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Influence of functionalized silicones on hair fiber–fiber interactions and on the relationship with the macroscopic behavior of hair assembly

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Synopsis

It is well established that silicones alter hair surface properties and that silicones have a significant impact on the macroscopic behavior of hair assembly, such as visual appearance, combing performance and manageability of the hair.

In order to fine-tune the chemistry of functionlized silicones for specific consumer benefits and hair types, we investigated the influence of silicones on hair fiber–fiber interactions and their correlation to hair volume. The incline plane fiber loop method, implemented with a high-precision motorized rotary stage, was used to quantify the fiber–fiber interactions. Low load static friction was studied as a function of polymer molecular weight, dose and chemical architecture. This information was related to the macroscopic behavior of hair assembly, using virgin curly hair in high humidity.

INTRODUCTION

Hair assembly behavior is driven by geometrical factors, mechanical properties and the local interactions between fibers. Although conditioning polymers primarily affect local interactions between fibers, a clear understanding of the role of polymers on fiber/fiber interactions is lacking.

In a recent study, Bushan investigated, at a very fine length scale using AFM technique (1), hair surface treated with conditioners. These measurements displayed evidence that conditioners accumulate along the edge of cuticles and increase the adhesive force between the AFM tip and the hair substrate. The magnitude of this adhesive force was attributed to the capillary force created by the conditioner fluid material on the AFM tip and, therefore, scaled with the size of the probe.

Earlier, an elegant method, which consisted of measuring the sliding angle of a single hair loop on two parallel fibers (2–3), was developed to measure fiber–fiber interactions. In this technique, the contact area is the intersection of two cylindrical hair fibers, crossing perpendicularly. The technique measures frictional and adhesive forces in the range of μN. In addition to its simplicity, the hair loop measurement technique presents several advantages:

(i) The contact materials are hair.

(ii) The technique operates in a force range, which is relevant to the hair assembly.

(iii) In spite of the fact that the technique involves very low load (10 μN) and a very small contact area, multiple slides along the hair length allow probing the distribution of interaction forces along the hair fiber length (cm).

In this work, the objective was to exploit the incline plane fiber loop method to determine hair fiber–fiber interactions induced by silicones, focusing in particular on understanding the properties of block copolymer silicones versus the traditional straight PDMS polymer. PDMS polymers are known to be very flexible and mobile, whereas the hydrophilic polar blocks of copolymer silicones interact with the hair substrate, restraining the mobility of the silicone segments. An additional objective was the identification of links between the hair fiber–fiber interaction measurements and the macroscopic behavior of hair assembly. The changes of volume and shape of curly hair tresses at high humidity were observed to determine whether the presence of silicones increased fiber-fiber interactions, reducing the frizziness of curly hair at high humidity.

EXPERIMENTAL

INCLINE PLANE FIBER LOOP APPARATUS AND PROCEDURE

An incline plane fiber loop method apparatus, adapted from Robbins and Howell and Mazur, was created for the quantification of the hair fiber–fiber interactions. A schematic of the apparatus is shown in Figure 1. The apparatus was enclosed in an environmental chamber at 25°C and 50% RH. A single hair loop, of diameter 3.8 cm, slid on two parallel hair fibers (L = 10 cm).

The two *parallel fibers* were mounted on an aluminum plate that was attached to a precision motorized rotary stage. The rotary stage (CZ7) from Thorlabs was controlled by a DC servo controller that was interfaced with a PC. Each parallel fiber was mounted at each end by a brass flat clamp from Diastron, A nylon thread with a closed loop connected to the hair fiber allowed the tension of the hair fiber to be adjusted, using standard

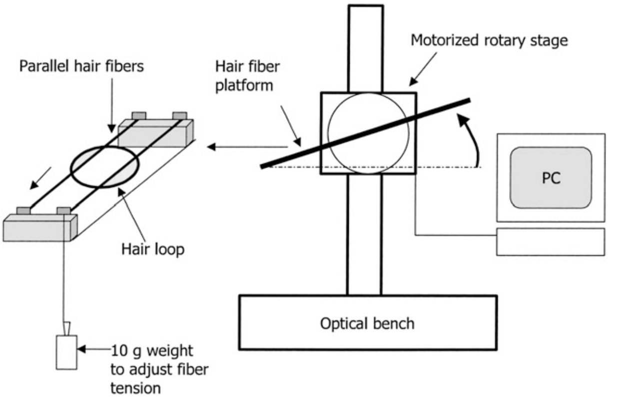

Figure 1. Incline plane hair loop apparatus.

weight. In all experiments, the tension was adjusted with a 10 g weight, unless indicated otherwise. There was a directional effect of the fiber on this hair loop friction measurement; sliding was consistently performed from root to tip of the hair fiber. The parallel fiber plane was tilted at a constant rotation speed of 2°/s, until it slid, or fell. The operator stopped the rotary stage when the loop started sliding or falling, and the angle was recorded by the motor driver software.

The *hair loops* were formed on a cylinder of 3.8 cm diameter, using very thin tape strip to close the loop. Additional thin tape strips were mounted on the loop to act as counterweight. Using that procedure, the total hair loop weight was approximately 2 mg.

For each treatment, 15 fibers were chosen randomly from a hair tress, to make 5 loops and 5 pairs of parallel fibers. The fibers were kept in the environmental chamber overnight prior to measurement. For a given loop and parallel fiber pair, 10 "slides" were performed, to probe the hair fiber–fiber interactions at different positions along the fibers. 50 slides were performed by treatment.

SILICONE MATERIALS

Four of Momentive's silicone polymers were used for the hair treatments. Silsoft* 1215 dimethiconol gum is a very-high-molecular-weight linear PDMS terminated by hydroxyl groups. The quat silicone, INCI name *silicone polyquaternium 18*, is a very high molecular weight block copolymers containing polyether group, amino quat group and silicone chain as described in (4). Silsoft A-843 copolymer, INCI name *Bisamino PEG/PPG-41/3 aminoethyl PG-propyl dimethicone,* is a block copolymer with an (AB)n structure, alternating polyether segments and silicone chain. The SME 253 aminosilicone is a linear silicone with pendant amigo groups. For simplification, in the following sections, silicone polyquaternium 18, Silsoft A-843 copolymer, SME 253, and dimethiconol gum will be called respectively silicone quat, amino ABn, aminosilicone and silicone gum. The neat polymers of amino Abn and aminosilicone were dissolved in isopropanol. The silicone quat and the dimethiconol gum were dissolved in cyclodimethicone (D4).

HAIR TREATMENT PROTOCOL

Virgin brown hair and brown curly hair were purchased from Hair International Hair Importers. Some curly tresses were relaxed using a commercial relaxer to make the loops. Bleaching was performed using a aqueous solution of 1.35% ammonium hydroxide and 3% hydrogen peroxide at pH = 10. The hair tress was dipped for 30 minutes in a fresh bath and then rinsed for 2 minutes in tap water. Four successive bleaching treatments were performed in this study. To apply a controlled amount of silicone to the hair, 1.4 g of solvent was applied to each 2-g tress, which was dried flat overnight at 50°C.

HAIR SURFACE DAMAGE ASSESSMENT

The hair surface damage level achieved by the processes described in the previous section was assessed using a wicking test. The hair tress was held taut by two paper clamps on a glass slide. A droplet of DI water was deposited on the flat taut hair tress and the time for

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the droplet to wick into the hair layer was recorded. On virgin hair, the droplet did not wick, due to high hydrophobicity (t > 5 min). In contrast, on "relaxed hair, wicking occurred in 6 s, indicating that the hair surface was hydrophilic and significantly damaged due to the relaxation process. On the 4X bleached hair sample, the hair was slightly discolored, but the water droplet did not wick within a 5-minute period, indicating a mild level of surface damage.

HAIR VOLUME EXPERIMENT

It is well known that curly hair assembly displays a significant increase of volume in high humidity. In the present experiment, the objective was to use this property to investigate the role of hair fiber–fiber interaction on the volume increase and shape retention of the hair assembly. The experimental design is shown in Figure 2. Prior to treatment with silicones, clean, curly tresses and relaxed tresses were placed for an hour in an environmental chamber at 25°C and 75% RH, and then a picture was taken of the untreated tresses. The tresses were then treated with silicones, as indicated in section 2.3. The treated tresses were placed for an hour in an environmental chamber at 25°C and 75% RH, for an hour and then a picture was taken of the treated tresses. Volume of the treated tresses was compared to the control (tress before treatment). Thereafter, fibers were taken from the curly tress and mounted to form pairs of parallel fibers for the incline plane hair loop measurement. Fibers were also taken from the relaxed tresses to create the hair loops.

THEORY

Sliding a block down an inclined plane is a very old method of measuring static friction (5). If the surface is inclined at a small angle, θ, a component of the gravitational force acts downward along the surface of the inclined plane (Figure 3a). The magnitude of this component is $mg \sin \theta$. If the block does not slide, it is acted on by the static frictional force, f_s. If the surface is inclined to the degree that the tangential component of the gravitational force exceeds f_s, then static friction is overcome and the block begins to

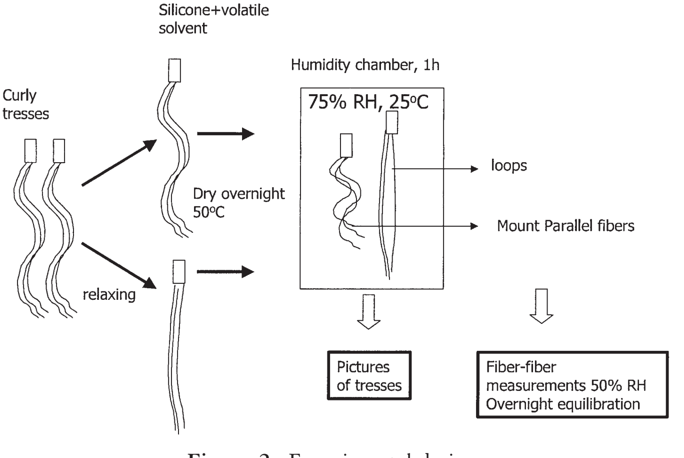

Figure 2. Experimental design.

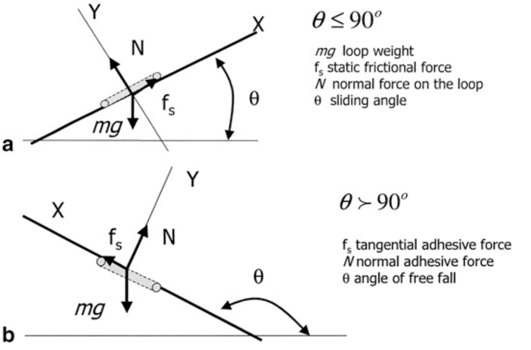

Figure 3. Force balance. (a) Hair loop sliding down an inclined plane with sliding angle θ <90°. (b) Free fall of a hair loop held by adhesion forces θ >90°.

slide. At the angle where the block is just on the verge of slipping, f_s is equal to $mg \sin \theta$ and the force balance leads to:

$$f_s - mg \sin \theta = 0 \Rightarrow \sin \theta = \frac{f_s}{mg} \quad (1)$$

$$N - mg \cos \theta = 0 \Rightarrow \cos \theta = \frac{N}{mg} \quad (2)$$

Note that the sin θ represents a frictional force, normalized by the weight of the block. The usual static coefficient of friction, which is defined by the relation $f_s = \mu N$, can be readily deduced from the sliding angle and is equal to $\mu = \tan \theta$.

The hair loop experiment is similar to the sliding block experiment except that the loop is in contact with the inclined plane at only four points. Equations 1 and 2 apply to the loop center of mass. The dimensional force can be derived by multiplying sin θ by the weight loop (20 μN). Because the weight of the loop is so light, the adhesion forces created by some of the silicone material allow the loop to stick to the parallel fibers. The parallel fibers can be inclined at angle higher than 90°. For angle higher than 90°, the force balance corresponds to a free fall problem involving adhesion forces (Figure 3b). The tangential and normal component of the force exerted on the loop are also described by equations 1 and 2. In that case, cos θ represents the normalized normal adhesion, whereas sin θ is the normalized tangential adhesion.

RESULTS

FIBER–FIBER INTERACTIONS

Untreated hair. The histograms of angle values for untreated virgin hair, bleached hair and relaxed curly hair are shown in Figure 4. A summary of the analytical data is shown in Table I. For untreated hair, the distribution was narrow and the average sliding angle was quite low (~26°), indicating weak hair fiber–fiber interactions. The variations of angle may be due to the variations of contact area for each sliding event (one or few cuticle

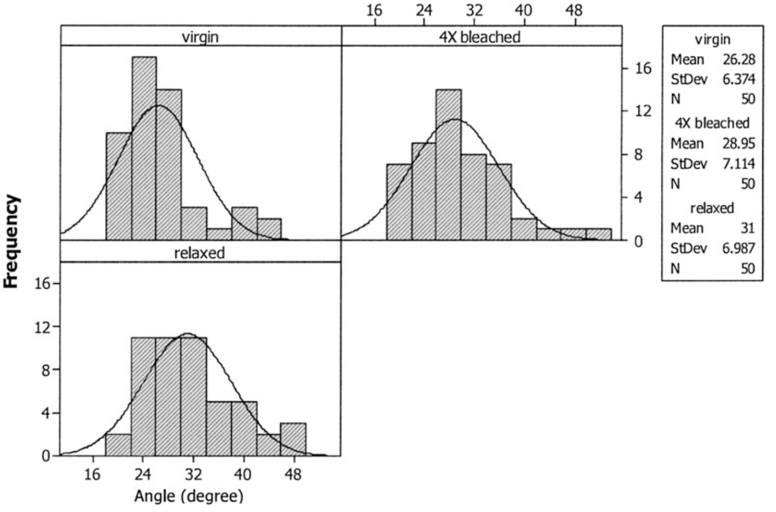

Figure 4. Sliding angle histograms of untreated hair (N = 50). X-axis: angle in degrees. Upper left: virgin Caucasin hair. Upper right: four time bleached hair. Lower left: relaxed hair. Black line is the normal distribution fit. {Note: Test data. Actual results may very.}

length, 5–10 μm) or the chemical heterogeneity of the hair surface. The average sliding angle for virgin hair corresponded to a total average frictional force of 8.8 μN, or 2.2 μN per contact and a static coefficient of friction of 0.5. The 4X bleached hair data were not significantly different from the virgin hair according to a t-test. This result reflected the mild surface damage of the hair, which was assessed by wicking test (section 2.4). In contrast, the relaxed hair, which was hydrophilic (and therefore has significant surface damage), displayed an average sliding angle of 31°—significantly higher than the virgin hair 26°. These data suggested that the incline loop technique might detect hair surface damage. The same hair fiber set (loops and pairs) was measured at two tensions (10 g and 50 g) and the data are displayed in Table I. The fiber tension decreased the friction slightly. This could indicate that, at higher tension, the reduced friction related to a decrease of contact area as a result of to cuticle lifting.

Treated hair. A typical histogram of angle values for silicone-treated hair is shown in Figure 5, in comparison with the untreated hair data. The treated hair clearly displayed a much broader distribution and a higher average sliding angle compared to the untreated hair. The average low load static coefficient of friction for untreated and treated hair is 0.6 and 1.1, respectively. The broad distribution is reflected by a high standard deviation value. These data suggest that the hair surface treated with silicones presented patches of different adhesion strength. Observations by Bushan with AFM probes also suggested that the hair surface treated with conditioners was patchy and displayed a distribution of adhesion force (1). Histograms of angle values for different silicone treatments at constant dosage 3000 ppm on the hair are shown in Figure 6. A summary table of the analysis data is shown in Table I. All data for silicone-treated hair displayed a broad distribution of angles, which differed clearly from untreated hair. The distribution was closer to a normal distribution for amino ABn, indicating a more even coverage. For the experiments in which the silicone was delivered by a volatile organic solvent, the normal distribution model did not fit the experimental data well. It is possible that the drying of volatile

Table I
Analysis Summary Table

	Tension (g)	Dose (ppm)	Average angle (degree)	Standard deviation	sin θ	Adhesive tangential force (μN)	cos θ	Adhesive normal force (μN)	Low-load static coefficient of friction	Angle >90 (%)
Virgin			26	6.4	0.44	2.2	0.89		0.5	0
4X bleached			29	7.1	0.48	2.4	0.87		0.6	0
Relaxed			31	7.0	0.51	2.6	0.85		0.6	0
Virgin	10		29	6.7	0.47	2.4	0.87		0.5	0
Virgin	50		25	5.8	0.42	2.1	0.90		0.5	0
Silicone quat		1000	47	15.0	0.71	3.5	0.66		1.1	0
		3000	53	27.2	0.71	3.5	0.55		1.3	12
Amino Abn		1000	49	19.2	0.71	3.6	0.62		1.2	4
		3000	71	28.5	0.83	4.2	0.32		2.6	22
Aminosilicone		1000	46	20.4	0.66	3.3	0.67		1.0	4
		3000	70	35.7	0.77	3.9	0.32		2.4	28
Silicone gum		3000	117	42.6	0.68	3.4	−0.32	1.6		68

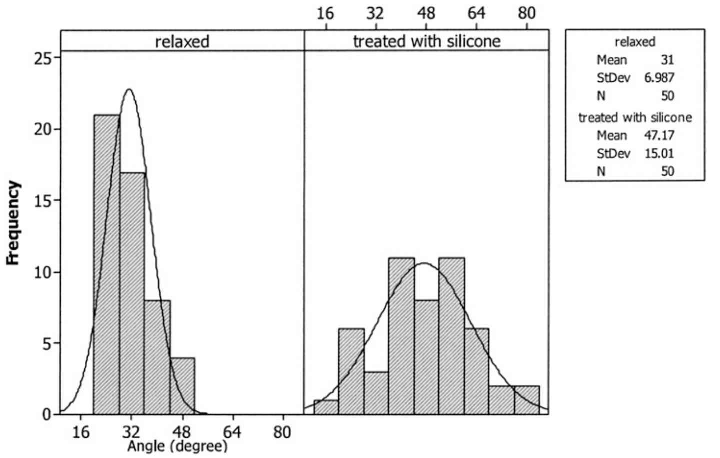

Figure 5. Sliding angle histograms of untreated hair and silicone-treated hair (N = 50, X-axis: angle in degrees). Treated hair has 1000 ppm of silicone quat. [Note: Test data. Actual results may vary.]

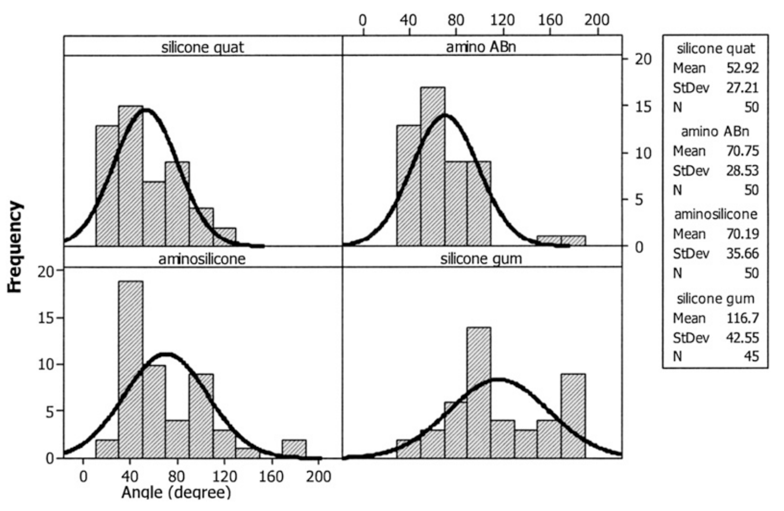

Figure 6. Sliding angle histograms of hair treated with different silicones at constant silicone dose of 3000 ppm (N = 50, X-axis: angle in degrees). Black line is the normal distribution fit. [Note: Test data. Actual results may vary.]

solvent affects the final spatial distribution of silicones on the hair sample and does not lead to a totally random distribution.

The strength of hair fiber–fiber interactions was the lowest for silicone quat (lowest sliding angle), and it was the highest for silicone gum (highest angle) (Figure 7). The silicone quat, the amino ABn and the aminosilicone treatment showed a rather low percentage of angles higher than 90° (column 11, Table I). These treatments were characterized by an increased adhesive tangential force from 2.6 μN (untreated) to 3.5–4.2 μN (column 7, Table I). In contrast, the silicone gum treatment wais characterized by a very high percentage of angles higher than 90° and a strong normal adhesion 1.6 μN (column 9, Table I).

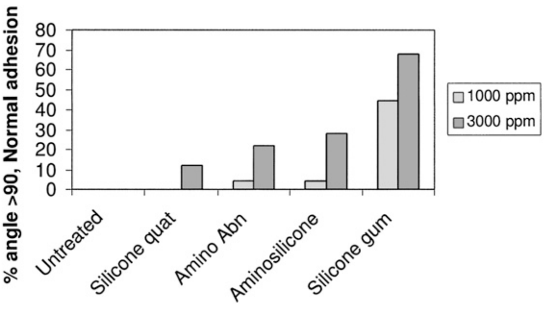

Figure 7. Percentage of angle higher than 90° for hair treated with different silicones. [Note: Test data. Actual results may vary.]

The large normal adhesion displayed by silicone gum may be attributed to the very large molecular weight of this linear flexible polymer, which may lead to the diffusive interpenetration of chain segments and entanglement across the fiber/fiber interface, providing bond strength (6). In contrast, the much shorter silicone chains of the silicone quat typically do not form entanglement and, therefore, form low-strength contact bonds. Generally, a very significant effect of concentration was observed when concentration was increased from 1000 ppm to 3000 ppm (Table I). The effect of concentration on the average angle was much more pronounced with the amino ABn and aminosilicone than in the case of silicone quat. For the silicone quat, increased concentration primarily influenced the percentage of high angle values and the broadness of the distribution.

QUALITATIVE RELATIONS TO HAIR VOLUME

Based on hair loop experiments, the different treated tresses were separated into 3 groups:

Group I: low interaction (silicone quat)
Group II: moderate interaction (amino ABn, aminosilicone)
Group III: strong interaction (silicone gum)

These three groups appeared to correlate qualitatively with three distinct hair assembly behaviors. The untreated curly and relaxed hair in a high humidity environment is shown in Figure 8a. The trees volume of the curly tresses was very high, compared to the relaxed tresses. The turbulence of the chamber air flow and the bending forces of the curled fibers separated the fibers. The curled fibers most likely separated due to the weak fiber–fiber interactions. The control experiment clearly contrasted with the silicone treated tresses. The tress volume pictures for quat, amino ABn, aminosilicone, and dimethiconol gum are shown in Figure 8b–e. In Group I, at low concentration (1000 ppm), the tress volume was quite similar to the control, whereas the tress volume was reduced at 3000 ppm (Figure 8b). Although the curl shape was maintained, individual fibers were separated from each other. In contrast, for Group II (aminosilicone, amino ABn), at both 1000 ppm and 3000 ppm concentration levels, the tress volume of the curly hair was reduced compared to the control (Figure 8c–d). At 1000 ppm, the curled fibers stayed parallel to each other and the wave shape was maintained to a much greater extent than that of the control tress, especially with amino ABn. The collective effects of the moderate fiber–fiber inter-

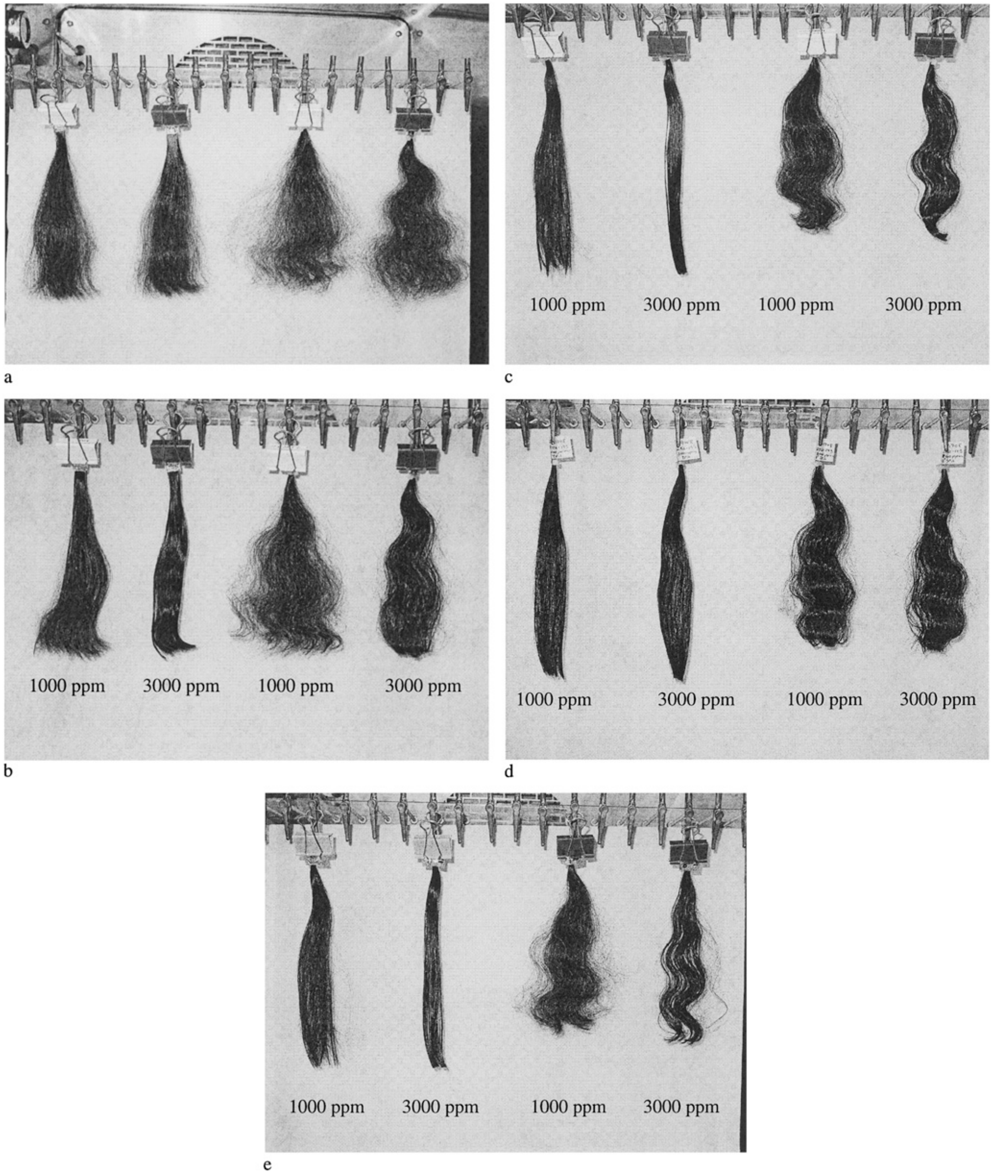

Figure 8. Hair tress pictures after 1 hour at 75% RH and 25°C. In each picture, two tresses on the left are relaxed, two tresses on the right are curly tresses. Silicone dose indicated in ppm: (a) untreated. (b) treated with silicone quat. (c) treated with amino Abn. (d) treated with aminosilicone. (e) treated with silicone gum. [Note: Test results. Actual results may vary.]

actions helped keep the fibers together and counteracted the forces that separate fibers. However, the fibers did not stick to each other. In Group III, tress volume reduction was observed at both 1000 ppm and 3000 ppm. However, at 3000 ppm, fiber grouping was observed, due to the strong adhesion interactions. When fiber–fiber normal adhesion is strong, groups of fiber stick to each other (Figure 8e).

CONCLUDING REMARKS

This study shows that the incline plane fiber loop method may detect adhesion forces in the range of 1 μN and elegantly separate the tangential and normal components of the fiber–fiber interactions. By collecting the data from a large number of sliding events and by controlling fiber tension, we were able to detect hair surface damage and differentiate silicone treatments. At concentrations of 1000 ppm and above, silicone treatments increased the fiber–fiber adhesive forces significantly. In addition, we demonstrated that the collective effect of these interactions influenced the behavior of curly hair assembly at high humidity. In particular, the study suggests that block copolymer silicone chemistry allows tuning the level of attractive fiber–fiber interactions and controlling the quality of the curly hair assembly appearance. Further measurements of the fiber–fiber interactions at lower silicone concentrations and different delivery vehicles will be evaluated in the future.

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