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Effect of oil films on moisture vapor absorption on human hair

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Synopsis

In this paper sorption and desorption of water vapor on hair fibers treated with various oils is investigated, using a dynamic vapor sorption (DVS) apparatus. Results show lower "equilibrium" sorption of moisture for various oil-treated samples compared to the untreated sample. Coconut oil-treated hair had a higher regain than mineral oil-treated hair. Although treating the hair samples with oil reduced moisture pickup, a considerable amount of moisture vapor was still able to penetrate into hair fibers. Calculated hysteresis plots show that the samples treated with different oils have slightly higher moisture retention at low relative humidities compared to that of the untreated sample, which suggests a beneficial effect. The calculated moisture diffusion coefficients for oil-treated samples were much lower compared to the untreated hair fibers, suggesting that surface oil films and penetrated oil molecules form a diffusion barrier. A moisture diffusion model is discussed in terms of the possible role of fiber swelling on restrictive narrowing of the cell membrane complexes (CMCs), which form the diffusion pathways in the fiber. The effect of film thickness on moisture absorption and the reverting of the sorption isotherm to that of the untreated hair after removal of the oil film shows that oil film is the main resistance to moisture diffusion. The lowering of the diffusion coefficient of water vapor by oil films will slow the loss of moisture, an effect similar to "moisturization" of hair.

INTRODUCTION

In many countries, vegetable oils are used as pre- or post-wash dressings for hair. Oils are known to lubricate the hair surface to prevent damage during grooming and to improve the luster of the hair by forming a thin coating on the surface. It has been shown that coconut oil prevents wet combing damage due to its hydrophobicity and the resulting reduction in fiber swelling (1,2). In earlier studies by Ruetsch *et al.* (2), it was shown that coconut oil penetrates into hair whereas mineral oil does not. In a later study by Hornby *et al.* (3), penetrability of different vegetable oils was investigated. Penetrability of oils into hair is an important aspect in this study because once the oil is applied to hair, the film thickness of the oil depends on the ability of the oils to penetrate hair. Oils that do not penetrate, such as mineral oil, will leave a thicker film on the surface as compared to coconut oil, which is known to penetrate hair. Such films left on the surface of hair can have a considerable effect on interfiber adhesion due to capillarity. This was investigated by Keis *et al.* (4) using several vegetable oils. This study attempts

to examine how the sorption of water vapor is affected by various oils applied to hair in relation to film thickness, which was controlled by the amount of oil applied to hair. No attempt has been made to determine film thickness on the hair surface.

For this study, three oils, namely coconut, mineral, and sunflower oils, were chosen based on their performance in an earlier study (1). Among these, coconut oil was known to penetrate the whole fiber, whereas sunflower oil showed limited penetration, especially into the cortex (3). Mineral oil was found not to penetrate the hair (2,3). The sorption and desorption of water vapor 24 hours after oil treatment, with the application of heat, and after removal of the oil film from the surface were studied. Additionally, hair samples were treated with various amounts of oil in order to demonstrate the effect of the film thickness on water vapor sorption behavior. It is known that oils have different abilities to penetrate into the cortex of the hair (1,3). In this study, we are attempting to see how the sorption of the water vapor is affected by the oil in the interior of the fiber and the oil film on the surface.

EXPERIMENTAL

All treatments were performed on dark brown European hair (purchased from DeMeo Brothers Inc., New York), which was washed with 1% sodium lauryl sulfate solution and rinsed thoroughly. The oils used for this study were commercially available mineral oil, coconut oil, and sunflower oil. Oils were applied to hair tresses in a ratio of 0.1 ml of oil per gram of hair. The oils were gently massaged into the hair swatch, and the samples were kept for 24 hours at room temperature (~25°C) before testing. Another set of tresses was treated with each of the oils as described above and then exposed to heat after the 24-hour time period. The samples were heated with a hair dryer on medium heat (~60–80°C) and air flow for 15 minutes before testing.

Additionally, samples were treated with a larger amount of coconut and mineral oil to form a thicker layer on the hair surface. This was achieved by applying oil in a ratio of 1.2 ml of oil per gram of hair. Finally, measurement on a coconut oil-treated sample was performed after the removal of the surface oil. This tress was treated with 0.1 ml of coconut oil, and kept for 24 hours. Then a Kimwipe® was wetted with acetone and the hair sample was pulled through the wipe multiple times until the fibers no longer showed any visual signs of the coconut oil treatment.

Sorption and desorption of water vapor was determined gravimetrically using a dynamic vapor sorption analyzer (DVS-1 from Surface Measurement Systems, NA, Allentown, PA). The description of the apparatus has been covered elsewhere (5). All experiments were conducted at 25°C and a total gas flow of 200 ml/min. Approximately 25 mg of hair snippets cut from the hair tress were dried overnight at 0% RH under dry nitrogen gas. Relative humidity was then increased by steps of 10% up to 90%, and then to 95%. Relative humidity was then decreased through the same steps back to 0%. The samples remained at each stage until its mass reached "equilibrium" (arbitrarily defined by a change in mass of less than 0.0015% per minute for 20 minutes). For the studies on the thicker oil coatings, only the sorption half of the experiment was performed.

RESULTS AND DISCUSSION

EFFECTS OF THIN OIL FILMS

At each relative humidity stage, moisture regain was calculated from the following formula:

$$R = \frac{M_V}{M_D} \times 100\% \quad (1)$$

Here, M_V is the mass of moisture in the fibers at a given relative humidity stage, M_D is the dry mass of the fibers, and R is percent moisture regain. Regain values were then plotted against relative humidity to give the sorption and desorption isotherms. The sorption-desorption isotherms for the untreated and oil-treated samples are displayed in Figure 1. For untreated and oil-treated hair a single run was performed. This was based on the high reproducibility of this measurement, which was established early in the validation study of this instrument, in which three replicates on a single sample gave essentially coincident sorption-desorption isotherms. Based on this observation and also considering the long time taken for a measurement (2.5 days), only one measurement was performed on each sample. The isotherms for the untreated hair behaved as expected, and a maximum regain of 27.38% occurred at 95% relative humidity. All of the oil-treated hair samples showed lower levels of moisture sorption compared to the untreated sample, with the coconut oil sample having slightly higher regain than the other oil-treated samples at high relative humidity. The maximum regains at 95% RH for the coconut, sunflower, and mineral oil samples were 23.65%, 22.53%, and 22.05%, respectively. The difference between the untreated control and the oil-treated samples is statiscally significant. The differences between the oil-treated samples may not be sig-

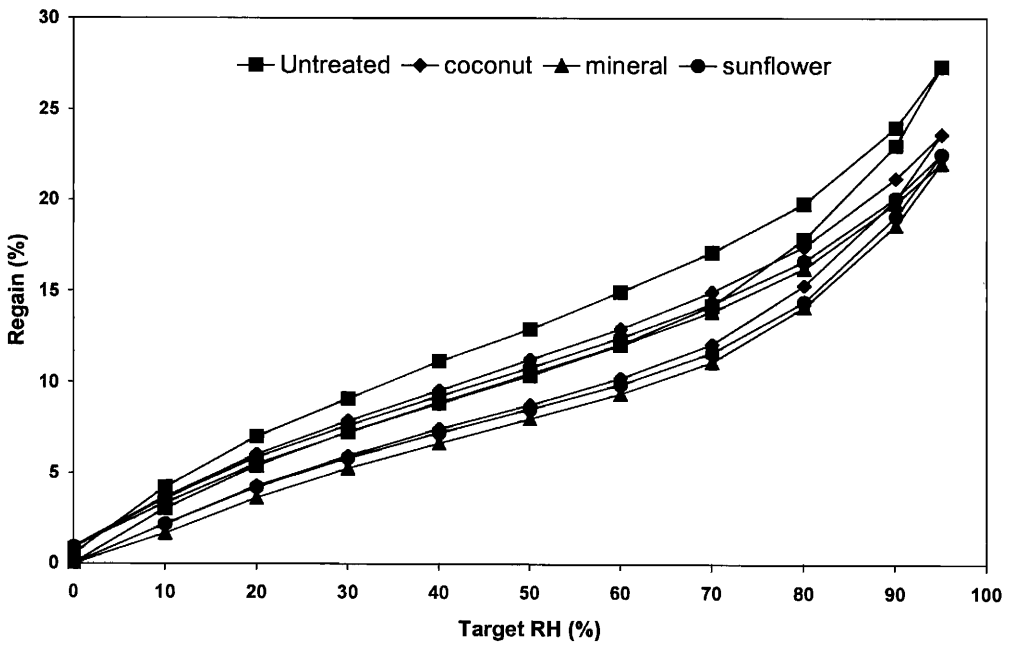

Figure 1. Water vapor isotherms at 25°C for untreated and oil-treated hair (thin oil coating).

nificant. Treating the hair samples with oil reduced moisture pickup; however, a considerable amount of moisture vapor was still found to penetrate into the hair fibers. The thin layer of oil on the surface may act as a barrier reducing the rate of penetration of water vapor. While this is the case for the mineral oil sample, there may be some penetration by the coconut and sunflower oil, which might hinder the absorption of water vapor. Several studies have indeed concluded that due to the long-chain nonpolar hydrocarbon structure, mineral oil does not penetrate into the hair fiber, leaving a layer on the fiber surface, even when exposed to heat (1–3). On the other hand, coconut and sunflower oils, which are polar and have affinity toward keratin, do penetrate into the cortex of the fiber. However, the amounts are expected to be too small to have a large effect on moisture vapor sorption.

The diffusion rates for moisture into and out of the fiber at each relative humidity were calculated for all of the samples from the sorption data of Figure 1. These calculations are based on the solutions of Ficks's diffusion equation applied to cylindrical geometry. A simplified version of this solution is given in equation 2:

$$C_t/C_{eq} = 4(D\ t/\pi\ r^2)^{1/2} \tag{2}$$

where C_t is the concentration of the diffusant at time t, C_{eq} is the concentration at equilibrium, D is the diffusion coefficient, r is the fiber radius, and t is time.

In a typical DVS sorption-desorption experiment, the humidity and the moisture regain data are obtained in the form shown in Figure 2. Each step in moisture regain is equivalent to a diffusion experiment. Therefore, the numerical data from the sorption (or desorption) experiment can be converted into a plot of (C_t/C_{eq}) Vs $(t/r^2)^{1/2}$. The initial

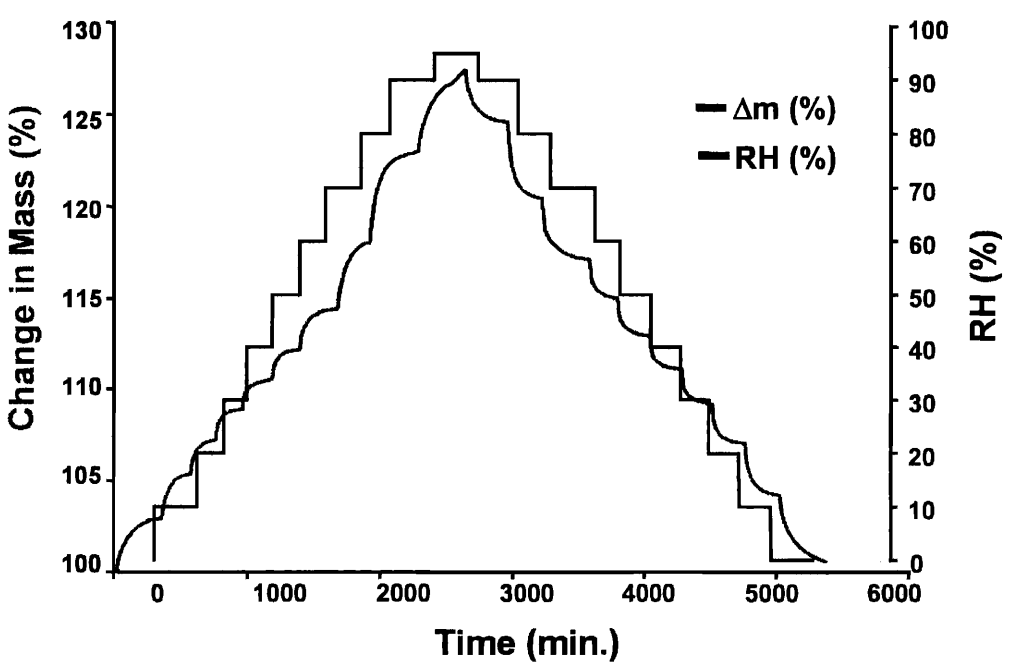

Figure 2. Target humidities and moisture regains as a function of time in a typical dynamic vapor sorption experiment.

part of this plot (for $(C_t/C_{eq}) < \sim 0.5$) will be linear and its slope (calculated by linear regression) is related to the diffusion coefficient as

$$D = (\pi/16)\,(\text{slope})^2\ \text{cm}^2/\text{s} \tag{3}$$

Diffusion coefficients for hair samples used in this work, calculated by equation 3, are displayed in Figure 3 for sorption and in Figure 4 for desorption as a function of RH. It should be noted that the diffusion coefficients obtained by this procedure are apparent diffusion coefficients because they are determined for a fiber sample and an average value of the radius is used in the calculation. True diffusion coefficients can be determined only by establishing concentration profiles as a function of time for diffusion into a single fiber. In Figure 3, we can see that as relative humidity increases from 0%, the diffusion coefficients increase, reach a maximum, and then decrease. In Figure 4, for desorption, we see the same pattern, although the values of the diffusion coefficients at all humidities are somewhat higher than those found in the sorption mode. This is because sorption takes place in an unswollen fiber in which diffusion is difficult, whereas desorption occurs from a swollen fiber in which diffusion is considerably easier. Swelling of the fiber is believed to open several pathways for diffusion. This is true of most materials. In the case of hair we see anomalous behavior, i.e., diffusion coefficients decrease with an increase in swelling. We propose the following hypothesis to explain the observed diffusion behavior.

The overall rate of diffusion into the hair cortex is controlled by two factors: (a) diffusion of water molecules through the cell membrane complexes (CMCs) and (b) diffusion into the matrix of the cortical cells. The latter involves the swelling of the cell, which can constrict the CMCs and reduce the rate of diffusion through these channels. This

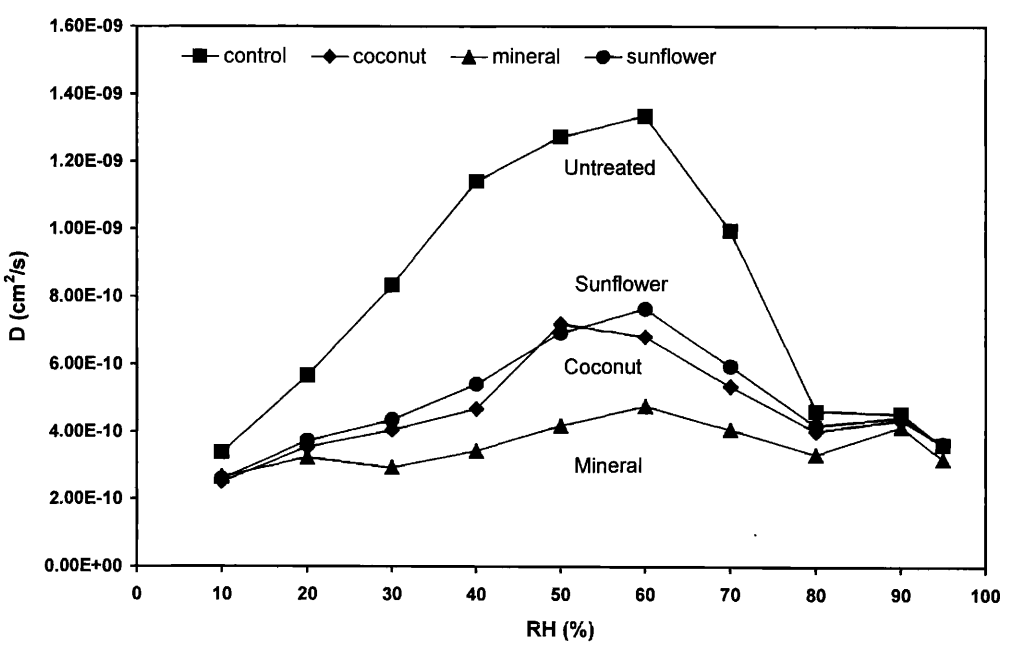

Figure 3. Plot of calculated water vapor sorption diffusion rates for various oil-treated hair as a function of RH.

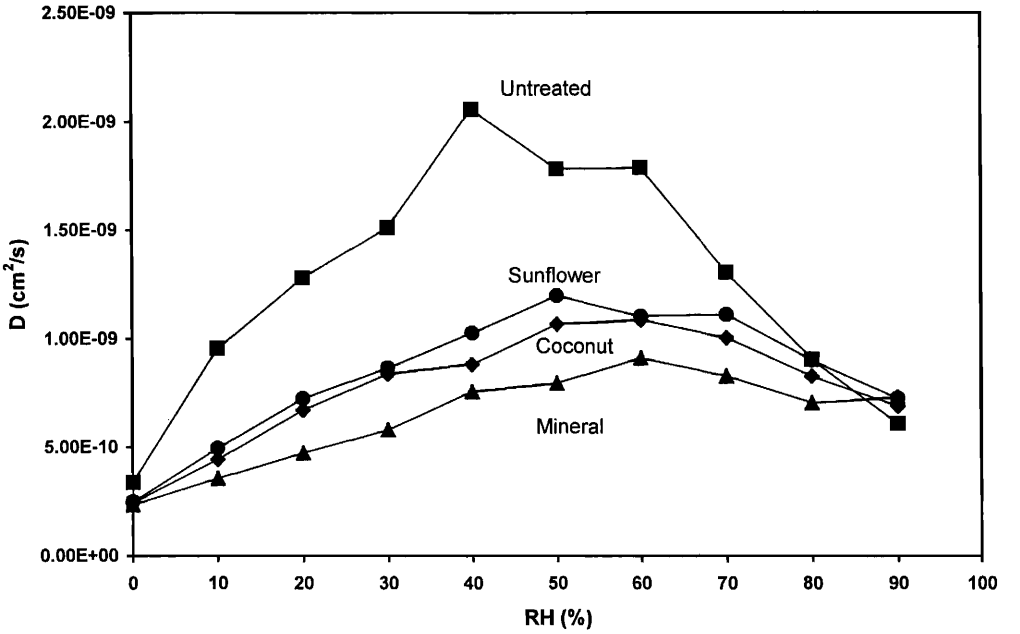

Figure 4. Plot of calculated water vapor desorption diffusion rates for various oil-treated hair as a function of RH.

happens mainly because the outward swelling of the cortex is restricted by the cuticle sheath. This directs the swelling pressure inwards, leading to the constriction of CMCs. Based on this realistic picture, we can explain the shape of the diffusion coefficient versus the RH curves seen in Figures 3 and 4. In the sorption mode, at low RH, diffusion through CMCs is fast, but slows down when the molecules cross over into the cell because the matrix is not swollen. As the humidity increases, the diffusion rate increases because the swelling leads to an increase in free volume. Beyond 70% RH, capillary condensation leads to excessive swelling of the cells, which constricts the CMCs, thus reducing the rate of diffusion through the CMCs. Therefore, it is reasonable to assume that during sorption, at low humidities (left side of the maximum), diffusion into the cells is the controlling step. At high humidities (right of the maximum), diffusion into the cells is fast, and therefore the rate-controlling step is the diffusion through the CMCs, which are constricted by the swelling of the cell. During desorption at high humidities (right side of the maximum), the rate-controlling step is the diffusion through the CMCs, which open up as the cells contract due to loss of water. At low humidities (left side of the maximum), as the cells contract, diffusion through these cells slows down and becomes the rate-controlling step. Diffusion through the CMCs is fast. This seems to be a reasonable hypothesis for the shape of diffusion coefficient versus RH curves. This concept is applicable to diffusion into the cuticular sheath also, except that in the cuticle the endocuticle adjacent to the CMC may participate in the diffusion.

For both sorption and desorption, the diffusion rates are substantially lower for the oil-treated hair compared to the untreated hair. Two possible reasons can be suggested for the lowering of the regain for the oil-treated hair: (a) the penetrated oil molecules block the sites for the sorption of water and (b) in the case of oil-treated hair, sorption

equilibrium has not been reached. This is possible since we use the same condition (dm/dt = 0.00015% for 20 min) for deciding the reaching of equilibrium for the untreated and the oil-treated hair. This will be discussed further in a subsequent section.

We note that the coconut and sunflower oil-treated samples show comparable diffusion coefficients while that of the mineral oil-treated sample is much lower. The possible reason is that, because of penetration into the fiber, the vegetable oil films left on the surface are thinner, for the same amount of oil applied, compared to the film of mineral oil, which does not penetrate into the hair. Thicker films give greater resistance to diffusion than thinner films.

EFFECT OF TEMPERATURE

The coconut oil-treated hair was subjected to a low level of heating to see its effect on absorption of oil from the film into the fiber. As can be seen from Figure 5, the sorption-desorption isotherms for oil-treated hair before and after application of heat are essentially identical, indicating the negligible effect of heat on oil absorption and the subsequent sorption-desorption of water vapor.

EFFECT OF THICK OIL FILMS

The thicker-surface oil films were formed by treating the hair samples with larger

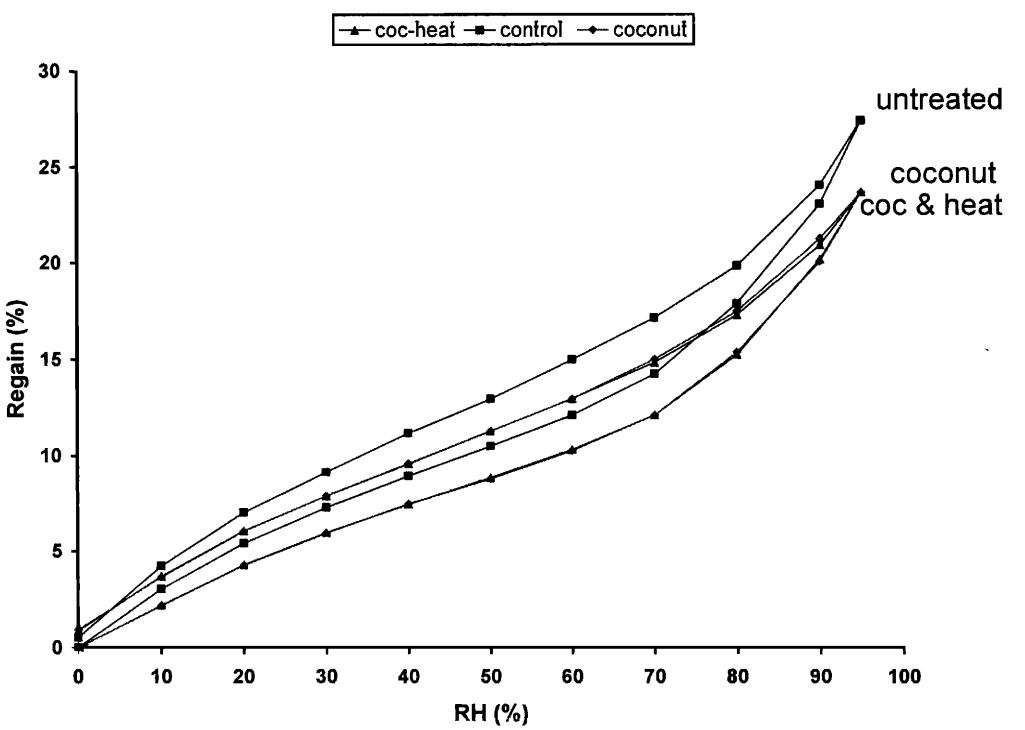

Figure 5. Water vapor isotherms for untreated hair sample and coconut oil-treated hair samples before and after exposure to heat. Effect of heat seems to be negligible (isotherms are essentially coincident).

amounts of oils. The effect of coating thickness on sorption isotherms for mineral and coconut oil-treated samples is shown in Figure 6. For both of the oils, the additional increase in coating thickness further reduced the amount of moisture sorbed by the fibers. As was the case for the thin oil coatings, the isotherms for the excess amounts of coconut and mineral oil are close together, with slightly higher moisture regain occurring in the coconut oil sample. This probably suggests that coconut oil film is thinner because of its ability to penetrate hair. Since mineral oil does not penetrate the hair, the film would be thicker; however, the differences in the sorption behavior are smaller because the differences in the two films are very small because of comparable viscosities.

The sorption diffusion coefficients for the coconut oil with two different coating thicknesses are plotted in Figure 7. With increasing coating thickness, the diffusion coefficients are decreased. The same trend appeared for the mineral oil sample (not shown here). While the sample with the thin coconut oil coating retains the general shape of the untreated plot, the sample with the thick coating has a flat sorption diffusion coefficient plot.

EFFECT OF REMOVING THE OIL

In order to determine if the reduction in moisture pickup and the slowing of moisture diffusion rates by the coconut oil are affected by the oil penetrated into the fiber, we performed the following experiment. As described in the Experimental section, the oil

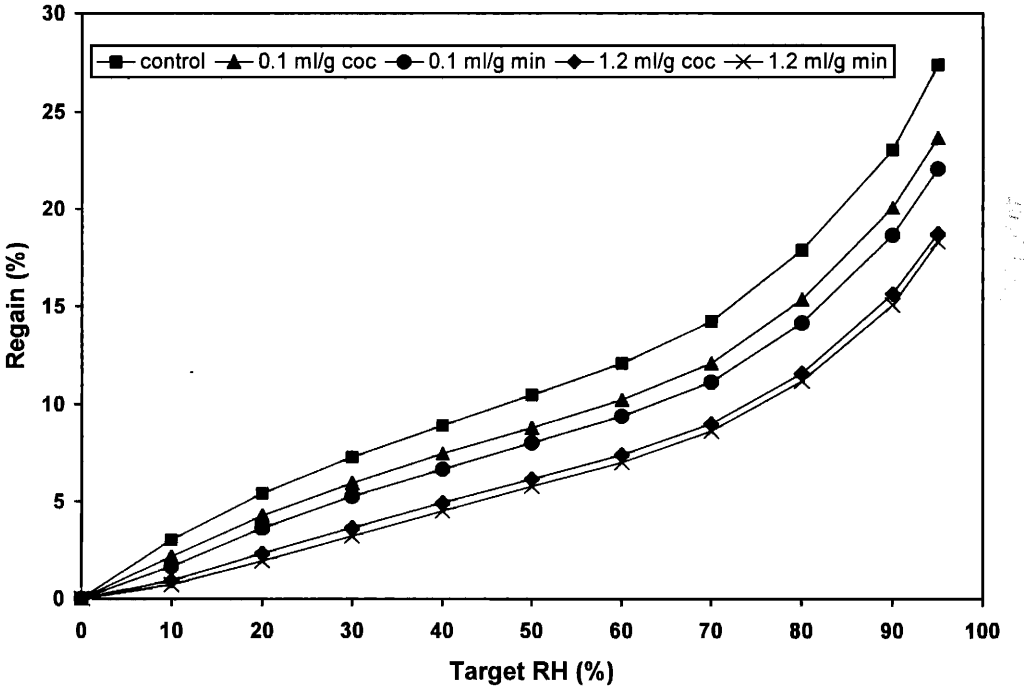

Figure 6. Water vapor sorption isotherms for hair samples with varying thicknesses of surface oil films. Samples with thicker films absorb less water vapor compared to thinner films. Mineral oil-treated hair consistently absorbs less water vapor compared to coconut oil-treated hair, in both cases.

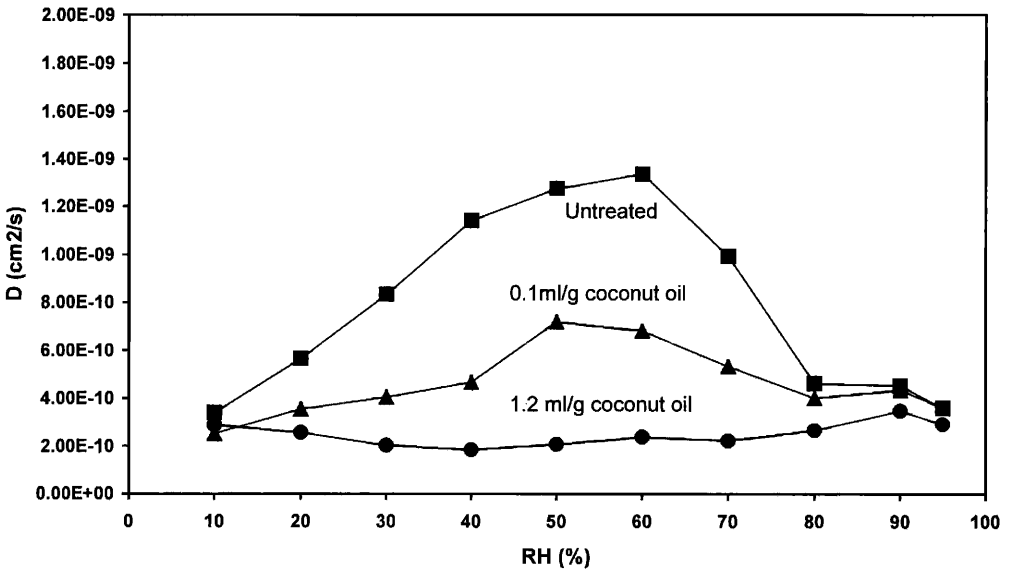

Figure 7. Plot of calculated water vapor sorption diffusion rates for hair samples treated with various amounts of coconut oil as a function of RH.

film from the surface of the fibers was removed with acetone. The sorption isotherms for acetone-wiped oil-treated hair along with that of the untreated hair are displayed in Figure 8. The original coconut oil-treated sample prior to wiping with acetone is also included in Figure 8. The sorption isotherm for the acetone-wiped sample is nearly

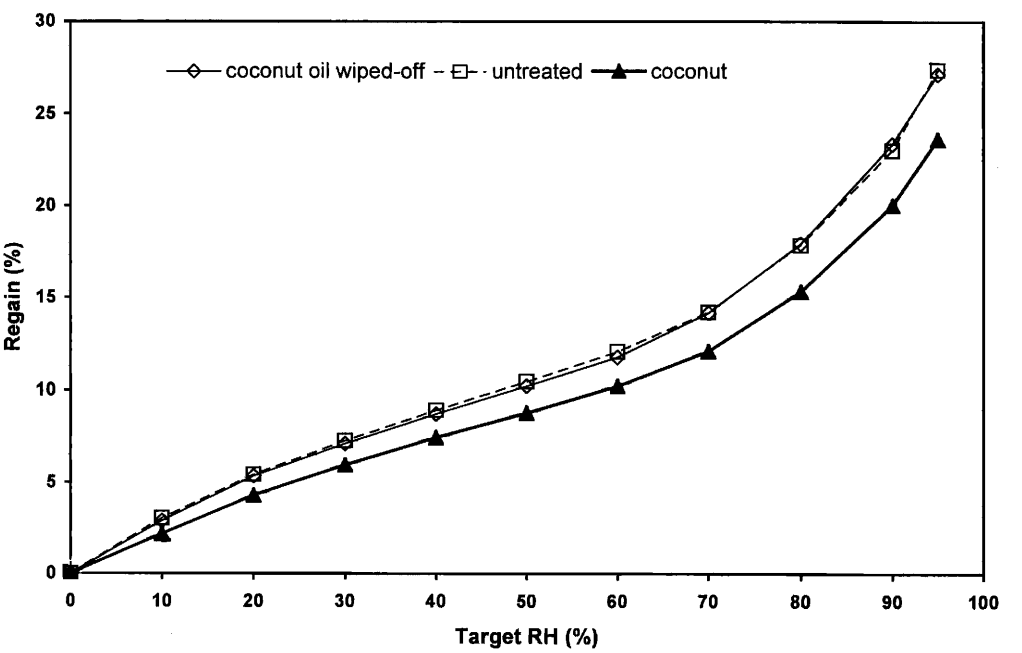

Figure 8. Water vapor sorption isotherms for hair sample after the removal of the surface coconut oil.

identical to that of the untreated sample, suggesting that the oil has been removed from the fiber surface. Also, the diffusion coefficients were similar to those of the untreated hair. This indicates that the coconut oil that had penetrated into the fiber cortex did not affect the moisture sorption behavior of the hair sample, probably because the amount is too small. Of course, this assumes that wiping the fiber with an acetone-soaked Kimwipe® does not remove the cortex-penetrated oil. The reductions in moisture uptake and diffusion rates found in our study seem to be caused mostly by the surface oil films.

NATURE OF THE OIL FILM

Oil applied to hair forms a thin film on the fiber surface where the amount applied is small (0.1 ml/g). Most of the oil ends up near the cuticle edge, as shown in Figure 9. From there it will penetrate into the cuticle through the endocuticle and the cell membrane complex. A small amount (as in the case of coconut oil) may also penetrate the cortex through cortical CMCs. Since these are the same pathways used by the water vapor to diffuse into the fiber, clogging of these pathways by oil molecules can retard the rate of diffusion. Since the sorption equilibrium depends on the set dM/dt (0.0015 %/min for 20 minutes), and because of the decrease in the rate of diffusion, it is possible that the dM/dt condition is satisfied before a true equilibrium is reached. However, when we performed an additional measurement with a coconut oil-treated hair sample, allowing the hair to remain at each RH for an extended time past the previous equilibrium condition (i.e., at least five more hours), the additional moisture uptake was negligible. This observation shows that the lowering of sorption levels is not related to the attainment of equilibrium. Thus, the more likely explanation is that the cuticle, which forms ~20% or more of the fiber volume, is partially penetrated by the oil molecules (endocuticle and CMCs), and therefore, that volume (these sites) is not available for the sorption of the water vapor. In other words, absorption of oil changes the sorption behavior of the substrate. This can lead to a lowering of the diffusion rate and the equilibrium uptake. The acetone-soaked Kimwipe® seems to remove the oil, which is penetrated into the cuticular zone.

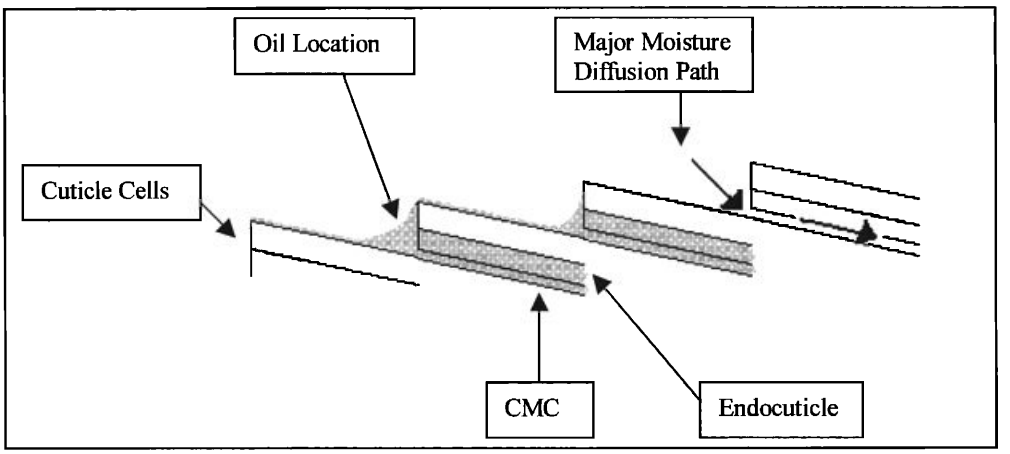

Figure 9. Schematic of location of oil on hair fiber surface.

CONCLUSIONS

Treating hair fibers with various oils reduced the amount of moisture regain and the diffusion rates of moisture in the fibers. These reductions are caused solely by the layer of oil on the surface of the fiber acting as a barrier. We suggest that differences between various oil-treated samples result partly from the differences in the molecular structure of the oils and their penetration behavior into the hair. Increasing the thickness of the oil layer on the fiber surface increased moisture regain and decreased diffusion rates. However, removing coconut oil from the fiber surface reversed the changes caused by the thin oil films. Our results using the DVS method indicate that moisture sorption behavior is not influenced by the oil that has penetrated into the cortex. This might be due to the relatively small quantities of oil present in the fiber interior. Greater changes are observed with oil penetrated into the cuticle layers and retained on the surface.

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