Surface Wettability of Human Hair.
II. Effect of Temperature on the Deposition of Polymers and Surfactants

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Synopsis

The effect of treatment temperature on the deposition and substantivity of surfactants and polymers on the surface of human hair has been investigated by measuring the surface wettability of the fiber with water before and after treatment. Advancing wettabilities indicate that the adsorption of low molecular weight cationic surfactants on the negatively charged hair surface goes through a maximum as treatment temperature is increased. This suggests an increase in the extent of chemisorption with increase in temperature, the decrease in wettability beyond the maximum being due, apparently, to orientation of the surfactant lipid chain toward the water making the surface more hydrophobic and less wettable. The adsorption and substantivity of anionic surfactants are low, due to the repulsion of negative charges on the hair surface. As with cationic surfactants, the adsorption of cationic polymers increases with treatment temperature, suggesting an increase in adsorption site activation. Increase in treatment temperature also increases polymer substantivity due to a lower probability of desorption resulting from multiplicity of attachments to sites on the fiber surface. Oxidation of the hair fiber surface, which involves disulfide cleavage to produce charged sites, leads to an increase in the extent of surface coverage and substantivity especially at lower treatment temperatures; reduction, on the other hand, does not result in significant increases. In those cases where desorption of deposited material does not affect the surface tension of the measuring liquid drastically, wettability data can be used to determine an average surface coverage if the contact angle of the liquid on the pure treatment material is known.

INTRODUCTION

Adhesive characteristics of single hair fibers play an important role in the aesthetic appearance of a hair assembly. In its natural state human hair acquires a coating of sebum secreted by the skin, which leads to an increase in interfiber adhesion and a loss of body (increase in bulk density). This condition is reversed by washing the hair with a surfactant which is usually anionic. Since the surface of a hair fiber is negatively charged, the amounts of anionic surfactants retained on the fiber are small. On the other hand, there are situations where deposition of cationic surfactants or polymers (generally referred to as conditioners) is beneficial to the grooming of hair. These materials can be incorporated into a shampoo, so that cleaning of the fiber surface and deposition of conditioning materials takes place in a single step, or into a separate formulation known as a cream rinse, which is applied to hair after washing with a shampoo.

Adsorption of cationic substances on the surface of hair occurs initially by physical adsorption followed by chemisorption. The treatment temperature plays an important role especially in the amount of chemisorbed material, and the adsorption characteristics of polymeric materials are also

highly temperature-dependent.[1] A study of the effect of temperature on the adsorption of surfactants and polymers on the surface of hair forms the subject of this communication.

It should be noted that this work is an outgrowth of observations made on hair fibers treated with cationic substances under conditions of practical use which led to changes in the surface characteristics of the fiber. It is not intended to be a systematic study of adsorption of surfactants and polymers from solution. Most of the work was done on single fibers so that adsorption isotherms could not be established for these systems.

EXPERIMENTAL

These studies were conducted on European dark brown hair cleaned by extraction with $CH_3OH/CHCl_3/CH_3OH$ in that order followed by exhaustive rinsing. The preparation of fiber specimens has been described.[2] Surface treatments involved immersion of the fiber snippet into a 1% solution of the treating material at a given temperature for 3.6 ks, followed by air drying and conditioning at 65% RH and 21°C. The polymers and surfactants used in this study were: Polymer JR-400 (JR-400) (Union Carbide Corp.), Gafquat-755 (GAF-755) (GAF Corp.), Triton-X-400 (TR-X-400) (Rohm & Haas Co.), Texapon-N-25 (Tex-N-25) (Henkel KGaA). The nature of the first three compounds has been given elsewhere.[3] Texapon-N-25 is an anionic surfactant similar to sodium lauryl sulfate but etherified with poly(ethylene glycol), having the general structure $R\text{---}(O\text{---}CH_2\text{---}CH_2)_n\text{---}OSO_3^-$, where R represents the lipid chain.

The wettability method used to characterize fiber surfaces has been discussed earlier.[2,3] Using a continuous immersion technique, about 3–4 mm of the fiber were scanned at 21°C, irrespective of treatment temperature, with double distilled water as the wetting liquid. Scans were repeated on the same fiber to study desorption and substantivity of the surface deposited material.

RESULTS AND DISCUSSION

TR-X-400

Hair fibers treated with TR-X-400 at temperatures ranging from 20°C to 80°C were scanned by the continuous immersion technique for characterizing wetting behavior. Typical advancing and receding wetting force curves for multiple immersions of these fibers are shown in Figures 1 and 2 for 20 and 80°C treatments, respectively. The general nature of these wetting force curves has been discussed elsewhere.[3] The characteristic stick–slip pattern obtained in the first immersion after treatment is due to desorption of surfactant at the contact line during the immersion. It has been pointed out that the Marangoni effect[4] plays a significant role in determining the nature of this particular wetting force behavior. In the second and third immersions (especially the third), the wetting force curves for fibers treated at 20°C are similar in appearance to those of the untreated fiber, indicating that desorption is virtually complete during the first immersion of the fiber in water, and suggesting therefore that at this treatment temperature sur-
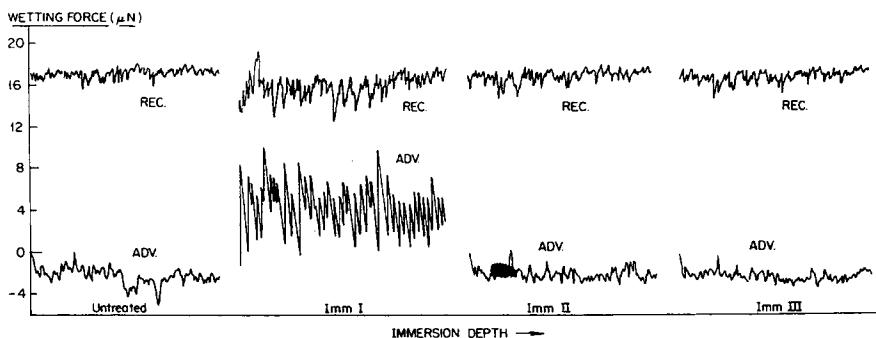
Fig. 1. Advancing and receding wetting force curves for a hair fiber treated with TR-X-400 at 20°C.

factant adsorption is mainly physical. However, when the treatment temperature is 80°C, the advancing wetting force curves show distinct regions of low wettability marked A, B, and C, which also show up in the receding mode. (They are in reverse order because the last part to immerse in the advancing mode is the first to emerge in the receding mode.) These patterns persist in the second and third immersions, indicating that the surfactant in these regions is chemisorbed and is difficult to desorb. Receding wetting forces after the third immersion of the treated fiber are lower in the marked regions (contact angles higher) than forces for the corresponding regions of the untreated fiber. If the surfactant is chemisorbed with the lipid chain oriented away from the fiber surface, a wettability lower than that of the untreated fiber would be expected.

An average wettability is obtained for each fiber by integrating the wetting force curves. Interfiber averages of advancing and receding wettabilities obtained for 6 specimens at each temperature are plotted in Figures 3(a) and 3(b). The average advancing wettabilities in the first and third immersions indicate a maximum at about 60°C. Although the difference is not statistically significant, the trend is reasonable. It is known that the extent of chemisorption increases with increase in temperature, mainly due
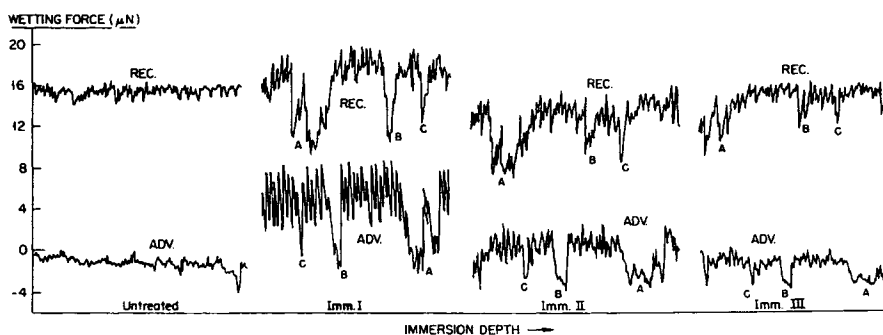

Fig. 2. Advancing and receding wetting force curves for a hair fiber treated with TR-X-400 at 80°C. In the first immersion the receding curve is displaced upward by 6 μN to avoid overlap.
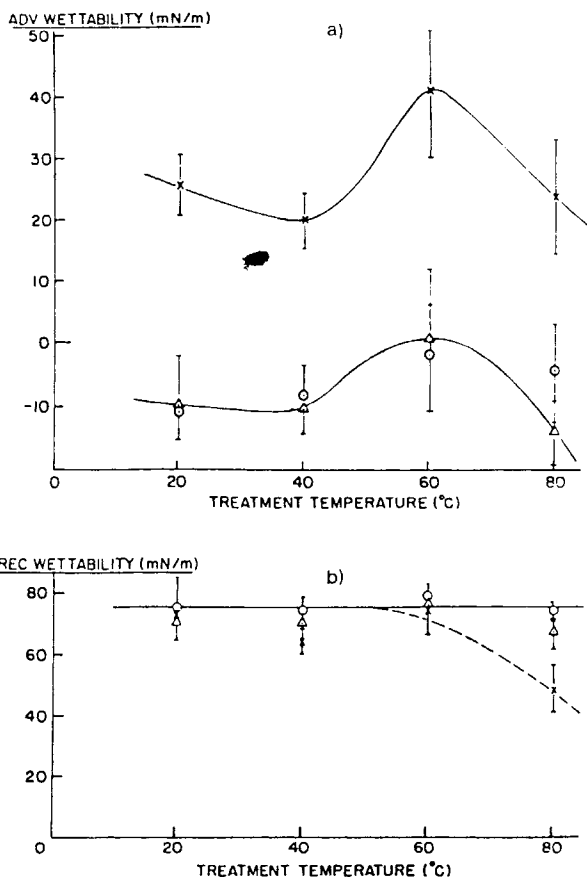
Fig. 3.   Advancing (a) and receding (b) wettabilities in the first (×) and third (△) immersions for hair fibers treated with TR-X-400 at four temperatures (bars indicate variations of the mean at the 95% confidence level): (○) untreated.

to an increased desorption rate of water molecules from adsorption sites which are then occupied by the surfactant molecules. It is likely that the chemisorbed surfactant is oriented with its lipid chain away from the fiber surface which would lead to a decrease in wettability. Physically adsorbed surfactant, on the other hand, is randomly distributed in multilayers, and the result is an increase in wettability. Since the amount of chemisorbed surfactant increases with temperature, the wettability may be expected to decrease at higher treatment temperatures (this is indeed observed with fibers treated at 80°C), especially in the third immersion when most of the physically adsorbed material has been desorbed. It should be noted that at higher treatment temperatures this low molecular weight surfactant can diffuse into the bulk of the fiber and slowly diffuse to the surface during measurement.

Although the receding wetting force curves show substantial differences in the uniformity of the fiber surface at different temperatures, there is relatively little effect of temperature on the average receding wettability values [Fig. 3(b)]. Only the first immersion value after an 80°C treatment

is significantly lower, the third immersion value again approaching that of the untreated fiber. This appears to be a reflection of the much slower rate of desorption of chemisorbed surfactant molecules during the measurement.

Tex-N-25

Advancing and receding wetting force curves for fibers treated with the anionic surfactant Tex-N-25 at 20°C and 80°C are shown in Figures 4 and 5, respectively. The finding that the advancing wetting forces are lower than those for TR-X-400 indicate, as expected, that anionic surfactants are not readily adsorbed on hair which has a negatively charged surface. In subsequent immersions, most of the surfactant is desorbed giving a wetting force curve similar to that of the untreated fiber especially in the third immersion. Third immersion wettabilities at 60°C and 80°C indicate some slight degree of surface modification, however; this is shown by the inter-fiber averages plotted in Figure 6 as a function of temperature. The values at 60°C and 80°C are significantly higher than that at 20°C, suggesting some degree of substantivity at higher treatment temperature.

Polymer JR-400

The general nature of advancing wetting force curves for hair fibers treated with polymer JR-400 has been discussed in an earlier paper.[3] The irregular nature of the first immersion curves for fibers treated at 20°C indicates an uneven and sometimes patchy distribution of the polymer on the fiber surface. This seems to be typical at treatment temperatures close to room temperature and to be due to the polymer film breaking up on the fiber surface as the fiber is withdrawn from the treatment solution. On immersion, most of the polymer is lost, leaving a relatively stable surface film which is more uniformly distributed, as can be seen from advancing wetting force curves in the second and third immersion.

Fibers treated at 80°C show basically the same behavior, except in the first immersion in which the appearance of the curve and the magnitude
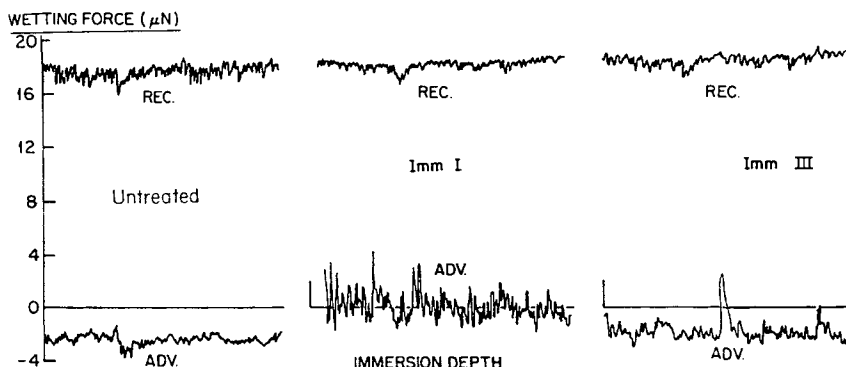

Fig. 4. Advancing and receding wetting force curves for a hair fiber treated with TEX-N-25 at 20°C.
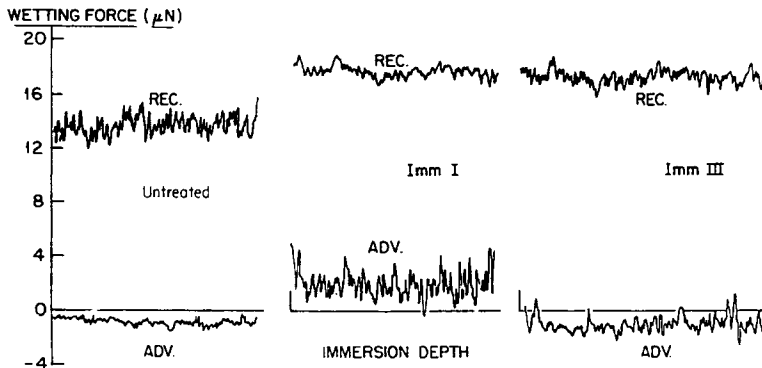
Fig. 5. Advancing and receding wetting force curves for a hair fiber treated with TEX-N-25 at 80°C.

of the wetting force indicate complete surface coverage. As would be expected for a surface uniformly covered by a hydrophilic polymer (contact angle with water ~0°), the advancing and receding wetting force curves are very close. It has been observed, though, that the receding wetting force curves for fibers treated with JR-400 at any of the treatment temperatures are essentially similar in the three immersions.

Interfiber average advancing wettabilities are plotted in Figure 7 as a function of temperature. A large variability is observed at 20°C, which decreases at higher treatment temperature. As in the case of TR-X-400, the wettabilities go through a maximum at 60°C in the first as well as the third immersion. This probably indicates that substantivity of the polymer is indeed affected by treatment temperature. It is known that polymer adsorption increases with increasing temperature, whereas adsorption of low molecular weight substances decreases because the desorption rate of the
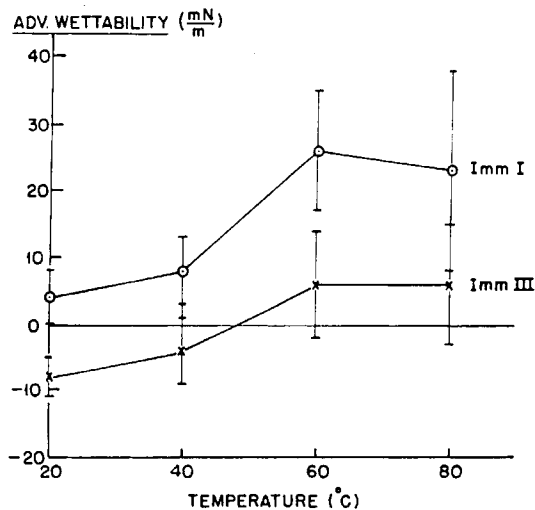

Fig. 6. Interfiber averages for the advancing wettability in the first and third immersions vs. temperature of treatment with TEX-N-25.
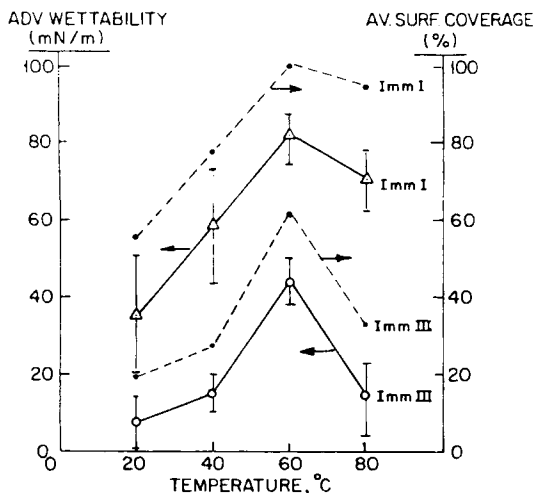
Fig. 7. Advancing wettabilities and surface coverage of hair fibers treated with polymer JR-400 as a function of temperature.

low molecular weight substances increases with increase in temperature. Polymer desorption, on the other hand, becomes more difficult because the number of attachments to the surface increases with temperature. In the case of polymer JR-400, cationic sites interact with anionic sites on the hair surface as water molecules are desorbed from these sites at higher temperature, thus leading to better substantivity.

It has been mentioned earlier[3] that any point on the wetting force curve corresponds to a contact angle averaged over the entire contact line, although the angle in different regions of the contact line may be quite different depending on the distribution of surface deposits. Therefore, the average contact angle calculated along a length of the fiber should be related to the average surface coverage along this length of the fiber. To be able to calculate surface coverage, however, the molecules must not have a specific orientation affecting wettability, and the surface wettability (or contact angle) of the pure component should be known. For the hydrophilic polymers used in this study, contact angles of the pure components are essentially zero. This is supported by the almost identical advancing and receding contact angles in the first immersion after treatment at 80°C. Further, the observed wetting forces agree with those calculated for $\theta = 0$, using the relation $p\gamma_{LV} \cos \theta$.

The wetting force at a given point along the fiber (neglecting buoyancy) is given by

$$F = p\gamma_{LV}[x \cos \theta_u + (1 - x) \cos \theta_t]$$

where x is the fraction of the wetted perimeter p not covered by the surface deposited material, so that $(1 - x)$ is the fraction covered by the treatment. γ_{LV} is the surface tension of the liquid, and θ_u and θ_t are the advancing contact angles of the untreated surface and the treatment material, respectively. If F_{av} is the average wetting force obtained by integrating the

wetting force curve, then the cosine of the average contact angle is given by

$$\cos \theta_{av} = \frac{F_{av}}{p\gamma_{LV}} = x(\cos \theta_u - \cos \theta_l) + \cos \theta_l$$

This rearranges to give

$$x = \frac{\cos \theta_{av} - \cos \theta_l}{\cos \theta_u - \cos \theta_l}$$

It should be noted that the above equations cannot be used to calculate cos θ_{av} if γ_{LV} is affected by desorption of the material, as, for example, in the case of TR-X-400. Since $\cos \theta_l \cong 1$

$$x = \frac{\cos \theta_{av} - 1}{\cos \theta_u - 1}$$

Average surface coverage $(1 - x)$ calculated from the above equation is plotted as the dotted lines in Figure 7, and it can be seen that surface coverage first increases with temperature, becoming a maximum at 60°C. The reduction in surface coverage and wettability at 80°C is probably not due to any specific orientation of molecules that leads to a reduction in wettability. If this were the case, it should have been reflected in the receding wetting force curves, as was the case for fibers treated with TR-X-400 at 80°C. The reason for the decrease in wettability or surface coverage at this temperature is not clear from these data, and further investigations of the sorption–desorption behavior of JR polymer are necessary. One possibility that might be explored is that the polymer undergoes hydrolysis at these temperatures (~80°C), splitting quaternary ammonium groups, and thus reducing the substantivity of the polymer. According to the manufacturers, the polymer is susceptible to hydrolysis in high or low pH environments.

It should be noted that surface coverage values cannot be calculated for TR-X-400-treated fibers because their wettability depends on the orientation of molecules on the surface. Chemisorbed molecules can orient with their lipid chain away from the fiber surface, leading to a reduction in wettability, even though the surface coverage may be substantial. Since the fraction of molecules with specific orientation and the appropriate value of cos θ_l are not known, this method cannot be used to calculate the average surface coverage.

Polymer GAF-755

The behavior of this system is similar to that of JR-400 except that a maximum in wettability or surface coverage is not observed within the temperature range studied. This is clearly seen from the temperature dependence of the interfiber average wettabilities and surface coverages shown in Figure 8.
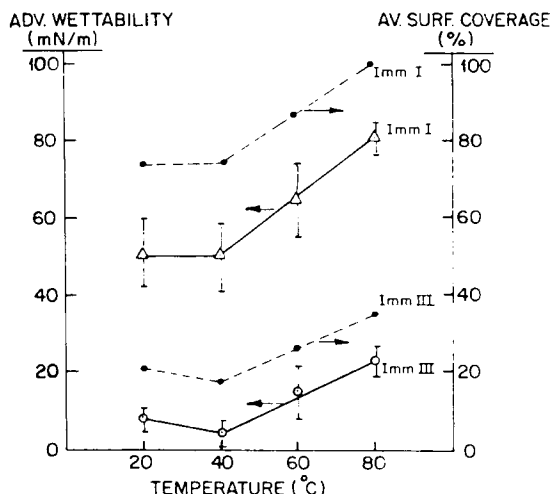
Fig. 8. Advancing wettabilities and surface coverage of hair fibers treated with GAF-755 as a function of temperature.

A numerical comparison of the surface coverages for the two polymers is shown in Table I. The data show a clear difference in the adsorption behavior of the two polymers at 60°C, whereas at other temperatures the differences are not statistically significant. Since adsorption of polymers from solution onto surfaces is influenced by phase transitions, it is likely that the difference between these two polymers at ~60°C (between 40°C and 80°C) treatment temperature may be due to the differences in the solution behavior of the two polymers. This aspect has not been investigated. In the temperature region relevant to the practical application of these polymers (40–60°C), GAF-755 seems to have lower substantivity than JR-400.

Effect of Chemical Modification of Fiber Surface on the Adsorption of JR-400

Chemical modifications such as oxidation and reduction are extensively used to alter the aesthetic appearance of hair. The effect of such treatments on the adsorption of conditioning polymers is important in the formulation of hair care products. Therefore, the effect of temperature on the adsorption of polymer JR-400 on reduced and oxidized hair was studied.

Reduction was carried out with an unbuffered $2.5 \times 10^{-2}M$ solution (pH ~ 6) of dithiothreitol for 0.48 ks. The fibers were rinsed with deaerated distilled water. Oxidation was carried out with 6% hydrogen peroxide with pH adjusted to ~10 with ammonium hydroxide. Treatment time was 0.9 ks followed by exhaustive rinsing in distilled water. Polymer JR-400 was then applied by immersion in a 1% solution for 3.6 ks, followed by air drying and conditioning at 65% RH and 21°C.

Interfiber average advancing wettabilities for reduced and oxidized fibers, shown in Figures 9 and 10, respectively, show that reduction does not produce significant changes in surface coverage or substantivity as reflected in first and third immersion wettabilities. Significantly, oxidation, on the

TABLE I

Average Surface Coverage (%) of Hair Fibers by Polymers JR-400 and GAF-755 as a Function of Treatment Temperature[a]

Immersion	20°C			40°C			60°C			80°C		
	I	II	III	I	II	III	I	II	III	I	II	III
JR-400	55±19	21±6	19±8	81±15	31±5	27±5	100	66±5	62±9	95±6	39±6	32±6
GAF-755	74±10	26±4	21±2	73±10	26±3	17±4	92±12	29±5	26±3	112±7	48±4	35±5

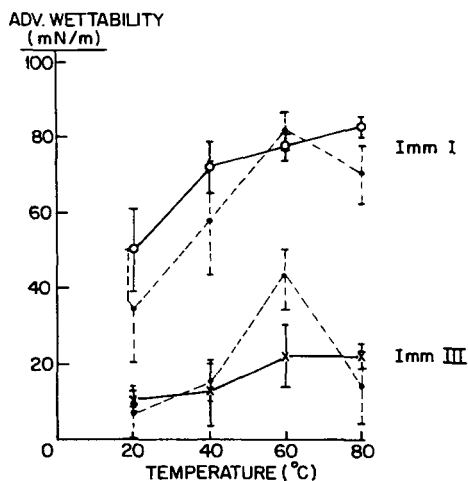[a] All entries at 95% confidence level.

Fig. 9. Advancing wettabilities of reduced hair fibers after treatment with JR-400 as a function of temperature: (- - -) untreated; (—) reduced.

other hand, improves both surface coverage in dip coating and substantivity, especially at low treatment temperatures, as evidenced by the significantly higher wettabilities in the first and the third immersion. Lower substantivities at 60°C obtained with both reduced and oxidized fibers lead to a disappearance of the maximum observed for the untreated sample, an effect that cannot be explained by the wettability method. Both reduction and oxidation produce an increase in the wettability of the fiber surface, reflecting an increase in the critical surface tension of the fiber surface as a result of the sulhydryl and cysteic acid groups generated by the cleavage of disulfide bonds.[5] This improves the adhesion between the surface and the polymer, leading to a higher surface coverage. The data indicate that
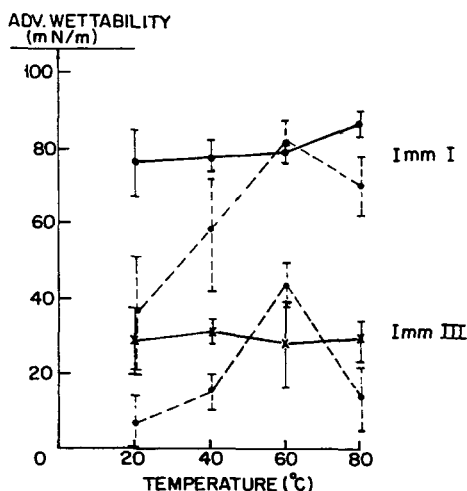

Fig. 10. Advancing wettabilities of oxidized hair fibers after treatment with JR-400 as a function of temperature: (- - -) untreated; (—) oxidized.

oxidation is more effective in this regard than reduction, suggesting that negatively charged cysteic acid groups in the surface domain of the fibers interact more effectively with the cationic polymer than sulfhydryl groups, which are only slightly ionized under neutral pH conditions. This increase in the number of binding sites by oxidative pretreatments would also be expected to affect substantivity of the cationic polymer. Reduction, on the other hand, increases the polarity of the surface by increasing the number of sulfhydryl groups without providing a significantly increased number of sites for chemisorption of the cationic polymer.

CONCLUSIONS

The results presented in this communication have shown that the adsorption of low molecular weight cationic surfactants on the negatively charged surface of hair fibers increases at first with treatment temperature, indicating an increase in the extent of chemisorption. It is suggested that different orientations of the chemisorbed and physically adsorbed surfactant molecules are the reason for the observation that the advancing wettability goes through a maximum at about 60°C. As expected, adsorption of anionic surfactants is not extensive because of the repulsion of the adsorbate molecules by the similarly charged hair fiber surface.

Adsorption of cationic polymers increases with temperature, which suggests an increase in site activation and a lower probability of desorption due to an increase in the number of attachments of the polymer molecule to the surface. In addition to improved surface coverage, chemisorption of cationic sites on the polymer molecule to anionic sites on the surface of the fiber contributes to improved substantivity. Oxidation of the hair fiber leads to an increase in surface coverage as well as in substantivity, especially at lower treatment temperatures, as a result of disulfide cleavage and generation of additional anionic sites on the fiber surface in the form of cysteic acid groups. This is not observed in the case of reduced fibers since few charged sites are created in the reduction process.

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