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Model-based analysis of the torsional loss modulus in human hair and of the effects of cosmetic processing

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Synopsis

Torsional analysis of single human hairs is especially suited to determine the properties of the cuticle and its changes through cosmetic processing. The two primary parameters, which are obtained by free torsional oscillation using the torsional pendulum method, are storage (G') and loss modulus (G''). Based on previous work on G', the current investigation focuses on G''. The results show an increase of G'' with a drop of G' and *vice versa*, as is expected for a viscoelastic material well below its glass transition. The overall power of G'' to discriminate between samples is quite low. This is attributed to the systematic decrease of the parameter values with increasing fiber diameter, with a pronounced correlation between G'' and G'. Analyzing this effect on the basis of a core/shell model for the cortex/cuticle structure of hair by nonlinear regression leads to estimates for the loss moduli of cortex (G''_{co}) and cuticle (G''_{cu}). Although the values for G''_{co} turn out to be physically not plausible, due to limitations of the applied model, those for G''_{cu} are considered as generally realistic against relevant literature values. Significant differences between the loss moduli of the cuticle for the different samples provide insight into changes of the torsional energy loss due to the cosmetic processes and products, contributing toward a consistent view of torsional energy storage and loss, namely, in the cuticle of hair.

INTRODUCTION

The behavior of human hair under torsional stresses and strains is an important contributing factor for the formation and maintenance of a hair style (1). Because of the nature of torsional deformation, the results for a fiber are biased toward contributions from its outer regions (2). For human hair, the method is thus especially suited to investigate the properties of the cuticle. In a recent publication (3), we presented a set of data from investigations on untreated and cosmetically treated human hair fibers using the torsional pendulum technique. For that investigation, we concentrated on considerations of the storage modulus G', which is derived from the frequency of the free torsional oscillation. A basic core/shell model of cortex and cuticle was applied to model the observed decrease

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of G' with fiber diameter or rather polar moment of inertia. This analysis enabled to obtain estimates for the torsional storage moduli of cuticle and cortex through nonlinear curve fitting and extrapolation. The results of the analysis supported the hypothesis that the torsional storage modulus of the cuticle is significantly higher than that of the cortex. Though the absolute value for the modulus of the cortex was too low compared to literature values, plausible changes of cuticle and cortex moduli were determined after cosmetic treatments.

This part of the investigation now is focused on the logarithmic decrement Λ, as a measure of energy loss in the fiber and as one of the primary variables from a torsional pendulum experiment. The loss modulus G'', as primary physical variable, is determined indirectly from the logarithmic decrement Λ and the torsional storage modulus G' for an individual measurement. G' is proportional to the energy stored and G'' to the energy lost during a torsional oscillation. The objective is to investigate whether the structure-based, basic core/shell model approach for G' (3) is also applicable for G''. This includes estimates of the loss moduli of cuticle and cortex as well as the effects of cosmetic treatments. The potential as well as the specific limitations of the approach are discussed.

MATERIALS AND METHODS

THEORETICAL BACKGROUND

Free torsional oscillation, *e.g.*, of a fiber in a torsional pendulum apparatus (2,4,5), yields the complex torsional modulus $G*$ as:

$$G* = G' + iG'' \tag{1}$$

where G' and G'' are the storage and loss modulus, respectively.

G' is given by:

$$G' = 4\pi^2 \frac{J\,l}{I\,T^2} \tag{2}$$

where J is the moment of inertia of the pendulum, l the length of the fiber, I the polar moment of inertia of the fiber, and T the time taken for one oscillation.

The cross-section of a hair fiber is generally assumed to be best described as elliptical so that the polar moment of inertia is given by:

$$I = (\pi/4)\,(a^3b + b^3a) \tag{3}$$

where a and b are the semiaxes of the ellipse.

The use of the polar rather than the torsional moment of inertia (6) assumes the limiting case that no warping of the test specimen occurs (7), which is plausible for small deformations and low resonance frequencies (8), as realized in this study. The situation is certainly different for combinations of high tensile and torsional strains (9). The approach was furthermore chosen to provide better comparability of data with previous investigations

(4,10,11) including those, which are based on the assumption of circular hair cross-sections (1,12,13).

Arithmetic means for oscillation time T were determined from five successive oscillations. G' values were determined from the mean oscillation times for fivefold measurements for a given fiber.

From the continuous decrease of the torsional amplitude due to damping, the logarithmic decrement Λ is determined through the following equation:

$$\Lambda = \frac{1}{n}\sum_{i=1}^{n} \ln \frac{A_i}{A_{i+1}} \tag{4}$$

where A_i and A_{i+1} are the amplitudes of successive oscillations and n is the number of oscillation from which the value for Λ is calculated. For the current investigation, $n = 5$ generally applies. Values are based on fivefold determinations for a given fiber.

For low degrees of damping, the connection between logarithmic decrement Λ and the torsional phase angle δ as $\tan\delta$ is given by the following equation:

$$\Lambda = \pi \tan\delta \tag{5}$$

With the loss factor:

$$\tan\delta = G''/G' \tag{6}$$

this yields:

$$\Lambda = \pi\, G''/G' \tag{7}$$

so that

$$G'' = \Lambda\, G'/\pi \tag{8}$$

Equation (8) enables to determine the value for G'' from the related values of G' and Λ for a given experiment.

In view of the fact that hair is not an uniformly isotropic, viscoelastic material, as may in principle be required, a core/shell model is suggested, which enables to estimate the separate contributions of cortex and cuticle to G'', in analogy to G' (3) as follows:

$$G'' = (G''_{\mathrm{co}}\, I_{\mathrm{co}} + G''_{\mathrm{cu}}\, I_{\mathrm{cu}})/I \tag{9}$$

with

$$I = I_{\mathrm{co}} + I_{\mathrm{cu}} \tag{10}$$

where subscripts co and cu relate to co̲rtex and cu̲ticle, respectively.

In accordance with the experimental evidence for the material used, the cuticle is treated for each fiber as a hollow, elliptical shaft with a constant wall thickness of 3 µm. This relates to about six layers of cuticle in the cross-section, which are assumed to be constant along fiber length and independent of fiber diameter.

Equation (9) was fitted to the G'' data using the established nonlinear regression method (3). This approach accounts for a certain fraction of the variance of the data and also yields estimates for the torsional loss moduli of cortex and cuticle together with their 95% confidence limits. The justification of this model-based approach, the applicability of which is considered as independent of the actual scatter of the data, is, namely, based on the observation that the torsional storage modulus of hair fibers drops significantly after the removal of the cuticle (10). Further considerations are given elsewhere (3).

EXPERIMENTAL

All experiments on hair fibers were conducted on a Single Fiber Torsion Pendulum apparatus (TRI Princeton, Princeton, NJ) as described by Persaud and Kamath (4). Effective hair fiber length was 3 cm, frequency about 0.1 Hz, and environmental conditions 22°C and 22% relative humidity. All tests and treatments were conducted on dark brown, commercial, Caucasian hair (International Hair Importers & Products Inc., Glendale, NY). For each fiber tested, the smallest and largest diameters were determined at five equidistant points and through 360° (Laser Scan Micrometer, LSM-500, Mitutoyo, Kanagawa, Japan). Hair tresses were taken from a collective of virgin hair (V) and subjected to a permanent waving treatment (7% thioglycolic acid, pH 9.5, 30 min) followed by reoxidation (2.2% H_2O_2, pH 4). This was followed by bleaching (8% H_2O_2, pH 9.4, 30 min). The perm-waved and bleached sample is referred to as WB. A group of fibers already prepared for torsional testing was furthermore treated with a commercial "repair" shampoo (30 min and 30 s rinse). The sample is referred to as WBS. For further, specific details the reader is referred to Wortmann *et al.* (3). Data analysis and nonlinear curve fits were conducted using Statistica (Version 13, Dell, Tulsa, OK) and SPSS (Version 20, IBM, Armonk, NY). Homogeneity or in-homogeneity of data sets was determined by analysis of variance (ANOVA) and nonconservative, *post hoc* least significant difference (LSD) tests, as implemented in the statistics programs.

RESULTS AND DISCUSSION

BASIC OBSERVATIONS

One of the primary experimental variables obtained from the free torsional oscillation test and in particular from the continuous decrease of the oscillation amplitude is the logarithmic decrement Λ [see equation (4)], as a measure of damping within the viscoelastic hair fiber. Figure 1 summarizes the results for Λ for the three samples.

Logarithmic decrement values at the chosen conditions (22% relative humidity, 22°C) are low compared to literature values for wool (14) and hair (12) at 65% relative humidity. This is attributed to the humidity-dependent glass transition of wool (15) and hair (16), where low humidity shifts the properties of a keratinous material further into the glassy region. The values show satisfactory agreement, however, with the values for wool at 25% relative humidity and $T < 30°C$ of $\Lambda < 0.06$ (17). Also reasonable agreement is

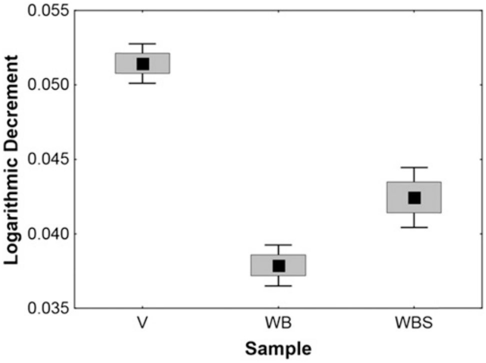

Figure 1. Summary of data for the logarithmic decrement Λ for the three samples. Data are given as means (■), standard errors (SE) (boxes), and limiting values for the 95% confidence range (1.96 × SE: whisker). Differences between all data sets are highly significant on the 95% level.

observed with the values for hair given by Persaud and Kamath (4) and Harper *et al.* (11) as well as from other sources on the basis of equation (5) (18–20).

Λ values drop after the waving and bleaching treatment compared to virgin hair, signifying a decrease of internal energy loss. Values increase again after the shampoo treatment. In line with the qualitative impression from Figure 1, ANOVA as well as LSD tests show that differences between all data sets are highly significant well beyond the 95% level. The results for logarithmic decrement thus show a high discriminative power for the cosmetic treatments.

G'' values are determined with equation (8) from the individually obtained values for Λ (see Figure 1) and G' (see Figure 2B) and are summarized in Figure 2A. G'' values are roughly by a factor 50–100 smaller than G', which is in agreement with observations by dynamic mechanical analysis (DMA) (19) and attributed to the general properties of hair as a glassy polymer well below its glass transition (16) under the conditions of the measurements. In line with expectations for such a material, G'' increases when G' decreases and *vice versa* (21).

Moving from the experimental variable Λ to the primary, physical variable G'', much of the discriminative power of the measurement of energy loss is lost. The insets in Figure 2A and B summarize the significance of the differences between the samples, as determined through the LSD test. Compared to G', the number of significant differences is smaller for G'', leaving only $V >$ WB as significant on the 95% level.

This difference of performance and loss of discriminative power are attributed to compensation effects between values for the storage and the loss modulus, respectively. Plotting G'' and Λ against G', as is done for the virgin sample in Figure 3, shows that the correlation between Λ and G' is only faint though significant ($r^2 = 0.08$), while it is quite pronounced for G'' ($r^2 = 0.69$). Similar observations were made for G'' versus G' for the WB ($r^2 = 0.74$) and the WBS sample ($r^2 = 0.77$), respectively.

Underlying the analysis for G'' above is the assumption that the data are essentially normally distributed. This assumption seems to be apparently correct, when inspecting the cumulative probability plots of the data, which all provide adequate straight lines.

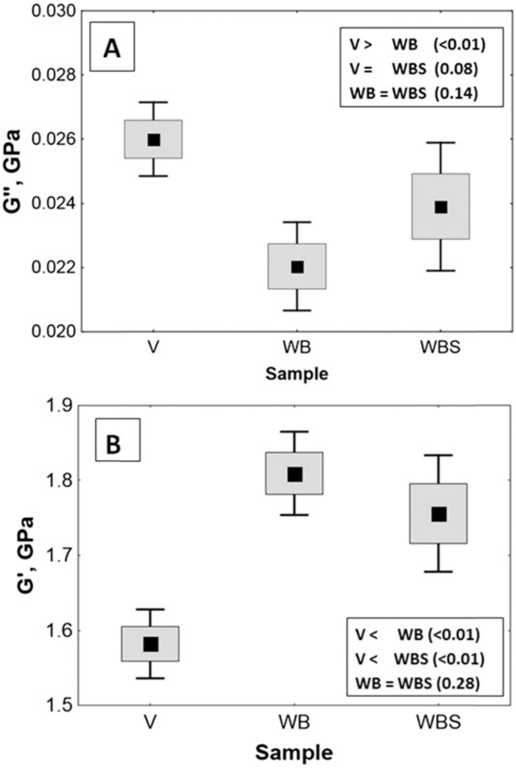

Figure 2. Summary of (A) G'' data and (B) G' data for all samples. Data are given as means (■), standard errors (SE) (boxes), and limiting values for the 95% confidence range (1.96 × SE: whisker). Insets give the results of least significant difference (LSD) multiple comparison of means tests with their levels of significance (p values). If $p < 0.05$, effects are significant on the 95% level.

APPLICATION OF THE CORE/SHELL MODEL

When plotting G'' against the moment of inertia for all samples, systematic decreases are observed (see Figure 4), similar as for G' (3,4). These observations are generally in line with data by Leray and Winsey (22) from torsional stress relaxation for both modulus and relaxation gradient. As for G', this highlights that G'' for hair is not a material constant. The decrease as such is in line with the core/shell model [equation (9)] and implies that the cuticle has a higher G'' value than the cortex, as related to the limiting values for G'' at low and high values of I, respectively.

The observation that G' and G'' values both decrease with increasing moment of inertia (3) implies that both storage and loss modulus are higher for the cuticle than for the cortex. For the current cases, the correlated changes of G'' and G', as shown in Figure 3, lead to the compensation effects for Λ, as mentioned earlier.

Equation (9) was fitted to the data applying nonlinear regression. The free optimization showed that the estimate for G''_{co} gave slightly negative values in all cases ($G''_{co} \geq -0.005$ GPa), which is physically not reasonable. For this reason, $G \geq 0$ was introduced as a boundary condition for the fit. Table I summarizes the results of the fits for G''_{co} and G''_{cu} together with the associated 95% confidence ranges and the coefficients of determination r^2. The solid lines through the data in Figure 4 are based on equation (9) and the parameter values in Table I.

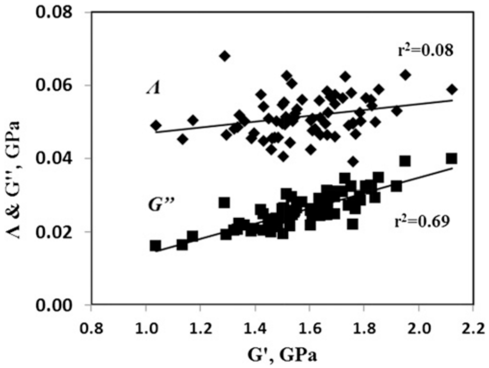

Figure 3. Plot of Λ data (◆) and G'' data (■) versus G' for virgin hair. Linear regression lines and the coefficients of determination r^2 are given.

Coefficients of determination for the fits of the core/shell model through equation (9) to the G'' data (see Table I) are substantial and comparable to those for G'. They may be used to reduce the unexplained variance of the data and thus to improve the discriminative power for G'', similarly as for G' (3). However, in the present case, this would need to be implemented with added caution in view of the boundary condition for the loss modulus of the cortex ($G''_{co} \geq 0$), which is expected to increase the risk of Type I errors, when identifying significant differences between samples.

The application of equation (9) is justified by the observation that the torsional moduli are not material constants of hair, but rather change with fiber diameter or rather moment of inertia (see Figure 4). This is attributed to differences of properties of cortex and cuticle in the core/shell structure of hair. The observed limitation of the model, as reflected by the r^2 values for the fit of equation (9), may be attributed to the fact that the torsional moduli of the cuticle are not true material constants. This may be related to the layered structure of the cuticle, which in practice is subject to damage (23,24), namely, by thermal stresses as, *e.g.*, reflected in delamination (25). Changes of structural integrity are expected to generate substantial and overriding contributions, namely, to frictional interactions within the cuticle layers, which will impact on G''. This may be considered as an explanation for the apparent lack of fit, namely, for the WB sample at low values of I (see Figure 4), that is for comparatively high-volume fractions of cuticle. Further complications are expected to arise from the limitations of the assumptions of constant cuticle thickness with fiber diameter as well as along fiber length, as well as the simplifications underlying equations (3) and (9) (7).

For all three samples, the boundary condition $G''_{co} \geq 0$ needed to be applied for the fits, where the necessity for this condition may be attributed to some extent to the required extrapolation to $I \rightarrow \infty$. Given this restriction, the upper 95% confidence limit for the loss modulus of the cortex in virgin hair is $G''_{co} = 0.005$ GPa. With the corresponding value of $G'_{co} = 0.61$ GPa (see Table I) this yields with equation (6) a maximum value of $\tan\delta_{co} = 0.008$. This value may be compared to $\tan\delta = 0.022$ of rhinoceros horn perpendicular to the growth direction under not too dissimilar conditions (110 Hz, 5.2% regain) (18). For this testing geometry, specifically the properties of the matrix, are determined, analogous to torsion. The comparison of the data shows that even the calculated maximum value for $\tan\delta_{co}$ is too low by a factor of about 3 using the extrapolation of the data in Figure 4. The

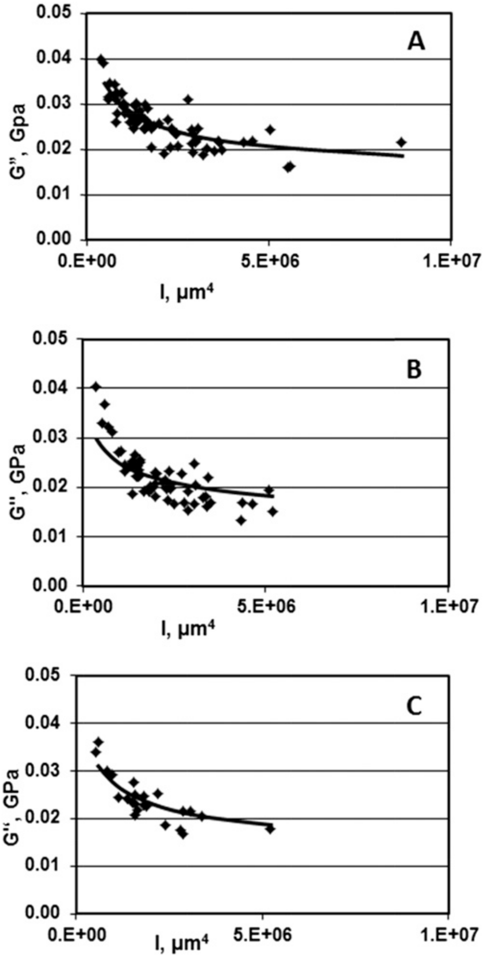

Figure 4. G'' versus polar moment of inertia for virgin (A:V), perm-waved and bleached (B: WB), and additionally shampoo-treated (C: WBS) hair. Solid lines are based on the fit of equation (9).

fits on the basis of the core/shell model thus turn out to not be suitable to estimate the torsional loss modulus of the cortex.

In contrast, tanδ – values for the cuticle with the applicable values for G''_{cu} and G'_{cu} (see Table I) yield a range of tanδ = 0.01–0.02, in acceptable agreement with expectation values for keratins for roughly comparable conditions (18–20,26–28). This gives some support for the overall validity of the estimated G''_{cu} values in the absence of reference values.

Because of the systematic decrease of G'' with I, the estimates for G''_{cu} are substantially higher than the G'' means, though they follow the same pattern for all samples. The overall behavior for G''_{cu} is as to be expected for a material below the glass transition, in that G''_{cu} decreases with an increase of G'_{cu} for a sample and *vice versa*.

The G'' value is reduced by a factor of about 2 compared to the virgin hair through the chemical processing of reduction and oxidation (WB), in line with considerations of increased stiffness and brittleness of the cuticle (3). Although the effect of the additional

Table I

Estimates for the Loss Moduli of Cortex (G''_{co}) and Cuticle (G''_{cu}) Together with their 95% Confidence Limits, as Obtained by Fits of Equation (9) to the Data in Figure 4

Sample	G''_{co}, GPa	G''_{cu}, GPa	r^2	G'_{co}, GPa	G'_{cu}, GPa
V (69)	0 ± 0.005	0.08 ± 0.01	0.722	0.61	3.60
WB (56)	0 ± 0.004	0.046 ± 0.004	0.600	0.40	4.84
WBS (23)	0 ± 0.009	0.11 ± 0.08	0.733	0.37	4.63

The number of measurements for each sample is given in brackets. r^2 are the coefficients of determination for the fits. Furthermore, values for the storage moduli for cortex (G'_{co}) and cuticle (G'_{cu}) are given (3) to aid the discussion.

"repair" treatment (WBS-sample) is small for G'_{cu}, the corresponding value of G''_{cu} increases well beyond the value for virgin hair. This not only indicates that the "repair" agent improves the overall structural integrity of the cuticle but also introduces through its components, possibly, namely, through the polymer content a strong viscous component, which contributes to the increase of G''_{cu}.

CONCLUSIONS

Using the values for the storage modulus, G' and the logarithmic decrement Λ as parameters obtained from the free torsional oscillation experiment on hair the values for the loss moduli G'' were determined. The raw data show a rather low discriminative power between the different samples, despite their rather strong chemical pretreatment. This can be attributed to a strong component of variance due to the systematic decrease of G'' with fiber moment of inertia. This decrease is associated with a decrease of the area fraction of the cuticle in the fiber cross-section, when the fibers get thicker. The effect is accounted for by a core/shell model for the cortex/cuticle structure of hair, yielding satisfactory coefficients of determinations. These model fits may be used, with due caution with respect to Type I errors, to improve the discriminative power for G'' measurements, when investigating hair samples with different processing histories. The more speculative aspects of the investigation relate to the determination of the loss moduli for cortex and cuticle. While the determination of G''_{co} proved to be unsuccessful, values for G''_{cu} show overall consistency. The distinct and plausible differences between the loss moduli for the cuticle for the samples support previous suggestions (3) that torsional measurements in the appropriate model context are a very sensitive tool to assess changes of the properties of the hair cuticle through cosmetic processes and ingredients, in line with expectations by Robbins (13). In conclusion and in agreement with Bogaty's (1) considerations, it is suggested that imparting the appropriate balance of torsional storage and loss moduli in hair by cosmetic processes and products will make a major contribution to their ability to control the dynamic movement of a hair style in line with consumer expectations.

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