

Investigation of penetration abilities of various oils into human hair fibers

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Synopsis

In this work we have explored capillary adhesion between hair fibers treated with different types of oils. With coconut, olive, and sunflower oils the capillary adhesion was found to decrease with time, but not with mineral oil. Application of heat reduced the capillary adhesion further for coconut and sunflower oils. Again, this was not observed with mineral oil. Based on an earlier study, where coconut oil was found to penetrate hair while mineral oil was unable to do so, it was hypothesized that the reduction in capillary adhesion resulted from the penetration of oil into the fiber, leaving a thinner oil film on the surface. Such a reduction in capillary adhesion can be explained by changes in Laplace pressure and in the areas of liquid bridges formed between the fibers.

The thinning of oil films on the surface of hair has been confirmed independently by goniophotometric measurements on single hair fibers treated with coconut, sunflower, and mineral oils. Thick films of oil (thicker than $\sim 0.5\ \mu\text{m}$) are known to mask the scale structure. As the oil is absorbed into the hair, the film thins with time and application of heat, and the scale structure reappears. This change can be conveniently determined by measuring the scale angle, using the well established goniophotometric protocol. The agreement between the two methods supports the concept that the reduction in capillary adhesion between hair fibers is most likely due to thinning of oil films by absorption of oil into the hair.

INTRODUCTION

Various natural oils are increasingly used in skin and hair care products, especially in ethnic hair products. In Asian and African countries, vegetable oils are commonly used as hair pomades and are known to lead to healthy-looking hair. Deposition of oils on hair has been claimed to have a beneficial protective effect. Oil-based hair conditioners are thus believed to help prevent moisture loss from hair, which causes dryness and loss of elasticity. Specifically, the beneficial effect of coconut oil on the prevention of cuticular damage during combing, when used as a prewash conditioner, has been demonstrated previously by protein loss and water retention measurements (1). In addition to providing a lubricating film, this effect was explained by the hydrophobicity of coconut oil, which reduces the water penetration into the fiber. For full beneficial effect, oil penetration throughout the hair fiber cortex is desirable, as mechanical properties of the hair fiber are determined by the cortex. However, the moisture-retention effect of oil is

dominated by surface-deposited oil. Recently, Ruetsch *et al.* (2) showed that coconut oil penetrates into the hair cortex and reduces the swelling of the hair fiber.

The presence of oil films on the surface of fibers leads to capillary adhesion between the fibers and increased specular reflection of light from the surface. The magnitude of these two effects depends on the thickness of the oil film, determined by the amount of oil applied. Penetration of oil into the fiber reduces the film thickness, which affects both capillary adhesion and light reflection. In this paper, the penetrability of various oils is studied by means of the changes in interfiber adhesion and light reflection measurements. The force of adhesion between fibers plays an important role in describing fiber assembly behavior and is measured using a recently described dynamic fiber pull-out method (3). The capillary adhesion force measured on a single fiber due to its contact with other fibers in the assembly is sensitive to the amount of oil on the fiber surface. Therefore, it is possible to determine which oils are more readily diffused into the hair fiber, thereby leaving thinner films of oil on the surface without "clumping" of the hair assembly.

A goniophotometer records the angular profile of reflected light and is frequently employed to quantify luster. This method is also known to serve as a sensitive probe of the hair surface, mostly used for detection of structural changes caused by cosmetic products and mechanical grooming (4–6). In this study we demonstrate that the changes in reflected light intensity, angular position for specular reflectance, and calculated scale angle can all be successfully used to detect the changes in the thickness of the surface oil film as a result of penetration.

EXPERIMENTAL

MATERIALS

The hair used in this study was black hair of Indian origin supplied by Marico Industries Ltd., Mumbai, India. Pure coconut oil, mineral oil, and ricebran oils were also provided by Marico Industries Ltd.. Cold-pressed extra-virgin olive oil (Filippo Berio, Italy), expeller pressed sunflower oil (Hain Pure Foods, Inc., New York), pure sesame oil (Kadoya, Summit Import Corp., New York), and pure mustard massage oil (KTC Edibles Ltd. England) were obtained from commercially available sources (health and food stores).

MEASUREMENT OF INTERFIBER ADHESION

Hair tress preparation. Prior to treatment, the hair tress was kept overnight at 21°C and 65% RH. A hair tress with a weight of 2 grams was gently combed in order to ensure parallel alignment of the hair fibers. Then 0.2 cc of the appropriate oil was directly applied to the tress with a syringe. The oil was gently massaged with gloved fingers into the tress for five minutes to distribute it uniformly into the hair assembly. In the application procedure a small amount of oil is left on the glove, but is considered to be negligible to have an effect on the measurement.

Packing density and hair fiber mounting. A detailed description of the method is given in reference 3. The hair tress (about 0.5 grams of hair per cm³) was packed into a specially

fabricated 3.8-cm-long brass cylinder with a diameter of 0.8 cm by pulling the hair tress through the cylinder. The excess of hair fibers was removed. From the packed hair assembly a single hair fiber was partly pulled out in the root-to-tip direction from the middle of the cylinder, and then attached to a Kevlar monofilament. The Kevlar monofilament was subsequently attached to a recording electrobalance (TRI-Scan) via a stainless steel hook. The force of withdrawal (mg) was recorded while the TRI-Scan stage was moving downward at a rate of 0.02 mm/sec. From the curve of force versus distance moved, an average force was calculated. For each oil treatment, measurement was repeated on ten specimens, i.e., pulling out ten single fibers, one at a time, from each packed hair assembly. Interfiber adhesion measurements were repeated after keeping the packed cylinder at a constant temperature and humidity (21°C and 65% RH) for 24 hours. A third set of measurements was performed after additional heat treatment using a blow-dryer at medium heat for five minutes. Warm airflow was directed on both cylinder walls and its openings. Even though this procedure is not highly reproducible in terms of the temperature experienced by the hair assembly compared to a constant-temperature oven, we used this procedure mainly because of its use in practice.

MEASUREMENT OF ANGULAR REFLECTED LIGHT PROFILE

The goniophotometer (GP) was used to record the scattered light intensity as a function of the angle. The light source was a He-Ne laser of 632 nm. The measurements were performed on single Indian hair fibers placed horizontally in the sample holder at an angle of incidence of 45°. The scale angle α was calculated from the GP curves of fiber in the root-to-tip (R-T) and tip-to-root (T-R) position, given by: $\alpha = (\theta_{TR} - \theta_{RT})/4$, where θ_{TR} and θ_{RT} stand for the angle of specular peak appearance for tip-to-root and root-to-tip positions, respectively (4). Measurements were performed on the same fiber as in the case of adhesion measurements, which were done on the same hair assembly, directly after oil application, 24 hours after oil application, and with short-term heat treatment using a blow-dryer. A thin oil layer was applied by moving the fiber through an oil drop at the tip of a needle. Additional scans were recorded after removing the remaining surface oil by dissolution, moving the fiber through a drop of acetone, as described previously.

RESULTS AND DISCUSSION

EFFECT OF VARIOUS OILS ON INTERFIBER ADHESION

Fiber withdrawal forces for hair treated with various oils are shown in Table I. Compared to untreated Indian hair, the withdrawal force is increased by a factor 3 to 9 for all oils used in this study. The withdrawal force of a fiber from a bundle is a function of the number of points of contact and the normal forces acting (laterally) at these points. Upon oil application, liquid bridges are formed between fibers and additional normal force arises from the negative Laplace pressures of these liquid bridges (capillary adhesion). The magnitude of the adhesive force is a product of the Laplace pressure of the liquid bridge and its area.

Comparing the initial withdrawal forces (i.e., directly after oil application) with forces measured after 24 hours, we observe a decrease of about 20% for mustard and olive oil.

Table I
Average Withdrawal Forces with 95% Confidence Levels for Various Oil Treatments Calculated from the Dynamic Interfiber Adhesion Measurement

Treatment	Initial force (mg)	Force (mg) after 24 hr	Force (mg) after 24 hr w/heat
Untreated	29.6 ± 8.1		
Coconut oil	116.2 ± 7.7	103.7 ± 9.6	63.9 ± 10.4
Mineral oil	107.4 ± 2.8	110.5 ± 1.7	108.1 ± 10.9
Sunflower oil	184.6 ± 24.3	108.3 ± 13.2	83.9 ± 12.9
Ricebran oil	109.4 ± 2.0	109.8 ± 1.8	
Mustard oil	287.3 ± 27.4	221.2 ± 19.3	
Sesame oil	203 ± 58.7	192.2 ± 85.5	
Olive oil	264.0 ± 45.0	192.0 ± 61.0	

For these oils, results showed considerable fiber-to-fiber variation, giving a large standard deviation. The reason for this could be the change in the area and thickness of the oil films, leading to uneven oil distribution on the fiber. There is no significant change in withdrawal forces for mineral, sesame, and ricebran oil, whereas for coconut oil and sunflower oil, forces after 24 hours have decreased by 10% and 40%, respectively. Further discussion will mainly focus on mineral, coconut, and sunflower oils, as these oils are found to give highly reproducible results representing different penetration characteristics. For these oils, results are summarized and presented graphically in Figure 1. For mineral oil, the withdrawal force remains unchanged even after heat treatment, suggesting that the nature of the oil film and the associated capillary adhesion remain unchanged. The difference in the initial adhesion force between sunflower, coconut, and mineral oil-treated fibers could be due to the different cohesive properties. The withdrawal forces for coconut oil and sunflower oil after heat treatment are further decreased by approximately 40% and 20%, respectively, compared to the force measured after 24

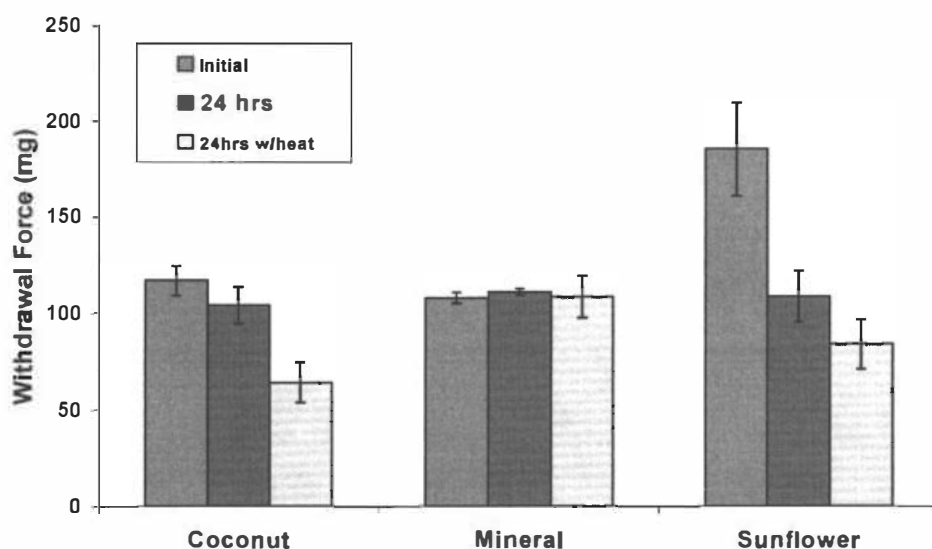


Figure 1. Average withdrawal forces for Indian hair tress treated with coconut, mineral, and sunflower oils, initially, after 24 hours, and with additional heat treatment.

hours. The major decrease in withdrawal force for sunflower oil-treated hair was found to occur within 24 hours, whereas for coconut oil-treated hair the short-term heat treatment had the largest effect. The lowest withdrawal force, i.e., the closest to the untreated hair, was found for the coconut oil-treated hair after 24 hours with heat treatment. In Figures 2–4 the typical withdrawal force curves are shown for mineral, coconut, and sunflower oil-treated hair fibers after 5 min, 24 h, and with heat treatment.

The decrease in withdrawal force is associated with changes in fiber-surface condition and can be explained as follows. The force of adhesion is determined by the effective area of the liquid bridges formed between fibers and by capillary pressure, which in turn depends on the surface tension of the oil, the contact angle of the oil on the fiber, and the curvature of the liquid bridge. An equation for the adhesive force due to capillarity for two parallel fibers has been derived by Brooks *et al.* (7). A decrease in the amount of oil on the fiber surface by penetration results in an increase in liquid bridge curvature and a decrease in contact area, shown in Figure 5. From this combined effect, an initial increase followed by a decrease in the withdrawal force is expected. Thus, decreased withdrawal forces found for sunflower and coconut oil-treated hair fibers indicate the penetrability of these oils into the hair fibers, leading to thinning of surface oil films. Unchanged withdrawal forces for mineral oil imply the possible lack of penetration and film thinning. These findings are in good agreement with fiber interior studies performed by secondary ion mass spectrometry (SIMS) in combination with a time-of-flight (TOF) mass spectrometer, where mineral oil was not detected within the hair fiber cross section, whereas coconut oil was found to penetrate partially or completely (2).

EFFECT OF MINERAL AND COCONUT OILS ON GP MEASUREMENTS

It was the work of Stamm *et al.* (4) that showed that the shift in the reflectance peaks

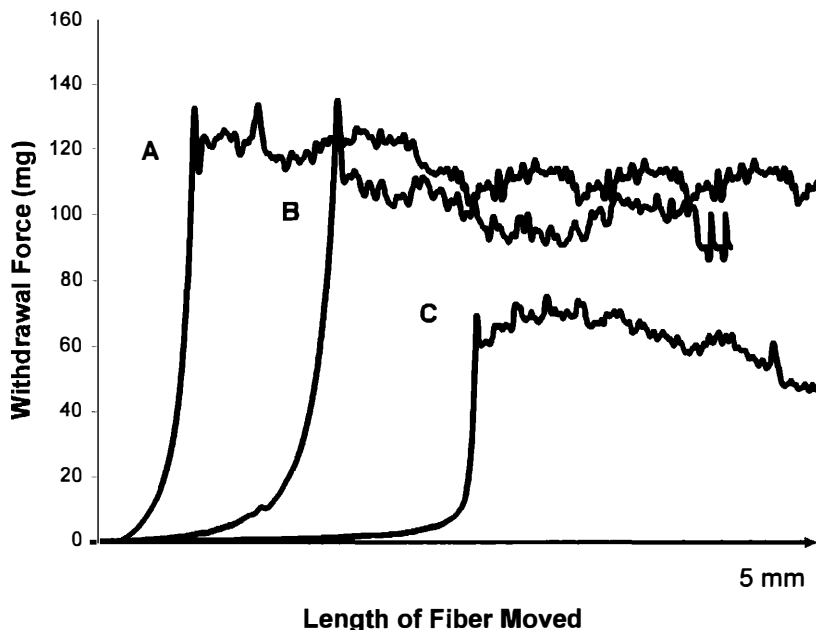


Figure 2. Typical withdrawal force curves for Indian hair fibers treated with coconut oil after 5 minutes (A), after 24 hours (B), and after 24 hours with heat treatment (C). Curves shifted arbitrarily.

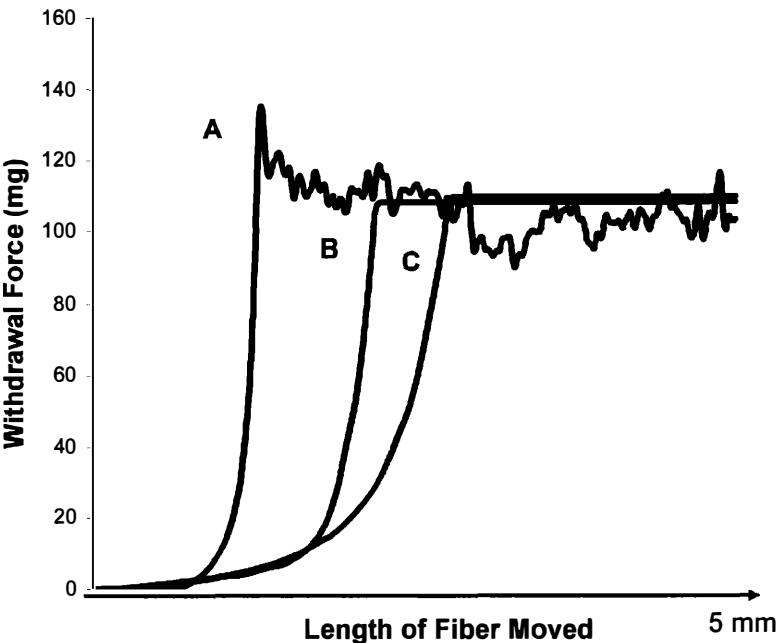


Figure 3. Typical withdrawal force curves for Indian hair fibers treated with mineral oil after 5 minutes (A), after 24 hours (B), and after 24 hours with heat treatment (C). Curves shifted arbitrarily.

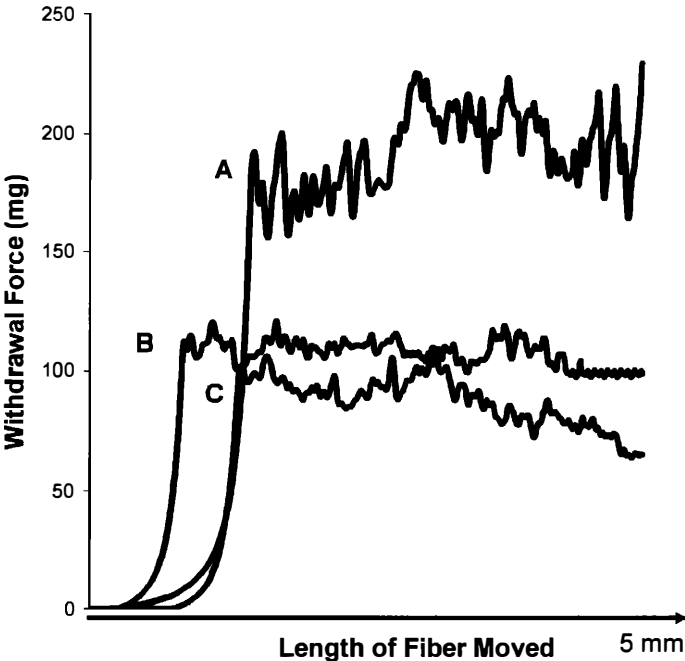


Figure 4. Typical withdrawal force curves for Indian hair fibers treated with sunflower oil after 5 minutes (A), after 24 hours (B), and after 24 hours with heat treatment (C). Curves shifted arbitrarily.

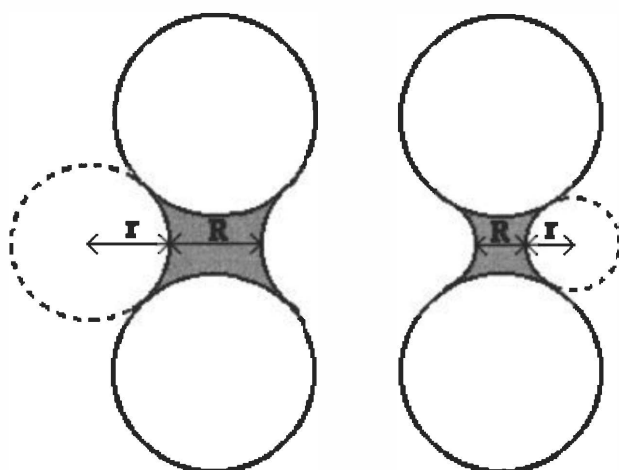


Figure 5. Schematics of the oil liquid bridge between two fibers. Oil penetration decreases the contact area, $A = \pi R^2$, and increases the Laplace pressure, $P = \sigma \cos \theta / r$, where σ is the surface tension of oil and θ is the contact angle. The combined effect of these two results in a decrease in adhesive force ($P_1 A_1 > P_2 A_2$).

for a hair fiber in the R-T and T-R modes at a given angle of incidence was due to the scale angle. Deposition of thick oil films eliminated this shift by masking the scale structure with the oil film. For such a system, the reflectance peaks in the R-T and T-R modes overlapped. In Figure 6A the GP curves recorded in the R-T and T-R positions for an untreated Indian single hair fiber and for the same fiber treated with a mineral oil are shown. For the untreated hair fiber the sharp specular reflectance peak occurs at an angle different from the angle of incidence, due to the inclination of scales relative to the axis of the fiber. For R-T and T-R scans, the specular peaks have a maximum at 38° and 52° , respectively. From these values a scale angle of 3.5° for untreated hair fiber is calculated. After application of mineral oil, the specular reflectance peaks overlap, both appearing at 45° . The angle of reflection being equal to the angle of incidence indicates the formation of a smooth mirror-like oil film on the fiber surface. Hair-fiber scale structure is no longer seen. Also, the sharper peaks with higher reflectance compared to untreated hair fiber illustrate the lustrous surface without diffuse reflectance. For mineral oil, the GP intensity scans, directly after oil treatment (not shown in Figure 6A) and after 24 hours, are similar regarding both the peak position as well as reflected light intensities. The additional shoulder on the specular reflectance peak for R-T at a higher angle is most probably caused by the discontinuity of film at certain locations. After heat treatment for five minutes, the intensity of reflectance has decreased by a factor of 1.6, as shown in Figure 6B. However, the shape of the GP curve remains similar to those obtained after 24 hours, with no separation indicative of the scale angle. Thus, even after the heat treatment, most of the mineral oil remains on the hair surface. It is worthwhile mentioning that the GP curves remained unchanged even with heat treatment over a longer period of time (20 minutes). Finally, in order to demonstrate the reproducibility and reliability of the results and the method, the hair fiber was dipped into acetone, removing the mineral oil film from the fiber surface. This resulted in the separation of scans from the R-T and T-R positions, giving a scale angle of 3.4° . Also, the reflection intensities are comparable to ones obtained from the initial measurements. To some

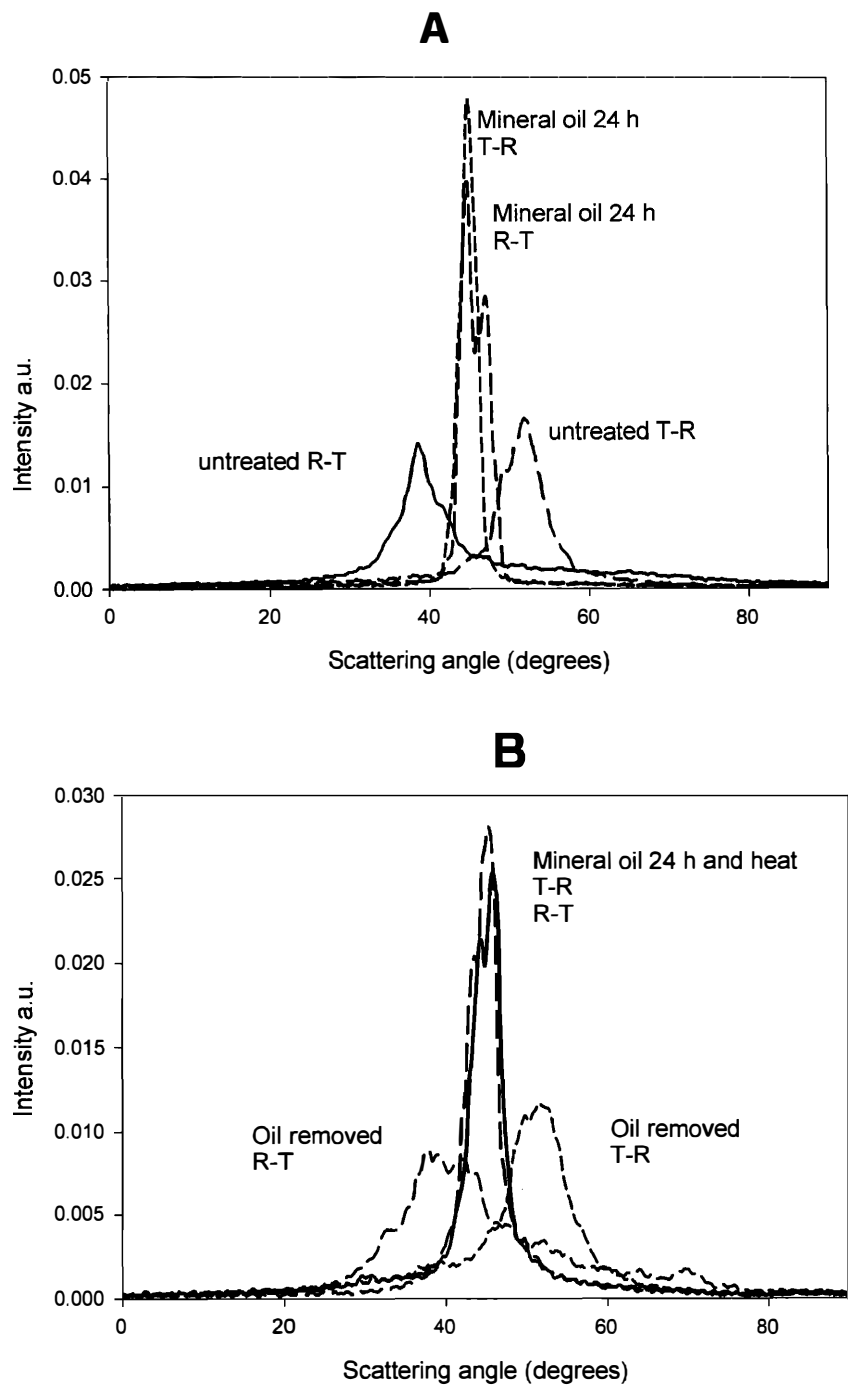


Figure 6. Goniophotometric intensity scans: (A) Individual untreated Indian hair fiber and 24 hours after mineral oil application. (B) 24 hours after mineral oil application with short-term heat treatment and after removal of oil film with acetone.

extent, increased diffuse reflectance may be explained by mineral oil residues, especially around the scale edges. Thus, using a goniophotometer as an optical tool to study the surface condition of the hair fiber, we conclude that mineral oil forms a smooth and stable film on the top of the cuticular sheath. Mineral oil does not penetrate extensively into the hair fiber in a 24-hour period, not even at elevated temperatures. Reduction in peak intensity after heat treatment is likely to be due to the penetration of a small amount of oil into the cuticular sheath, leaving most of it on the surface.

In Figure 7A the GP intensity scans are shown for untreated Indian hair fiber recorded in the R-T and T-R positions. Figure 7 also displays the reflectance curves when the same fiber was treated with coconut oil. As described above, a scale angle of 3.6° is found from the displacement of specular peaks from the angle of incidence. Coconut oil treatment covers the scale structure and results in sharp specular reflectance with increased peak intensities. After 24 hours the reflection intensity has decreased by a factor of 1.9 (see Figure 7B). However, peaks are still positioned around the angle of incidence. Application of heat treatment for only a few minutes induces a tremendous change in the GP curves, with partial separation, as seen in Figure 7C. Intensity scans from the T-R and R-T positions show a reduction in total intensity and separation. Although multiple reflections are observed, indicating the change in the surface distribution of oil residues, the fiber scale structure is likely to be exposed. Thus, the major amount of deposited oil film on the surface has indeed penetrated into the hair fiber. Dipping the fiber into acetone removes the remaining oil and results in scans matching those of the untreated fiber, as shown in Figure 7D. The scale angle is again 3.5° .

Results from coconut oil treatment differ from those from mineral oil treatment in several ways. Although measured intensity does not allow exact quantification, the changes in relative intensities can be used as estimates as long as measurements are performed on the same fiber under identical conditions. Hence, the reduction in intensity after 24 hours could indicate the decrease in coconut oil film thickness covering the hair fiber. For mineral oil, the reflected light intensity remained constant. Therefore, we can suggest that coconut oil may have at least partially penetrated the hair fiber within 24 hours. After 24 hours the remaining smooth coconut oil film must be very thin, considering the effect of short-time blow-drying. Several studies conducted at TRI have demonstrated the loosening of scale edges and the formation of half-domes upon heat treatment of hair fibers. Under such conditions, oil can wick into the cuticular structure. If so, then both mineral and coconut oil should penetrate into the hair because their surface tensions are similar. Although oils can wick by capillarity between separated cuticle cells at the surface where the cells may be separated, their penetration into the entire cuticle sheath and the cortex does not occur by capillarity. The fact that coconut oil was found to penetrate and mineral oil does not supports this hypothesis. Because of the much smaller volume, the cuticle can accommodate only a small amount of oil. Therefore, these GP observations show that oils penetrate into the bulk of hair and skin by molecular diffusion.

EFFECT OF OTHER OILS ON GP MEASUREMENTS

We also conducted measurements with various other plant-derived oils. For hair treated with mustard oil, the scale structure remained covered after 24 hours, even after addi-

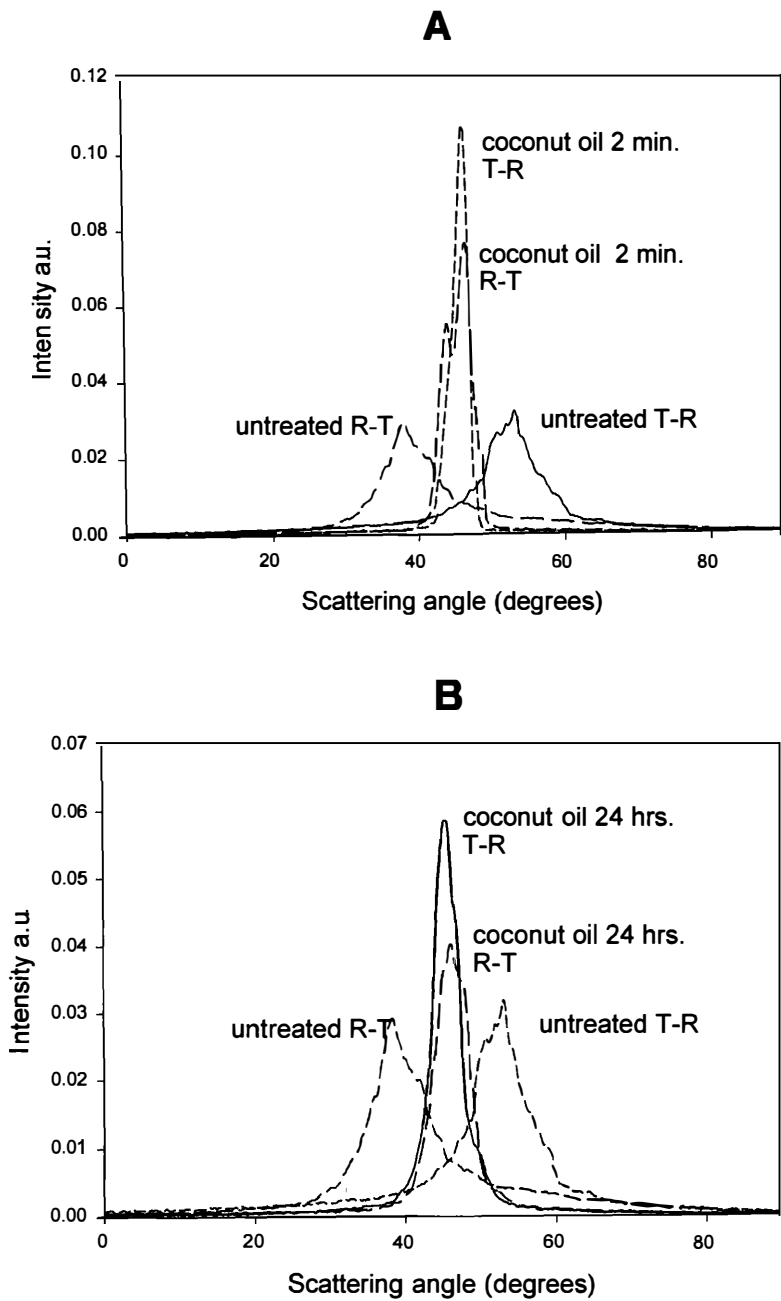
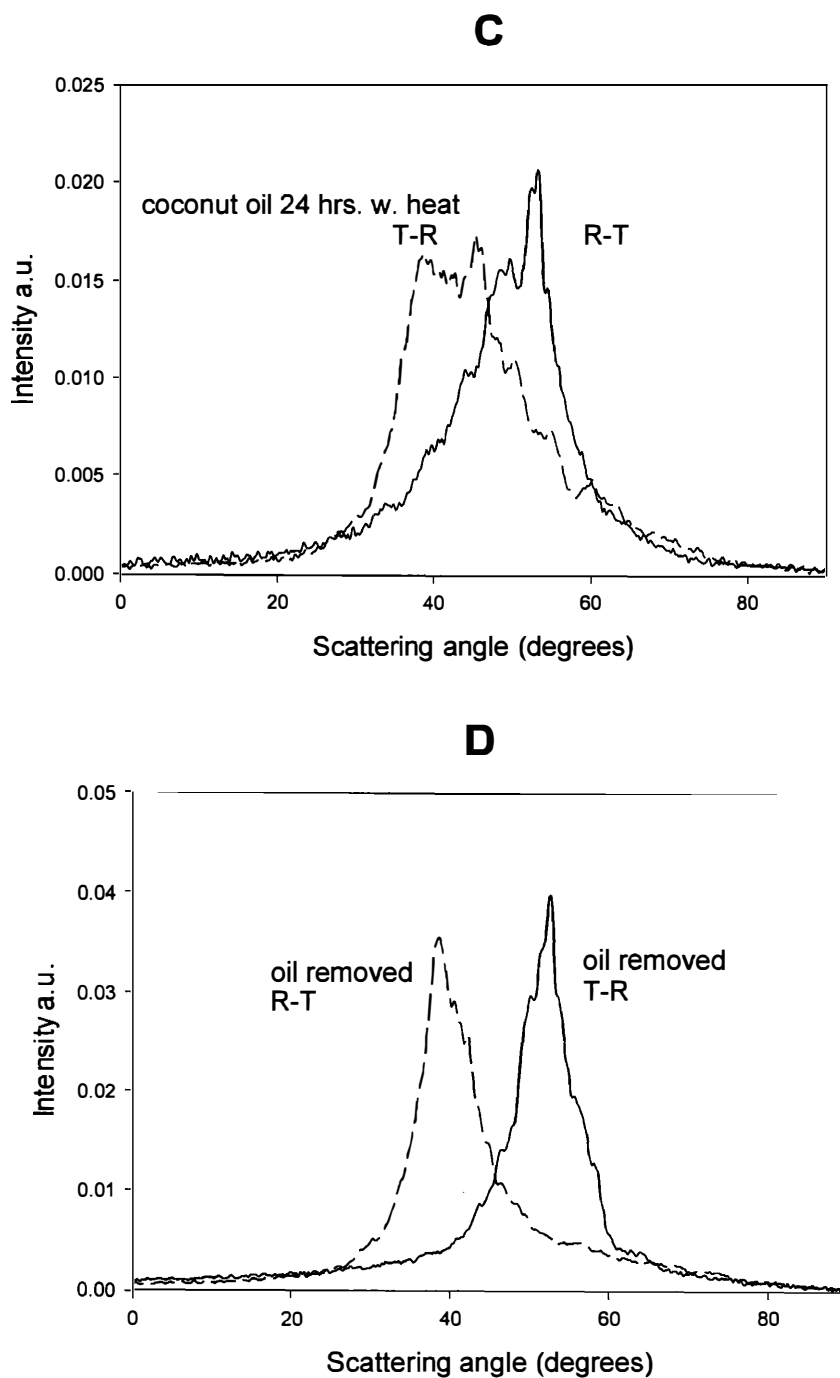


Figure 7. Goniophotometric intensity scans: (A) Individual untreated Indian hair fiber and immediately after coconut oil application. (B) 24 hours after coconut oil application compared to untreated fiber. (C) 24 hours after coconut oil application with short-term heat treatment. (D) After removal of oil film with acetone.

tional heat treatment. Also, for hair treated with sesame, ricebran, and olive oils, the scale structure was not apparent from the GP curves even after 24 hours, suggesting no penetration. For olive oil, however, partial separation of reflectance patterns from the

Figure 7. *Continued.*

T-R and R-T positions appeared after additional heat treatment. Surprisingly, for hair treated with sunflower oil, the scale edges were partly exposed after 24 hours, indicating at least partial penetration of sunflower oil into the fiber. As GP scans characterize only

the hair surface condition, it is not possible to determine if sunflower oil penetration has occurred only within the cuticular layer or throughout the hair fiber, involving the cortex. In general, polyunsaturated oils do not seem to diffuse into hair. Saturated and monounsaturated oils seem to diffuse into the hair structure.

DIFFUSION MECHANISM

It is known that diffusion of small molecules such as dyes and surfactants in wool fibers occurs through intercellular pathways known as cell membrane complexes, CMCs (8). It is also known that surfactants such as sodium lauryl sulfate diffuse into protein structures effectively because of their ability to solubilize proteins by complexation (9). Since we are considering the diffusion of oils that are uncharged triglycerides, this may be irrelevant in this instance. Based on the work referenced above, the diffusion or penetration ability of small molecules would be expected to be through the CMCs, controlled by the affinity of the molecules for nonkeratinous proteins in the CMCs, molecular structure, and molecular weight. For example, mineral oil does not diffuse into hair because it is nonpolar, containing long linear hydrocarbon chains with lengths above C-20. Even though the straight-chain molecular structure is favorable for diffusion by reptation, lack of affinity seems to prevent it from diffusing into hair. Vegetable oils, on the other hand, consist of triglyceride molecules in which three fatty acid molecules are naturally esterified to the three hydroxyl groups of a glycerol backbone. For example, coconut oil is rich in lauric acid (C-12 triglyceride), whereas in sunflower oil linoleic acid (C-18:2 triglyceride) is predominant. Because of its polar character, coconut oil seems to have an affinity toward protein molecules in the CMCs, and, therefore, this oil penetrates more readily into hair fibers compared to mineral oil. Since C-12 fatty acid is a straight-chain fatty acid, the molecular structure of the triglyceride is also favorable for diffusion. Diffusion occurs by an acid-base type of interaction involving the ester groups in the oil and the carboxyl and amine groups in the protein. Oils containing triglycerides with unsaturated fatty acids seem to encounter greater resistance to diffusion. These molecules tend to be more spread out because of the presence of multiple double bonds and are therefore difficult to enter and move through the narrow channels of the CMCs. These aspects need to be explored further, based on the dynamics of these molecules in a protein environment.

CONCLUSIONS

The work reported in this paper shows that the formation of oil films in hair fiber assemblies can be studied by two very different methods, interfiber adhesion and reflectance of light. There seems to be good correspondence between the two methods, as shown by the agreement between the two methods for coconut, mineral, sunflower, and olive oils. In general, saturated and monounsaturated oils penetrate into the hair because of a compact molecular structure and the polar head group of the triglyceride molecules that constitute these oils. In a dynamic mode these molecules can reptate and squeeze through the CMCs. On the other hand, polyunsaturated oils do not penetrate into hair, most likely because of the more open and spread-out structures of their triglyceride molecules and because of the presence of multiple double bonds. The results reported in

this work show a complex relationship between capillary liquid films, interfiber capillary adhesion, light reflectance, fiber surface and bulk structure, and molecular diffusion.

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