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Fatigue Strength of Panelist Hair and Correlation With Hair Damage Measures

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Synopsis

The objective of this work was to investigate fatigue strength differences between root and tip hair for 41 Caucasian and 12 Asian panelists and correlate fatigue strength data to other measures of hair damage. In most cases both fatigue α- and β-values significantly decreased at tips, indicating a higher likelihood of fiber breakage and premature failure as hair became more damaged. This decrease in tip fatigue strength correlated positively with panelist coloring frequency for Caucasian panelists. In addition, a correlation was found between fatigue cycles to break (α-value) and oxidative damage ($R^2 = 0.73$), as measured by Fourier Transform Infrared Spectroscopy, and with cuticle integrity as measured by a scanning electron microscopy damage score ($R^2 = 0.77$). An increase in oxidative and cuticle damage correlated with a lower α-value (i.e., lower cycles to break). The fatigue α-values were also compared with internal lipid levels including fatty acids, cholesterols, and wax esters as measured by gas chromatography–mass spectrometry. For root hair, there was a reasonable correlation ($R^2 = 0.36$) between internal lipid levels and fatigue strength, but no correlation was seen for tip hair. For Asian panelists, a decrease in fatigue strength was also found with increasing oxidative damage, especially for those using powder bleaches. Both panelist groups had high person-to-person variability and no clear difference between Caucasian and Asian panelists.

INTRODUCTION

Hair strength and breakage is a critical area of research for the cosmetics industry because consumers regard "strong hair" as a desirable attribute. Hair strength assessments include the number of broken fibers shown when brushing and in the bathroom and broken hairs/split ends still on their head. The cosmetics industry has developed multiple methods to measure hair strength: measuring the inherent mechanical properties of single fibers (1) and mimicking the combing/brushing process (2). The focus of this paper is on single-fiber fatigue mechanical properties and a comparison of fatigue strength measurements between different panelist samples and between root and tip.

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Tensile testing measures the mechanical behavior of extended hair by obtaining a stress/strain curve (where stress is defined as average force/unit area). This measure of fiber damage is well established and accepted in the cosmetic industry (3). Fatigue testing is a more recent addition to single-fiber testing that instead measures hair exposed to a repetitive force until failure occurs. Failure occurs due to the creation of flaws that propagate, ultimately fail, and lead to breakage. Evans has proposed that this method is relevant to a consumer where repeated stimuli received simulates repeated grooming (4). Data can be generated in two ways. The first is at constant load (i.e., stress will vary according to fiber diameter) to generate an S–N plot where stress is plotted against the log of number of cycles to failure. The second is at constant stress (i.e., load is altered according to fiber diameter) to generate a survival distribution where survival probability is plotted against cycles to failure. The survival data are fitted to a cumulative Weibull distribution (see Equation 1) where $f(x)$ is the probability of the fiber breaking in x cycles, α is the characteristic life at which 63.2% of fibers have broken, and β is the shape factor (i.e., the shape of the curve). The failure rate is constant when $\beta = 1$ and shows early life failures when $\beta < 1$.

$$f(x) = 1_{-e}^{-(x/\alpha)\beta} \tag{1}$$

As shown by Evans and Park (4), chemical damage from bleaching decreases fatigue cycles to break, likely due to flaws created during the coloring/bleaching process and/or the resistance of these flaws to propagate under fatigue conditions. This chemical damage can be due to changes in the protein matrix (e.g., disulfide bond breakage) or from changes in the cell membrane lipid structure (5).

In previous studies, hair fatigue breakage has been compared between samples created in a controlled lab environment; however, limited fatigue studies have measured panelist hair samples and no studies have compared root versus tip breakage. The objective of this work was to study fatigue breakage of panelist hair samples and to compare fatigue masurements with other relevant measures of hair damage.

EXPERIMENTAL

HAIR SOURCE

To allow for root and tip measurements, hair samples of ~500 fibers were cut a few mm from the scalp's of 41 Caucasian panelists (age 18–35) with hair >30 cm long. The samples were wrapped in aluminum foil and refrigerated for lipid analysis. The hair was equilibrated for 48 h at room temperature and 50% relative humidity before measurement. Hair samples were also taken from nine Asian panelists (age 18–40) with hair >30 cm. Both sets of panelists were asked about their habits and practices (wash frequency, color and bleach use, etc.).

FOURIER TRANSFORM INFRARED SPECTROSCOPY MEASUREMENTS

A Perkin Elmer Fourier transform infrared (FTIR) system equipped with a single-bounce diamond attenuated total internal reflection (ATR) accessory was used to measure the

cysteic acid level on the first few microns of the hair surface. Approximately 30–50 fibers per panelist were bundled and measured at different locations from root to tip. Each measurement was conducted with eight scans from 600–4,000 cm^{-1} and 4 cm^{-1} resolutions. Due to the specificity of cysteic acid peaks, ATR-FTIR has been used as an industrial method for assessing the level of chemical damage present on hair surface. In the conventional method (6), the second derivative of the cysteic acid peak at 1,040 cm^{-1} (normalized to the 1,450 cm^{-1} protein CH_2 stretch peak) was taken as the relative chemical damage on clean hair. Silicone is commonly used in most hair care products and can easily be deposited on human hair. The cysteic acid and silicone peaks appear at the same region (1,000–1,250 cm^{-1}) and may interfere with one another. Chemometric approaches are used to measure cysteic acid level in the presence of silicone.

The classical least square method was the first used to estimate silicone in hair, based on pure component spectrums that can be measured separately (i.e., silicone, hair keratin, and cysteic acid). Then the silicone value, together with hair spectrums (700–1,800 cm^{-1}) at different damage levels with corresponding mass spectrometry data (the range was normalized from 0 to 1), were used as a calibration data set to build a partial least square (PLS) model using PLS Toolbox 8.61 (Eigenvector Research Inc., Wenatche, WA, USA). The spectrum preprocessing and analysis was done in MATLAB 2018b environment. The root means square error cross validation of the PLS model for both cysteic acid and silicone are 0.0068 and 0.00134 with R^2 values of 0.99 and 0.97, respectively.

FATIGUE MEASUREMENTS

Fibers were cut for fatigue strength measurements from the root and tip end of the panelist samples (7–10 cm long) and crimped at 30 mm using a Dia-Stron Auto-Assembly System (AAS 1600) (Andover, Hampshire, UK). The average cross-sectional area along each fiber was analyzed using a Dia-Stron Fiber Dimensional Analysis System (FDAS 770), which incorporates a Mitutoyo laser micrometer (LSM-6200) (Malborough, MA, USA). The average cross-sectional area was calculated from three diameter measurement points along each 30 mm crimped fiber. The average cross-sectional values for each of the fibers were then used to set the Dia-Stron Cyclic Tester (CYC801) in controlled stress mode. Stress was 140 MPa with a speed 40 mm/s. Data were analyzed by Weibull statistical tools (JMP Pro 12.1.0, SAS Cary, NC). Fit with the Weibull distribution was confirmed for each data set. Fibers with break cycles less than 10 were omitted from the analysis due to premature breakage and were mostly between 2–4 fibers. Fifty fibers per sample were measured and all measurements were made at a relative humidity of 50% and temperature of 23°C.

CUTICLE MEASUREMENTS

For the Caucasian panelists, 25 fibers from either the hair mids or tips (less than 5 cm from the fiber distal end) were mounted for scanning electron microscopy (SEM) analysis. Each fiber was graded at 750× magnification according to the scale on a Hitachi S-3000N (Krefeld, Germany).

Low damage: cuticle aligned and spaced regularly but some irregularity or slight lifting of the cuticle is observed (up to ~15% lifting). Mid damage: cuticle is irregularly spaced due to missing cuticle edges, but all cuticle is present; tightly packed cuticle with lifted cuticle

edges. High damage: any cuticle missing up to 50% of fiber; significant cuticle chipping and partial removal of cuticles. Stripped: majority of fiber stripped (must be >50%).

Hair Damage Severity Scale (HDSS) was calculated from this assessment: HDSS = (1× low) + (3× medium) + (5× high) + (7× stripped)*(100/175).

LIPID MEASUREMENTS

For each sample of Caucasian panelist samples ~0.1 g of hair was cut into 20–40 mm segments and placed in vials (n = 4). First, the hair was extracted gently with hexane to remove the external cetyl and stearyl alcohol and lipids. The hexane extraction consists of extracting the hair with hexane two times then concentrating the dried residue in a second solvent and BSTFA derivatizing reagent for the gas chromatography. Next the internal cetyl and stearyl alcohol and readily extracted internal lipids were extracted using 2:1 then 1:1 chloroform–methanol. The chloroform contained 10 mM dimethylhexylamine (DMHA) and the methanol 1% formic acid. Each extraction was heated for 30 min at 65°C with the hair, then combined, and the dried residue derivatized with BSTFA + 1% TMCS. Cetyl and stearyl alcohol and internal lipids were quantified by gas chromatography (GC) with flame ionization detection using a polydimethylsiloxane capillary column with hydrogen mobile phase. Nonadecanoic acid and eicosanoic acid were used as internal standards. For the sebum, an artificial sebum formula was used containing a mixture of fatty acid, squalene, cholesterol, waxes, and triglycerides.

RESULTS

CAUCASIAN PANELIST RESULTS

The Caucasian panelist hair samples were all between 30 and 45 cm long and were either straight or very slightly wavy (curl pattern I or II according to the L'Oreal curl scale) (7). A 10 cm section was cut at the root and tip end for a total of 50 fibers for fatigue testing. Figure 1 shows the α-value for each panelist's root and tip samples calculated from the survivial probability after confirming the data fit a Weibull distribution. This α-value is the number of cycles for 63.2% of fibers to break and was found to highly correlate with median cycles to break (0.96 correlation for root and 0.88 for tip across all the samples). The data show high variability between samples, especially for root samples with a maximum α-value for panelist 2,078 of 36,228 cycles and a minimum α-value for panelist 2,147 of 1,726 cycles. The root samples were exposed to some coloring and physical damage but this does not explain this wide variability. Although not studied in this work, protein content or other factors can also impact this difference; however, this work does show a correlation of α-value with internal lipids. The average root α-value across all panelists was 6,276 versus 4,536 for tips, showing an overall decrease in fatigue strength as hair became damaged. About 30% of panelists showed a decrease in fatigue of more than 3,000 which was driven in part by oxidative treatments (i.e., hair coloring). About 40% of panelists showed a minor increase or decrease in α-value.

Figure 2 shows each panelist's β-value for root to tip. A decrease in β-value was measured for 80% of panelists and the average dropped from 1.03 to 0.748. The β-value describes the shape of the Weibull distribution and a lower number indicated increased premature

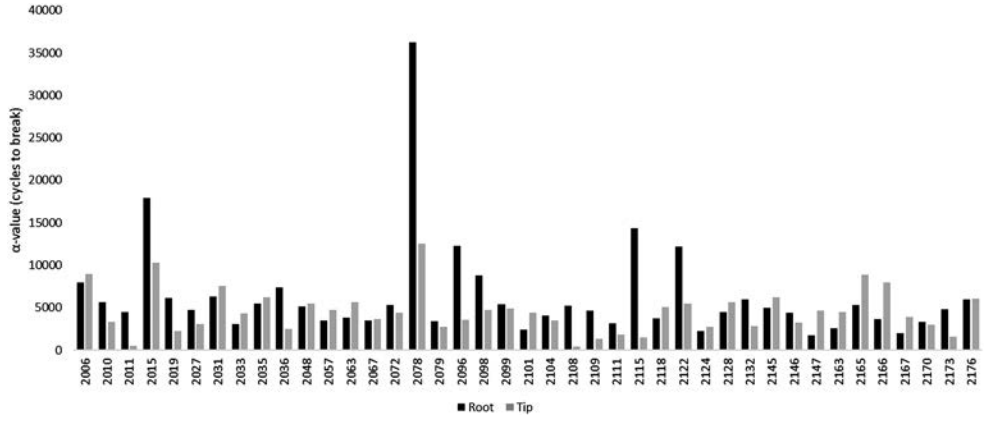

Figure 1. Root and tip α-values for 41 panelists.

failure (i.e., more fibers are breaking after just a few fatigue cycles). This may indicate that as hair grows there are increasing numbers of fibers containing significant flaws that rapidly propagate and lead to fiber breakage. Data shows that both α- and β-values decrease from root to tip, indicating increased chance of breakage as hair grows longer and increased chance of premature breakage. An alternative way to show this data is to calculate the likelihood of failure after a given number of cycles from the Weibull distribution (Equation 1). Figure 3 shows the percentage chance of a fiber breaking at 500 cycles. This percentage is almost double at tips, 20.6% broken fibers after 500 cycles at tips versus 11.5% at roots.

Panelists were asked several questions related to their habits and practices (e.g., use of shampoo, conditioner, and leave-on treatments, frequency of washing, use of heated implements, and chemical treatments). Specifically, the panelists were asked when they last colored their hair. No correlation of fatigue values was found with product use, wash frequency, or use of heated tools at either roots or tips.

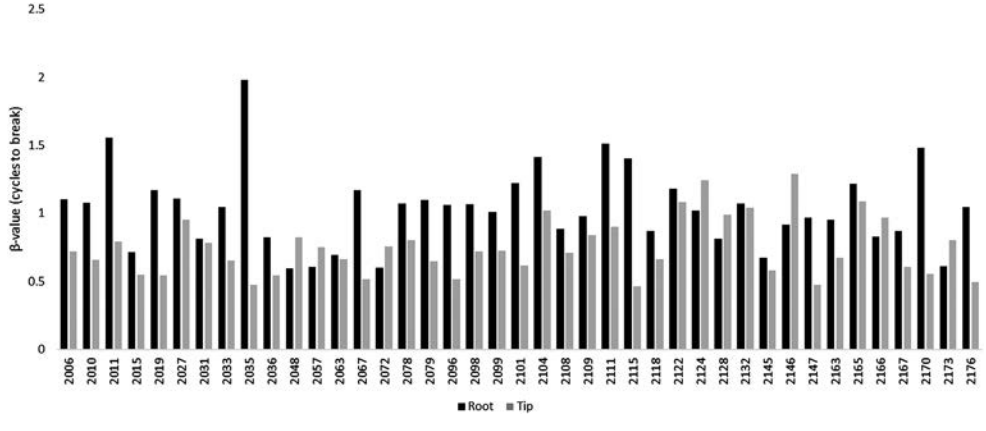

Figure 2. Root and tip β-values for 41 panelists.

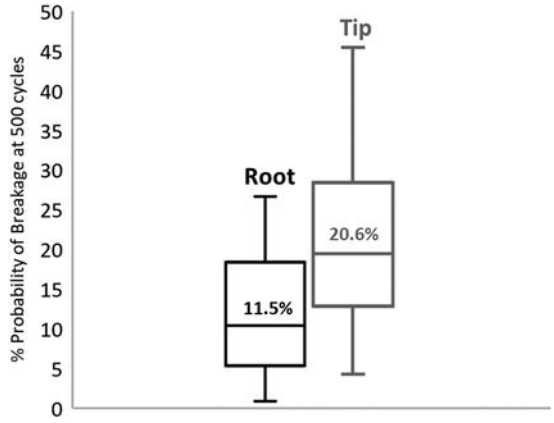

Figure 3. Percent probability of breakage at 500 cycles.

Some correlation was observed regarding coloring frequency but variability in individual α-values meant variability between groups was large. To reduce variability, α-values for each panelist response were averaged, indicating that time since last color does correlate with fatigue breakage (Figure 4). Panelists were asked "time since last color," but if we assume that this can be translated into coloring frequency (i.e., longer time since last color equals a lower color frequency), these data indicate that a higher color frequency will increase fatigue breakage at tips. In addition, the decrease in breakage from root versus tip is also higher for colorers (40% for past 4-week colorers versus 10% for noncolorers). This fits with anecdotal information from consumers (i.e., those who color more frequently also claim that hair breakage is an issue for them).

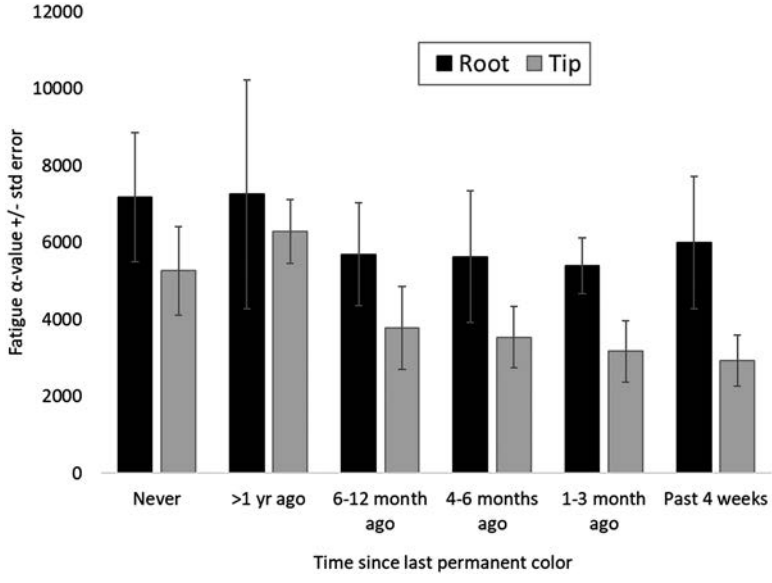

Figure 4. Fatigue α-value versus time since last color.

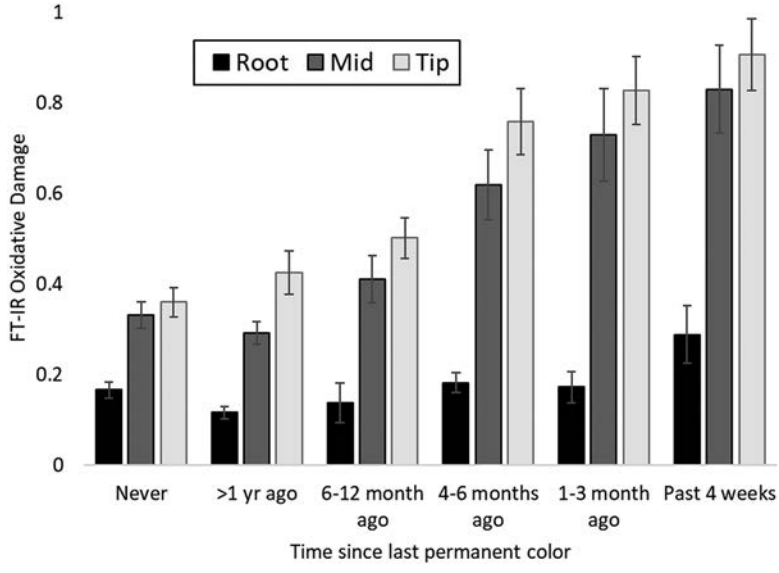

Figure 5. Cysteic acid FTIR value versus time since last color.

Two other measures of damage were performed on the same 41 panelists: cysteic acid measurement using FTIR and cuticle integrity using a SEM damage scale. Cysteic acid is an industry method that has been shown to correlate with oxidation from colorants and bleaches (8). It is a nondestructive method that quantifies formation of cysteic acid via the S–O stretch at 1,040 cm^{-1}. This study measured every 5 cm down the hair from root to tip. As expected, panelists who claimed to have never used hair color showed only a slight increase in cysteic acid (~10%, likely due to UV oxidation). Panelists who had colored in the last year or more frequently showed a much higher level of increase. Average cysteic acid values increase for mid and tip hair as time since last color decreases (Figure 5). This supports for our assumption that time since last color can be corelated with frequency of coloring. No difference is seen for root hair other than an increase for the group who colored in the last 3 mo. All other groups had noncolored regrowth at their roots and showed a low FTIR score. We did not see a linear increase in FTIR score from root to tip and the mid value was consistently only about 10–20% lower than the tip value. This may be due to not all-over coloring habits or, more likely, due to cuticle removal via brushing/combing. The FTIR method only measures surface cysteic acid (penetration depth 2–5 μm) and overall cysteic acid decreases or flattens as cuticle with high-cysteic acid is physically removed.

Cuticle damage was assessed via SEM grading where 25 fibers at mids and tips were graded on a four-point scale. Low damage: cuticle aligned and spaced regularly but some irregularity or slight lifting of the cuticle is observed (up to ~15% lifting). Mid damage: cuticle is irregularly spaced due to missing cuticle edges, but all cuticle is present; is tightly packed with lifted cuticle edges. High damage: any cuticle missing up to 50% of fiber; significant cuticle chipping and partial removal of cuticles. Stripped: majority of fiber stripped (must be >50%). HDSS was calculated from this grading to calculate a single number: HDSS = (1× low) + (3× medium) + (5× high) + (7× stripped)*(100/175). Figure 6 shows example images of each grade. Cuticle damage was minimal at mids but increased significantly at tip (Figure 7). The increase was notably higher as time between

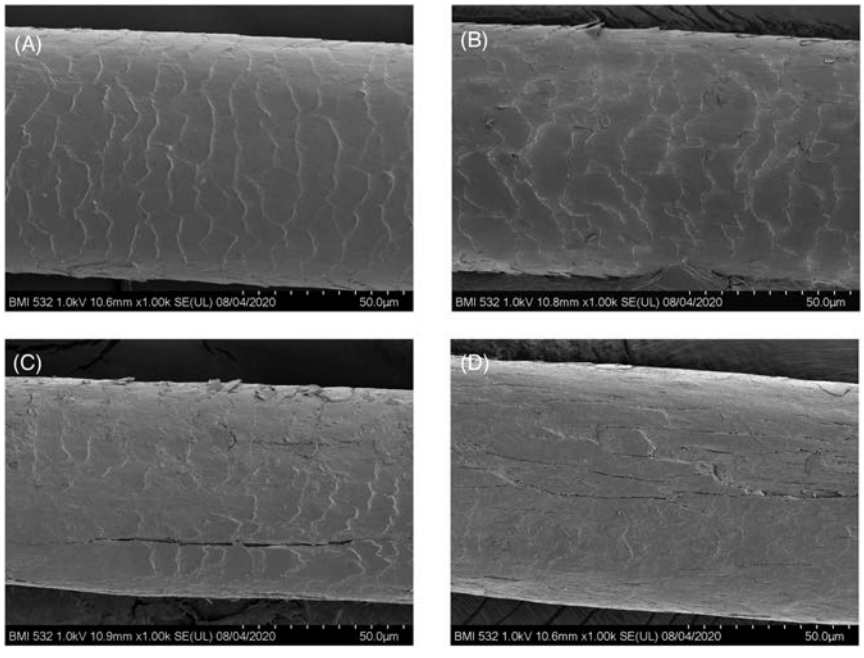

Figure 6. Example images for SEM grading scale. (A) Low damage, (B) medium damage, (C) high damage, (D) stripped.

color decreased (i.e., as color frequency increased cuticle damage also increased). Cuticle removal increases as consumers color more frequently because oxidative damage increases and more disulfide bonds and other protein bonds are broken. Hair subjected to extensive oxidative damage has also been previously shown to have higher propensity for physical damage (9).

These two well-established damage measures were then correlated with fatigue breakage data (Figure 8) for tips. SEM grading was not performed at roots and FTIR showed a very

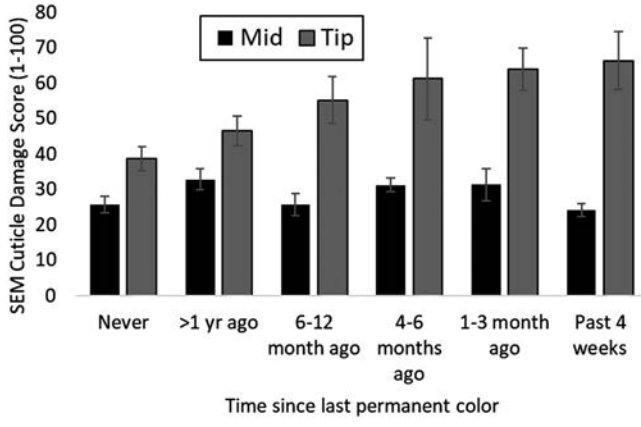

Figure 7. SEM cuticle damage score versus time since last color.

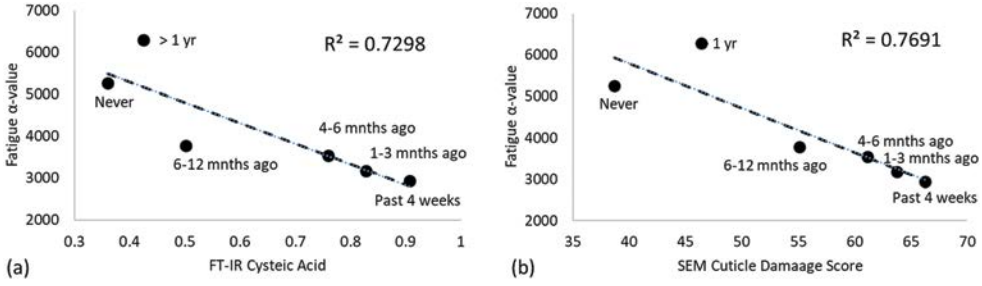

Figure 8. Correlation of fatigue α-value with (A) FTIR cysteic acid and (B) SEM cuticle grading score.

weak correlation at roots. However, using the mean scores for each coloring time point,, a good correlation for tips is seen between fatigue α-value and FTIR score ($R^2 = 0.73$) and cuticle SEM damage score ($R^2 = 0.77$). The FTIR score at tips also strongly correlated with cuticle SEM damage score ($R^2 = 0.91$). This correlation implies oxidative damage also weakens hair to fatigue breakage in panelist hair samples, as seen in lab created tresses (2).

The panelist variability in fatigue breakage at roots did not strongly correlate with oxidative damage and this is likely related to differences in hair structure. Cuticle damage was minimal in the first 6–8 cm of growth and oxidative damage was relatively low even for panelists who color regularly. Previously published data show that internal lipids can influence fatigue strength and hair can be strengthening via the addition of lipid materials (e.g., cetyl and stearyl alcohol) (3). Camacho-Bragado proposed a technical model where failures in the lipid-rich cell membrane complex structure play a key role in breakage of curly hair (10). In this study, internal lipid levels and composition were quantified using a differential extraction method. First, hair samples were cut into 5 cm lengths from root to tip and then extracted with hexane to remove surface lipids. A second extraction was then performed with chloroform–methanol to remove internal lipids and this extract was then analyzed by gas chromatography. As expected, most lipids extracted were fatty alcohols (~80%) along with cholesterols, wax esters, and squalene from sebum (11). A reasonable correlation in internal fatty acid levels with fatigue breakage at roots was observed with $R^2 = 0.36$ (Figure 9) supporting the hypothesis that lipid levels are important for fatigue breakage. Lipid levels do not explain all the root hair fatigue breakage, indicating that

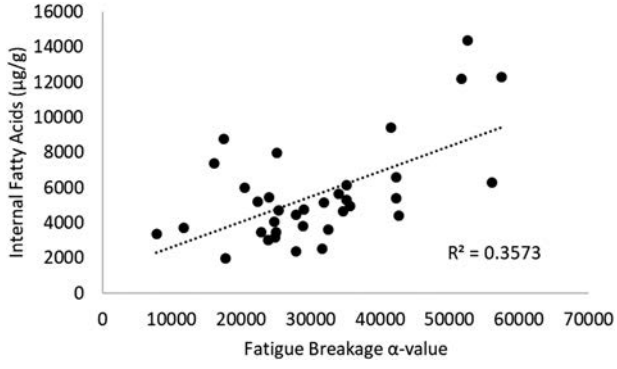

Figure 9. Correlation of internal fatty acid levels versus fatigue α-value.

Table I
Panelist FTIR and Fatigue Values Root and Tip

Panelist number	Coloring habits	Perming habits	FTIR cysteic acid		Fatigue α-value (63.2% cycles to break)		Fatigue β-value	
			Root	Tip	Root	Tip	Root	Tip
S71	Uncolored	No	0.15	0.26	3,783	3,381	2.68	0.71
S78	Uncolored	No	0.15	0.19	7,050	5,909	1.43	1.46
S79	Uncolored	No	0.19	0.20	4,432	16,867	1.66	1.39
S52	Level 3 Colorant	Yes	0.19	0.24	9,111	5,835	0.61	0.81
S35	Level 3 Colorant	Yes	0.43	0.67	12,694	11,201	1.93	0.62
S73	Level 3 Colorant	No	0.35	0.57	8,846	25,616	1.83	0.67
S07	Powder Bleach	No	0.21	1.03	2,173	773	1.92	0.81
S09	Powder Bleach	No	0.80	0.78	5,490	16,266	2.07	0.83
S25	Powder Bleach	No	0.17	1.19	2,929	798	1.73	1.45
S100	Powder Bleach	Yes	1.27	1.29	403	150	0.72	0.84
S107	Powder Bleach	No	1.27	1.19	512	1,067	0.65	0.63
S112	Powder Bleach	No	1.34	1.35	1,025	420	0.86	0.60

protein differences may also be contributors. More work is required to confirm this hypothesis. No correlation is seen for lipid levels at tips, likely due to additional damage that contributed to fatigue breakage.

ASIAN PANELIST RESULTS

The Asian panelist's hair samples were all between 30 and 45 cm long and all very straight. Table I shows the cysteic acid and fatigue resuts for root and tip hair as well as the coloring/bleaching and perming details. In general, there were similarities between the Asian and Caucasian panelists. As oxidative damage increased, either by coloring or powder bleaching, fatigue cycles to break decreased, especially panelists using powder bleaches. The oxidative damage was much higher for a powder bleach as compared to the oxidant in a Level 3 permanent colorant and, with the exception of panelist S09, the α-values were 1,000 or less at tips. S09 had a relativly high α-value although she had a powder bleach and she also had a much higher α-value at tip than at the roots. This was also seen in S73 and S79, but there was nothing obvious in the given habits and practices information that would explain this. Additional fatigue fibers were run to ensure this difference was significant and not a sampling issue. As with the Caucasian panelists, the α- and β-values mostly decreased from root to tip, meaning the probability of breakage and chance of premature failure of fibers increased at tips. The wide variation of α- and β-values was also similar.

CONCLUSION

Breakage is a concern for many consumers, especially those with long hair. In this study, analysis of panelist hair indicated that regular use of permanent coloring or powder bleaching products can lead to increased breakage, as measured using a fatigue protocol where hair was subjected to repeated low-level stress. Fatigue breakage was also found to correlate closely with measured damage by two methods: FTIR cysteic acid and SEM cuticle damage score at hair tips where damage is at its most advanced. As expected, fatigue breakage also

increased from root to tips, but there was significant variation between panelists, even at roots where damage was lowest. This variability was shown in part to be driven by internal lipid levels, but it is proposed other differences (i.e., curl level, protein composition, etc.) may be driving this variability.

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