

Thermal degradation of hair. I. Effect of curling irons

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Accepted for publication July 15, 1998.

Synopsis

The effects of thermal treatments on human hair induced by conventional curling irons, operating in the temperature range from 130°C to 164°C, have been investigated. The fibers were thermally exposed by continuous heating for extended periods of time (5–15 min) or by short (15 s) intermittent heating cycles. The model calculations of heat transfer through a fibrous assembly, based on heat conduction through a semi-infinite solid, were performed. The calculated data have shown that near-uniform temperature distributions are reached in the hair samples within a few seconds of thermal exposure, suggesting that continuous and intermittent modes of treatment are equivalent. The resulting damage to the fibers has been investigated and quantified by the use of fluorescence spectrophotometry, Hunter colorimetry, and combing analysis. The fluorescence analysis has shown that thermal treatment results in a decomposition of hair chromophores, specifically tryptophan (Trp) and its oxidation products (kynurenes). The calculated first-order rate coefficients of Trp decomposition were in the range from 0.03 to 0.12 (min⁻¹), with an estimated activation energy of 6.6 kcal/mol. Hunter colorimetry was employed to quantify thermally induced color changes in hair, such as an increase in the yellowness of white and Piedmont hair or simultaneous yellowing and darkening of bleached hair. Combing analysis has revealed a gradual increase, as a function of exposure time, in combing forces that were measured in the tress sections exposed to curling irons. The extent of the combing increase was found to be dependent on the mode of thermal treatment in which intermittent heating cycles, separated by rinsing, resulted in a higher degree of fiber damage.

INTRODUCTION

The deleterious effects of chemical treatments on hair, such as permanent-waving, bleaching, relaxing, or oxidative dyeing, have received significant attention in cosmetic literature (1). Also, physical changes produced as a result of grooming operations have been thoroughly discussed (2). In addition to this, the photodegradation of human hair has been of growing interest to scientists and has warranted considerable attention (3,4). On the other hand, the literature reflects a limited amount of research focusing on the irreversible chemical or physicochemical changes occurring in hair as a result of thermal treatments applied to hair in conjunction with the use of curling irons or hairdryers, i.e., in the temperature range from 100°C to 170°C (5–9). This area has been investigated primarily in the context of reversible thermally induced effects such as hair drying (5,6) or hair softening at elevated temperatures (<96°C) in aqueous solutions (7). Also, high-temperature decomposition of keratin at temperatures greater than 200°C has been

studied by using differential scanning calorimetry (DSC) (5,8), thermomechanical analysis (8), and thermogravimetric analysis (8).

The key structural elements found in hair and wool that could undergo thermal degradation on contact with hot curling irons or hot air include the cuticle and its outermost layer (epicuticle), which is constructed of fatty acids covalently bound to the protein; the cortex, which accounts for the major portion of the fiber's dry mass and holds most of the water; intercellular binding material, known as the cell membrane complex, which provides adhesion between cortical cells; and the crystalline phase, which is responsible for the mechanical strength of the fibers (10). DSC was used to identify the thermal transitions in hair when subjected to temperatures ranging from 30°C to 250°C (5,8). This study characterized three processes: removal of water (50°–120°C), which occurs during drying; a "toughening transition" in the amorphous matrix (140°–170°C); and denaturation of the crystalline phase (233°C) (5). A detailed study of water desorption/absorption curves related to heat drying of hair at temperatures ranging from 50°C to 110°C, followed by equilibration at 55% relative humidity and 22°C, has shown a reduction in moisture regain (6). Based on this, it was concluded that heat-dried hair becomes more susceptible to static charge accumulation and flyaway during subsequent grooming procedures. The processes occurring at temperatures ranging from 100°C to 170°C are of interest to cosmetic scientists, since conventional curling irons typically operate in this range. One of the physical transformations in hair structure, occurring as a result of annealing between 70°C and 180°C, is an increase in fiber crystallinity, demonstrated by Milczarek *et al.* (5). This effect is similar to wool fiber strengthening, which has been observed after short-term (6–30 min) heat treatments ranging from 130°C to 150°C (11). According to the same paper, longer heating times can also cause destabilization of the α -helical component, as detected by mechanical stress-strain or relaxation measurements. Furthermore, using low-angle X-ray diffraction, Lee was able to postulate the formation of amide cross-links in wool heated at temperatures ranging from 170°C to 235°C (12). Earlier work, completed by Asquith and Otterburn (13) and Menefee and Yee (14), also provides evidence for the formation of cross-links as a result of heat application. Crosslinking could also be responsible for a decrease in urea-bisulfite solubility and a loss in moisture regain (15), observed as a result of short thermal treatments of wool at temperatures ranging from 110°C to 230°C, for as little as 30 seconds.

Chemical reactions in thermally treated keratin fibers were investigated by analyzing the gaseous product of wool degradation at 160°C. Identified products include H₂O, CO₂, CH₄, CO, H₂S, and COS, suggesting decarboxylation and other decomposition pathways for keratin protein (16). The effects of temperature on hair were also investigated using electron spin resonance (ESR) spectroscopy to monitor the signal produced from melanin (9).

The yellowing of wool represents another important aspect of thermally induced keratin degradation, which has been of great interest within the textile industry. This phenomenon is also significant from a cosmetic scientist's point of view, since hair yellowing is commonly perceived as undesirable, especially in the discoloration of unpigmented grey hair. In wool, yellowing can be produced by irradiation and by thermal treatments exceeding 100°C. Several papers were published on this topic, but the mechanism of color formation has not yet been firmly established. Decomposition of cysteine and tyrosine and oxidation of tryptophan (Trp) to kynurenine were proposed as likely path-

ways for the formation of yellow-colored chromophores (17–19). In the case of thermal degradation, the process of yellowing is accelerated at high pH levels and can be controlled under acidic conditions or in the presence of certain reactive reagents, such as maleic anhydride or various antioxidants (20,21). Our results, discussed below, indicate that white, Piedmont, and bleached hair also experience yellowing as a result of short-term thermal treatments induced by hot irons.

The objective of this communication is to analyze hair damage resulting from the use of conventional curling irons. We have employed fluorescence spectroscopy to quantify the decomposition of hair chromophores (i.e., Trp), and color analysis to measure the extent of color changes resulting from thermal treatments. In addition to this, combing measurements were used to detect changes in the fiber frictional properties of hair, which could reflect thermal damage to the surface elements (e.g., surface lipids) of the fiber structure.

EXPERIMENTAL

INSTRUMENTATION

Thermal treatment of hair was performed using curling irons purchased from several manufacturers. We have elected to refer to these as curling iron A, curling iron B, curling iron C, and curling iron D. Figure 1 presents a dependence of temperature as a function of temperature setting for the four appliances employed in this work. The results indicate that the temperatures produced by these devices can range from 80°C to 300°C. These measurements and the analysis of similar appliances suggest that a more typical range is 130°C to 170°C. Within these limits, the process of hair drying occurs very rapidly, and fiber damage may be controlled by proper timing, even at 170°C.

In order to maintain uniformity of the experimental conditions and to assure reproducibility of the obtained data, the thermal treatment to each hair tress was administered in the same position, as indicated by the discolored band present on the hair tresses in Figure 9. Throughout this report we will refer to intermittent and continuous conditions with respect to the mode of curling iron application. Intermittent are those conditions in which heat treatment of a short duration (15 s) was applied to hair. Between each treatment interval the tresses were rinsed and towel-dried to a moist condition. The sum of all heating cycles constitutes a total treatment time. Continuous conditions of thermal exposure, on the other hand, represent the case in which a tress (initially containing 15–25% water) is subjected to thermal exposure for a long period of time, typically 5–15 min, without interruption. The intermittent mode of treatment emulates consumer usage conditions more closely than the continuous mode. Several experiments, discussed in subsequent paragraphs of this paper, were designed to compare the extent of hair damage resulting from both procedures.

Fluorescence measurements were performed using a Fluorolog-2 fluorescence spectrophotometer (Model 212) manufactured by Spex Industries, Edison, NJ. The experimental conditions were similar to those described previously (4). We used a bifurcated fiber optics probe to collect the spectra directly from the surface of hair. The emission and excitation slits were set at 2-nm bandpasses. The measurements were performed in both emission and excitation modes by irradiating hair in the wavelength range of 290–380

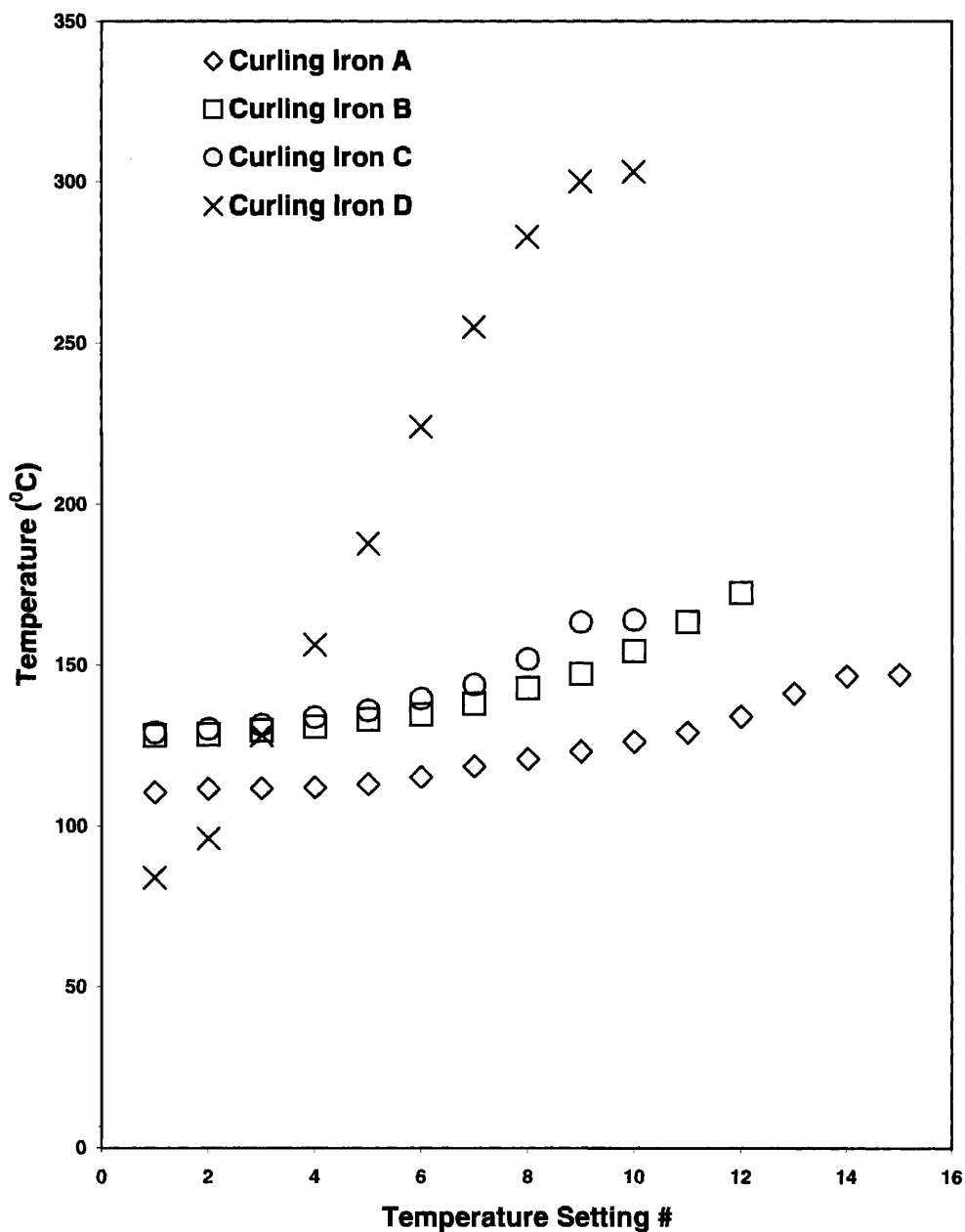


Figure 1. Temperature profile comparison of several commercially available curling irons.

nm. This range of wavelengths was monitored in order to probe hair chromophores absorbing and emitting light in various parts of the UV/Vis spectrum.

Spatially resolved combing analysis was achieved using a miniature tensile tester (Model 160), manufactured by Dia-Stron, Ltd., Hampshire, UK. The combing measurements were performed on wet hair with the following instrumental parameters: range, 2000 G; gauge, 2 G; sample size, 50 mm; phase 1 (extension), 350%; phase 2, 0%; phase 3, 0%;

and phase 4, 0%. In all experiments, the hair tresses were combed several times to remove entanglements prior to performing the combing measurements. The combing traces were always collected before and after thermal exposure, and after one or more shampoos as specified in the text of the paper. Subsequently, the effect of treatments was quantified by force-difference combing curves obtained by subtracting untreated control traces from the curves obtained after the treatment. The data are also reported in terms of combing work difference, which represents integrated values of difference combing curves in the region subjected to thermal treatment. The data analysis was performed by employing Microsoft Excel or MathCad software. All combing measurements were performed on wet hair.

In order to quantify the degree of color changes resulting from heat treatment in various types of hair, we used a HunterLab ColorQUEST sphere spectrophotometer manufactured by Hunter Associates Laboratory, Inc., Reston, VA. The use of the spectrophotometer enabled us to obtain the tristimulus (L , a , b) values, which were utilized to calculate discoloration parameters that can be used to describe the adverse effects of thermal treatments. The reported data, in terms of total color difference $\{\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}\}$ (Eq. 1), chromaticity difference $\{\Delta C = \sqrt{(\Delta a)^2 + (\Delta b)^2}\}$ (Eq. 2), and the yellowness index difference (ΔYI) between unexposed and exposed sections of a hair tress, represent the average of measurements performed at several positions in the designated region on two different tresses. The yellowness index (YI) was calculated using the following equation:

$$YI = 100 \frac{1.28 X - 1.06 Z}{Y} \quad (\text{Eq. 3})$$

where the CIE tristimulus values X , Y , Z are defined as:

$$Y = 0.01 L^2 \quad (\text{Eq. 4})$$

$$X = 0.9804 \left(0.01 L^2 + \frac{aL}{175} \right) \quad (\text{Eq. 5})$$

$$Z = 1.181 \left(0.01 L^2 - \frac{bL}{70} \right) \quad (\text{Eq. 6})$$

MATERIALS

The majority of the experiments were performed on light-brown hair purchased from International Hair Importers & Products Inc., Valhalla, NY. In order to examine the thermal effects on different types of hair, several experiments were performed on bleached and Piedmont hair purchased from DeMeo Brothers Inc., New York, NY, as well as on Asian and unpigmented (white) hair purchased from International Hair Importers, Inc. Hair tresses were prepared by gluing 2 g of fibers to a 1.5-in \times 1.5-in plexiglass tab with Duco Cement. The resulting dimensions of all hair tresses were 6.5 inches in length and 1.25 inches in width. Hair tresses were precleaned with a 3% ammonium lauryl sulfate solution and rinsed thoroughly prior to use in the experiments.

RESULTS AND DISCUSSION

Curling irons are normally applied to dry hair for a short period of time, in the range of 5–20 seconds, at temperatures dependent on the type of hair to be curled. The temperature range of 100°–120°C is prescribed for very fine or damaged hair, 120°–130°C for fine hair, 130°–140°C for normal hair in good condition, 140°–150°C for thick and wavy hair, and 150°–170°C for coarse, thick, and extremely curly hair. After the application of curling irons, hair is allowed to cool down before combing or brushing or the further application of styling aids. This procedure is frequently repeated several times during the course of a day, resulting in a total treatment time totaling the order of tens of minutes over a time span of a few weeks. In this study we have employed two modes, continuous and intermittent, for the application of curling irons as described in the Experimental section of this report. Using the intermittent mode, each treatment cycle of 15 s was repeated several times for a total treatment time of 3–15 min, while in the continuous mode the sample was treated continuously for a similar period of time. In order to answer the question on how equivalent these two modes of hair treatment are, in terms of temperature as a function of time and distance within the sample, we have performed theoretical heat-transfer calculations on a model fiber assembly. Equations describing heat transfer for the semi-infinite solid model, proposed by Carslaw and Jaeger (22), were employed. It was assumed that heat transfer, via conduction, occurs through several layers of fibers in perfect thermal contact with each other. In reality, the fibers would not assume a position of perfect thermal contact, and both the presence of air and water would most likely increase the rate of heat transfer by convection.

The physical constants used in the heat transfer calculations, including thermal diffusivity values defined by Equation 8 in the Appendix, are displayed in Table I. The parameters characterizing fiber assemblies were calculated as a superposition of the corresponding parameters for hair (79%) and air (21%). In the calculated values for the thermal diffusivity of the fiber, we also account for a 15% water content in the fiber structure, which is approximately an equilibrium amount at room temperature and 65% relative humidity.

Figure 2 presents the results of heat transfer calculations through a model fiber assembly characterized by a thickness of 25 fiber layers with a fiber diameter of 70 μm , i.e., a total thickness of 1750 μm . The data are plotted in terms of normalized temperature θ (as defined by Equation 9, Appendix) as a function of the dimensionless distance parameter.

Table I
Parameters Characterizing Thermal Properties/Hair Fiber Assemblies

	Conductivity, k (W/m · K)	Specific heat, c_p (J/Kg · K)	Density, ρ (Kg/m ³)	Thermal diffusivity, α (m ² /s × 10 ³)
Hair fiber*	0.43 (23)	795.492 (24)	1324 (1)	0.04083
Air	0.02624 (25)	1006.3 (25)	1.1769 (25)	2.216
H ₂ O	0.597 (25)	4181.8 (25)	998.21 (25)	0.0143
Fiber assembly	—	—	—	0.497

* The thermal conductivity (k) and specific heat (c_p) values for Polyamide-66 and wool, respectively, were used to represent the constants for a hair fiber.

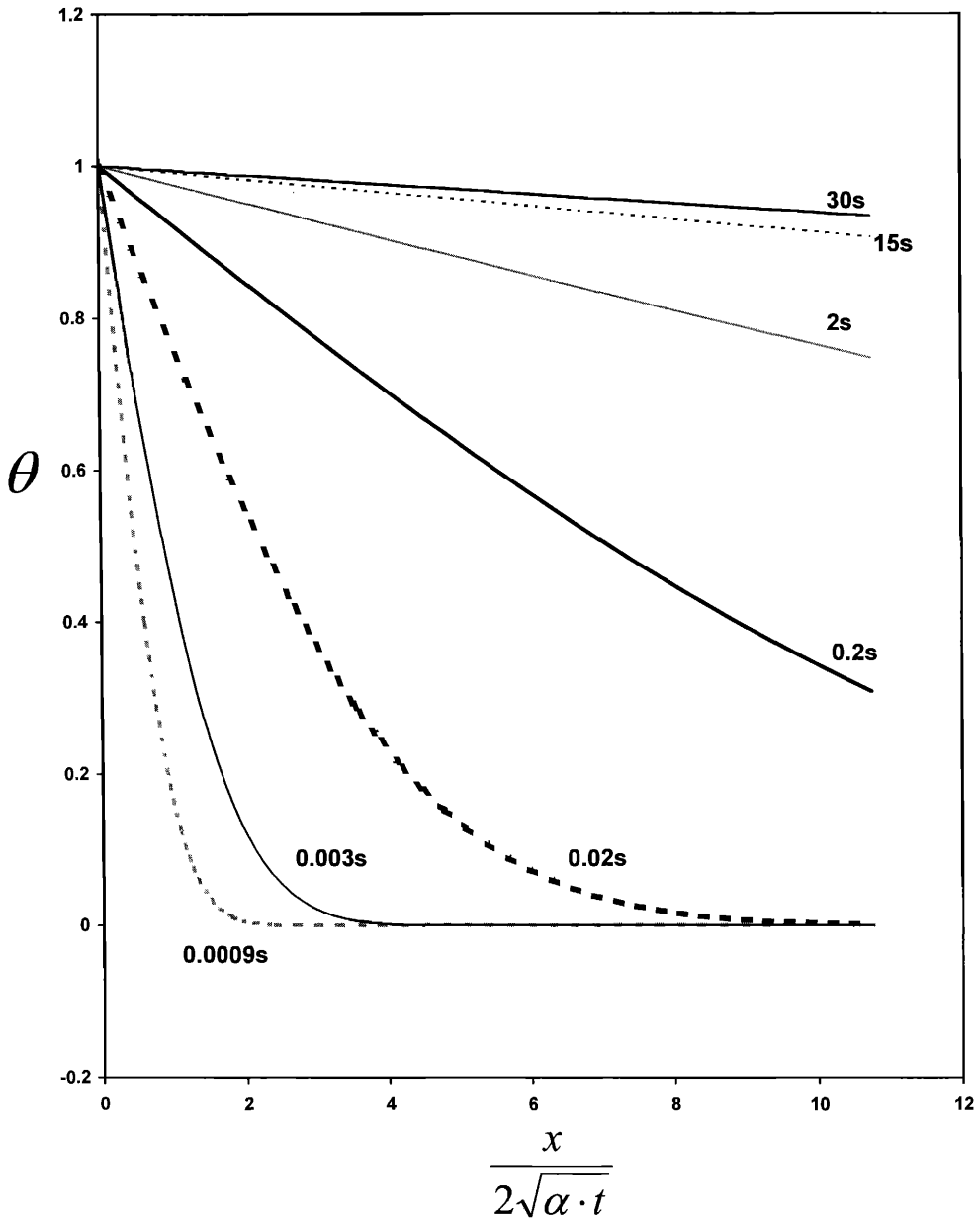


Figure 2. Dimensionless temperature response in a semi-infinite solid (superpositioned fiber assembly) exposed to a high-temperature surface.

The largest value of the distance parameter (10.69) corresponds to the fiber assembly thickness (1750 μm). Also, the calculations for the temperature distribution throughout the fiber assembly were performed for exposure times ranging from 0.0009 s to 30 s. The calculated data presented in Figure 2 clearly demonstrate that near-uniform temperature distributions in hair samples are reached within a few seconds of thermal exposure. Under real conditions, the uniform temperature distributions are probably reached even

faster, since hair is heated from both sides of the curling iron assembly. The results of the theoretical heat-transfer calculations suggest that the thermal conditions of continuous and intermittent treatment modes are nearly equivalent and should lead to similar degrees of fiber damage.

FLUORESCENCE ANALYSIS

Figure 3 presents the fluorescence spectra of white, unpigmented hair, subjected to thermal treatment at 164°C for various periods of time ranging from 0 to 30 min. The spectra were obtained using excitation wavelengths of 290, 320, and 350 nm and show emission bands at 345, 420, and 465 nm. The emission band, with a maximum at 345 nm, was previously shown to correspond to Trp, which absorbs light with a maximum at 285 nm (14). The peak at 465 nm, obtained by excitation at 320 and 350 nm, matches the emission band of 1-kynurenine, which has an absorption maximum at approximately 360 nm (26,27). Evident from the spectra is a peak at 465 nm, obtained by excitation at 290 nm, which is probably related to disulfide bonds in the keratin structure (26). The emission maximum at 420 nm can be ascribed to N-formylkynurenine, which according to the literature has an absorption maximum at 320 nm (27).

The spectra obtained after thermal exposure indicate a decrease in the emission intensities of all bands, which is probably related to thermal decomposition of the corresponding chromophores. The largest reduction in the emission intensity is evident for the band at 345 nm, corresponding to Trp. Figure 4 presents the time dependence of Trp decomposition for various types of hair, including unpigmented (white), Piedmont, commercially bleached, light-brown, and Asian hair. The values of % Trp were calculated as the ratios of Trp emission intensities obtained before and after the thermal exposure ($\% \text{ Trp} = I_e/I_u$, where I_e and I_u represent the Trp emission intensities of the thermally exposed and unexposed regions of a hair tress, respectively). All types of fibers exhibit rapid Trp decomposition, with only 20% of the Trp residues remaining after 30 min of thermal exposure. Further analysis of the data has also shown that the process of Trp decomposition follows first-order reaction kinetics for which the calculated rate constants are given in Figure 4. The temperature effect on the extent of Trp decomposition is illustrated with the data presented in Figure 5, which were obtained after a total treatment time of 3 min. The results include measurements obtained using intermittent and continuous modes of treatment. As predicted by the heat-transfer calculations, which showed nearly uniform temperature distributions within a few seconds of exposure time, both intermittent and continuous modes of hair treatment yielded similar (within experimental error) extents of Trp loss in the temperature range of 140°C to 165°C. As stated previously, one side of a hair tress was exposed to the high-temperature surface of the curling iron while the other side of a tress was in contact with the lower-temperature arm. We found that both sides of the hair tresses experienced a comparable degree of Trp decomposition. A high rate of heat transfer is presumably responsible for the similar degrees of Trp decomposition on both sides of a tress. The data presented in Figure 5 also demonstrate that the process of Trp decomposition is thermally activated with an estimated activation energy of 6.6 kcal/mol. Such a small value of activation energy suggests a free radical mechanism for the oxidation of Trp (28).

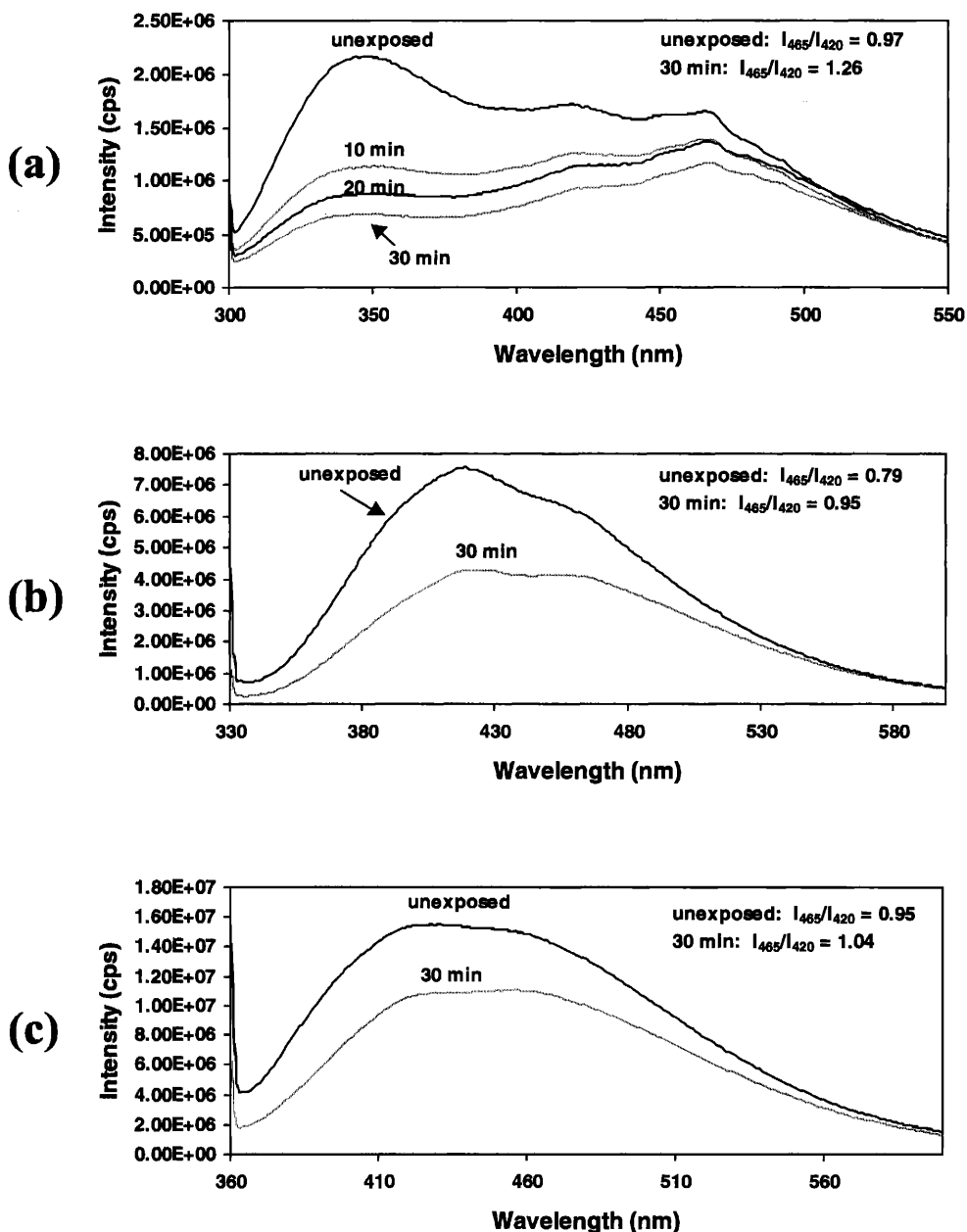


Figure 3. The emission spectra of white (unpigmented) hair, at excitation wavelengths of 290 nm (a), 320 nm (b), and 350 nm (c), before thermal exposure after 30 min of treatment. Thermal treatment was administered at 164°C.

The fluorescence spectra of unpigmented hair obtained at excitation wavelengths of 320 nm (Figure 3b) and 350 nm (Figure 3c) suggest thermal decomposition of both N-formylkynurenine (emission peak at 420 nm) and l-kynurenine (emission peak at 465 nm). The extent of decomposition of these two species is not nearly as severe as in the case of Trp, judging from the emission intensity ratios for these chromophores before and

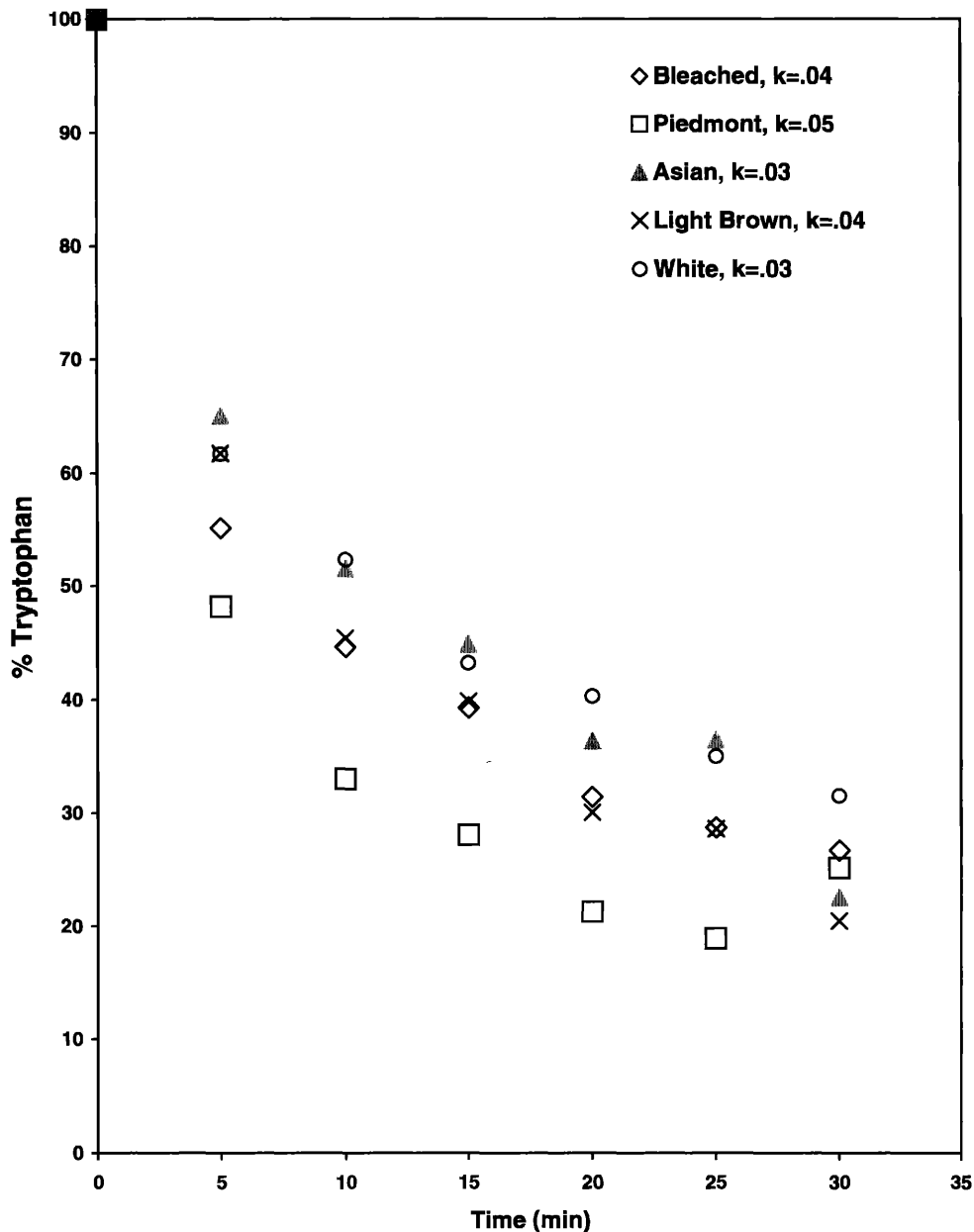


Figure 4. Decomposition of Trp for various fiber types as a function of thermal exposure time. Thermal treatment was administered at 164°C. k is reported in min^{-1} .

after thermal treatment. This may be due to the higher thermal stability of N-formylkynurenine and l-kynurenine, or may arise from the fact that kynurenines are the products of Trp decomposition. It must also be addressed that thermal treatment produces a change in the relative emission intensities for the peaks corresponding to N-formylkynurenine (420 nm) and l-kynurenine (465 nm). For the spectra obtained at

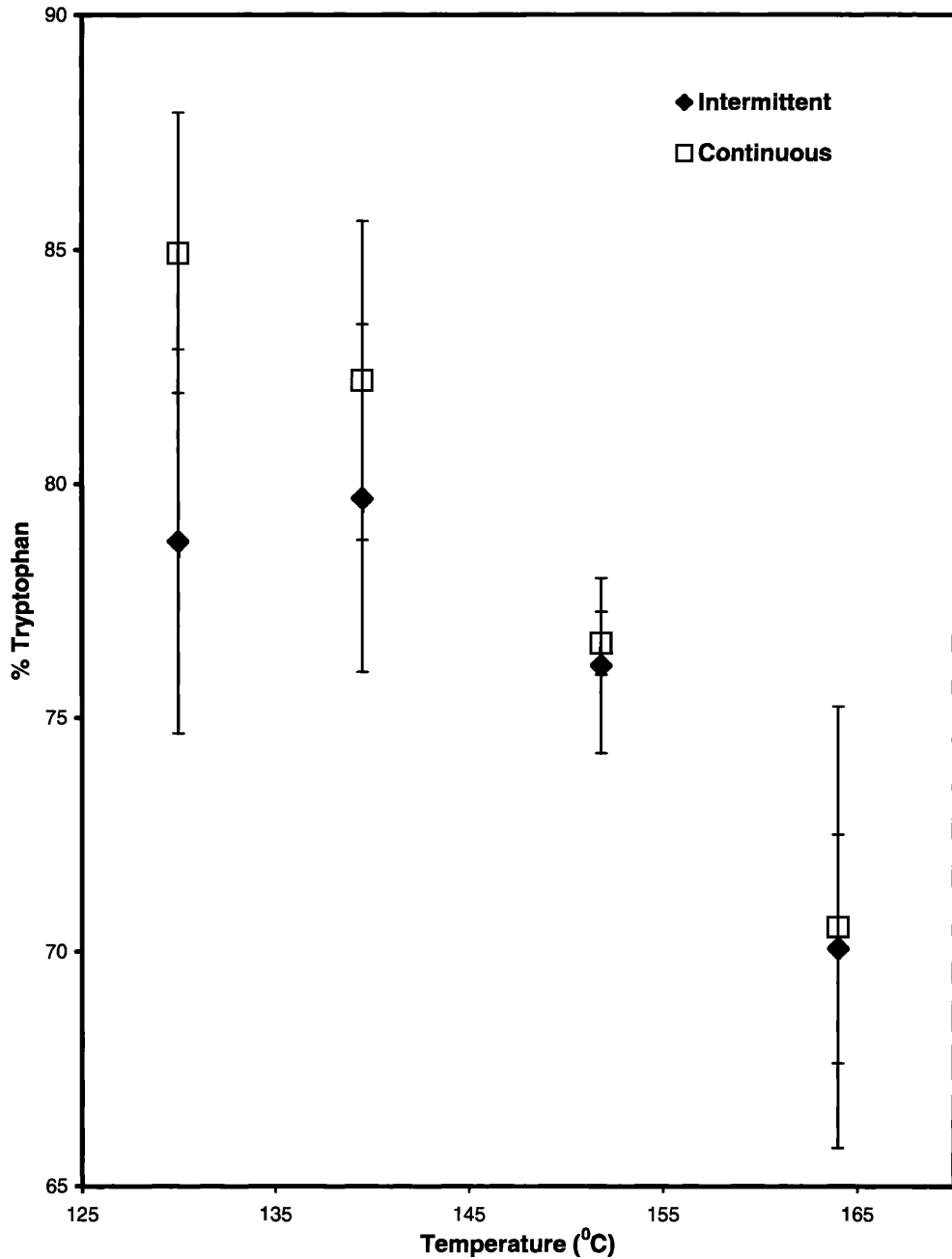


Figure 5. Comparison of Trp decay for fibers exposed to several curling iron temperatures for 3-min under continuous conditions and intermittent conditions (15-s intervals).

the excitation wavelength of 320 nm, the ratio I_{465}/I_{420} increased from 0.79 to 0.95, while the corresponding change for the spectra obtained at an excitation wavelength of 450 nm increased from 0.95 to 1.04. These results suggest a shift, in favor of the

formation of l-kynurenine, that could also be responsible for the yellow coloration of thermally treated unpigmented hair. Similar variations in emission intensities, as in white hair, can also be observed in Piedmont hair.

Somewhat different spectral changes are observed in other types of hair such as bleached (Figure 6), light-brown Caucasian (Figure 7), and Asian (Figure 8). For bleached hair, the Trp emission appears at 345 nm and is reduced as a result of thermal treatment. The longer wavelength emission band is narrower than that corresponding to white hair and appears as a superposition of two peaks with maxima at 433 and 450 nm. The intensity of this band also decreases, without a change in the ratio of I_{450}/I_{433} , as a result of treatment with curling irons. It should also be mentioned that bleached hair becomes black-yellow colored as a result of thermal treatment, a result discussed in the following section of this paper. As in the case of unpigmented hair (white, Piedmont, or bleached), the Trp emission appearing at 335 nm also decreases significantly for pigmented hair (Figures 7 and 8). However, the longer wavelength emission intensity, corresponding to kynurenines, revealed an increase rather than a decrease. The extent of change is clearly evident for light-brown hair, which has also shown a small increase in the ratio of I_{450}/I_{433} . Similar trends, with a smaller magnitude of change, can also be seen in the spectra obtained for Asian hair. The difference in behavior of thermally degraded pigmented and unpigmented hair is similar to that observed in irradiated hair, which has also shown increases in the emission intensities for bands at 420 and 450 nm (26). To explain this, it was suggested that melanin provides a selective photoprotection to kynurenines, or that bleaching results in higher absorption and, consequently, fluorescence emission by hair chromophores. Both of these explanations do not hold in the case of thermally degraded hair. An additional argument may invoke an antioxidant or free-radical scavenging nature of melanin, which may contribute to the retardation of both the photo and thermal degradation of kynurenine chromophores.

COLOR ANALYSIS

One of the clear manifestations for the effect of high temperature on unpigmented hair is the resulting change in color. As illustrated by Figure 9, white and Piedmont hair become perceptibly yellowish even after 2 min of treatment at 164°C. Bleached hair acquires both yellow and dark-brown or black coloration after similar treatment. Table II presents the results of Hunter colorimeter measurements (tristimulus L, a, b values) for white, Piedmont, bleached, light-brown Caucasian, and Asian hair treated at 164°C for a total of 30 min. The data are presented as differences in readings between the thermally treated and untreated sections of a hair tress, and also include calculated parameters such as the total color change (ΔE), chromaticity change (ΔC), and change in the yellowness index (ΔYI).

The total color change, ΔE , was the largest for unpigmented fibers, i.e., bleached, Piedmont, and white hair. Pigmented hair, light-brown Caucasian, and Asian hair experienced only small color changes. The largest contributing factors to ΔE were the variations in lightness, L , especially in the case of bleached hair, which becomes dark-colored after the application of curling irons. The reason for the dark-brown or black color formation in bleached hair may be attributed to thermally induced condensation of melanin fragments, produced during bleaching by reaction with hydrogen peroxide.

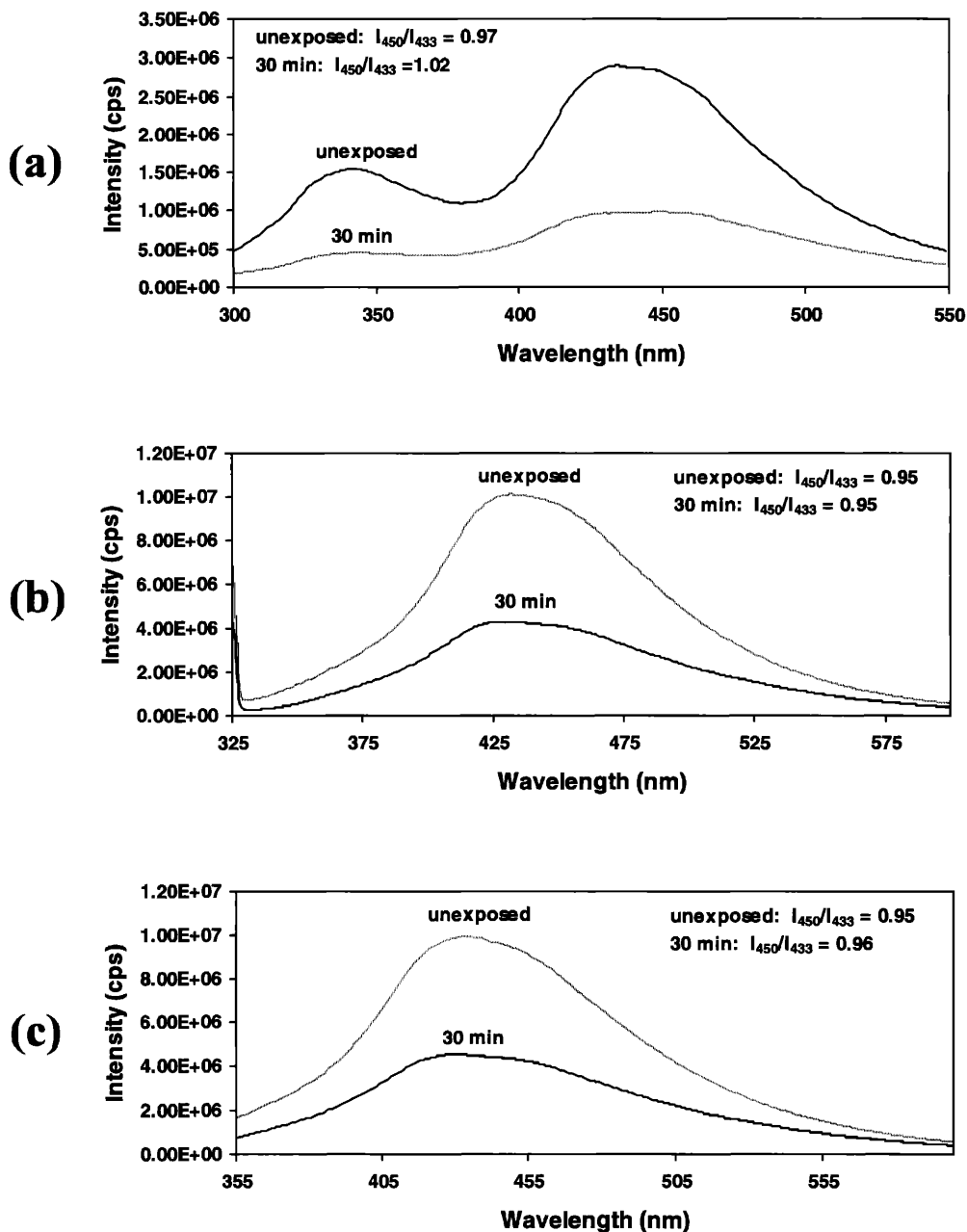


Figure 6. The emission spectra of bleached hair, at excitation wavelengths of 290 nm (a), 320 nm (b), and 350 nm (c), before thermal exposure and after 30 min of treatment. Thermal treatment was administered at 164°C.

In this reaction, higher-molecular-weight residues of melanin decomposition, which cannot be removed by rinsing due to their large size, undergo polycondensation, resulting in the reformation of the melanin pigment. In the case of Piedmont and white hair, changes in lightness (ΔL) are accompanied by a significant variation in the parameters

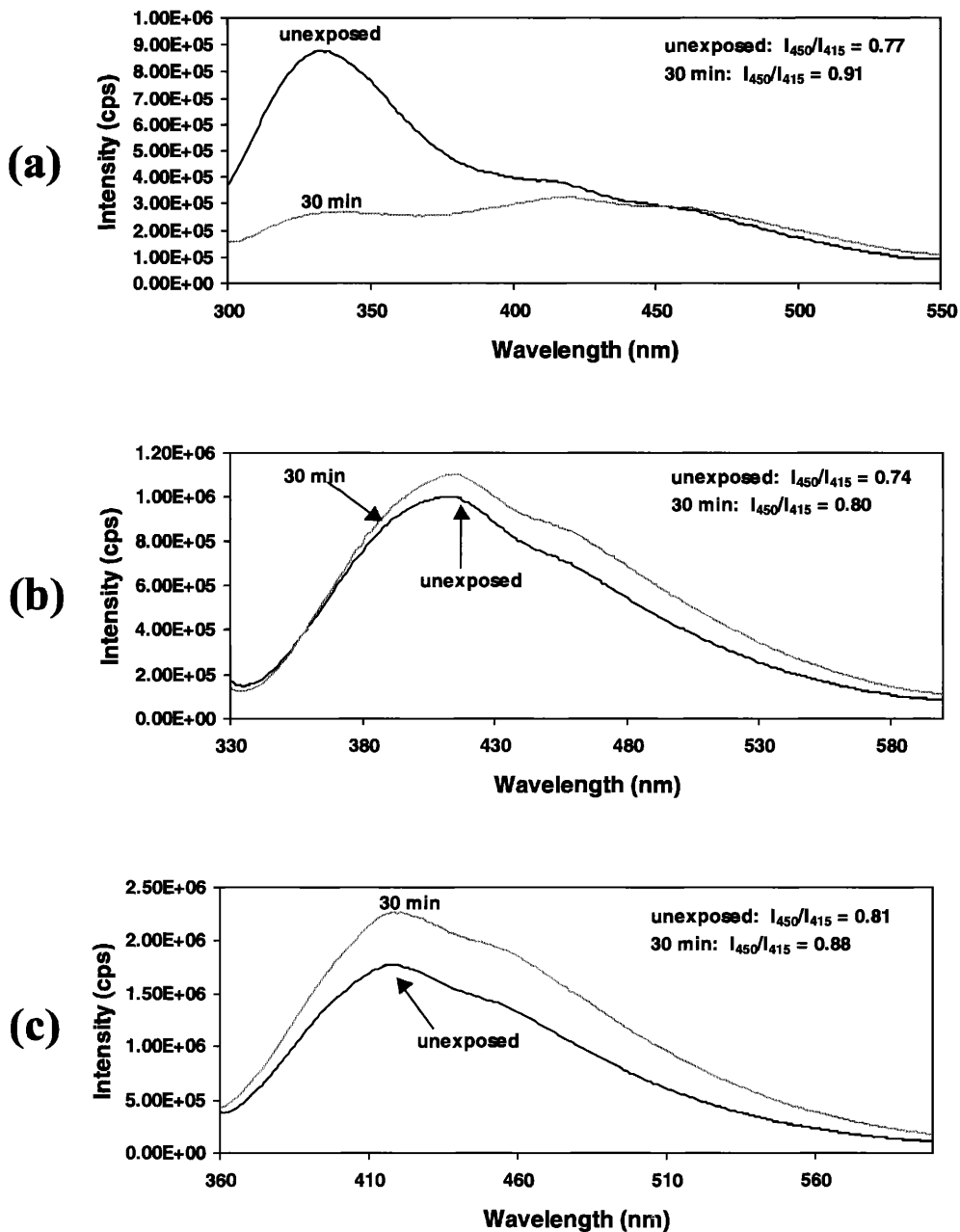


Figure 7. The emission spectra of light-brown Caucasian hair, at excitation wavelengths of 290 nm (a), 320 nm (b), and 350 nm (c), before thermal exposure and after 30 min of treatment. Thermal treatment was administered at 164°C.

Δa and Δb , which leads to a large change in chromaticity (ΔC). This is also reflected by large increases in the yellowness indices for these two types of hair, as well as for bleached hair. Pigmented hair, on the other hand, experienced small differences in yellowness.

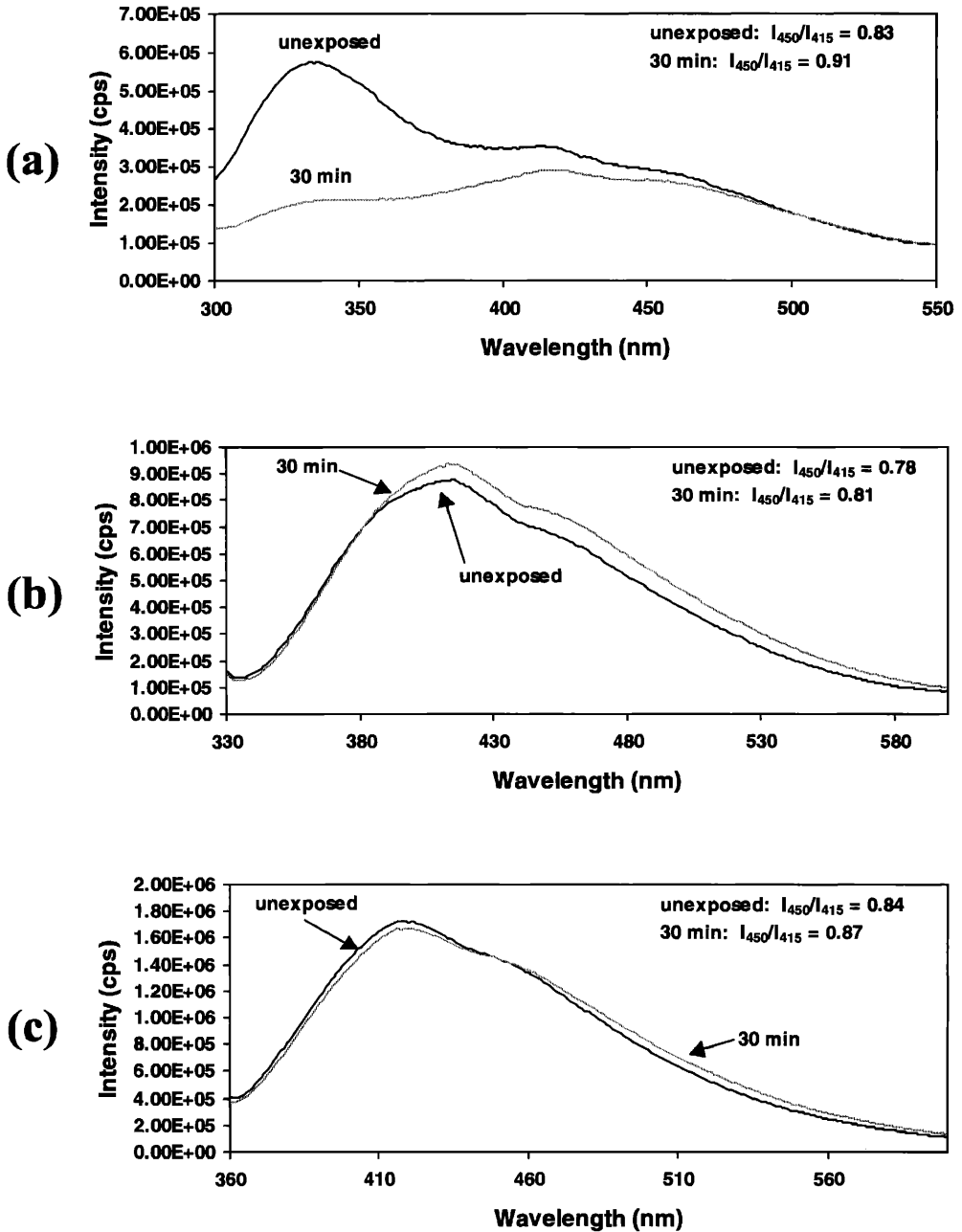


Figure 8. The emission spectra of Asian hair, at excitation wavelengths of 290 nm (a), 320 nm (b), and 350 nm (c), before thermal exposure and after 30 min of treatment. Thermal treatment was administered at 164°C.



Figure 9. Bleached, Piedmont, and white (unpigmented) hair after 30 min (5-min intervals) of thermal treatment at 164°C.

Table II
Hunter Colorimeter Data for Thermally Treated Hair

	ΔL	Δa	Δb	ΔE	ΔC	ΔYI
White	-2.85	1.46	2.98	4.37	3.32	10.13
Piedmont	-3.05 ± 0.88	1.95 ± 0.35	2.18 ± 0.36	4.23 ± 0.68	2.93 ± 0.36	14.61 ± 0.81
Bleached	-6.41 ± 2.32	0.04 ± 1.00	0.88 ± 0.64	6.47 ± 2.30	0.88 ± 0.64	7.55 ± 2.06
Light-brown	-0.82 ± 0.08	-0.44 ± 0.23	-0.25 ± 0.14	0.96 ± 0.13	0.51 ± 0.21	-2.38 ± 2.25
Asian	-0.48 ± 0.11	-0.31 ± 0.25	-0.15 ± 0.10	0.59 ± 0.16	0.34 ± 0.23	-2.46 ± 2.02

COMBING ANALYSIS

The quantification of combing measurements has been widely employed in the evaluation of hair care products (29–31). This technique is very sensitive to small changes in the chemical composition or physical modification of the hair surface that accompany

treatment of hair with hair dyes, bleaches, and permanent lotions, as well as photo-degradation or even combing. The latest modification of the technique involved the application of a treatment to a localized segment of a hair tress, while leaving the rest of the fibers intact as an internal reference (32). Similarly, in the analysis of the thermal degradation of hair, curling irons were applied to a relatively small selected area on each hair tress as illustrated by Figure 9. Consequently, the combing traces revealed the appearance of a peak in the thermally treated area, as a result of fiber damage. The sensitivity of the combing evaluations can further be enhanced by subtracting the untreated control traces from the curves obtained after the treatment.

The effect of thermal treatments at 164°C for light-brown fibers is illustrated in Figures 10a and 10b. The fibers were exposed to curling irons continuously for 15 min, followed by two shampoos, then evaluated by combing measurements. A total treatment time of 60 min represents, thus, four heating cycles. A gradual increase in combing forces, probably related to thermal decomposition of the surface lipid layer, is observed. Similar trends were evident in the analysis of combing traces obtained for other types of hair, such as unpigmented white, Piedmont, and Asian. Figure 10b provides the combing-work difference values, which were obtained by integrating the area of the combing curve where thermal treatment was administered and subtracting this value from the similarly obtained value prior to thermal exposure. Additionally, Figure 10b contains a plot for both, a 1-in- and a 1.5-in-diameter curling iron. The data for the 1.5-in-diameter iron (Figure 10b) were determined by integrating the thermally exposed areas of the curves in Figure 10a. Recognize, also, that the 1.5-in-diameter curling iron results in much higher combing-work difference values than the corresponding 1-in-diameter iron values. This difference is due to much larger integration boundaries provided by the larger iron, which provides the same extent of damage as the smaller iron but covers a much larger surface area of the hair tress. The 1.5-in.-diameter curling iron was used for all the data reported in this communication. Figure 11 presents the temperature dependence of combing work, for both intermittent and continuous modes of thermal treatment, for a relatively short period of time (3 min). These data indicate that, in general, the use of a higher heating temperature results in higher combing-work values, although the effect is not very pronounced. The data also demonstrate that the intermittent mode inflicts a greater amount of damage to hair, at least in the short time span of this experiment (3 min). One factor, which could have contributed to the larger extent of damage, is the increased handling of samples treated in the intermittent mode, which involves rinsing, towel-drying, and low-temperature hair dryer drying after each heating cycle. The total number of handling cycles for intermittently treated fibers is thus twelve. In contrast, the samples subjected to a continuous thermal treatment were only rinsed and dried once after the continuous 3-min treatment.

Finally, it should be pointed out that shampooing is an important step in the evaluation of thermally degraded hair. It was frequently observed, at short exposure times, after the thermal treatment but before shampooing, that hair could actually show a small decrease in combing forces. This could presumably be related to the presence of hair lipids, possibly brought to the fiber surface at elevated temperatures by diffusion from the fiber interior. These lipids are solubilized by shampoo detergents, removed by rinsing with water, and most likely unmask the thermally damaged hair surface, characterized by increased friction.

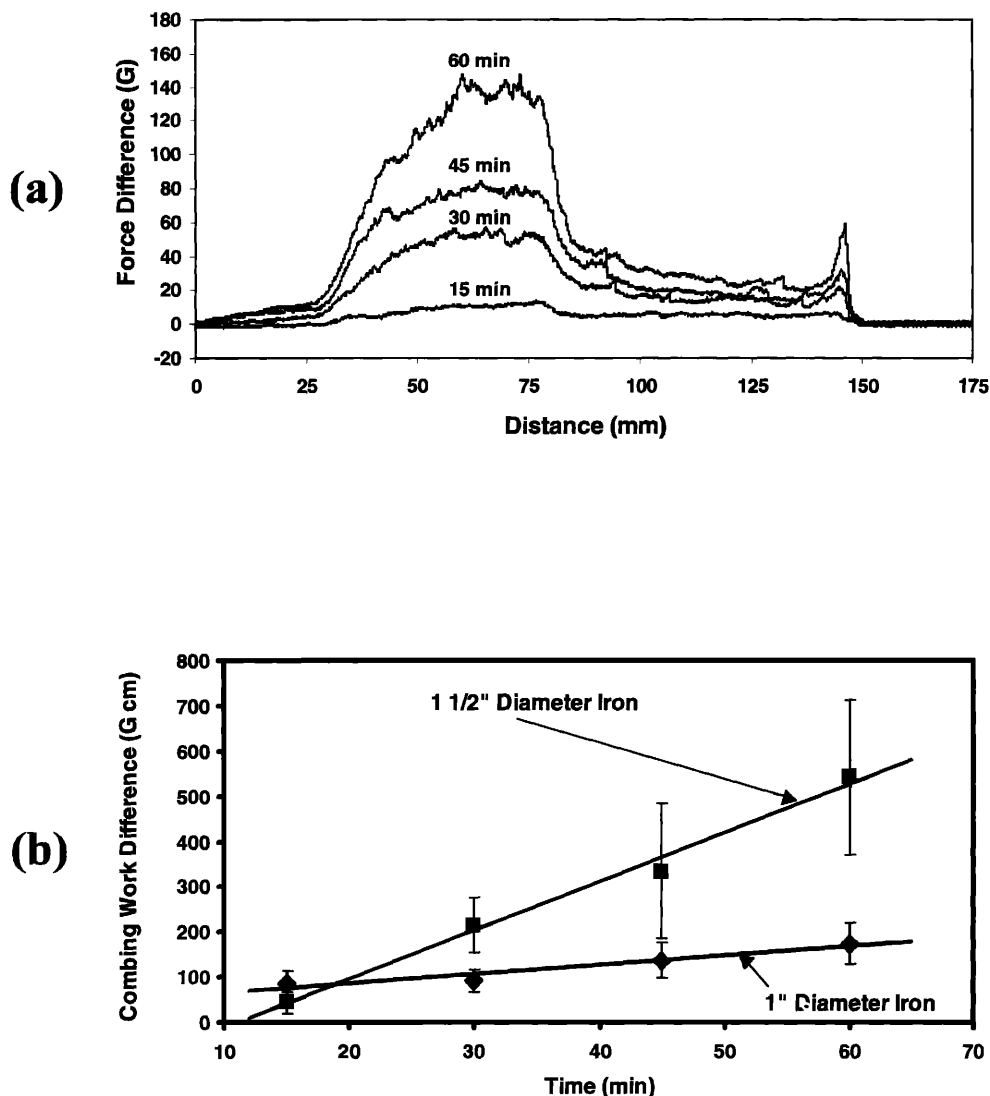


Figure 10. (a) Combing curve differences for light-brown fibers monitored after 15, 30, 45, and 60 min of curling iron application (164°C). (b) Combing work difference for light-brown fibers as a function of thermal exposure time reported for two curling irons with different barrel diameters.

CONCLUSIONS

The thermal treatment of hair with curling irons, at temperatures ranging from 130°C to 170°C , was found to result in significant damage to a variety of fiber types, including white (completely unpigmented), Piedmont, Caucasian light-brown, and Asian hair. The extent of damage was quantified in terms of (a) hair chromophore decomposition determined by fluorescence spectroscopy and Hunter colorimetry, and (b) hair surface modification determined by combing measurements. Both Trp and its oxidation products (kynurenines) were affected. As judged by a reduction of its emission intensity, Trp was found to undergo decomposition in all types of hair, with the first-order kinetic rates

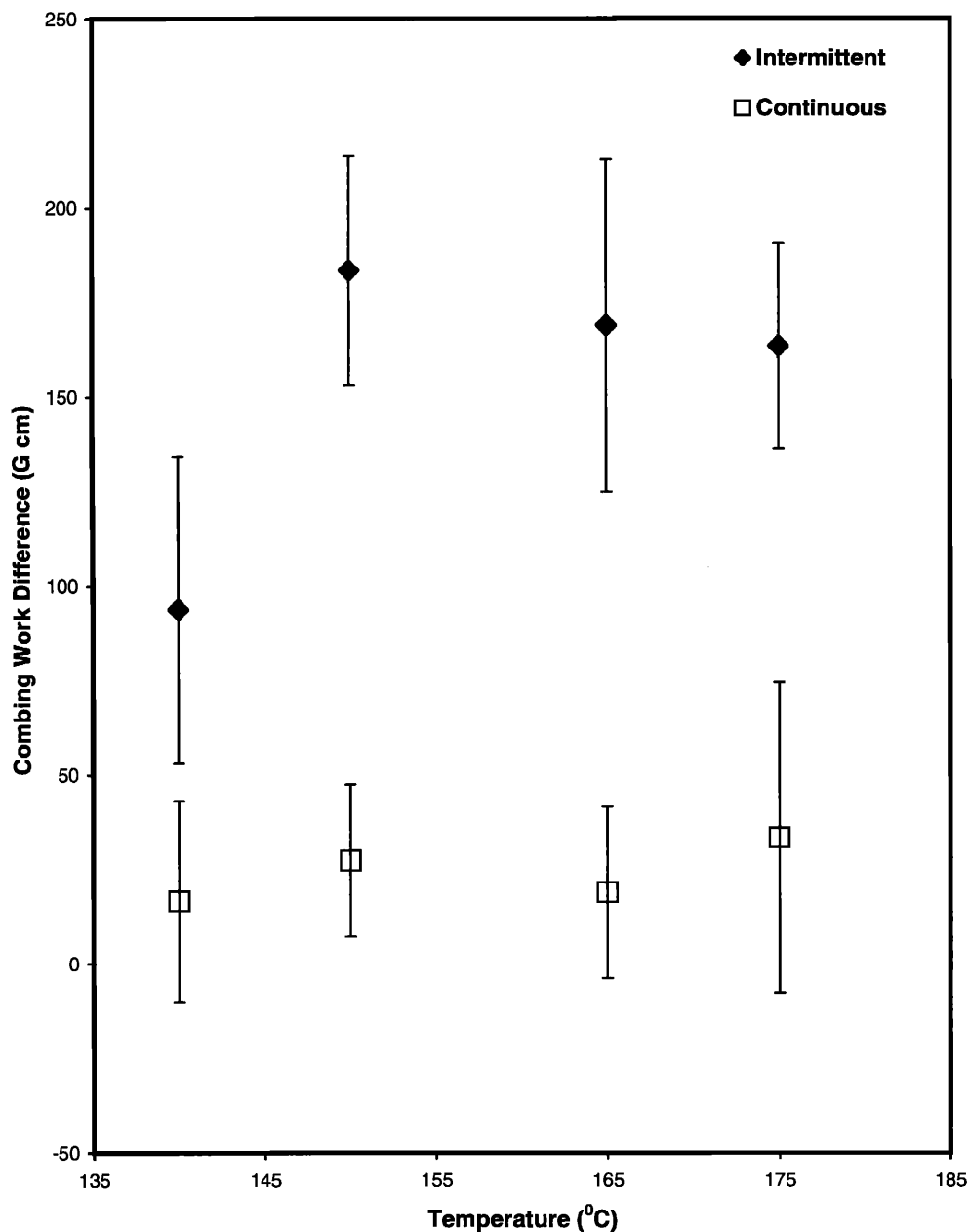


Figure 11. Combing work difference as function of temperature for fibers subjected to 3 min of thermal treatment using intermittent (15-s intervals) and continuous modes of treatment.

in the range of 0.03 to 0.12 (min^{-1}) and an estimated activation energy of 6.6 kcal/mol. The products of Trp oxidation, which emit light in the visible range (400–500 nm), were found to undergo decomposition in unpigmented types of hair (white, Piedmont, and bleached). Thermal treatments were also found to produce discoloration of hair, especially unpigmented hair, which becomes yellow (white or Piedmont hair) or dark-

colored (bleached hair). In addition to this, combing measurements demonstrated the damage to hair as reflected by an increase in combing forces.

APPENDIX: HEAT TRANSFER CALCULATIONS

In order to complement the experimental results, which investigated the differences between continuous and intermittent modes of thermal treatment, we have performed calculations for the temperature distribution as a function of time and distance through a fiber assembly. This was achieved by utilizing the heat-transfer solution for the semi-infinite solid model proposed by Carslaw *et al.* (22,33).

For illustration, we have included Figure 12, which depicts the arrangement of fibers in an ideal assembly. The arrangement of fibers in a cubic lattice provides a fiber (79%) and air (21%) contribution to the composite semi-infinite solid. In addition to this, a 15% contribution of H₂O to the fiber itself was also considered. For the calculations, it is assumed that heat transfer, via conduction, flows through each fiber and into the next fiber while in perfect contact with one other. In practice, the fibers would not assume a position of perfect thermal contact nor would conduction be the only mode of heat transfer. The presence of air in the fiber assembly could decrease heat transfer by conduction while increasing it by convection. Also, the effect of water evaporation is neglected in the calculations. For the purposes of this model, we will only consider conductive heat transfer and not the combined effects of convection or water evaporation.

One-dimensional heat transfer through a semi-infinite slab, representing a fiber assembly with no internal heat generation and constant thermal conductivity, is given by the Fourier equation:

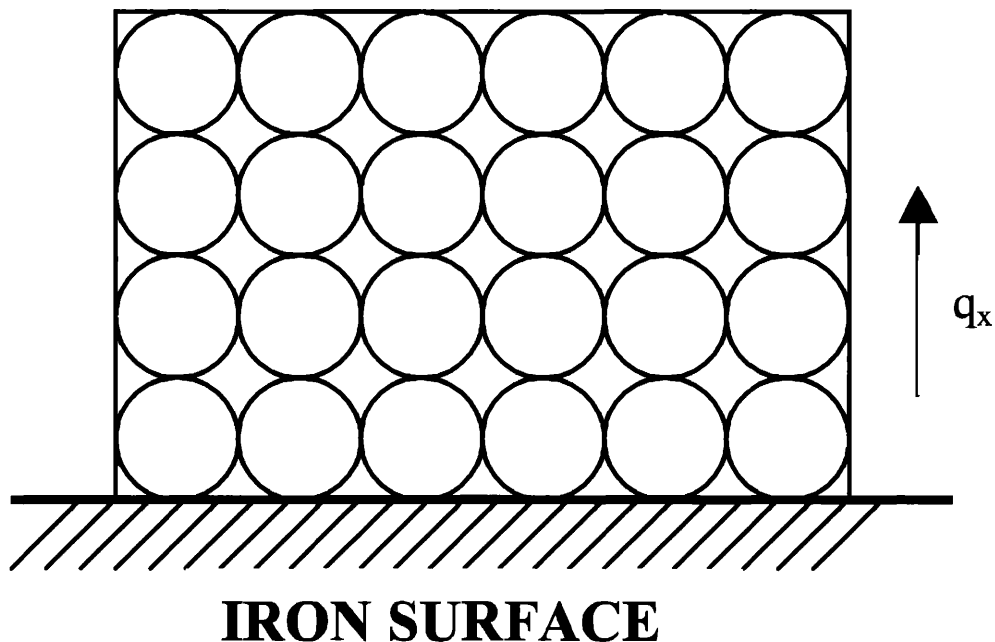


Figure 12. A series of cylinders representing an ideal hair fiber assembly.

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (\text{Eq. 7})$$

where T and t represents the temperature and time, respectively. The thermal diffusivity, α , of the solid can be calculated using the following relationship:

$$\alpha = \frac{k}{\rho \cdot c_p} \quad (\text{Eq. 8})$$

in which case the thermal conductivity (k), density (ρ), and specific heat capacity (c_p) of the material are assumed to be constant throughout the heating process.

Solution of Equation 7, with respect to the initial and final boundary conditions, provides the following relationship (34):

$$\theta = \frac{T - T_o}{T_s - T_o} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{\alpha \cdot t}}} e^{-u^2} du \quad (\text{Eq. 9})$$

where u is a dummy variable for the integration, T_o is the initial hair temperature, T_s is the surface temperature of the heat source, and $T(x,t)$ is the temperature of hair as a function of distance (x) and time (t). For the sake of algebraic convenience, the dependent variable $T(x,t)$ has been normalized, resulting in the single variable, θ . The results of the calculations, in the form of a plot of θ as a function of the dimensionless distance parameter, are presented in Figure 2.

We also performed calculations for a fiber arrangement in the form of a hexagonal lattice in which the composite consisted of fiber (91%) and air (9%). In comparison to the cubic arrangement, the hexagonal formation results in a smaller contribution of air, resulting in decreased thermal diffusivity and, consequently, a slower rate of heat transfer.

ACKNOWLEDGMENTS

The authors acknowledge useful discussions with J. Kosiek and K. Krummel.

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