

Surface Wettability of Human Hair. I. Effect of Deposition of Polymers and Surfactants

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Synopsis

Monitoring the wetting force exerted on a single fiber while the fiber is slowly and continuously immersed in a liquid and then withdrawn can provide several kinds of information about the physicochemical heterogeneity of the fiber surface. This method for scanning the fiber surface with an appropriate liquid has been found useful for studying the distribution of materials deposited on the surface of human hair to improve hair assembly properties, such as cationic polymers used in hair conditioners. It is shown how wetting force vs. immersion depth curves can reflect not only the average distribution of the material on the surface, but also the degree of uniformity of the deposit; further, wetting force curves for multiple immersions of the same treated fiber indicate the ease of desorption of the surface material. The results for the systems studied, which include mildly oxidized hair and smooth nylon fibers for comparison, show how the relation between the critical surface tension of the fiber and the surface tension of the treating solution influences distribution and substantivity. Finally, data on the difference between advancing and receding wettability indicate how this hysteresis is related to the nature of the surface and to surface coverage by treating agents.

INTRODUCTION

In recent years a large number of shampoos and conditioners have come on the market which are intended to enhance the esthetic appearance of hair. Washing hair with these products is claimed to impart "body" (one of the attributes of which is low bulk density), smoothness, and luster. These favorable changes in the behavior of the assembly are brought about by subtle changes in the surface characteristics of individual fibers. In the process of washing hair with shampoos and conditioners, the natural deposits of sebum, an oily secretion produced by the sebaceous glands, are replaced by the polymers and surfactants that constitute the particular hair-care product. The nature of these deposits can influence interfiber interactions and thereby affect the behavior of the fiber assembly.

The amounts of residue left on the fiber surface are extremely small, necessitating sophisticated methods for analyzing surface concentrations. Some of these, principally tracer techniques, involve either extraction or destruction of the sample, and therefore they provide only an average surface concentration. Elemental analysis obtained by surface analytical techniques are sometimes ambiguous because of the presence of the same elements in the substrates as in the deposited material.

It appeared useful, therefore, to explore a new approach to the characterization of hair surfaces that would provide information about surface deposits, namely, a simple method involving wettability measurements on individual fibers. It

will be shown that wettability parameters measured by this method provide information not only about the average distribution of the material on the surface, but also about the nature and uniformity of the deposited film and about its substantivity, i.e., whether it is removed in subsequent processes. The surface wettability method can be adapted to study the desorption of surface deposits into liquid environments. This is particularly important in the case of hair, where irreversible deposition can lead to buildup of deposits that can affect hair appearance adversely.

EXPERIMENTAL

Materials. The hair sample used in this work was "European dark brown hair" (EDBH), supplied by DeMeo Bros. of New York. The hair was cleaned by extraction either with methylene chloride or with $\text{CH}_3\text{OH}/\text{CHCl}_3/\text{CH}_3\text{OH}$ in that order, followed by exhaustive rinsing in distilled water, and drying and conditioning at 65% RH and 21°C. Nylon 6 fibers used in this work were extracted with CH_3OH to remove the spin finish and were also rinsed with distilled water and conditioned at 65% RH and 21°C.

The following quaternary compounds were used in the fiber treatments: (1) Polymer JR-400 (Union Carbide): water-soluble, high molecular weight (~400,000), cationic, cellulosic polymer used in hair conditioners. (2) Gafquat-755 (GAF-755) (GAF Corp.): high molecular weight, quaternized poly(vinyl pyrrolidone) copolymer used in hair conditioners. (3) Triton X-400 (Tr-X-400) (Rohm and Haas): low molecular weight surfactant, mainly stearyl dimethyl benzyl ammonium chloride.

Treatment of Fiber Specimens. Fiber snippets mounted on stainless steel hooks were treated with 1% solutions of the polymer or surfactant for 3.6 ks at 21°C and were then air-dried without rinsing and conditioned at 65% RH and 21°C overnight.

Wetting Force Measurements. A modified Wilhelmy plate technique was adapted to single fibers using a recording microbalance. The technique, the method of specimen preparation, and the relevant theory of wetting of solids by liquids have been described earlier.¹⁻³ Wetting force measurements were at first performed using stepwise immersion; however, it was soon realized that the technique can be used to scan the surface of a fiber with a liquid immersion medium. In this procedure the fiber snippet is moved continuously into the liquid to a depth of 3-5 mm while the wetting force is recorded; the immersion speed was 2.8 $\mu\text{m}/\text{s}$. Such a wetting force curve as a function of the depth of immersion reflects the surface properties along the length of the fiber.

The wetting force curve is integrated electronically to obtain an average wetting force \bar{F}_W . The perimeter of the fiber was calculated from the microscopically measured major and minor axes of the cross section, which approximates an ellipse. From these measurements it is possible to calculate an average contact angle θ using the equation:

$$\bar{F}_W = p\gamma_{LV} \cos \theta,$$

where \bar{F}_W is the average wetting force, p is the fiber perimeter, and γ_{LV} is the surface tension of the liquid. In most of these measurements with hair, buoyancy corrections can be neglected. For example, the buoyancy force on a hair of di-

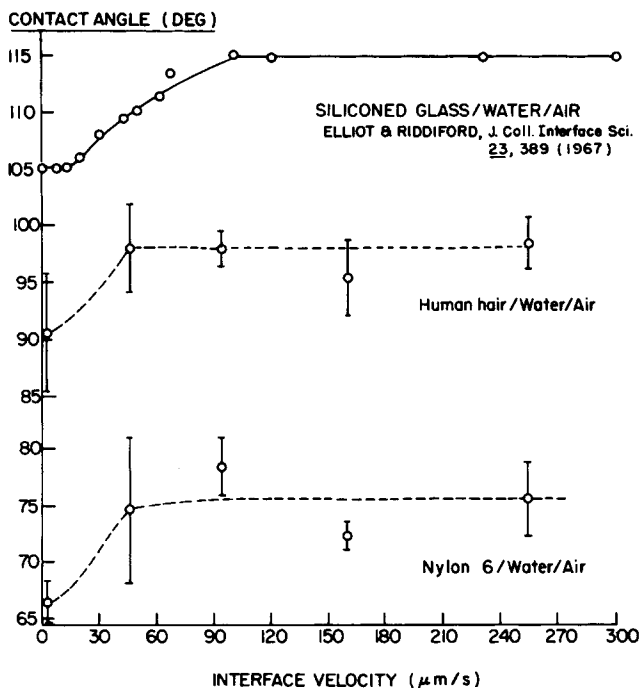


Fig. 1. Dependence of contact angle on interface velocity for three moving solid/water/air interfaces.

ameter $50 \mu\text{m}$ immersed to a depth of 5 mm amounts to $\sim 0.1 \mu\text{N}$, which is negligible compared to the wetting forces generally encountered in this work.

In multiple immersions the fiber specimens were air-dried and conditioned overnight at 64% RH and 21°C between successive recordings of wetting force curves. Doubly distilled water was used for wetting force measurements throughout this work, and all measurements were done in the against scale mode (scales pointing towards the liquid).

RESULTS AND DISCUSSION

Effect of Interfacial Velocity on Contact Angle. In a continuous immersion process the contact angle of a liquid against the surface of a solid depends on the interfacial velocity. Elliott and Riddiford⁴ found for a system consisting of a siliconed glass/water/air that the contact angle for such a hydrophobic surface was independent of interfacial velocity up to about $15 \mu\text{m/s}$, after which it increased until the interfacial velocity reached about $120 \mu\text{m/s}$ and then remained constant. The authors discussed this phenomenon in terms of differences between the relaxation times of molecules in the surface layers and those in the bulk of the wetting liquid. Equilibrium conditions prevail only at the lower interfacial velocities, while at higher speeds the surface molecules do not have enough time to reorient themselves at the interface. This results in lower work of adhesion and, consequently, higher contact angles.

In order to establish whether fiber surfaces follow a similar dependence on interfacial velocity to that observed by Elliott and Riddiford, average contact

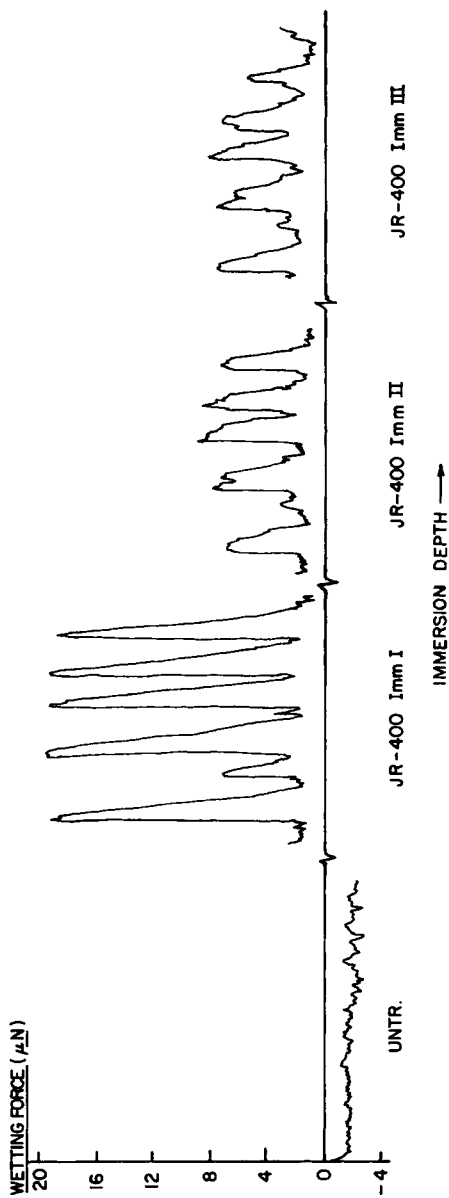


Fig. 2. Advancing wetting force curves in successive immersions in water of a hair fiber treated with JR-400 at 20°C.

angles were determined from integrated wetting forces for the systems human hair/water/air and nylon 6/water/air. It can be seen from the plots of contact angle as a function of interfacial velocity in Figure 1 that both systems follow a pattern similar to that for siliconed glass/water/air at higher speeds of immersion. However, because of interfiber variability the effect of speed could not be established within statistically significant limits. Because the low interface velocity range was limited, it was not possible to establish the point at which the velocity begins to have an effect on contact angle. It was presumed that nonequilibrium considerations would be minimized by choosing an interface velocity of $2.8 \mu\text{m/s}$ for the wettability measurements, since the work of Elliott and Riddiford suggests that at this low velocity the contact angle is independent of interfacial velocity.

Effect of Surface Deposits on Wetting Force Curves. Advancing wetting force curves for a hair fiber treated with polymer JR-400 together with that of the corresponding untreated fiber are shown in Figure 2. These curves were obtained with the same fiber specimen in multiple immersions. The wetting force is negative for the untreated fiber, reflecting the hydrophobicity of the epicuticular layers of hair.^{2,3} The apparent stick-slip nature of these curves is a result of the scale structure (surface roughness) and the chemical heterogeneity of the fiber surface along the wetted perimeter. After treatment with polymer JR-400, the fiber shows a positive wetting force that changes drastically as a function of depth of immersion, which is attributed, as will be discussed, to an uneven distribution of the hydrophilic polymer on the surface. The same fiber in the second immersion gives a lower wetting force, reflecting partial desorption of the polymer from the fiber surface during the first immersion. In the third immersion the wetting force curve shows very little further change, suggesting that after the first immersion the polymer-treated fiber surface has attained a relatively stable condition as far as its wetting behavior is concerned. It should be noted that in these experiments about 3–4 mm of the fiber are immersed in the liquid, and the total immersion time is about 1.5 ks.

In an effort to establish whether the large variations in the first immersion wetting force curve were due to uneven distribution of the polymer on the fiber surface, a fiber was investigated having polymer deposited at specific locations using a microsyringe. Wetting force curves of this fiber after drying and conditioning are shown in Figure 3. Large increases in wetting force are seen when the liquid meniscus contacts the resin deposits on the surface. The fiber is

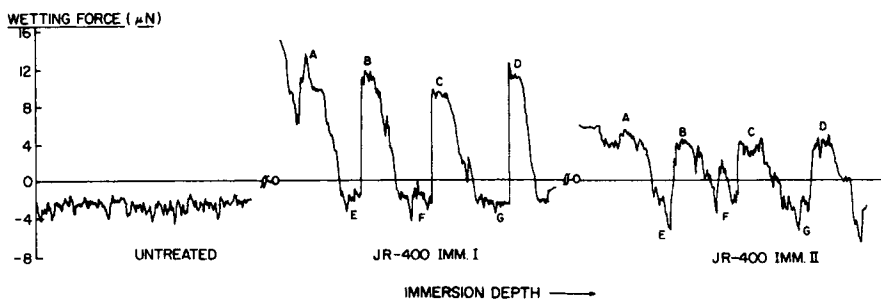


Fig. 3. Advancing wetting force curves in two immersions in water of a hair fiber treated with JR-400 solution at specific locations.

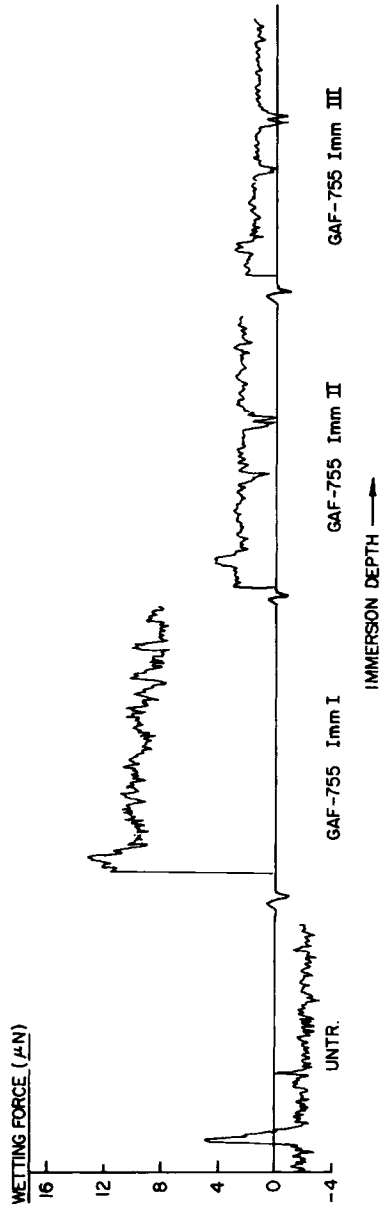


Fig. 4. Advancing wetting force curves in successive immersions in water of a hair fiber treated with GAF-755 at 20°C.

covered with the polymer in locations A, B, C, and D and is bare in locations E, F, and G. In the first immersion, part of the polymer is desorbed so that the wetting forces in the second immersion are lower at locations A, B, C, and D.

The wetting force at any position on the fiber is given by

$$F_W = p\gamma_{LV} \cos \theta$$

If a fiber is completely covered with the hydrophilic polymer (contact angle = 0° , $\cos \theta = 1$), the wetting force curve with water would be expected to show a more or less uniform value of $\sim 18 \mu\text{N}$ for a fiber of perimeter $247 \mu\text{m}$. A wetting force value between that of the untreated fiber and that of a completely covered fiber indicates unevenness in the distribution of the resin along the wetted perimeter; in such a case the meniscus at the three-phase line of contact will be irregular. The situation is similar to that described by Boruvka and Neuman⁵ of a cylindrical body with stripwise heterogeneity on the surface along the axis of the cylinder, for which these authors solved the LaPlace equation. Thus every point on the wetting force curve represents the surface chemical characteristics of the wetted perimeter at that instant, and the entire curve shows the distribution of hydrophobic and hydrophilic areas on the fiber surface. Wetting force curves such as those in Figure 2 indicate distribution of the hydrophilic polymer in relatively large domains, whereas those in Figure 4 suggest a comparatively uniform distribution of smaller domains covered by the polymer. The wetting force curve can be integrated to obtain an average wetting force which is related to the average surface coverage. However, this value does not indicate the nature of the distribution of the polymer, which can be deduced only from the shape of the wetting force curve itself.

The first immersion wetting force curve for a hair fiber treated with GAF-755 (Fig. 4) indicates a much more uniform deposition of this compound than of JR-400. Again, significant amounts of the material are desorbed during the first immersion, leaving a somewhat lower surface coverage, as indicated by the wetting force curve obtained in the second and third immersions.

The wetting force curves for hair fibers treated with the surfactant TR-X-400 (Fig. 5), on the other hand, show a regular pronounced stick-slip effect in the first immersion which is not seen in the second and third immersions. In these immersions, the wetting force curves appear similar to that of the untreated fiber, suggesting that most of the surfactant has been desorbed in the first immersion. Hair fibers show a high degree of interfiber variability in their wetting behavior, but the wetting force curves generally fall into the patterns described above.

In order to characterize the wetting behavior of a hair sample, average wetting forces (obtained by integration of the wetting force curve) were determined for

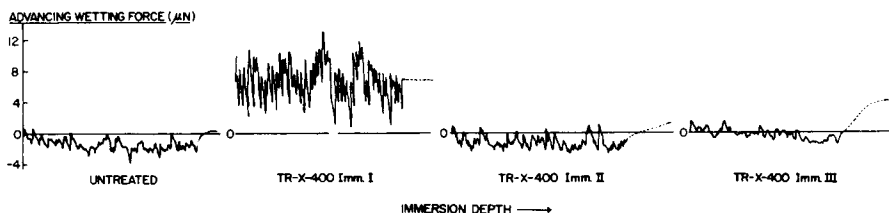


Fig. 5. Advancing wetting force curves in successive immersions in water of a hair fiber treated with TR-X-400 at 20°C .

TABLE I
Advancing and Receding Wettabilities (mN/m) of Surface-Treated Hair Fibers in Multiple Immersions^a

Treating agent	Untreated		Immersion I		Immersion II		Immersion III	
	Adv	Rec	Adv	Rec	Adv	Rec	Adv	Rec
JR-400	-8 ± 3	70 ± 5	35 ± 16	75 ± 4	8 ± 7	74 ± 4	7 ± 7	74 ± 4
GAF-755	-9 ± 3	80 ± 4	51 ± 9	86 ± 3	12 ± 4	86 ± 4	8 ± 3	84 ± 3
TR-X-400	-11 ± 5	75 ± 11	26 ± 5	73 ± 10	-7 ± 5	74 ± 12	-10 ± 5	71 ± 13

^a All values reported at 95% confidence level for six specimens.

TABLE II
Surface Tensions of 1% Solutions of the Treating Agents

Treating agent	γ_{LV} (mN/m)
JR-400	64.2
GAF-755	66.9
TR-X-400	26.9
Water	70.9

several specimens, and the interfiber averages are given in Table I in terms of wettability ($\gamma_{LV} \cos \theta$), the average wetting force normalized for the fiber perimeter. Although the data show high interfiber scatter, certain trends can be noted. The finding that wettabilities of the polymer-treated fibers in the second and third immersions are close to the value for the untreated fiber indicates that most of the polymer is desorbed in the first immersion, and that these polymers do not bind strongly to the surface in a room temperature (20°C) treatment. In general, advancing wettabilities are more sensitive to the treatment than receding wettabilities. This aspect will be discussed further in connection with wetting hysteresis.

Critical Surface Tension of Hair. The uneven distribution of the hydrophilic polymers on the hair fiber surface can be understood by considering the interactions between the hair surface and the polymer solutions. If the surface tension of the treatment solution is much higher than the critical surface tension of the hair surface, a uniform liquid film does not form and the treatment solution distributes itself in a patchy manner on the surface. An effort was made, therefore, to determine the critical surface tension of untreated hair using water and methylene iodide according to the method described by Wu.⁶ This method yields the dispersion ($\gamma_S^d = 24$ mN/m) and nondispersion ($\gamma_S^e = 4$ mN/m) or polar contributions to the critical surface tension of hair, $\gamma_C = 28$ mN/m, where

$$\gamma_C = \gamma_S^d + \gamma_S^e$$

The extremely small polar contribution reflects the essentially hydrophobic, low energy nature of the epicuticle of the hair fiber.

The surface tensions of the 1% treatment solutions, measured by the Wilhelmy technique using a platinum wire, are shown in Table II. Neither of the polymers are surface-active, and the surface tensions of their 1% solutions are close to that of water and thus much higher than the critical surface tension of the untreated hair surface. Therefore, they do not wet the fiber surface, which explains the breakup of the film and the patchy distribution of the polymer on the surface. The low molecular weight surfactant solution, on the other hand, has a much lower surface tension and therefore wets the surface easily.

Effect of Oxidation. The wettability of hair can be altered by exposing the fibers to oxidative or reductive treatments.³ Such treatments increase the critical surface tension of the fiber and so permit better wetting with liquids of higher surface tension. During oxidation the disulfide bonds in the keratin, especially in the exocuticular layer, are oxidized to cysteic acid, introducing anionic sites at or near the fiber surface for the chemisorption of cationic compounds like the

TABLE III
Wettabilities of Hair Fibers Surface-Treated after Oxidation^a

Treating agent	Adv wettability (mN/m)			
	Untreated	Oxidized	Surface-treated	
			Immersion I	Immersion II
JR-400	-0.8 ± 4.0	27.3 ± 3.4	51.5 ± 8.5	27.9 ± 5.0
GAF-755	-8.1 ± 2.6	26.7 ± 2.8	65.7 ± 3.7	39.5 ± 1.9
TR-X-400	-7.4 ± 7.9	27.8 ± 2.9	35.0 ± 13.0	21.6 ± 7.4

^a All values reported at 95% confidence level for five to six specimens.

polymers and surfactants used in this work. Oxidation of hair fibers was carried out with 6% H₂O₂ at a pH of 10 (adjusted with ammonium hydroxide) for 0.9 ks at 20°C. The short treatment times confined oxidation to the surface regions of the fiber without extensive bleaching of the bulk fiber.

Wetting force curves for the oxidized fibers treated with polymer solutions were much more uniform in the first immersion, suggesting better wetting of the fiber surface as well as improved binding of the cationic polymer to the oxidized hair surface. For fibers treated with TR-X-400, the wetting force curves were still nonuniform, but this was probably due not to nonuniformity of surfactant deposition, but to variations in the orientation of the surfactant molecules. On an unoxidized surface the orientation can be more random because both chemisorption and physical adsorption occur. On an oxidized surface the relative amount of chemisorption increases, the surfactant molecules becoming oriented with their lipid chains pointing towards the liquid and the cationic ends bound to anionic sites on the fiber surface. This can increase the hydrophobicity and decrease the wettability of the fiber compared to that of the unoxidized fiber.

Average wettabilities of fibers before and after oxidation and after subsequent surface treatment are shown in Table III. Very significant increases in wettability are seen after oxidation and again after treatment with polymers and surfactant. Higher wettabilities in the first and second immersions of the oxidized and treated fibers compared to those in Table I suggest higher surface coverage and improved substantivity, respectively. In the case of fibers treated with TR-X-400, the relatively low wettabilities are probably due to a reduction in the surface tension of the liquid as a result of surfactant desorption rather than to poor surface coverage.

Treatment of Nylon 6 Fibers. Wettability studies have shown that, although human hair fibers are hydrophobic, they do interact to a certain extent with cationic substances. To confirm the effects that were observed in the treatment of hair with cationic polymers and surfactants, similar experiments were conducted with nylon 6 fibers. These fibers are hydrophilic but have no specific sorption sites for cationic substances. Treatments were carried out with 1% solutions for 3.6 ks at 20°C as before, but the fibers were not rinsed prior to measurements.

Advancing wetting force curves for fibers treated with GAF-755 are shown in Figure 6. Because of the smooth fiber surface, a relatively uniform pattern is seen for the wetting force of the untreated fiber with water. The polymer-treated fiber shows a high wetting force in its first immersion corresponding to a contact angle close to 0°. In the second immersion the wetting force curve is

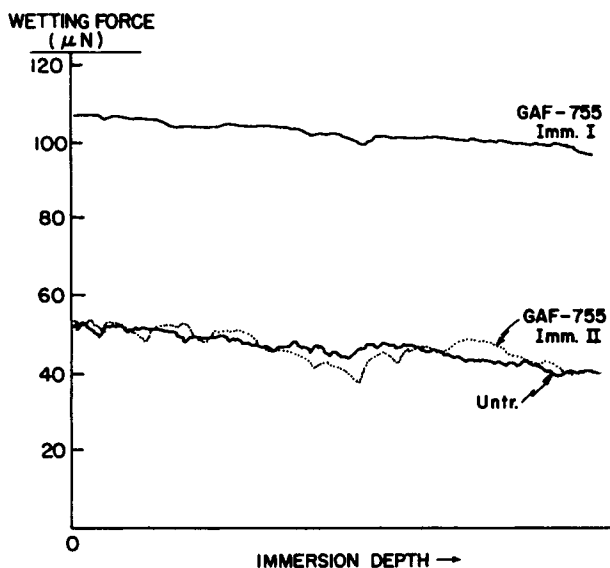


Fig. 6. Advancing wetting force curves for untreated and GAF-755-treated nylon 6 fibers.

close to that of the untreated fiber, suggesting almost complete desorption of the polymer from the surface. Similar behavior is shown by fibers treated with polymer JR-400.

Fibers treated with TR-X-400, however, show a regular stick-slip pattern in the first immersion which does not occur in the second immersion (Fig. 7). This is probably due to the desorption of excess surfactant (these fibers were not rinsed after treatment), which affects the surface tension of the liquid near the three-phase boundary during the measurement. This aspect will be discussed in detail in a separate communication. In the second immersion slightly higher wetting

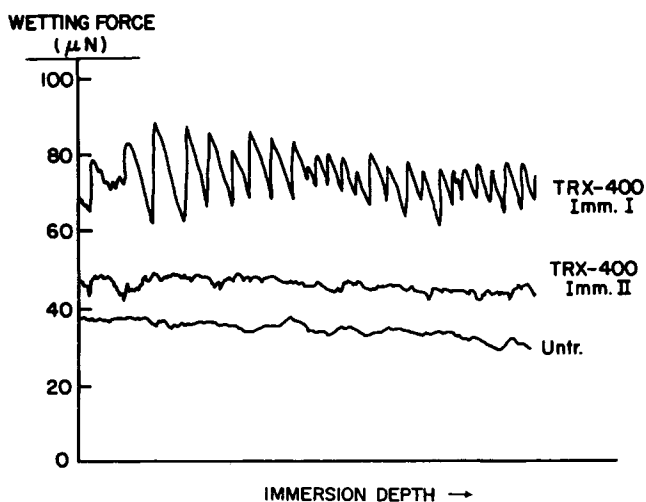


Fig. 7. Advancing wetting force curves for untreated and TR-X-400-treated nylon 6 fibers.

TABLE IV
Wettability of Surface-Treated Nylon 6 Fibers

Treatment	Adv wettability (mN/m)	Rec wettability (mN/m)
Untr.	30.6 ± 2.3	73.2 ± 1.4
JR-400 Imm. I	74.7 ± 2.4	76.5 ± 3.0
JR-400 Imm. II	37.6 ± 6.7	75.3 ± 5.2
GAF-755 Imm. I	70.7 ± 6.5	73.3 ± 2.7
GAF-755 Imm. II	35.8 ± 2.5	74.8 ± 4.2
TR-X-400 Imm. I	52.5 ± 4.7	59.5 ± 5.2
TR-X-400 Imm. II	27.9 ± 12.2	65.8 ± 4.0

force values are observed than those for the untreated fiber. This may be due to penetration of the low molecular weight surfactant into the fiber resulting in slow, diffusion-controlled desorption. It should be noted that this is only a trend and not a statistically significant effect because of the high scatter in the data.

Interfiber average wettabilities for surface-treated nylon 6 fibers are shown in Table IV. First immersion wettabilities with polymer-treated fibers reflect contact angles close to zero, suggesting complete coverage of the surface during treatment. This improved surface coverage in comparison with that for hair is attributed to the higher critical surface tension of nylon fibers ($\gamma_C = 38.4$ mN/m). In the case of TR-X-400, values are lower, probably because the desorption of the surfactant during the measurement affects the surface tension of the measuring liquid. It should be remembered that the polymers are not surface-active, whereas TR-X-400 is highly surface-active. In the second immersion the wettabilities are not statistically different from that of the untreated fiber, suggesting complete removal of the deposited material.

Receding wetting force curves, also recorded for these fibers, are smooth, like the advancing wetting force curves, but have a negative slope resulting from the decreased buoyancy as the fiber is pulled out of the liquid. Since buoyancy is not negligible with these rather large diameter (~ 0.5 mm) monofilaments as it is with hair fibers, buoyancy has been taken into account in the calculation of wettabilities. Average receding wettabilities obtained by integration, are also shown in Table IV. Reference will be made to receding wettabilities in connection with the discussion of wetting hysteresis.

Surface Heterogeneity and Wetting Hysteresis. Wetting hysteresis refers to the difference in contact angles measured in the advancing and receding modes. It has been attributed to several causes,⁷⁻⁹ including surface heterogeneity, molecular volume of the liquid molecules, and orientation of molecules at the interface. Which of these causes is primarily responsible for the wetting hysteresis of hair is debatable. The unique water-wetting behavior of hair is due to the heterogeneity of its composition, especially its cuticular cell structure with the hydrophobic epicuticle which is easily damaged to expose the hydrophilic interior, the endocuticle. In general, the advancing contact angle is greater than 90° ($\sim 100^\circ$) for undamaged fibers.² The receding contact angle seems to depend more on the scale direction—whether the scales point towards (against scale) or away from the liquid surface (with scale) during the withdrawal of the

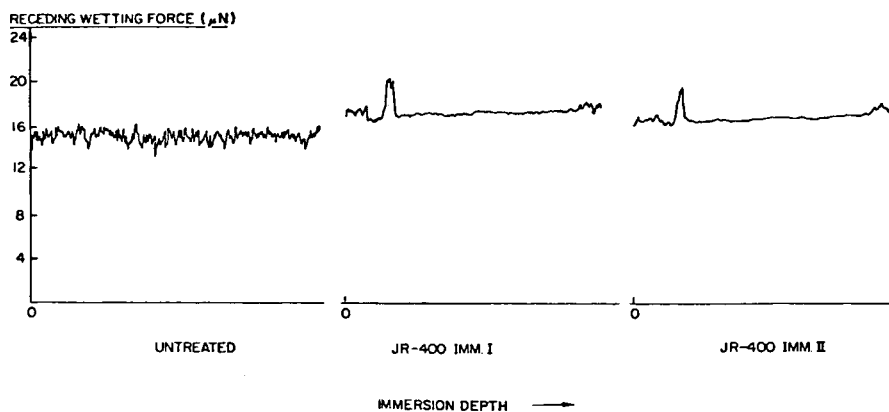


Fig. 8. Receding wetting force curves for untreated and JR-400-treated hair fibers.

fiber from the liquid²—but is generally low (0 – 50°) for a hydrophobic surface. It is possible that reorientation of lipoproteins of the cell membranes occurs during contact with water, with the protein moieties orienting themselves towards the water. Capillary water held between loose scales seems to contribute to lower contact angles, especially in the against-scale receding mode.

In the case of the surface treatments considered in this work, surface heterogeneity seems to play a role in hysteresis mainly because of incomplete surface coverage by the deposited compounds. At low surface coverage, advancing wettabilities are very sensitive to the presence of hydrophilic areas, but receding wettabilities do not show this sensitivity since both the hydrophilic areas and the untreated areas have similar values. This can be seen from Figures 8 and 9 and the data in Table I. Whereas the average advancing wetting forces are different for the untreated and treated fibers in the first and second immersions, the receding wetting forces are essentially identical. In the case of surface active TR-X-400, desorption during the measurement reduces γ_{LV} near the three-phase boundary and thus reduces the advancing wettabilities. Desorption can also lead to a large scatter in the data, especially in the advancing mode.

Since advancing wetting forces are drastically affected by surface coverage while receding wetting forces remain essentially unaltered, the hysteresis ratio

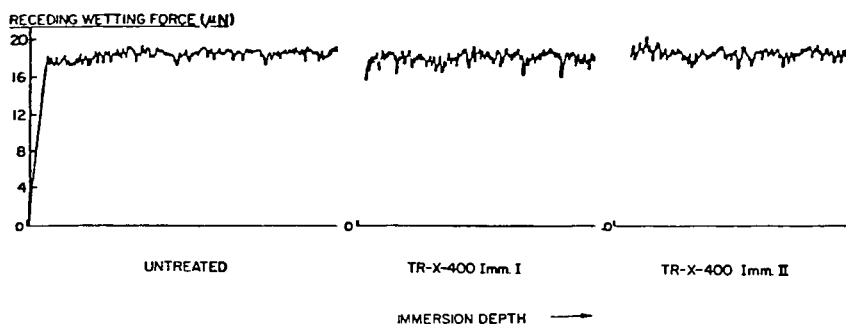


Fig. 9. Receding wetting force curves for untreated and TR-X-400-treated hair fibers.

TABLE V
Hysteresis Ratios for Untreated and Surface-Treated Hair and Nylon 6 Fibers

	Hair	Nylon 6	Nylon 6 in 1% solution of treating agent
Untreated	2.23	1.42	—
JR-400 Immersion I	1.39	1.01	1.40
JR-400 Immersion II	1.83	1.34	—
JR-400 Immersion III	1.86	—	—
Untreated	2.31	1.41	—
GAF-755 Immersion I	1.29	1.02	1.34
GAF-755 Immersion II	1.85	1.38	—
GAF-755 Immersion III	1.96	—	—
Untreated	2.40	1.40	—
TR-X-400 Immersion I	1.49	1.06	1.04
TR-X-400 Immersion II	2.25	1.38	—
TR-X-400 Immersion III	2.32	—	—

should be qualitatively related to surface coverage. Wetting hysteresis ratio is defined as²

$$h = \gamma_{LV}(1 + \cos \theta_r) / \gamma_{LV}(1 + \cos \theta_a)$$

where θ_a and θ_r are advancing and receding contact angles. Hysteresis ratios calculated for human hair and nylon fibers in contact with water and polymer or surfactant solutions are given in Table V.

The high hysteresis ratio for untreated hair reflects that $\theta_a \gg \theta_r$. In the first immersion for JR-400-treated fibers the value of h is considerably lower but still greater than unity, suggesting a level of surface coverage well below 100%. The increase in the value of h in subsequent immersions is probably due to the reintroduction of surface heterogeneity as a result of desorption of the polymer from the surface during the first immersion. For the GAF-755-treated fibers the value of h in the first immersion is somewhat lower, suggesting somewhat more complete coverage of the surface. The surface coverage in the case of TR-X-400 is difficult to establish, since desorption leads to changes in the surface tension of the wetting liquid during advancing measurements.

The hysteresis ratio for the nylon-water system is significantly lower than that of hair, suggesting that the nylon fiber contains larger proportions of better wetting regions. To a certain extent this is borne out by the relative contributions of dispersion and nondispersion forces to the critical surface tension (γ_C) of the nylon fiber³:

	γ_S^d (mN/m)	γ_S^g (mN/m)	γ_C (mN/m)
Hair	24	4	28
Nylon 6	31	7	38

The dispersion contribution to γ_C arises from hydrocarbon regions which are poorly wetted by water, whereas the nondispersion contribution arises from polar regions more easily wetted by water. An h value close to unity in the first immersion in the case of surface-treated nylon is indicative of complete surface coverage. The value of h in the second immersion is essentially the same as that of the untreated fiber, suggesting almost complete desorption of the material from the surface.

TABLE VI
Wettability of Nylon 6 Fibers in 1% Solutions

Treating agent	Adv wettability (mN/m)	Rec wettability (mN/m)
JR-400	22.8 ± 6.5	60.7 ± 7.7
GAF-755	31.8 ± 10.4	67.3 ± 3.7
TR-X-400	21.5 ± 5.2	25.2 ± 5.7

Advancing and receding wettabilities for nylon 6 fibers in polymer and surfactant solutions are shown in Table VI. For the polymer solutions advancing and receding wettabilities are very different, whereas for TR-X-400 they are similar in magnitude because of the low γ_{LV} of the solution. Hysteresis ratios for nylon 6 treated with polymer solutions are not very different from those of the untreated fiber with water (Table V). This is because the surface tensions of these solutions are relatively close to that of water. However, with a 1% TR-X-400 solution ($\gamma_{LV} \cong 26$ mN/m) the hysteresis ratio is close to unity. This shows that if the surface tension of the wetting liquid is low, the liquid does not distinguish between the high and low energy areas on the fiber surface in the advancing mode.

In order for a system to exhibit wetting hysteresis, then, surface heterogeneity of the solid surface is required, but it is also important that the liquid have an appropriate surface tension which can perceive this heterogeneity. If the surface tension is too low, then both high- and low-energy areas are completely wetted, thus eliminating wetting hysteresis.

CONCLUSIONS

The work presented in this paper shows that wetting force curves obtained as a function of depth of immersion can reveal information concerning the surface chemical heterogeneity of a fiber, and so can be used to study the distribution of materials deposited on the fiber surface. The relation between the critical surface tension of the fiber and the surface tension of the treating solution plays an important role in the nature of the distribution of the surface-deposited material. Wetting force curves obtained for the same substrate in multiple immersions after a given treatment provide useful information about the ease of desorption of the treating agent. Data presented here indicate how wetting hysteresis is related to the surface chemical heterogeneity of the solid surface and the surface tension of the liquid.

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