 1; an otherwise healthy tress (Figure 1A) subjected to the model damage process, consisting of a single perm treatment and bleached five times (with 15 shampooing and conditioning cycles after each step), becomes unruly, while individual hair fibers adopt an irregular form that causes visual misalignment of the bundle (Figure 1B). Although misalignment from such damage may, in some cases, be attributed to the altered surface properties of the hair (11), the fact that individual fibers adopt such irregular shapes must be related to some, as yet undetermined, internal changes. To elucidate how such irregular fibers and misaligned hair bundles can affect the perception of softness,

Table II AFM Experimental Parameters	
Parameter	Setting
Cantilever (TESP type), Spring constant, k	24.3 N m ⁻¹
Z-scan rate	1 Hz (600 nm s ⁻¹)
Ramp size	300 nm
Trigger deflection	10–15 nm



Figure 1. The generation of misaligned hair in an otherwise healthy tress by repeated damage treatments: (A) healthy Japanese tress and (B) same tress after $1 \times$ perm and $5 \times$ bleaching/shampooing/conditioning cycles.

naturally curly hair collected from a Japanese female were incorporated into straight tresses to various levels and each tress was assessed by blindfolded volunteers (Figure 2A). Clear changes in the alignment of the tresses can be observed as the level of unruly curly hair increases.

Figure 2B shows the results of the softness perception test; a clear trend in the rating for these tresses was observed, with the tress containing 20% unruly hair assessed as having the lowest softness. This result clearly shows the effect that even a small number of irregular hair can have on the overall perception of hair softness and also shows how important fiber alignment is to the feeling of softness. Figure 2B also includes the assessment of a tress containing 20% unruly hair (low softness feeling) after treatment with GG. The softness perception for this tress was much higher than that for the untreated 20% tress, with the treated tress being judged somewhat similar to the 5% unruly hair-containing tress. To support this assessment, a Kendall's coefficient of concordance test was performed (see the Appendix). Table III shows the rank order evaluations from each judge and the results of the coefficient of concordance test, as calculated from equations (1-3). A value of the coefficient of concordance, W, of 0.76 was obtained, which indicates good agreement between the judges. Using this value of W, and since both the number of judges, *p*, and the number of variables, *n*, were large (15 and 6, respectively), a Friedman distribution factor, χ^2 , of 57.0 was calculated [equation (3)]; at (n-1) degrees of freedom, it was thus established that this result was statistically significant (p < 0.001). Close observation of the treated tress in Figure 2A also showed that the hair bundle was visually well aligned and had fewer hairs projecting from the bunch, further indicating that the fiber



Figure 2. (A) Tresses, made from straight tresses with additions of varying levels of unruly hair, used for softness evaluation, and (B) softness evaluation results for these tresses.

shape was indeed adjusted by the GG treatment. Curl radii measurements were again implemented, this time for the treated hair, and a mean curl radius of 33.3 ± 23.8 mm was determined. This value was intermediate between the values of 56.6 ± 22.0 and 21.7 ± 17.9 mm measured for the curl radii of straight and curly hair, respectively. The difference in curl radius between the curly hair and GG-treated curly hair was found to be statistically meaningful at the 99% confidence level (as determined by the Student's *t*-test), again an indication of the straightening effect of the treatment.

To deepen the understanding of the mechanism behind the improvement in alignment and softness brought about by GG treatment, physical measurements on individual hair fibers were carried out. In this regard, it was considered important to connect the perception of softness experienced by consumers to a realistic stress range for measurement. The first step in doing this was to ask the panelists to describe how they felt softness when touching their hair, in an open answer format. Analysis of their responses identified "smoothness during touching or finger combing" as dominant, with "ease of combing/ less snagging during combing" and "less bounce or stress when I hold or bend" judged equally in second place. These answers, therefore, highlighted alignment and the flexibility of the hair fiber itself as important factors, respectively, and indicated that consumers are aware of such points. To estimate the load required to just straighten and align unruly and curly tresses, a force meter was used to monitor the loads experienced by such tresses during typical finger combing and bunching actions. This arrangement is shown in Figure 3. A range of values between 0.3 and 5 g per fiber were recorded. In correlation with simple stress-strain measurements on single hair fibers under high (>95%) humidity conditions, carried out in preliminary experiments (data not shown), this upper load limit of 5 g was found to correspond to strains of <0.5%, a value that was estimated to be

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Judge	Unruly hair content of tress (by weight)							
	Straight (0%)	2%	5%	10%	20%	20% + GG		
A	1	2	5	4	6	3		
В	1	2	3	5	6	4		
С	1	2	3	4	6	5		
D	2	1	3	5	6	4		
E	1	2	3	5	6	4		
F	1	4	2	6	5	3		
G	1	3	4	5	6	2		
Н	1	2	3	6	5	4		
Ι	1	3	4	5	6	2		
J	2	1	3	5	6	4		
K	1	2	5	4	6	3		
L	1	3	2	6	4	5		
М	2	1	3	6	4	5		
Ν	2	1	5	4	6	3		
R_i	21	30	50	75	84	55		
\overline{R}	52.5							
S	3009.5							
W	0.76							
χ^2	57.0							

 Table III

 Rank Responses and Statistical Results for Control Tresses in Perception Tests

below the Hookean region and approaching the toe-in region. The subsequent measurements of hair physical properties were, therefore, limited to within this range to reflect the real loads experienced by hair fibers during everyday consumer manipulation and to study the perceived effects of GG under such conditions.

STRESS RELAXATION MEASUREMENTS

A typical grooming procedure in which the application of the GG treatment might be used is given in Figure 4. Misaligned and disordered hair (Step 1) are washed and the treatment is applied (Step 2), after which a slight stress is applied to the damp hair (Step 3) to align the bunch (Step 4). The magnitude of this stress directly correlates with the final alignment of the hair bundle; the meniscus force arising between fibers in the wet state is enough to attain a certain degree of alignment (11), although in this study, it has been observed that combing will give greater alignment, in addition to any detangling effect. It is preferable that the hair will maintain this alignment to some degree; typically, however, the hair will tend to revert to their original state on drying (Step 5), with any improvement in alignment coming from residual water set. Thus, to realize an



Figure 3. Force meter (A) used to evaluate load per fiber when hair is gently pulled into alignment (B).

agent's effectiveness, this irregular nature should be resisted and the aligned state stabilized, in a form more closely resembling Step 4. In this study, the effect of GG during the procedure outlined in Figure 4 would thus appear to increase the stability of the alignment from the wet state to the dry state and to greatly reduce the incidence of irregularly shaped hair visibly "breaking away" from the bundle. To model this behavior, stress relaxation measurements on single hair fibers under high humidity conditions were used. Using the upper limit of 0.5% strain, the relaxation characteristics of untreated, control treatment-treated, and GG-treated hair fibers were studied. Figure 5 shows a stresstransient plot of the averaged relaxation data (N = 10) collected for curly damaged Japanese hair fibers at high (>95%) relative humidity and normalized against the initial values of stress. The greater relaxation after treatment with the control treatment and,



Figure 4. Typical grooming procedure in which the application of a GG treatment might be used.



Figure 5. Normalized stress-transient plots under high humidity for curly damaged Japanese hair after various treatments. Solid line, untreated hair; dashed line, hair treated with control treatment; dotted line, GG-treated hair. Each plot is the average of the data of 10 fibers.

more so, after the GG treatment is evident. So, as described by Zuidema *et al.* (7), this would indicate the higher setting ability of these two technologies. If the relaxation rate is constant at strains of <1%, as described by Feughelman *et al.* (9), then the effect of the control treatment and the GG treatment on the initial relaxation, from T = 0 to T = 2 min, is also apparent. In the case of the control treatment, the most likely explanation for this effect is due to the breakage of ionic bonds in hair caused by the low pH value of 3.7 of the formulation. Although the GG treatment also has a pH of 3.7, clearly the presence of GG further increases the efficacy of this formulation. The further significance of the result for GG is that the increased relaxation rate means less time is needed for it to be effective and thus this fits within a realistic timeframe for a typical grooming procedure. Combined with the increased relaxation brought about by GG overall, the effectiveness of this agent in setting the hair is evident.

EVALUATION OF INITIAL ELASTIC MODULUS

Consumers typically determine the softness of their hair under ambient conditions, as well as during the treatment phase when the hair is damp, and the pliability of the hair fiber itself was also identified as important to the perception of softness, from the panelists responses previously described. With regard to the typical grooming procedure outlined in Figure 4, it was thus considered whether GG could also affect the pliability of individual hair fibers in addition to its effect on alignment. Stress–strain measurements over the initial 0.25% (the initial strain was reduced from 0.5% to overcome the effect of the shift in the stress–strain relationship for hair on moving from high to low humidity) were performed under 20% humidity conditions and the change in modulus before and after treatment was used as an indicator of the pliability change of each fiber. Figure 6 shows the change in modulus over this low strain region for untreated control, control treatment–treated, and GG-treated hair fibers, expressed as a relative modulus value. Although the moduli of the untreated and control fibers did not change with treatment, those fibers treated with GG showed a 20% decrease in modulus, indicating the increased pliability of these fibers at 20% relative humidity.



Figure 6. Relative initial modulus results for curly damaged Japanese hair after various treatments, under dry (20%) relative humidity conditions (N = 5).

NANOINDENTATION AND FORCE MAPPING BY AFM

After treatment with GG, the changes in physical property of hair indicated that some modification of the hair components had taken place. To investigate this further, and attempt to elucidate which subcomponent(s) of hair may be affected by GG, AFM force measurements were used. In Figure 7A, a force map of an untreated hair section, taken from the root, shows the cortex CMC as dark lines among the lighter cortex cells. This contrast between the CMC and cortex cells is lost, however, in images of the highly damaged tip region of curly damaged hair (Figure 7B). After treatment with GG, similar regions of the hair again show strong contrast between the CMC region and the cortex cells (Figure 7C). The control treatment did not show any significant effect (data not shown). Nanoindentation measurements performed on the cortex CMC confirmed that the modulus of the cortex CMC was higher in the damaged tip but had recovered and was indeed softer than that of the undamaged root, as shown in Figure 7D.



Figure 7. Young's modulus maps of hair cross sections after various treatments, (A–C), and comparison of Young's modulus for the cortex CMC region of each cross section (D).

In summary, it has been shown that GG can have a significant effect on the properties of hair, improving alignment and the flexibility of the fiber. AFM nanoindentation measurements have indicated that the cortex CMC may be involved in this process, although the possibility that some other region of the hair also contributes cannot be discounted. Two important physical property changes after treatment with GG were shown in this article; the first was an increase in stress relaxation in the very low strain region under the very high (>95%, almost wet) relative humidity condition, and the other was a decrease in the modulus in the very low strain region in the dry (20% relative humidity) condition. In the Hookean region, stress mainly comes from stretching of hydrogen bonds but in the region of very low strain, before the Hookean region, the deformation by the strain may occur not in keratin but in amorphous parts, such as the CMC or intermacrofibrillar materials. This would be consistent with our findings that GG affects the cortex CMC.

The precise nature of this action is not known, but it may be hypothesized that GG is capable of forming many hydrogen bonds with hair proteins through its anionic carboxyl group, amino group, and also centrally located amid group. It is our contention that, on drying, GG resides in the same areas previously occupied by water, forming hydrogen bonds with hair proteins. In the case of the anionic carboxyl group, particularly, such bonding may be considered stronger than either hair protein-water or hair protein-hair protein bonds, as has been suggested for the action of organic acids containing multiple carboxyl groups in hair (12). Even under high humidity, the strong and stable hydrogen bonds of an anionic carboxyl group are not easily replaced by water, and then hair-set durability against humidity is improved (12). In wet conditions, however, an abundance of water molecules allows the exchange of hydrogen bonds between the carboxyl group and hair proteins as well as between hair proteins themselves; such exchange is a cause of stress relaxation. According to the data presented in this study, concerning the stress relaxation measurement in the almost wet condition, the stress relaxation increases more for treated hair. This means that further interactions exist between the ingredients included in the treated solution, in particular GG, and hair proteins. In water-abundant conditions, the links remaining after hydrogen bond exchange are chemical bonds, hydrophobic interactions, van der Waals interactions, and the hydrogen bonds of protein-protein sites that are inaccessible to water molecules. The GG molecule also has an amide group, and hence, it can interact with proteins. It seems very possible that GG in the test formulation interacts with protein segments in hydrophobic regions protected from water molecules. In the cortex CMC, this would most likely be within the centrally located proteinaccous δ -layer itself. These interactions diminish protein-protein interactions, and GG acts as a plasticizer. This could be the reason of the stress relaxation decrease by GG under the almost wet condition. Similarly, the plasticization of the water inaccessible areas may be responsible for the modulus decrease of the low strain region in the dry state. In total, it is felt that the specific distribution of these chemical functionalities, combined with the small size of the molecule, provide GG with a uniquely high capability for modifying the physical properties of hair. The multifunctional nature of GG is another unique feature of this agent; such actions have not previously been described for this, or any other, molecule.

CONCLUSIONS

This study has clarified the contribution of hair fiber alignment to the perception of softness. Furthermore, the low strain (<0.5%) region has been identified as being important for consumers awareness of hair softness. Stress relaxation measurements at slight strains

have been used to show the potential that active agents have for achieving and stabilizing hair alignment.

GG has been shown to improve hair alignment and increase the pliability of the hair, thereby creating hair softness. For the first time, the cortex CMC has been directly implicated as a contributor to hair properties in the low strain region and as a target for the plasticizing action of GG. It is proposed that the stabilization of the hair alignment occurs through hydrogen bonding between GG and proteins of the hair. On drying, GG also improves the pliability of individual fibers. The results of this study clearly show the benefits of utilizing GG as an additive for hair care products and the properties imparted by this additive indicate a total caring effect from the wet to dry states of hair. That these effects are so readily perceivable also highlights the sensitivity of the human sense of touch to small changes in fiber properties.

APPENDIX

KENDALL'S COEFFICIENT OF CONCORDANCE

Kendall's coefficient of concordance, W, is a useful measure of the degree of agreement among a number of judges (p) assessing a given set of n variables, i (13). The value of Wvaries between 0 and 1, where 0 indicates no agreement and 1 indicates unanimous agreement. The coefficient of concordance may be calculated by (14)

$$W = \frac{12S}{p^2(n^3 - n)},$$
 (1)

where S is the sum of the squared deviations, according to

$$S = \sum_{i=1}^{n} \left(R_i - \overline{R} \right)^2, \tag{2}$$

where R_i is the sum of each rank and \overline{R} is the mean of the R_i values. From W, it is possible to obtain a value for Friedman's χ^2 distribution statistic (15) via

$$\chi^2 = p(n-1)W. \tag{3}$$

If the number of judges, p, and the number of variables, n, are above 15 and 4, respectively, Friedman's χ^2 is asymptotically distributed like χ^2 with (n - 1) degrees of freedom (13) and the significance level can be obtained from p tables (16), based on this approximation.

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