Effect of Low-Temperature Plasma and Chitosan Treatment on Wool Dyeing with Acid Red 27

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ABSTRACT: This study examines in detail the influence of low-temperature plasma and biopolymer chitosan treatments on wool dyeability. Wool knitted fabrics were treated and characterized by whiteness and shrink-resistance measurements. Surface modification was assessed by contact-angle measurements of human hair fibers, which were used as a model to study the wetting properties of the treated wool knitted fabrics. The dyeing behavior was assessed from the diffusion mechanism point of view. The dyeing kinetics were measured at two different pHs (4.2 and 6.5) and three different temperatures (60, 85, and 100°C) to gain information about the contribution of the surface modification treatment to the dyeing mechanism. The exhaustion and reflectance data were compared, and the apparent diffusion coefficients were calculated. On the basis of the obtained results, a model for the dyeing mechanism of the chitosan treated wool was proposed. When treated with chitosan, the polymer sheath spread on the surface of the fibers acted as a predominant dyeing site in very short dyeing times, thus interacting with the dye and in later stages imparting the dye to the wool fiber. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2204–2214, 2005

Key words: biopolymers; cold plasma; diffusion; dyes/pigments

INTRODUCTION

Dyeing is one of the most sensitive steps in wool processing because it reflects even the slightest changes in the wool fibers due to different previous processing steps and treatments. To minimize fiber quality deterioration, many chemical, physical, and biochemical methods that modify only the fiber surface have been developed. Even with the modification confined to the fiber surface, dyeing is still very sensitive to the modification. Hence, to determine the most appropriate dyeing method for accordingly modified wool, the mechanism of dyeing needs to be revealed, and the fine structure of wool fibers and the diffusion pathways of dyes in wool fibers should be considered. Thus, the complex chemical constitution and structure of wool fibers, as well as their complicated surface structure and properties, are of great research interest today.[1]

The main substance of wool is a protein, keratin, the main chains of which are crosslinked with cystine residues and contain a variety of side chains, some basic and some acidic, depending on the side-chain groups present. From a structural point of view, the main part of the wool is the cylindrical core of the fiber (elongated spindle-shaped cells), which is called the cortex and is divided into ortho and para segments. Surrounding the cortex is a cuticle (flattened cells) made up of an outmost scale layer and a thin outer layer (epicuticle). Both layers have a tremendous influence on dyeing because of their hydrophobic characteristics. The cuticle is separated from the underlying cortex by the intercellular material, which is called the cell membrane complex (CMC) and consists of non-keratinous proteins (δ layer) and lipids (β layer).

The hydrophobic nature of wool is known to be due to the specific properties of the exocuticle and epicuticle. The exocuticle is hydrophobic because it contains a high degree (≈35%) of disulfite crosslinkage in the A-layer.[2] The epicuticle surrounds each cuticle cell of the wool fiber, and it consists of fatty acid (≈25% by mass) and protein (≈75% by mass). The main component of the fatty acid fraction (≈65%) is 18-methylei-

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cosanoic acid, which is covalently bound to the fiber as a thioester to cysteine residues of the protein. The epicuticle membrane is 5–7 nm thick, and 18-methyleicosanoic acid is about 2.8–3.0 nm long. Fatty acid chains of 18-methyleicosanoic acid are oriented away from the fiber to produce a polyethylene-like layer at the fiber surface, and this makes the epicuticle hydrophobic and resistant to the attack of different agents.[3,4] This is the reason that wool is known to have a hydrophobic water-repellent surface even after the removal of wool grease by aqueous scouring or a solvent reaction.

With different wool treatments, it is possible to reduce the hydrophobic nature of the fiber surface and thus enhance some important textile properties. By the partial removal of the covalently bound fatty acid monolayer, an increase in the hydrophilicity of the fiber surface occurs, and this could enhance dye diffusion and polymer adhesion. During aqueous chemical treatments with the aim of modifying the wool-fiber surface, the highly resistant epicuticle acts as a semipermeable membrane, enabling the influx of reactants and the outflow of products, particularly soluble proteins of low molecular weight.[5] Today, because of increased environmental awareness, wet chemical treatments may soon need to be replaced by more favorable physical means of fiber surface modification, which are called dry treatments.

Cold plasma, that is, low-temperature plasma (LTP) treatment is the most commonly used physical method for a surface specific fiber modification, as it affects the surface both physically and chemically without altering the material bulk properties. Plasma treatments modify the fatty acid monolayer present in the outermost part of the fiber, generating new hydrophilic groups as a result of the hydrocarbon chain oxidation and reducing the fatty acid chain length.[6] The oxidation process also promotes the formation of Bunte salt and cysteic acid residues on the polypeptide chain.[7] Particularly when oxidizing gasses are used, plasma induces cystine oxidation in the A-layer of the exocuticle, converting it into cysteic acid and thus reducing the number of crosslinkages in the fiber surface.[8] Although plasma species can penetrate to a depth of tens of nanometers into the fiber, which is deep enough to remove surface lipids, there are also some indications that the internal lipids of the CMC are modified to a certain extent.[9,10]

Synthetic polymers can be applied to wool textile materials to improve their shrink resistance (silicone polymers), stain and water repellency (fluoropolymers), and flame resistance. For direct adsorption to wool material under appropriate conditions, it is preferred for the polymer to have lower critical surface tension than the wool fiber and for the polymer particles to be positively charged.[11] Today, much attention is focused on natural polymers as possible substitutes for synthetic polymers. A range of naturally occurring polysaccharides (alginates, carrageenan, cellulose, dextrans, pectin, and starch) are widely used in textile industry. Although commercially available, another polysaccharide, chitosan (CHT), is still not sufficiently used. Given its natural occurrence and its biodegradability and the fact that it differs from other polysaccharides by exhibiting basic rather than acidic characteristics, CHT is a good candidate to become a regular textile finishing or auxiliary agent. The positive charge gives CHT its unique chemical and biological properties and makes it attractive for a wide number of textile applications, whereas its solubility in acidic solutions makes it easily available for industrial purposes. The chemistry of CHT is similar to that of cellulose, but it reflects also the fact that the 2-hydroxyl group of the cellulose has been replaced with a primary aliphatic amino group.

CHT treatment is nowadays considered a useful method for modifying the surface topography and thus controlling the surface-related properties of the fiber. CHT improves the dye coverage of immature cotton fibers in dyeing cotton[12,13] and can be successfully used as a thickener and binder in the pigment printing of cotton.[14] In wool finishing, CHT has been used as a shrink-resistance agent[15–17] and as an agent for improving the dyeability of wool.[18,19]

The main problem for CHT applications to wool is that it is weakly bound to the substrate as it is supposed to interact electrostatically with available anionic groups. Therefore, to enhance CHT binding, it could be useful to promote the formation of new anionic groups on the fiber[20] and to increase the surface tension of wool fibers. To achieve this, one of today's established methods is the LTP treatment of wool.[8,21,22]

The results of LTP and CHT treatments on wool dyeability still have to be examined in detail.[23,24] Therefore, in this study, wool knitted fabrics were treated with LTP, CHT, or both; they were characterized, and their dyeing behavior was assessed from the diffusion mechanism point of view. Contact-angle measurements of human hair fibers were used as a model to study the wetting properties of the treated wool.

EXPERIMENTAL

Materials

The experiments were performed with 100% wool plain knitted fabric (single knit) (Pulligan International S.A., Barcelona, Spain) with a cover factor of 1.22 $tex^{1/2}$/mm. Before the treatment, the fabric was cleaned by Soxhlet extraction with dichloromethane rinsed with ethanol and water and equilibrated in a conditioned room (20°C and 65% relative humidity). This removed processing residues, that is, oils and lubricants. CHT (Vanson Ha-

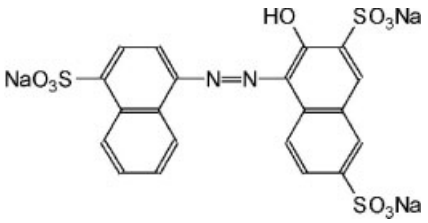

Figure 1 Structure of AR27.

loSource, Inc., Redmond, WA) of declared viscosity (369 cps) and degree of deacetylation (84.9%) was used. For dyeing experiments, we selected Acid Red 27 (AR27; Amaranth/Azorubin S, Aldrich Chemical Co., St. Louis, MO; Fig. 1) for its known sensitivity to dyeing variability in wool fibers (C.I. number 16185; 80% purity). AR27 is a threefold sulfonated monoazo leveling dye with increased ionic charge of the molecule and is, therefore, known to have a suppressed aggregation tendency and a low affinity. This is a rather hydrophilic dye, and it was chosen to mark the contrast in the dyeing of unmodified and modified wool. Its molecular weight is 604.5 g/mol.

Wool treatments

An LTP treatment was carried out in capacitively coupled, radio-frequency-induced (13.56 MHz) air plasma. The samples were treated under 0.20 mbar of pressure for 40 s, and the power was maintained at a constant level (100 W). These treatment conditions were selected as optimal on the basis of a previous investigation.[21] CHT solutions (1 g/L) were freshly prepared by the dissolution of CHT in distilled water containing acetic acid. The treatments were done by the exhaustion method: a wool knitted fabric (untreated or LTP-treated) sample was immersed in the treatment solution at a liquor/wool ratio of 20 : 1 and was subjected to shaking in a thermostatically controlled laboratory shaker at 25°C for 20 min; after the treatment, the wool samples were run through squeeze rolls to remove the excess solution with an HVF laboratory padder (Mathis, Zürich, Switzerland) at a padding speed of 3 m/min and a squeeze roll pressure of 3 bar. The samples were dried at room temperature.

Wool characterization

The degree of whiteness (CIEGanz 82 and Berger 76) was measured with a Color-Eye 3000 spectrophotometer (Macbeth, New Windsor, NY) with a D_{65} illuminant and a 10° observer. The area shrinkage was determined in accordance with Woolmark TM 31 with an FOM 71Lab washing machine (Electrolux Wascator, Ljungby, Sweden) with a 5A washing cycle.

Dark brown European human hair (average diameter = 80 μm; treated with the same methods used for wool) was used as a model for wool fibers for the contact-angle measurements with the Whilhelmy balance method.[25] Advancing contact angles (θ_{ADV}) were calculated from the dynamic wetting force measurements carried out in a KSV Sigma 70 tensiometer electrobalance (KSV Instruments Ltd., Helsinki, Finland).[6,26] A single hair fiber was scanned for 1 mm at a velocity of 0.5 mm/min for both the advancing (Adv) and receding (Rec) modes. The vessel containing the wetting liquid was raised and lowered with a motorized platform. Corresponding advancing adhesion tension (F/L) values were recorded, and one wetting hysteresis cycle was evaluated for each fiber. All measurements were made at room temperature (20°C) for both scale cuticular directions of immersion: against-scale (AS) and with-scale (WS).

Dyeing of the wool samples

The dyeing was performed with a Labomat BFA-12 (Mathis) at a liquor-to-wool ratio of 100 : 1. Ten identical dye baths were prepared, and 10 2-g wool samples were used. The dyeing procedure was as follows. The fabric sample was equilibrated for 10 min at 50°C in a bath containing 10% o.w.w. sodium sulfate at a chosen pH (4.2 or 6.5). Then the dye (0.25% o.w.w.) was added, and the temperature was raised at a rate of 1.5°C/min to the dyeing temperature (60, 85, or 100°C), at which it was held to complete the dyeing time of 240 min. The dyeing system was buffered with a sodium acetate/acetic acid buffer (pH 4.2) or a potassium dihydrogen phosphate/disodium hydrogen phosphate buffer (pH 6.5). The pH measurements taken during the dyeing showed that the pH did not change during the whole process. All the dyeings were carried out without leveling agents to avoid the influence of the auxiliary treatments on the dyeing results.

The rate of dyeing was followed by the sampling of the dye bath at the beginning and after known time intervals (5, 10, 15, 20, 30, 45, 60, 90, 120, and 240 min). The absorbance of the dye bath samples was measured with a UV-265FW ultraviolet–visible spectrophotometer (Shimadzu, Kyoto, Japan) at the wavelength of maximum absorption (λ_{max} = 521 nm) at room temperature with a 10-mm-path-length cell. The exhaustion [E (%)] can be expressed as the percentage of the decrease in the dye-bath concentration:

$$E = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 is the optical density (initial dye concentration) of the dye bath at the very beginning of dyeing,

TABLE I
Degree of Whiteness and Area Shrinkage of Wool Fabrics

	Whiteness degree		Area shrinkage (%)		
Sample	CIE Ganz 82	Berger 76	1 × 5A	2 × 5A	3 × 5A
Untreated	−7.98	10.7	35.0	55.5	62.8
LTP	−7.08	11.0	3.5	9.0	12.4
CHT	−8.82	10.3	34.5	54.8	63.0
LTP+CHT	−11.40	8.4	7.5	10.6	14.0

A_t is the optical density (dye concentration) of the dye bath at a particular time interval t, and E_∞ is the dye exhaustion at equilibrium. From a previously prepared calibration curve of the absorbance versus the dye concentration at the same wavelength (λ_{max}), the concentration of dye remaining in the dye bath (C_t) at various dyeing times was calculated, and the amount of dye on the fiber at time t (C_F) was obtained by the difference. The diffusion coefficient was measured with the relationship between C_F/C_∞ (the relative amount of dye sorbed) and $t^{1/2}$ (C_∞ is the concentration of dye in the fiber at equilibrium). According to Fick's second law, at some stage of the dyeing process, this relationship should be approximately linear, as long as the dyeing process is controlled by diffusion and C_F is neither too small nor too large.[27] Both E_∞ and C_∞ usually correspond to 240 min of dyeing, but they had to be determined independently for the samples dyed at pH 6.5 and 60°C (dyed for 24 h) and 85°C (dyed for 48 h) as they had not reached equilibrium exhaustion in 240 min. The apparent diffusion coefficient could be estimated as the linear-fit slope with the following equation:

$$\frac{C_F}{C_\infty} = 2\sqrt{\frac{Dt}{\pi}}, \qquad (2)$$

where D is the instrinsic diffusion coefficient.

As the fabric samples were taken at various times during the dyeing (5, 10, 15, 20, 30, 45, 60, 90, 120, and 240 min), they were rinsed and dried, and the color measurements were performed (D_{65} and 10°) with a Color-Eye 3000 (Macbeth) diffusion reflectance spectrophotometer. The Kubelka–Munk K/S values were obtained at λ_{max}, and metric lightness L^* and psychometric chroma C^* were calculated in the CIELAB color space. At each of the dyeing times, the color difference values (ΔE) between the untreated samples and each of the treated samples were derived and plotted against dyeing time t.

For the samples dyed at pH 4.2 and 85°C, the color fastness to washing was determined after 45, 90, and 240 min of dyeing time according to TM 193 (ISO 105-CO6).

RESULTS

Substrate characterization

The results presented in Table I show that the fabric whiteness slightly increases after the LTP treatment. This effect can be attributed to the oxidation effect brought about by the plasma treatment on the fiber surface. It includes creating polar groups by oxidation and removing the surface lipids.[21] On the contrary, the treatment with CHT provokes some yellowing, which is more pronounced when the sample has previously been treated with LTP. The yellowing is due to the natural color of CHT, and it is obvious that better polymer deposition occurs on LTP-treated wool. Moreover, the LTP treatment reduces the felting shrinkage of the knitted fabrics, as shown in Table I. This effect is not significantly altered by the subsequent application of CHT, the result being different from our previously published results, mainly because of the aging effect.[21] Anyhow, the CHT application stabilizes the surface characteristics, and the effect remains stable with time.[21]

Figure 2 shows the F/L wetting hysteresis cycles for untreated and CHT-, LTP-, and LTP+CHT-treated human hair fibers versus water as the wetting liquid, and Table II shows the corresponding values of the contact angle calculated from the dynamic mean wetting force values obtained in the Adv mode.

θ_{ADV} tends to decrease with the LTP treatment, and the hydrophobic untreated fiber surface ($\theta_{ADV} > 90°$) becomes hydrophilic ($\theta_{ADV} < 90°$). The CHT treatment does not influence the contact angle for the previously untreated fiber, but when the fiber is LTP+CHT-treated, the contact angle (78°) considerably increases with respect to the value of the LTP-treated fiber. This confirms the presence of the CHT on the fiber surface, which remains more hydrophilic than the untreated fiber but more hydrophobic than the surface of the fiber treated with LTP only.

The wetting hysteresis cycles for untreated fibers clearly show that the fibers are very hydrophobic as they have a negative advancing F/L value [$F/L \approx -20$ mN/m; Fig. 2(a)]. The receding F/L values are very dependent on the scale direction of the fibers, as previously mentioned by Kamath et al.[28] This could mean

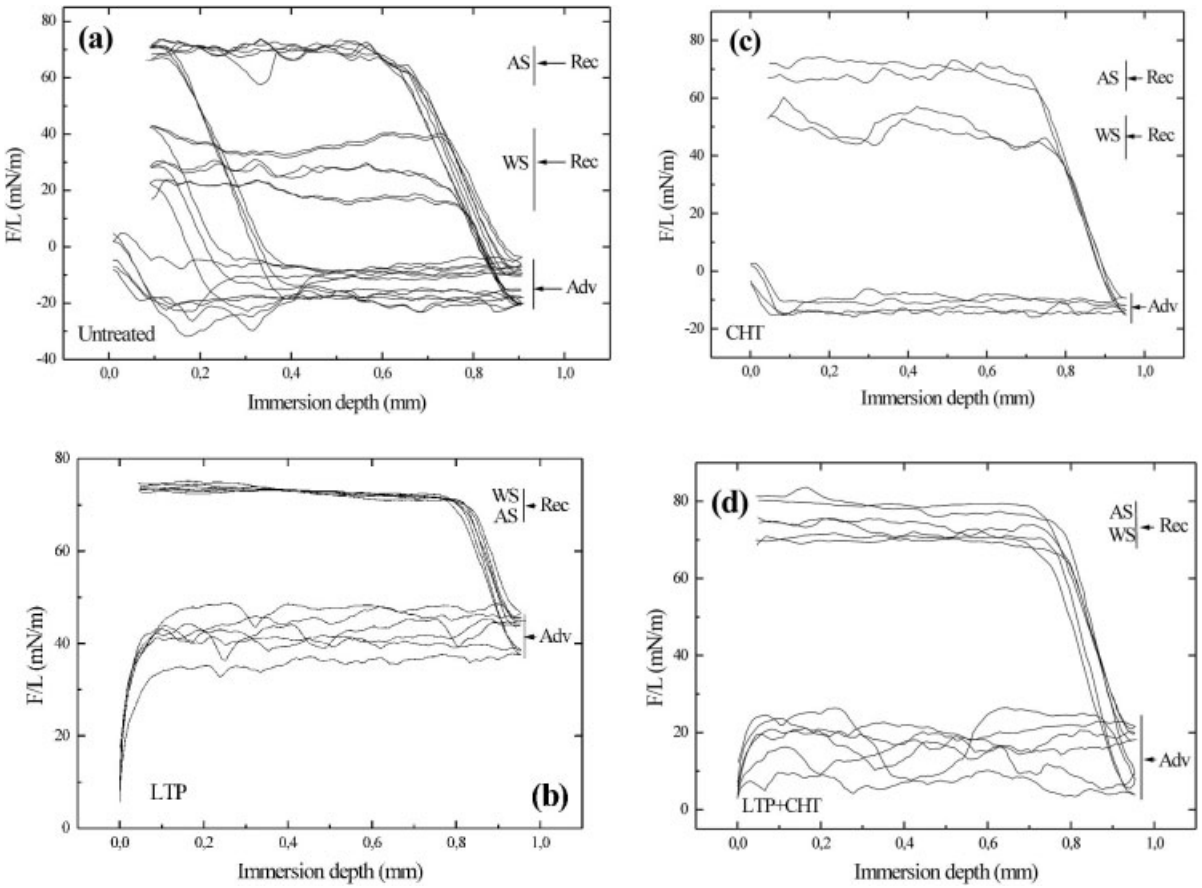

Figure 2 F/L wetting hysteresis cycles for (a) untreated, (b) LTP-treated, (c) CHT-treated, and (d) LTP+CHT-treated human hair fibers versus water as the wetting liquid for the AS and WS cuticular directions of immersion.

that there has been some CHT deposition on the fiber surface, even though the value of θ_{ADV} does not confirm it. The wetting hysteresis cycles for LTP-treated fibers show that F/L decreases a lot in comparison with that of the untreated fiber, and this has been attributed to the formation of hydrophilic groups in the hydrocarbon chains of the lipid layer and/or its elimination, which makes the fiber surface more hydrophilic[6,21] [Fig. 2(b)]. By analyzing the receding F/L values, we can see there is no influence of the scale direction anymore. The wetting hysteresis cycles for CHT-treated fibers show a pattern similar to that of the untreated fiber, maintaining a similar value of the advancing F/L values but showing a much higher value for the receding F/L values [Fig. 2(c)]. The wetting hysteresis cycles for the LTP+CHT-treated fiber are similar to the LTP-treated-fiber wetting hysteresis cycles, and there is no difference between the scale directions [Fig. 2(d)]. It clearly shows that polymer deposition occurs on the fiber surface because of the change in the advancing F/L value and because of the unusually irregular pattern of the advancing part of the wetting hysteresis curve, which could be attributed to irregular CHT deposition on the fiber surface.

TABLE II
θ_{ADV} Values for Untreated, LTP-, CHT-, and LTP+CHT-Treated Human Hair Fibers Measured by the Whilhelmy Balance Method

	Sample			
	Untreated	LTP	CHT	LTP+CHT
θ_{ADV} (°)	102 ± 4	55 ± 4	100 ± 2	78 ± 4

Dyeing

Other authors[18] and our previously published results[19] show that it seems likely that CHT treatment leads to increased dye exhaustion. From these results, we have learned that various factors, mainly the pH and temperature, have to be considered. Therefore, for the first dyeing experiment, pH 4.2 and 85°C were chosen. pH 4.2 was chosen to be near the isoelectric point of wool because under these conditions the concentration of charged amino and carboxyl groups is known to be maximum, and so their stabilizing effect on the wool protein is the greatest. Thus, the level of fiber damage as a result of dyeing can be minimized.

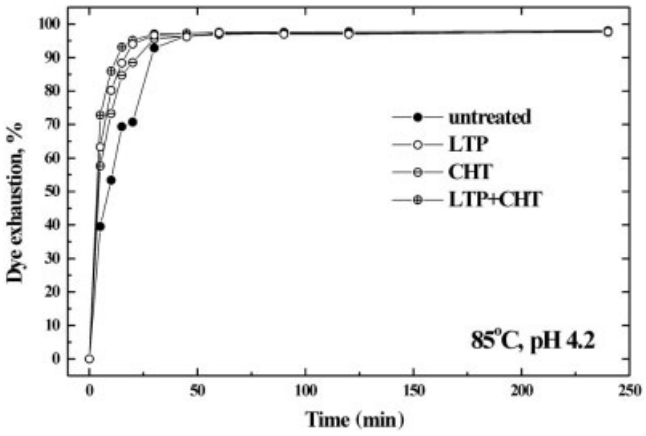

Figure 3 Dye-exhaustion curves at pH 4.2 and 85°C (low-temperature dyeing at the recommended pH): LTP-, CHT-, and LTP–CHT-treated wool versus untreated wool.

The dyeing rates at 85°C and pH 4.2 of wools treated with LTP, CHT, and LTP+CHT are shown in Figure 3 and compared with the dyeing rates of untreated wool. In the early stage of the dyeing cycle, the dyeing rates of LTP-, CHT-, and LTP+CHT-treated wool increase significantly, and the time to reach the dyeing equilibrium is also shorter as a result of surface modification. CHT promotes the dye exhaustion at this pH because its amino groups are protonated. Because of the rapid initial strike, it is difficult to distinguish and discuss the dyeing behavior of differently modified wools. Therefore, to explain the possible dyeing mechanism, we had to facilitate the examination of the diffusion of dye into wool by changing the dye-bath pH.

General experience in the dyeing of wool with acid dyes has shown that a low dye-bath pH generally leads to a greater equilibrium uptake. This is because a low pH favors protonation of carboxyl groups and greater amounts of dye are taken up. Below the isoelectric point of wool (pH 4.2), wool is positively charged, mainly because of the presence of basic groups in lysine and arginine, whereas above that point, carboxyl groups confer a net negative charge on the fiber. When the pH is less than 6, the amino groups within the wool, either at the ends of protein chains or in amino acid side chains, will be mainly protonated. When the pH is greater than 6 almost all carboxylate groups in wool will be present as anions.[29] In acid solutions, CHT behaves as a cationic polyelectrolyte because of the protonation of the amino groups. Because the p*K* value of the amino groups of CHT is 6.3 and the p*K* value of the monomer is close to 7.7, above pH 6.5 the amino groups ($R—NH_2$) should be only partly (ca. 20% at pH 6.9) protonated into $R—NH_3^+$. Therefore, the amino groups of CHT are at pH 4.2 protonated to form cationic amino groups, but at pH 6.5 CHT should have a very low positive charge.[30] Knowing these facts, in the second dyeing experiment, we applied the dye intentionally at pH 6.5 instead of pH 4.2, under otherwise unchanged dyeing conditions, thus minimizing the presence of charged amino groups on wool and on CHT and promoting anionic repulsion at the wool-fiber surface. Because dye diffusion is very slow at pH 6.5, the surface-barrier effect is expected to be predominant. Furthermore, we chose pH 6.5 in the knowledge that this is too high for dye fixation but at the same time sufficiently low to appreciate the differences in the dyeing behavior, these differences being produced by the diverse wool treatments.

Moreover, at pH 6.5, different dyeing temperatures were chosen: conventional dyeing at 100°C, low-temperature dyeing at 85°C, and cold dyeing at 60°C. Figure 4 shows the dyeing rates for the three different dyeing temperatures at pH 6.5 versus the corresponding dyeing rates of untreated wool. The surface-barrier effect is confirmed by the LTP-treated-wool dyeing behavior. The influence of the CHT treatment becomes significant when the temperature is increased to 100°C as other effects, mainly concerning the fiber swelling and water uptake, then become important.

However, it can be assumed that the CHT sorption on wool is due to the ionic interaction between the negative charges of carboxylate and sulfonate groups in the keratin molecule and the protonated amino groups of CHT and to hydrogen bonding between hydroxyl or amide groups of wool and hydroxyl groups of CHT. Both types of interactions are known to be weak, and hence CHT affinity for wool can be generally regarded as weak. Because of its unique molecular structure, CHT has an extremely high affinity for many classes of dyes. According to Giles et al.,[31] the adsorption of sulfonated dyes by chitin and CHT may be regarded as an ion-exchange process at the cationic sites of the polymer, and the similarity of this substrate–dye system to wool dyeing has been confirmed.[32] Consequently, once adsorbed on wool, CHT, which is rich in protonized amino groups, increases the attractive force to negative sulfonate groups of the dye, and enhanced dye uptake during the dyeing of CHT-treated wool is expected.

Table III summarizes the $t_{1/2}$ (the time of the half-dyeing) and E_∞ results obtained from dyeing experiments. $t_{1/2}$, calculated from exhaustion curves, is the time (min) taken for the material to absorb 50% of that at equilibrium. The $t_{1/2}$ values are considerably reduced with the treatments, as already evident from the dyeing rates shown in Figures 3 and 4. In dyeing at pH 4.2 and 85°C, all values decrease by the order of 90%. In dyeing at pH 6.5, the values for LTP- and LTP+CHT-treated wools always decrease independently of the dyeing temperature, but the CHT-treated sample shows an increased or unchanged $t_{1/2}$. These results confirm that at pH 6.5 CHT is not protonated,

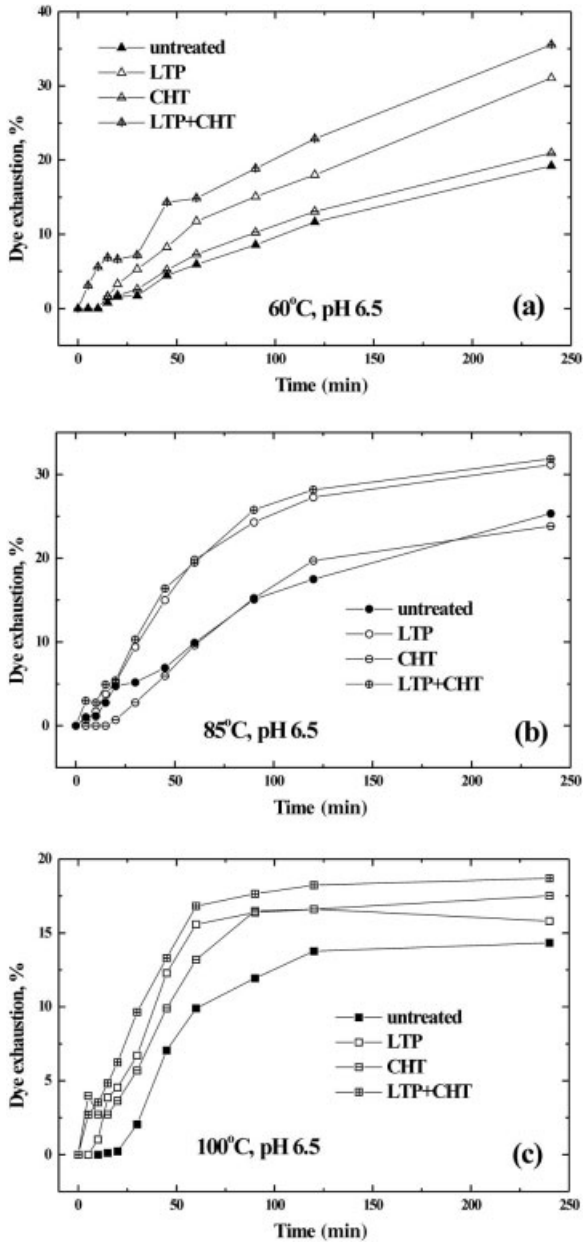

Figure 4 Dye-exhaustion curves at pH 6.5 and (a) 60°C (cold dyeing), (b) 85°C (low-temperature dyeing), and (c) 100°C (conventional temperature dyeing): LTP-, CHT-, and LTP+CHT-treated wool versus untreated wool.

and hence its influence on the dyeing behavior is limited to other factors. Therefore, at pH 6.5, the LTP-treatment contribution is the main factor influencing the dyeing behavior of wool.

Saturation dye exhaustion is almost unchanged in dyeing at pH 4.2. This is due to the fact that LTP treatment is confined to the surface of the wool fiber. In dyeing at pH 6.5, the results are inconsistent.

Diffusion is the process by which dye molecules penetrate the interior of the fibers. There are two possibilities for the mechanism of dye diffusion into the wool fiber: intracellular diffusion through the cuticle layer and intercellular diffusion through the CMC of the intercuticle.[33,34] Neither can explain all phenomena that are observed in wool dyeing, as the process is very complex. The second theory mostly refers to the early stages of a dyeing cycle. Moreover, the lipid materials present at cuticular junctions and inside the fiber, as well as the presence of non-keratinous proteins within the CMC, impede dye penetration. The diffusion characteristics of the bulk fiber phase are appreciated by the apparent diffusion coefficient. The behavior observed in dyeing-rate curves can be confirmed through the relation between C_F/C_∞ and $t^{1/2}$, which gives the slope of the straight line that corresponds to the apparent diffusion coefficient of dyes into wool. The relationship between C_F/C_∞ and $t^{1/2}$, after a short induction period, is usually linear, even beyond the early stages of dyeing (Table III). This initial deviation from the linearity is due to surface-barrier effects.

In dyeing at pH 4.2 the linear region exists only at short dyeing times, mainly for the first 15 min of dyeing. Nevertheless, untreated wool shows a prolonged linear region to 30 min of dyeing. In dyeing at pH 6.5, after a short induction period, that is, a non-linear region at short times, C_F/C_∞ versus $t^{1/2}$ shows a more linear region characteristic of a penetration mechanism in the bulk phase. In dyeing at pH 6.5, the slope of LTP-treated wool is always larger than the slope of untreated wool, independently of the dyeing temperature. It is obvious that dye diffusion in LTP-treated wool is very rapid early in the dyeing process versus that in untreated wool, and this implies that the barrier effect in wool dyeing is diminished, quite clearly reflecting the changes in the fine structure of the wool surface with LTP treatment.

Figure 5 shows the apparent diffusion coefficient for differently treated wool samples at pH 6.5 and for each dyeing temperature investigated. The value $2(D/\pi)^{1/2}$ of LTP-treated wool is always larger than the corresponding value of untreated wool, independently of the dyeing temperature. At 60°C, apparent diffusion coefficients of differently modified wools are very low and almost of the same value, with the exception of LTP-treated wool, which has a somewhat improved diffusion coefficient. Diffusion in the LTP-treated sample begins almost immediately, and the other samples have somewhat delayed diffusion. At 85°C, the differences are appreciable, and the influence of the CHT treatment is noticeable in wool previously treated with LTP. Once again, diffusion in the LTP-treated sample begins earlier than in other samples, which initiate the linear region of the plot after 45 min of dyeing. At 100°C, diffusion in the LTP-treated sample continues to improve, but the difference between the untreated and LTP-treated samples almost disappears. Both CHT-treated samples show considerable diffusion retardation, having slower diffusion

TABLE III
Dye Exhaustion and Diffusion Parameters of Untreated and LTP-, CHT-, LTP+CHT-Treated Wool Samples at Different pH Values and Dyeing Temperatures

pH	Dyeing temperature (°C)	Sample	$t_{1/2}$ (min)	E_∞ (%)	Linear region of C_F/C_∞ vs $t^{1/2}$ (min)	$2(D/\pi)^{1/2}$ ($min^{-1/2}$)	Linear-fit correlation coefficient
4.2	85	Untreated	8.3	98.1	5–30	0.163	0.988
		LTP	0.8	97.7	5–15	0.159	0.992
		CHT	1.5	97.6	5–15	0.170	0.999
		LTP+CHT	0.3	97.8	5–15	0.128	0.996
6.5	60	Untreated	>240	55.7	30–240	0.031	0.999
		LTP	170	49.5	10–240	0.050	0.998
		CHT	>240	61.6	30–240	0.029	0.999
		LTP+CHT	147	53.4	30–240	0.033	0.999
	85	Untreated	84	28.2	45–90	0.106	0.999
		LTP	53.5	35.2	30–60	0.129	0.999
		CHT	99	32.8	45–120	0.100	0.999
		LTP+CHT	43.5	30.6	30–60	0.146	0.995
	100	Untreated	40.3	14.3	30–60	0.262	0.985
		LTP	31.9	15.8	30–60	0.266	0.995
		CHT	40.3	17.5	30–60	0.201	0.999
		LTP+CHT	29.6	18.7	30–60	0.150	0.999

than the untreated sample. Hence, by measuring the diffusion coefficients at different dyeing temperatures, we show that the CHT/dye interaction is strongly temperature-dependent.

Figures 6 and 7 present the results of reflectance measurements. As the color difference in all samples is mainly due to the chroma increase, it can be considered as the contribution to dye uptake that corresponds to the extent of wool modification. The ΔE values for untreated and LTP-, CHT-, and LTP+CHT-treated wool show that for every dyeing system there is a time in the dyeing process when the color difference, which is the result of the fiber modification, becomes nearly constant. In the early stage of dyeing, during the first 20 or 30 min of dyeing, ΔE always increases until the maximum value occurs. From this point on, the color differences are always diminishing until the time when they become nearly constant. This implies that some kind of equilibrium between the dye and active sites on the fiber (wool or CHT) is reached and that from this moment on the dyeing behavior, including the dyeing mechanism, of both treated and untreated wool is similar. The initiation of this equilibrium is always later when the dyeing temperature is lower.

The color differences obtained in dyeing at pH 4.2 and 85°C are similar for all wool samples, and the only noticeable difference exists in the first 30 min of dyeing. In the first 20 min of dyeing, it seems that both LTP and CHT treatments contribute to dye uptake, and the obtained effect could be considered a sum of both treatments. In dyeing at pH 6.5, the main differences exist in the first 20 min of dyeing. Moreover, the

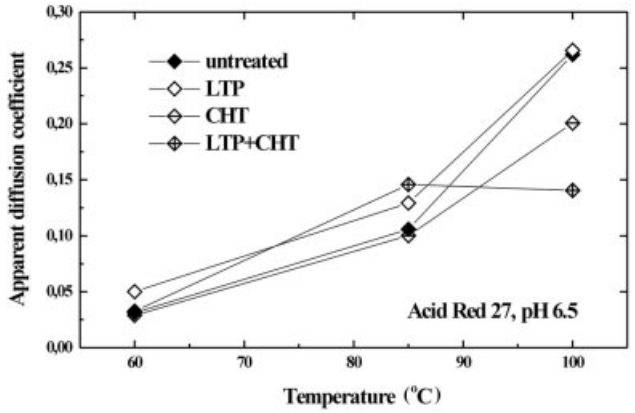

Figure 5 Apparent diffusion coefficient versus the dyeing temperature at pH 6.5.

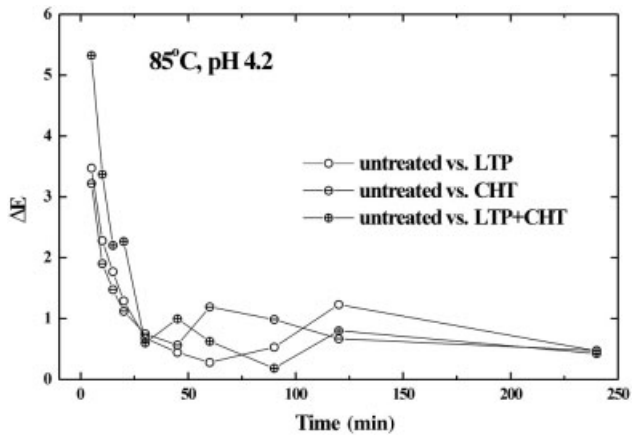

Figure 6 ΔE as a function of the dyeing time at pH 4.2 and 85°C (low-temperature dyeing at recommended pH): LTP-, CHT-, and LTP+CHT-treated wool versus untreated wool.

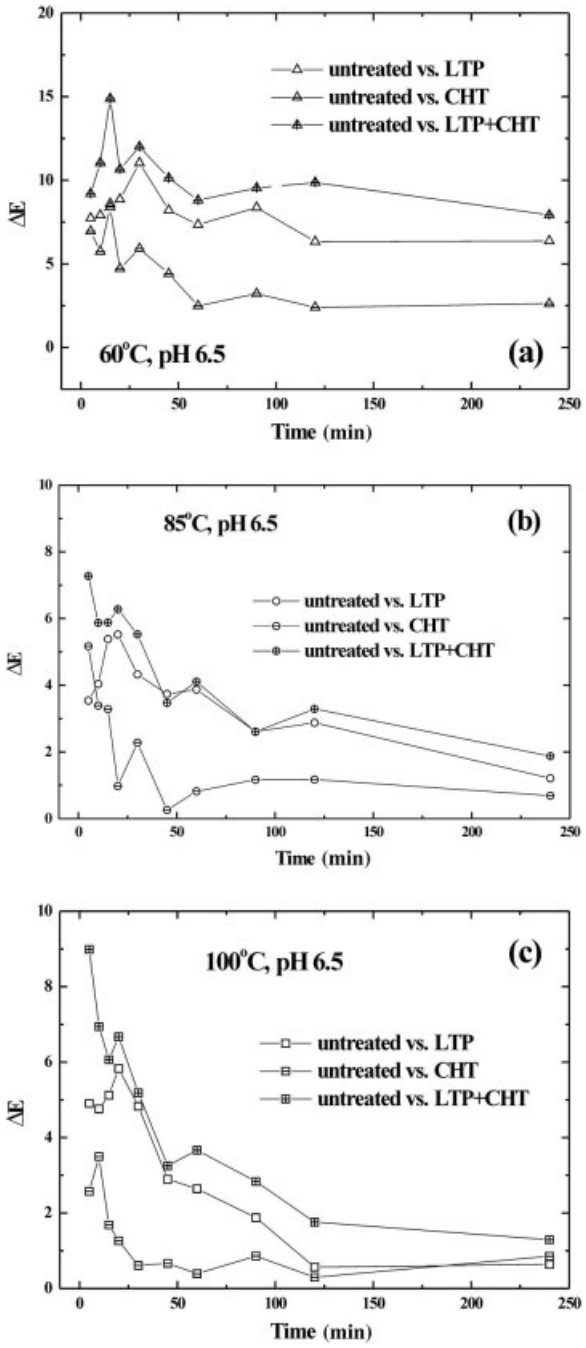

Figure 7 ΔE as a function of the dyeing time at pH 6.5 and (a) 60°C (cold dyeing), (b) 85°C (low-temperature dyeing), and (c) 100°C (conventional temperature dyeing): LTP-, CHT-, and LTP+CHT-treated wool versus untreated wool.

curves for the LTP- and LTP+CHT-treated wools are always very similar and close to each other, and the curve of the CHT-treated wool is always displaced to the lower part of the diagram, having noticeably lower values of ΔE. This behavior is independent of the dyeing temperature. Therefore, the LTP treatment seems to contribute much more than the CHT treatment in the early stage of dyeing, but later on the influence of CHT is predominant. At the end of the dyeing process (240 min), the color differences are very small for dyeing at pH 4.2 and 85°C, mainly because of the dyeing equilibrium established early in the dyeing process. On the contrary, the final color differences for the dyeing at pH 6.5 differ noticeably, always in the order CHT < LTP < LTP+CHT, and the magnitude of the differences generally decreases with an increase in the dyeing temperature.

Table IV shows the color fastness to washing (TM193) of the wool samples dyed at low-temperature conditions (pH 4.2 and 85°C). Compared with that of the untreated wool, the color fastness of CHT-treated wool does not change (90 and 240 min) or is even improved (45 min). On the contrary, the color fastness of LTP-treated wools does drop a little bit (90 and 240 min). However, as this dyeing is performed with a low-temperature procedure (85°C) and a leveling-type acid dye is used, the results could be considered satisfactory. In no cases is there staining of the adjacent wool and cotton fabric.

On the basis of all available results, it can be suggested that the LTP and CHT treatments influence the dyeing process in different ways, always influencing the kinetics of dyeing. In untreated fiber, because of the existence of the surface barrier, the dye enters the fibers most readily by diffusion through the intercellular region between the cuticle scale cells (untreated; Fig. 8). Within the cuticle cells, from the outmost ends of the cuticle cells, the endocuticle and then the exocuticle become colored as the dye travels through the intercellular cement and penetrates the cells from their undersides. This mode of dye penetration means that the whole cuticle cell plays a role as a barrier retarding the direct penetration of the dye into the cortex. Within the cortex, the dye diffuses through the intercellular cement to reach the cortical cells. The dye enters the nuclear remnants of paracortical cells soon after it begins to move into the cortex. Thus, in the case of wool without the modification in the cuticle cells, it is assumed that the dye uptake in the early stage of adsorption is subject to the dyeing behavior of the intercellular region of the cuticle–cuticle (surface) layer. With this assumption, it is reasonable to postulate that the apparent dyeing rate of the wool fiber is treated as consisting of two distinct dyeing rates: the dyeing rate for the intercellular region of the surface layer and the dyeing rate for the bulk (cuticle and cortex) phase.

LTP pretreatment more or less removes the surface barrier present on the fiber surface, and this means that dyes can enter the treated fibers more easily by both intracellular (transcellular) and intercellular diffusion (LTP; Fig. 8) in comparison with untreated wool, for which only intercellular diffusion is possible. The content of hydrophilic groups on the surface is increased, and the part of the cystine on the surface layer (A-layer of the exocuticle) is converted to cysteic acid.[21] Apart from this, there are some indications that the endocuticle and the interscale CMC are also mod-

TABLE IV
Color Fastness (TM 193) of Untreated and LTP-, CHT-, and LTP+CHT-treated Wool

	Dyeing time (min)					
	45		90		240	
Sample	ΔE	Grey-scale grade	ΔE	Grey-scale grade	ΔE	Grey-scale grade
Untreated	6.73	2	6.61	2	7.74	2
LTP	7.82	2	8.41	1–2	8.96	1–2
CHT	4.49	2–3	6.15	2	6.62	2
LTP+CHT	7.33	2	6.83	2	8.24	1–2

Fastness was measured on samples after different dyeing times at pH 4.2 and 85°C.

ified, and this facilitates dye diffusion into the fiber. As a result, the dye molecules diffuse more quickly into the treated fibers, and so the LTP treatment definitely alters the dyeing system kinetically.

When a wool sample is treated with CHT, the polymer presumably forms a layer on the wool-fiber surface (CHT and LTP+CHT; Fig. 8). During the dyeing of CHT-treated fiber, there are two possible sites of interaction between CHT and dye: on the fiber surface and in the bulk of the fiber. If the dyeing conditions give a chance for CHT to desorb, some CHT could find itself in the solution, thus making a third interaction site possible. This possibility is viable mostly for dyeing at a low pH, and it is less probable for dyeing at pH 6.5. If CHT is preferably deposited on the fiber surface, the dye will be accumulated at the surface of the fiber, and this could give rise to an additional surface-barrier effect in the early stage of dyeing. With time, the dye adsorbed in CHT should migrate to the fiber surface and diffuse in the fiber bulk. If CHT penetrates the wool fiber, it will influence not only superficial properties but also some other fiber properties, thus changing the number of binding sites on the fiber, and this could lead to greater mobility of the dye inside the fiber.

Therefore, when CHT is present on the fiber, the rate-determining step for the process of dye uptake is not always diffusion within the fiber to appropriate sites, but it could be the transfer of the dye to the fiber surface as this transfer may be from CHT to the fiber. CHT-treated-wool samples take up the dye faster than untreated wool because the amino groups of CHT create additional active sites for dyeing on the surface of treated fibers. Also, the CHT present on the fiber surface apparently assists the migration of the dye in the later stage of the dyeing process, when more dye migrates into the fiber structure.

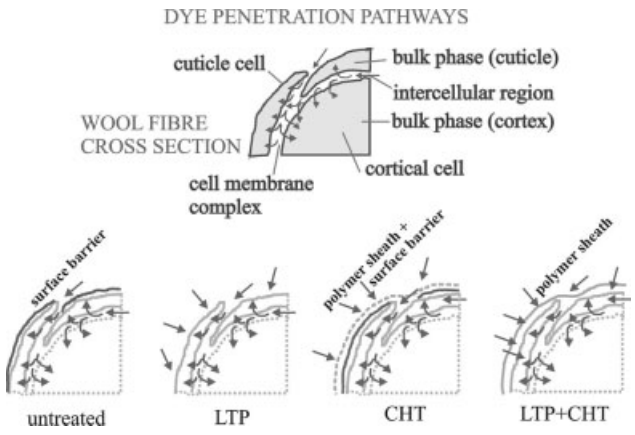

Figure 8 Dye diffusion pathways of LTP-, CHT-, and LTP+CHT-treated wool versus untreated wool.

This behavior depends on the pH of the dye bath and the dyeing temperature. For dyeing at pH 4.2, during the early stage of dyeing, CHT-treated-wool samples take up dye quickly and homogeneously because of an increased number of dye sites on the wool surface, and on average there is more dye on CHT-treated wool than on untreated wool. The dye molecules are then ready to migrate into the fiber structure. As the pH is increased to 6.5, the electrostatic forces of attraction progressively decrease because of decreasing positive charge on the wool and CHT. This inhibits dye adsorption. Therefore, in the absence of electrostatic attraction, only van der Waals forces provide attraction between the dye and wool. Under these conditions, it is expected that the rate of dyeing will be independent of electrostatic forces and that it will be diffusion-controlled.

For untreated fiber, higher dye-bath temperatures always aid the penetration of the dye molecules into the fiber interior, leading to a more uniform coloration. In the case of CHT-treated wool, for dyeing at 60°C, the treatment helps the initial strike but does not affect dye migration. Higher dyeing temperatures (85 and 100°C), because of the opening of the wool structure as the result of the temperature increase, help the dye migrate from the CHT sheath into the wool structure, causing some dye sites to be vacated on the CHT-treated-wool surface. These dye sites probably subsequently take up more dye from the dye bath, with consequently higher exhaustion and even penetration being obtained in the later stages of dyeing.

The dyeing behavior of CHT- and LTP+CHT-treated fibers is different, presumably for two different reasons. First, we suppose that there is more CHT adsorbed onto

the surface of LTP-pretreated wool, and second, we suppose that dye desorbed by CHT in the later stages of the dyeing process could enter the LTP-pretreated fiber more easily by two possible penetration ways (intercellular and transcellular). Both facts are the results of the surface-barrier-layer removal.

Generally, it is likely that CHT enhances dye uptake, thereby facilitating dye penetration of the fiber. Hence, the CHT-treated wool accommodates more dye, not only on the wool surface but also in the fiber structure, this resulting partly from more dyeing sites available on the treated wool surface and partly from more dye having migrated into the treated fiber structure.

CONCLUSIONS

Improved CHT adsorption is clearly shown on wool pretreated with LTP. The dyeing properties are significantly improved and the contact angle is different in comparison with those of wool treated with CHT only.

The interpretation of the dyeing behavior of CHT-treated wool is difficult because the CHT layer deposited on the fiber surface can interact with dye in different ways, depending on the dyeing conditions (pH and temperature) and dye-bath composition.

As it clearly interacts with acid dye, the CHT sheath spread on the surface of the fiber acts always as a predominant dyeing site in very short dyeing times, thus accumulating dye and in later stages desorbing the dye to the interior of the wool fiber.

The dyeing properties of wool treated with LTP are considerably improved versus those of untreated wool. The influence of the LTP treatment is clear enough, and we have confirmed the conclusions of other authors that the surface-barrier effect in dyeing is diminished by the treatment. The dye diffusion is improved, this effect being clearly independent of the dyeing temperature.

When treated with CHT, the polymer sheath spread on the fiber surface acts as a predominant dyeing site in very short dyeing times, thus interacting with the dye and in later stages giving the dye to the wool fiber. This effect is obviously independent of the dyeing temperature, but its duration diminishes with increasing temperature.

For dyeing at pH 6.5, there are always differences in the final exhaustion, that is, the equilibrium exhaustion values between differently treated wools. As there are not protonized amino groups present on wool or CHT, the effect is due to the increased capacity of the treated fiber to adsorb dye, mainly because of the structural changes (plasma treatment) or additional dye adsorption sites (CHT).

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