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The effect of treatments on the shear modulus of human hair measured by the single fiber torsion pendulum

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Synopsis

Previous studies with the single fiber torsion pendulum have alluded to the ability of this device to selectively measure different regions of a fiber, namely, the core and the sheath. This selective ability of the torsion pendulum was explored further as a means of better understanding treatments effects. First, a substantial reduction in shear modulus was caused by simply abrading the hair fiber surface to remove the cuticle layer. In another experiment, bleaching was found to have a softening effect on the cuticle layer since the shear modulus was reduced significantly. Next, the fibers were subsequently treated with either Polyquaternium-10 or cetyl trimethylammonium bromide (CETAB) and measured again. The CETAB treatment resulted in an increase in the shear modulus indicating fortification of the cuticle layer. Polyquaternium-10 treatment increased the shear modulus slightly. These different effects are explained by the molecular sizes of these compounds—CETAB is a small molecule which can penetrate into the cuticle layer while Polyquaternium-10 is too large to do so. Lastly, the effect of moisture was evaluated by varying the humidity inside a chamber surrounding the sample mounted in the torsion pendulum. This showed a substantial inverse relationship between humidity level and shear modulus that was much more pronounced for bleached hair fibers than for untreated.

INTRODUCTION

In the field of hair damage alleviation, manufacturers of hair care products have often attempted to show improvements on hair strength as a result of application of a specific conditioning formulation. Very often these attempts have failed because the tensile strength measurements are carried out at high rates of deformation which masks the very small effects of these actives on hair strength. However, it was noticed recently that these subtle effects were observable by a shear modulus measurement using a single fiber torsion pendulum (1). The positive effects of a high molecular weight and a low molecular weight cationic conditioner were shown in these studies.

Earlier studies of single fiber torsion pendulum were almost entirely dedicated to the study of fiber damage by chemical treatments of hair (2,3). The work done at TRI was the first attempt to show the beneficial effect of conditioners on human hair.

In the present work we have expanded these studies to include larger number of hair specimens. An attempt has been made to distinguish between the contribution of the cuticle and the cortex to the overall shear modulus of hair. These studies have been expanded to include the effect of relative humidity on shear modulus. This type of study will be useful in evaluating moisturizing effect of certain hair care products on hair.

BACKGROUND

SIMPLE HARMONIC MOTION

Simple harmonic motion is the type of motion that occurs when an object at rest is displaced by a force and the object tries to restore itself to its resting position. Figure 1 displays three examples of simple harmonic motion—a simple pendulum, a vertical spring, and a torsion pendulum. Simple harmonic motion has a specific frequency. The period (time for one oscillation cycle) remains constant even though the amplitude of the oscillation decays. In the case of a torsion pendulum, the period can provide information about the torsional rigidity of the sample connecting the pendulum to the vertical support.

TORSIONAL SHEAR OF FIBERS IS GREATEST AT THE PERIPHERY

The surface of a fiber to which torque is applied has the maximum influence on the shear modulus determination. For hair fibers, the surface consists of the cuticle layer. Figure 2 is a diagram showing a cylinder to which torque is applied. Torsion generates varying levels of shear within the cylinder as a function of distance from the center. In Figure 2, a gray square is shown in (a) before torque is applied while (b) and (c) show the effects of shear on the gray square after torque is applied. The wedge on the top of the cylinder in Figure 2 (c) shows the diminishing shear towards the center of the cylinder. The shear stress will be $r\theta$, where r is the distance from the center. At the fiber surface it will be $R\theta$, R being the radius of the fiber. At the center the shear stress will be 0 ($r = 0$).

EXPERIMENTAL

MEASUREMENT OF SHEAR MODULUS

Measurement of shear modulus of single hair fibers using the single fiber torsion pendulum have been discussed in detail in an earlier communication (1).

For humidity dependent shear modulus measurements the hair fiber mounted on the pendulum was surrounded by a small humidity chamber. The relative humidity was changed by 10% intervals using wet and dry nitrogen (±1–2% RH).

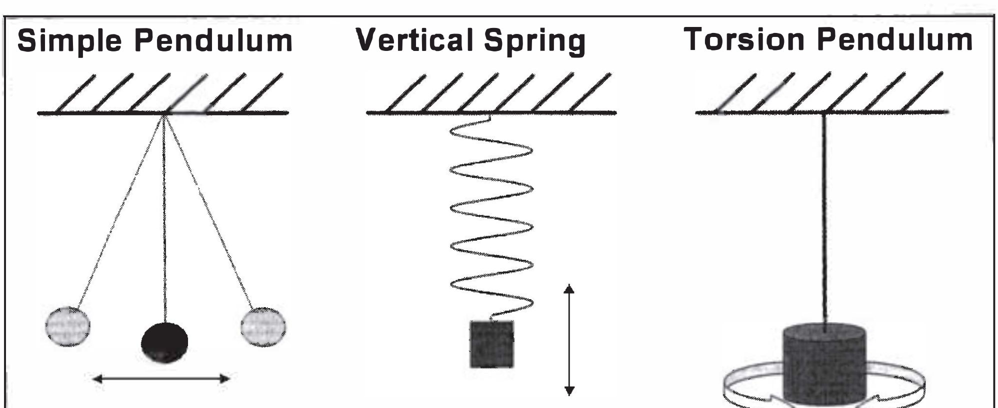


Figure 1. Examples of simple harmonic motion.

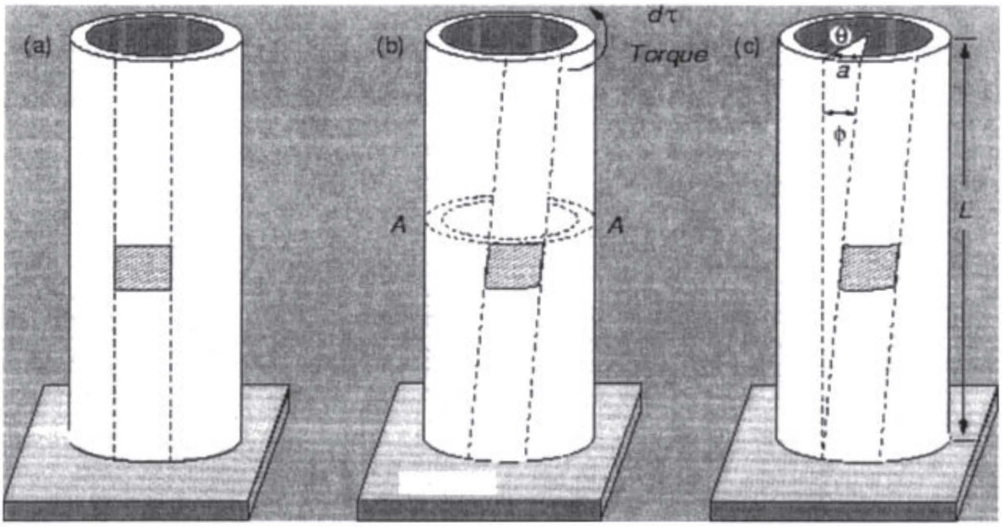


Figure 2. Torsional shear of a cylinder.

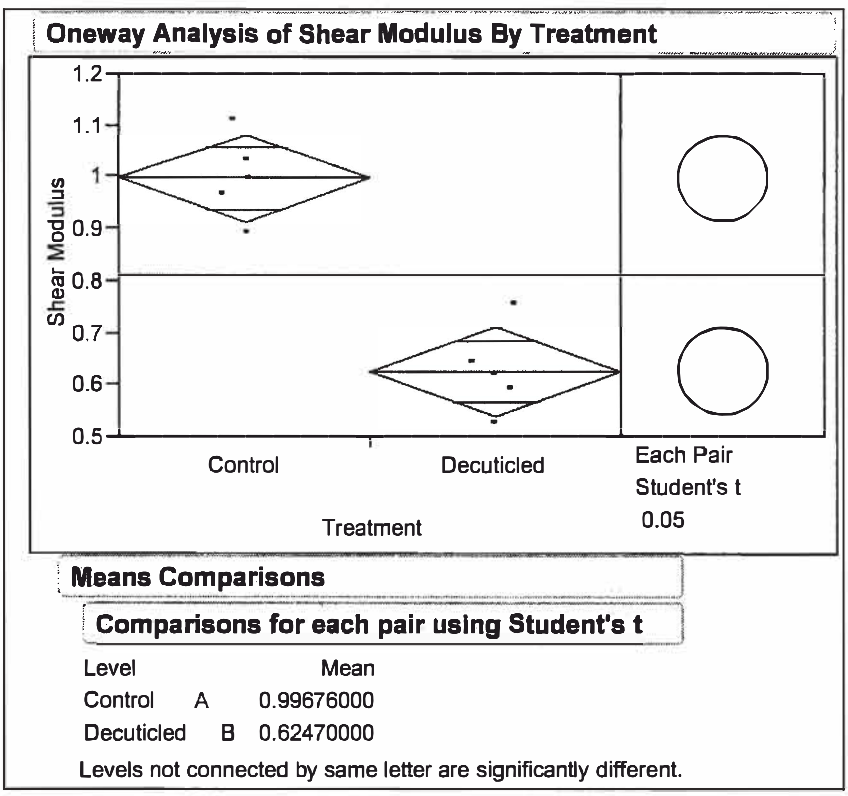


Figure 3. Effect of cuticle abrasion on shear modulus.

The shear modulus (G) of the fiber was calculated by the following equation, assuming an elliptical cross section.

$$G = \frac{16\pi LM}{T^2(a^3b + ab^3)}$$

where L = length, M = moment of inertia for the pendulum mass, T = period, a = semi major axis, and b = semi minor axis.

The semi axes of the elliptical fiber cross section, were determined with a laser micrometer by rotating the fiber on its axis in the laser beam.

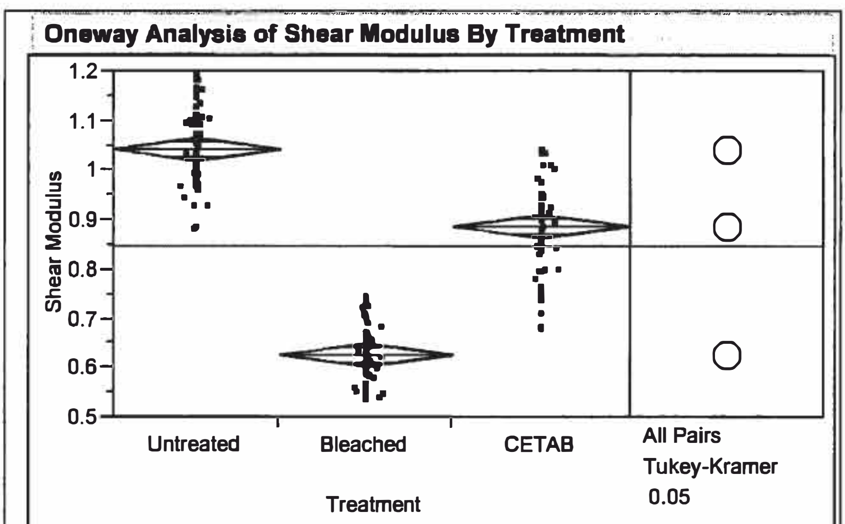
RESULTS

EFFECT OF CUTICLE REMOVAL

Figure 3 shows the results of an experiment in which the shear modulus of hair fibers was measured before and after abrasive removal of the cuticle layer. The shear modulus of untreated (i.e., control) hair fibers was measured and found to be approximately 1.0 GPa. The same specimens were abraded to remove the cuticle layer (i.e., decuticled) and measured again. The shear modulus of the decuticled fibers was on average approximately 0.6 GPa which is 40% less than that of the fibers before they were abraded. The two non-overlapping significance circles (right side of the graph) and the comparison table (below the graph) show that this difference is highly significant. These results clearly show the major influence of the cuticle layer on the shear modulus of hair fibers.

EFFECT OF TREATMENTS ON SHEAR MODULUS—EXPANDED STUDIES

Bleaching + cetyl trimethylammonium bromide (CETAB). Figure 4 shows the results for the



Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

Level			Mean
Untreated	A		1.0404402
CETAB	B		0.8843395
Bleached		C	0.6253302

Levels not connected by same letter are significantly different.

Figure 4. Effect of bleaching and subsequent CETAB treatment on shear modulus.

effects of bleaching and the effects of subsequent cetyl trimethylammonium bromide treatment. Initially, the shear modulus of untreated hair fibers was measured and found to be in the range of 1 to 1.1 GPa. The same specimens were bleached (commercial product, 90 min.) and measured again. The shear modulus dropped to 0.6 to 0.7 GPa which is a 40% reduction indicating that the cuticle layer and the cortex was softened by the bleaching process. Subsequent treatment with CETAB (0.5%, 30 min., rinsed) resulted in the shear moduli increasing to 0.8 to 1.0 GPa which is midway between that of the Untreated and the Bleached fibers. The non-overlapping significance circles and the comparison table show that these differences are highly significant.

The bleaching process oxidizes cystine by breaking disulfide bonds and creates cysteic acid groups both in the cuticle and the cortex. Breaking the disulfide bonds lowers the shear modulus of the fiber. However, it is important to note that the shear modulus of the fiber is dominated by the cortex because it contributes more to the volume of the fiber. The greater effect of CETAB in restoring the shear modulus comes from its ability to penetrate into the cortex of hair. This has been shown independently by mass spectroscopy methods (4). The penetrated CETAB molecules form salt linkages and hydrophobic bonds which act as secondary valence cross-links, thus fortifying the internal structure of the endocuticular proteins in the cuticle and the keratin associated proteins in the cortex as shown in Figure 5.

Bleaching + Polyquaternium-10 (PQ-10). Figure 6 shows the results for the effects of bleaching (commercial product, 90 min.) and the effects of subsequent polyquaternium-10 (PQ-10) treatment (0.5%, 30 min., rinsed). The experimental design of this study was the same as the CETAB study. The shear moduli of the untreated (1 to 1.1 GPa) and bleached fibers (approximately 0.7 GPa) are similar to the CETAB study. The effect of subsequent treatment with PQ-10 is much different—only a slight increase in shear modulus to approximately 0.8 GPa. Other studies have shown that polyquaternium-10

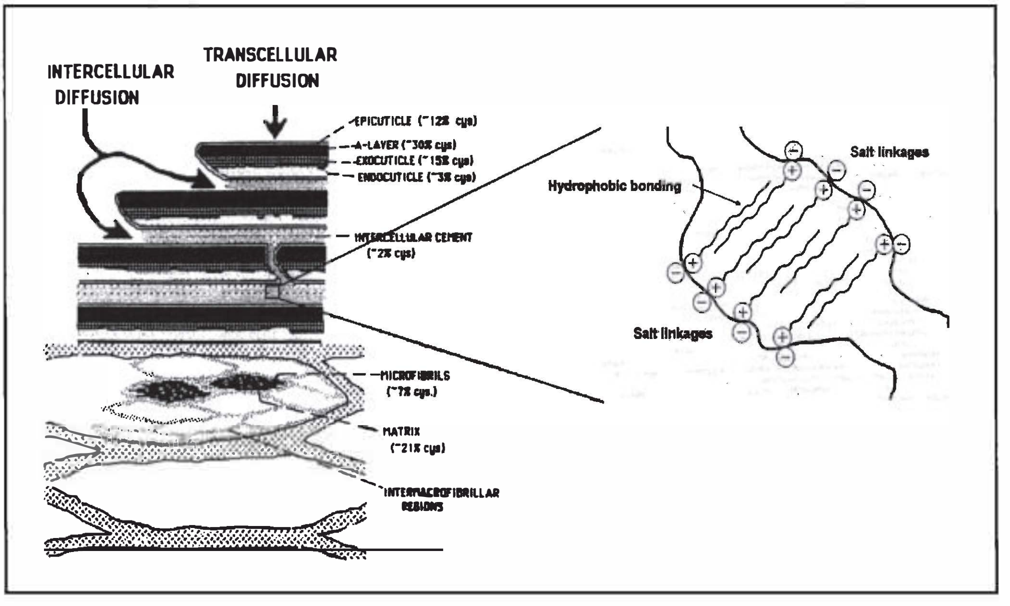


Figure 5. Possible mechanism of fortification via hydrophobic bonding.

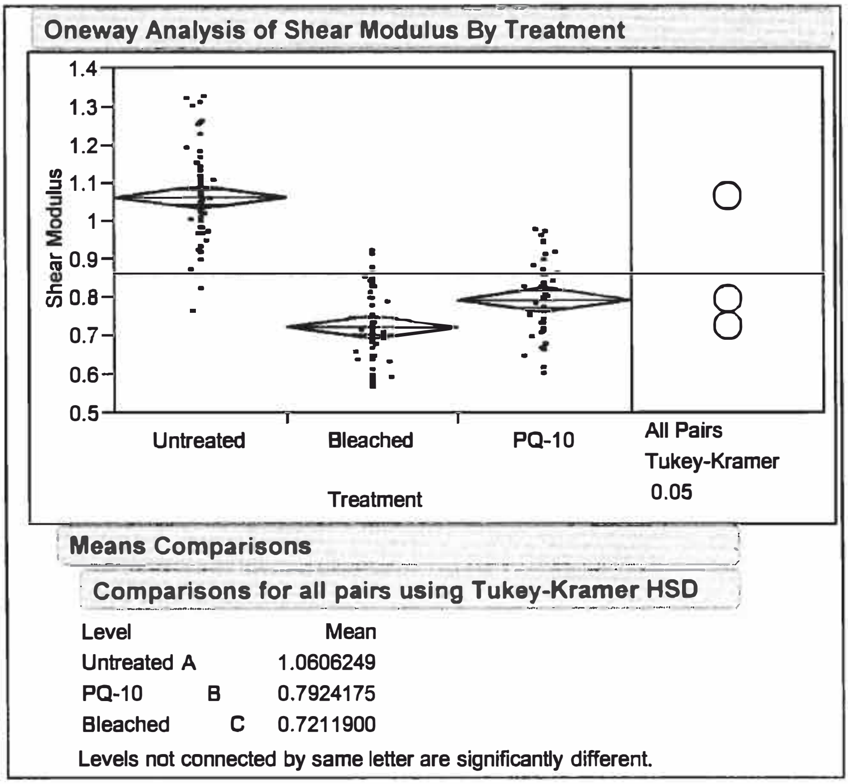


Figure 6. Effect of bleaching and subsequent PQ-10 treatment on shear modulus.

molecules are too large to penetrate into the cuticle layer (4) and merely adhere to the outer surface and therefore, less effective in fortifying the fiber structure.

EFFECT OF MOISTURE ON UNTREATED AND BLEACHED HAIR

Water is one of the simplest and best known "plasticizer" which softens hair fibers. The effect of relative humidity surrounding the fibers, was investigated by measuring the torsional behavior after equilibrating the fiber at different humidity levels from less than 10% RH to 80% RH or higher. The humidity effect on the shear modulus of untreated hair (solid lines) and of bleached hair (dashed lines) is shown in Figure 7. For untreated hair, the effect is sizeable with shear moduli in excess of 1.5 GPa at low humidity levels (10% RH or less) and drops steadily to about 0.7 GPa at 90% RH. The effects are even more extreme for bleached hair with shear moduli in the vicinity of 2.0 GPa at 10% RH and dropping below 0.5 GPa in the 80% to 90% RH range. These responses were very rapid when the humidity was changed indicating that equilibration of single fibers is quite fast. The interesting feature in Figure 7 is that the Sorption isotherm of the bleached hair crosses that of the unbleached hair at approximately 55% RH. Bleached hair has more negative changes from cysteic acid formed by disulfide cleavage. They can form salt linkages with the positive charges in the protein. At low humidities these salt linkages become strong and their number is higher than those in the unbleached hair

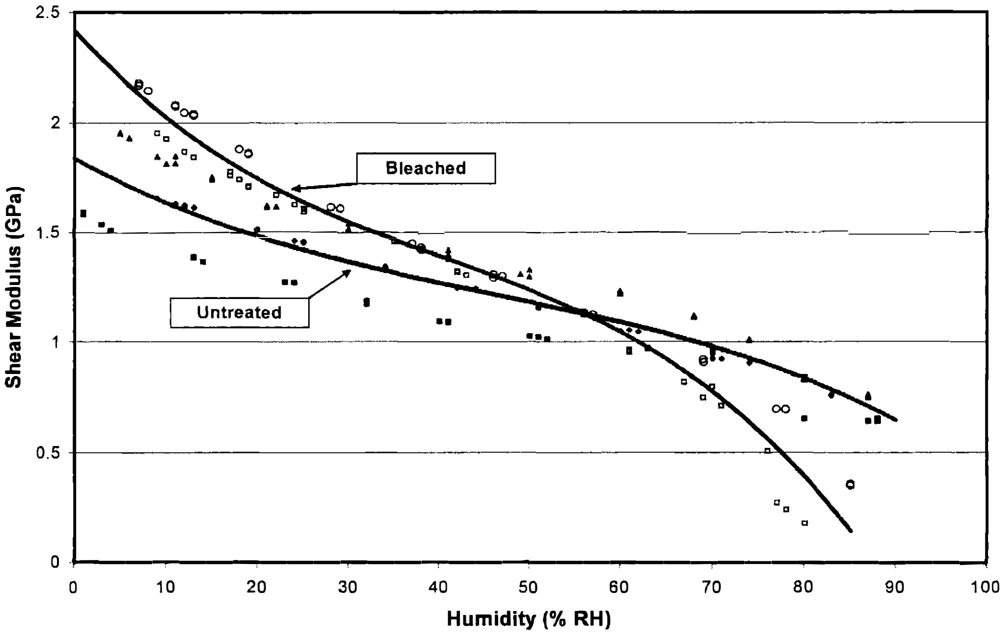


Figure 7. Effect of humidity on the shear modulus of untreated and bleached hair.

fiber. Therefore, we see a higher shear modulus compared to the untreated fiber at low humidities (below 55% RH). Above 55% RH these salt linkages become weak and therefore the shear modulus goes below that of the unbleached (untreated) fibers.

Sorption—Hysteresis. Figure 8 is an example of the hysteresis effect for untreated hair measured gravimetrically. Hysteresis at a given RH is the difference in the moisture content between the desorption (where moisture content is decreasing) and the sorption curves (where moisture content is increasing). Sorption hysteresis reflects the ability of the hair to retain moisture.

Figure 9 shows the shear modulus of untreated hair as a function of relative humidity. The data indicated by "START" were collected after the untreated hair sample was thoroughly dried and the line connects the data as the humidity was incremented upwards. Unlike the gravimetric response to moisture sorption, the shear modulus is substantially reduced as moisture is absorbed. Upon reaching almost 90% RH, the humidity was decreased by the same steps and the shear modulus increases. The two curves show the sorption hysteresis measured by a mechanical method involving shear modulus measurements.

The shear modulus curve for desorption lies below that for sorption, indicating that the moisture content is higher (shear modulus lower) in the desorption mode at a given humidity as observed in Figure 8.

CONCLUSIONS

On a theoretical basis, torsion measurements are dominated by the periphery of hair fibers allowing sensitivity to factors affecting the cuticle layer. Cuticle abrasion was

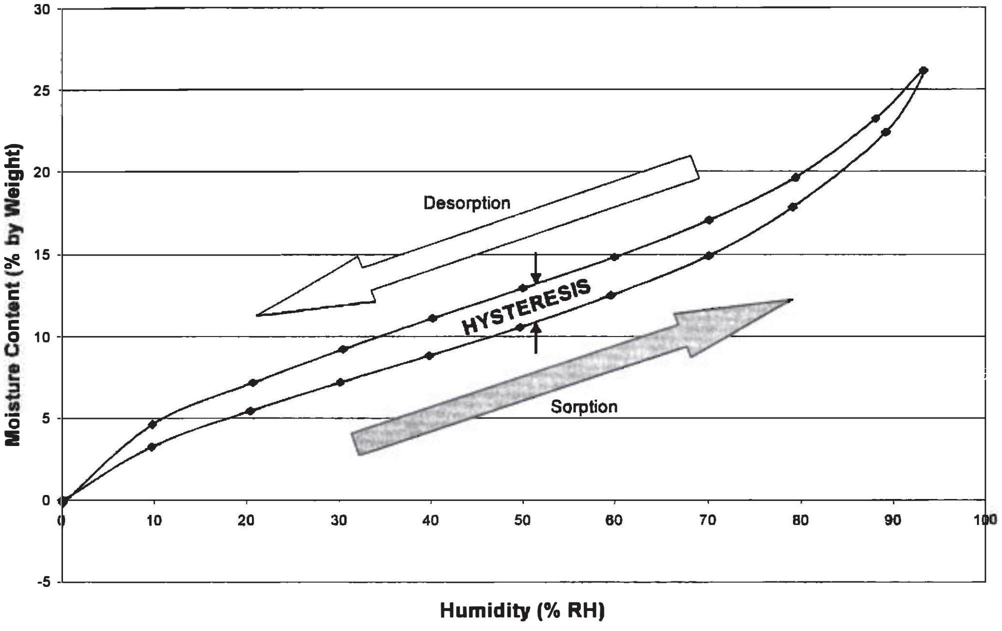


Figure 8. Example of hysteresis of moisture sorption-desorption measured gravimetrically.

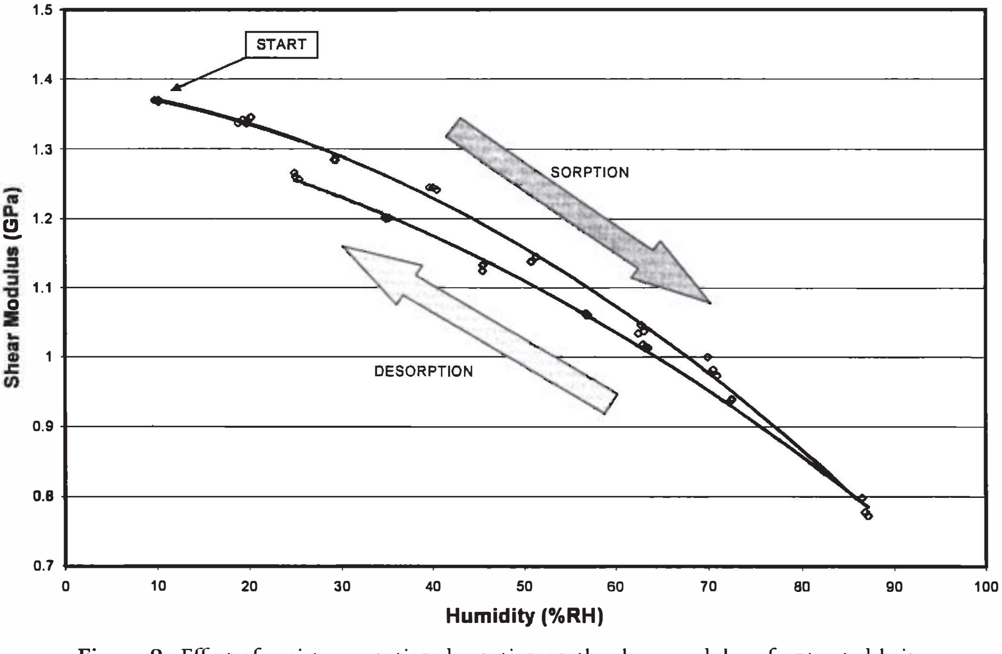


Figure 9. Effect of moisture sorption-desorption on the shear modulus of untreated hair.

found to lower the shear modulus of untreated hair fibers by 40% showing the effect of the cuticle layer in this measurement. Bleaching also lowers the shear modulus of hair by approximately 40% indicating softening of the cuticle layer. Subsequent treatment with CETAB increases the shear modulus of hair indicating fortification of cuticle layer.

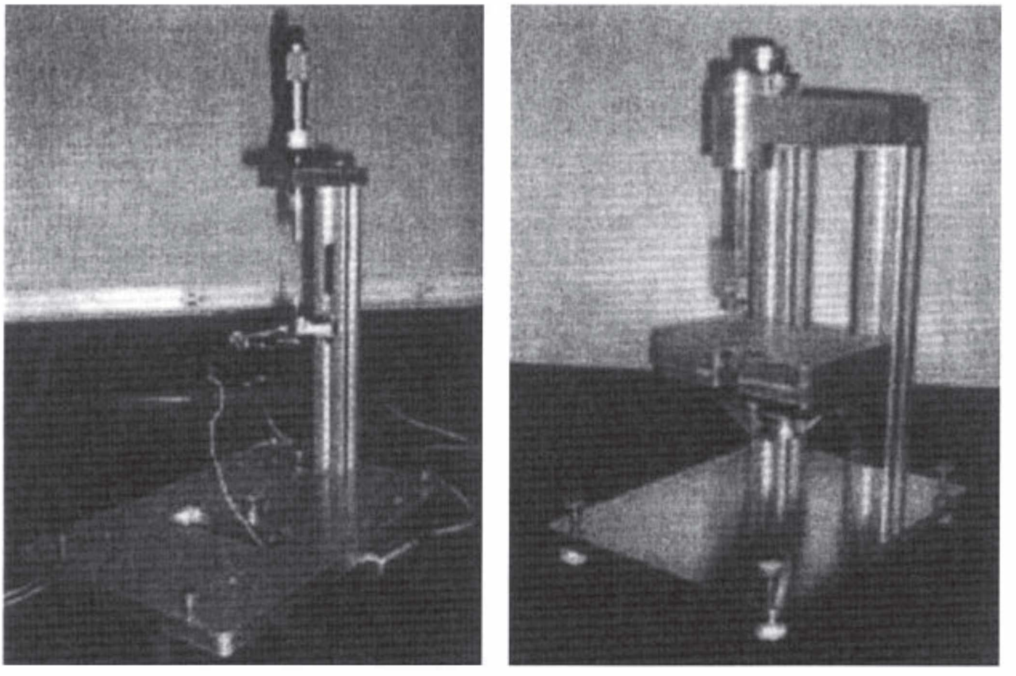


Figure 10. Original torsion pendulum (left) and next generation torsion pendulum (right).

PQ-10, on the other hand, has little effect most likely due to its inability to penetrate into the cuticle layer. Measuring the shear modulus as a function of humidity, changes showed an inverse relationship between humidity and shear modulus which was much more extreme with bleached hair than untreated hair. The shear modulus response to changing humidity was large and rapid indicating that moisture has a dominant effect on the cuticle layer and the cortex pf the fiber.

ACKNOWLEDGMENTS

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