

The effect of various cosmetic pretreatments on protecting hair from thermal damage by hot flat ironing

Y. ZHOU, R. RIGOLETTO, D. KOELMEL, G. ZHANG,
T.W. GILLECE, L. FOLTIS, D. J. MOORE, X. QU, and C. SUN,
*International Specialty Products, Wayne NJ (Y.Z., R.R., D.K., G.Z.,
T.W.G., L.F.), and ISP Shanghai Global R&D, Shanghai, China
(X.Q., C.S.).*

Synopsis

Hot flat irons are used to create straight hair styles. As these devices operate at temperatures over 200 °C they can cause significant damage to hair keratin. In this study, hair thermal damage and the effect of various polymeric pretreatments were investigated using FTIR imaging spectroscopy, DSC, dynamic vapor sorption (DVS), AFM, SEM, and thermal image analysis. FTIR imaging spectroscopy of hair cross sections provides spatially resolved molecular information such as protein distribution and structure. This approach was used to monitor thermally induced modification of hair protein, including the conversion of α -helix to β -sheet and protein degradation. DSC measurements of thermally treated hair also demonstrated degradation of hair keratin. DVS of thermally treated hair shows the reduced water regain and lower water retention, compared to the non-thermally treated hair, which might be attributed to the protein conformation changes due to heat damage. The protection of native protein structure associated with selected polymer pretreatments leads to improved moisture restoration and water retention of hair. This contributes to heat control on repeated hot flat ironing. Thermally stressing hair led to significantly increased hair breakage when subjected to combing. These studies indicate that hair breakage can be reduced significantly when hair is pretreated with selected polymers such as VP/acrylates/lauryl methacrylate copolymer, polyquaternium-55, and a polyelectrolyte complex of PVM/MA copolymer and polyquaternium-28. In addition, polymeric pretreatments provide thermal protection against thermal degradation of keratin in the cortex as well as hair surface damage. The morphological improvement in cuticle integrity and smoothness with the polymer pretreatment plays an important role in their anti-breakage effect. Insights into structure-property relationships necessary to provide thermal protection to hair are presented.

INTRODUCTION

Hair damage from thermal treatment with styling appliances such as hot flat irons, blow dryers and curling irons has become an increasing concern in hair care. This is especially true with hot flat irons that can exceed temperatures of 200°C. Because of the growing popularity of using high temperature thermal styling appliances, there is a need for thermal protective ingredients/products and test methods to show their efficacy. To meet this challenge, understanding and assessing hair damage from thermal treatment is needed. In recent decades, thermal damage of hair by curling irons has been discussed by several publications (1–3) that have studied various effects on hair thermal damage, such as

moisture content, conditioners, polymers and heating modes. Changes in hair mechanical properties, combing force and tryptophan by curling ironing treatment at 120–160°C were demonstrated in the literature as well. High-temperature decomposition of hair keratin has been studied by using DSC (4,5). On the other hand, the literature reflects limited amount of research on hair damage and protection from using hot flat ironing at a temperature over 200°C.

In this work, hair damage from thermal treatment was studied in different aspects by several techniques towards understanding hair thermal damage and the protective effect by cosmetic pretreatment. It is also our objective to understand the thermal protection mechanism, such as the role of moisture regain of hair on controlling hair temperature from repeated heating. Also, the alleviation of weakening of hair and the consequent reduction in hair breakage through combing using polymers with different functional groups highlights the structure-property relationships important for thermal protection efficacy.

MATERIALS AND METHODS

POLYMERS

VP/acrylates/lauryl methacrylate copolymer, PEC (polyelectrolyte complex of methylvinylether/maleic acid copolymer and polyquaternium-28 (6,7)), polyquaternium-55, copolymer of VP and DMAPA acrylates, and other polymers used in this study were supplied by International Specialty Products (ISP). Hydroxyethylcellulose (HEC) was supplied by Aqualon. These ingredients are used as supplied and not purified and modified in any way.

HAIR SAMPLES

European dark brown hair was purchased from International Hair Importers. Each hair tress was 1.5" wide, 3.5 g in weight and 6.5" in length of loose hair. Asian hair tresses were supplied from a local commercial source in China made with the same specifications.

THERMAL TREATMENT OF HAIR

Hair tresses were hot flat ironed by a controlled 12-minute treatment schedule. The temperature of hot iron used in this work was 232°C unless specified elsewhere. First, the hair tresses were washed with 10% sodium lauryl ether sulfate (SLES) and dried with a hair blow dryer set on hot. Then hair tresses were thermally exposed for a short (12 seconds) intermittent heating cycle separated with SLES washing every 4 minutes for a total of 12 minutes thermal treatment. If a protective agent was tested, tresses were pretreated with 0.5 g of a 1% polymer solution for Asian hair or 0.5 g of a 1% polymer solution made into 0.5% hydroxyethyl cellulose (HEC), after the SLES wash, then dried and followed with hot flat ironing. At the end of the 12-minute hot ironing, the tresses were washed with 10% SLES again and dried for subsequent combing to quantify hair breakage. The polyelectrolyte complex (PEC) was supplied and tested at 2%, unless specified.

ASSESSING HAIR DAMAGE BY PHYSICAL TOOLS

Differential scanning calorimetry (DSC). DSC was used to measure hair damage by assessing hair keratin degradation and the effect of cosmetic pretreatments. DSC measurements were performed on tresses after the 12-minute controlled hot ironing treatment schedule. Two thermal parameters derived from the DSC peak were used to assess hair damage: the denaturation temperature, T_d , of the helical protein and the denaturation enthalpy, ΔH . All hair samples were run on a Q2000 DSC (TA Instruments) at a heating rate of 2°C per minute. Between 8 to 13 milligrams of cut hair fibres were used per run in high volume stainless steel pans. Fifty microliters of water were added to each pan prior to sealing. The sealed hair fibers were hydrated in their pans overnight before running.

FTIR spectroscopic image analysis of hair fibers. Fourier transform infrared imaging spectroscopy (FT-IRIS) was utilized to examine the molecular modification of hair keratin from thermal insult with and without protective treatment. This novel technique provides significant advantages of direct spatially resolved concentration and molecular structure information for sample constituents. In this study, hair cross sections were imaged by a Perkin Elmer Spotlight system which couples a FT-IR spectrometer to an optical microscope. The system consists of a linear array mercury-cadmium-telluride (MCT) detector and an automated high precision XY sample stage. In the FTIR images, each pixel size is $6.25\mu\text{m}$ and 16 scans were collected for each spectrum with $8\mu\text{m}^{-1}$ spectral resolution. Five-micrometer-thick hair cross sections were prepared by slicing a short hair bundle which is embedded into ice mounted on the top of a sample holder under -30°C using a Leica CM 1850 Microtome. Hair cross sections were collected on CaF_2 windows for conducting FT-IR imaging analysis. Spectral Dimensions Isys 3.1 software was used for data analysis and image construction. Spectral data were baseline-corrected before peak heights and integrated area were measured.

Scanning electron microscopy (SEM). SEM was used to examine the morphological changes of cuticle layers on the hair surface after thermal treatment with and without the protective treatment. The Amray Model 1820 SEM was used to collect digital photomicrographs. Four to five fibers were examined for each hair sample treatment.

Dynamic vapor sorption analysis (DVS). The sorption and desorption of water vapor on hair were determined with a DVS Advantage-1 gravimetric vapor sorption analyzer (Surface Measurement Systems Ltd., London, UK). The experimental temperature was $25.0 \pm 0.1^\circ\text{C}$ and the total N_2 gas flow was 200 ml/min. Approximately, 40mg of hair samples formed into a 20-30 strands of loop were loaded onto a tared quartz sample pan. The diameter of the hair fiber, which was chosen as the average of 30 fibers (59 μm), was determined using a Mitutoyo micrometer. The sorption sequence consisted of the following steps:

1. The hair sample was initially wet at 95% RH for 1 hour.
2. The hair was dried at 25°C and 0 %RH for 12 hours.
3. The hair samples were exposed to an isothermal humidity ramp from 0–90 % RH followed by a 90–0% RH desorption in 10% RH steps. Each sorption-desorption step was 4 hours in duration to approximate gravimetric equilibration.
4. At the end of each partial pressure, step points were averaged to produce an isotherm plot, which showed the change in mass of hair samples as a function of relative humidity.

Atomic force microscopy (AFM).

- Specimen preparation. European dark brown hair fibers were mounted onto a steel sample disk using a nail polish liquid. A thin layer of the liquid was brushed on the surface of the metal disk. When the liquid hardened into a tacky state, hair fibers were carefully placed on the metal disk. The liquid dries quickly to keep the hair fibers firmly in place.
- Instrumentation. AFM was performed using a Multimode Nanoscope V supplied by Veeco Instruments, Inc (Santa Barbara, CA) at ambient conditions (22°C, 50% humidity). A sharp Nitride lever (SNL) probe combining a sharp silicon tip with a silicon nitride cantilever was used for the topographic imaging acquisition. The nominal radius of the tip was about 2 nm and the spring constant of the cantilever is 0.06 N/M. The scan was first carried out perpendicular to the longitudinal axis of the hair fiber. After the tip was centered over the cross section and located at the very top of the fiber, the scan direction was changed to parallel with the longitudinal axis of the hair fiber. A scan rate of 1Hz was used for all measurements. The data collection was set to deflection channel and the error signal images, which are very sensitive to the changes in height, were recorded at 15×15 and 5×5 μm². The image data presented in this paper are raw and unfiltered.

Hair temperature measurement during hot flat ironing with thermal image analysis. In order to evaluate the heat control effect of polymer pretreatment, hair temperature during hot flat ironing was measured. An infrared camera (Flir P series) was used to measure hair temperature after hot flat ironing with an IR beam aiming on hair. Hair tresses were hot flat ironed from the top of the tress to the bottom, with three 5-second strokes as one heating cycle, and the maximum temperature was taken during the third stroke. Three hair tresses were tested for each treatment and the average temperature of hair was taken from the three tresses.

ASSESSING HAIR THERMAL DAMAGE BY QUANTIFYING HAIR BREAKAGE FROM COMBING

Hair breakage is quantified by combing the dried tresses that was exposed to the 12 minutes thermal treatment and washed with 12% SLES. To do so, a translucent plastic is first placed under the tress. The tress is then combed vigorously 100 times with a fine-toothed comb. The fragments of hair that are collected as a result of combing are secured by tape and numbered. Five hair tresses were tested for each treatment and the average number of hair breakage was taken from the tests of five tresses. The % hair breakage reduction by a cosmetic pretreatment is calculated as the number of hair pieces of control (untreated) minus the number of hair pieces from the polymer pretreatment test divided by the number of hair pieces of the control:

$$\% \text{ Hair breakage reduction} = \frac{C - T}{C} \times 100$$

where C = the number of hair pieces collected for the control and T = the number of hair pieces collected for the test.

RESULTS AND DISCUSSION

THERMAL DEGRADATION OF HAIR KERATIN FROM THERMAL TREATMENT

Hair is composed primarily of proteins. The cortex region contains the bulk of the hair keratin fibers. There are different types of protein components in human hair, with the

organized α -helical protein accounting for about 40% of the fiber's cross section (8) in the fibrous cortex surrounded by the multicellular flat cuticle sheath.

One way of showing the degradation of hair by thermal treatments is through DSC. Figure 1 shows the DSC results of thermally treated hair at two temperatures, 205°C and 232°C. DSC yields two thermal parameters from protein thermal transition: protein denaturation temperature or the DSC peak temperature, T_d and the denaturation enthalpy or the area of the peak, ΔH . The results in Figure 1 show the reduction of T_d and ΔH after thermal treatment of European hair, indicating protein degradation. With the heating temperature increasing from 205°C to 232°C, T_d is reduced by an additional 20 degree. Also, ΔH is reduced by an additional 14.9J/g. Therefore, at higher heating temperature, the protein degradation becomes more severe.

THERMAL PROTECTION OF HAIR KERATIN BY VARIOUS POLYMER TREATMENTS AND THEIR ANTI-BREAKAGE EFFECT

A thermal protection route was developed aiming to putting polymer barrier on the hair surface to reduce overheating spots, and to improve hair vapor retention/restoration which can serve as a heat sink to reduce thermal damage from repeated heat treatment. Polymers with different chemistries are evaluated for their effect on hair thermal protection. Figure 2 shows the structures of these polymers. From a structure-property point of view, high molecular weight polymers having film-modifying groups for a smooth and flexible film formation and polymers having hydrophobic units were evaluated. The polyelectrolyte complex (PEC) of a high molecular weight anionic polymer and cationic polymer was included in the study as it forms a smooth film on drying. All polymers studied contain PVP (polyvinylpyrrolidone) in the repeated unit. A copolymer of VP and DMAPA acrylates contains a film modifying group, DMAPA (dimethylaminopropyl methacrylamide) for smooth and flexible film formation. Its analogue, polyquaternium-55 (PQ-55) contains a quaternary group with a lauryl chain. Another VP copolymer, VP/acrylates/lauryl methacrylate copolymer, is anionic with a lauryl chain.

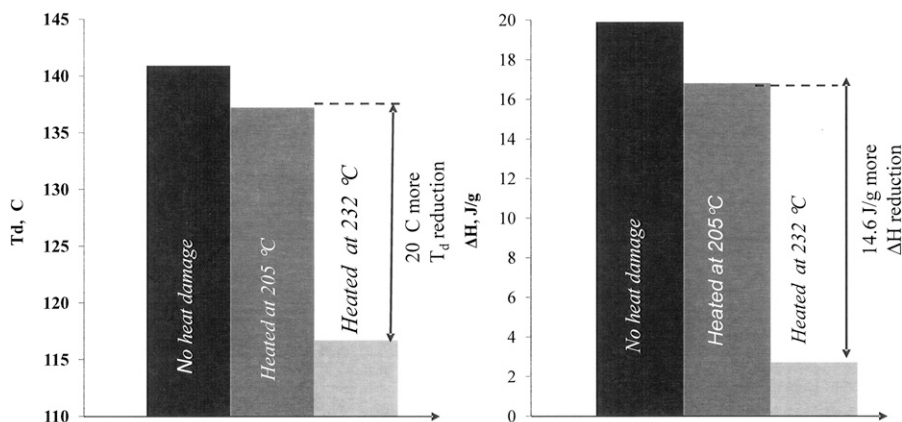


Figure 1. DSC results of thermally treated hair at two temperatures, 205°C and 232°C. Dark brown European hair.

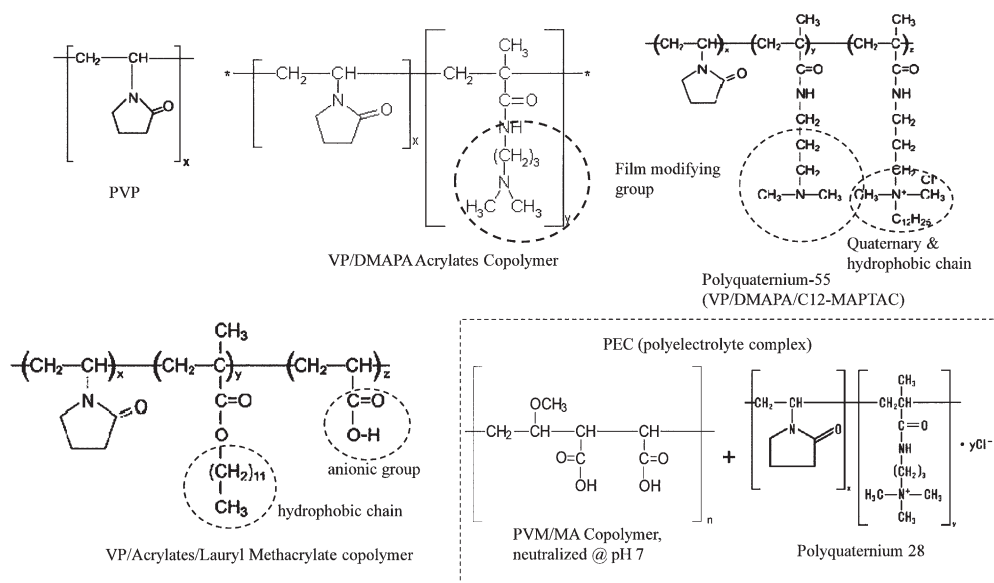


Figure 2. The chemical structures of polymers tested for their thermal protective effects.

Table I summarizes the results of peak temperature and denaturation enthalpy from the DSC analysis of thermally treated Asian hair at 205°C with and without cosmetic pretreatment. The hair breakage results during the subsequent combing are listed in Table I as well. The thermally treated hair shows reduction in both parameters, T_d and ΔH , indicating that thermal treatment causes hair protein damage. The shaded areas in Table I is the hair fibers pretreated with the polymer containing a film modifying group or a hydrophobic unit and made in 1% polymer solutions. The results demonstrate that the polymer pretreatment provide significant reduction in T_d and ΔH loss. The percentage of protein thermal protection was calculated based on the difference in ΔH reduction between the untreated hair sample and the polymer pretreated hair sample. The polymer

Table I
DSC Results of Peak Temperature and Denaturation Enthalpy from DSC Analysis of Thermally Treated Asian Hair at 205°C with and without Polymer Pretreatment and Hair Breakage Results During Subsequent Combing

Asian hair, 205°C thermal treatment	T_d (°C)	ΔH (J/g)	T_d loss	ΔH loss	% Protein protection	No. of breakage/anti-breakage (%)
No thermal treatment	140.4	20.5				
Thermal treated, no protection	136.5	16.0	3.9	4.5		193
Polyquaternium-55	139.6	18.6	0.8	1.9	57.7	132/31%
VP/acrylates/lauryl methacrylate *copolymer	138.7	17.9	1.7	2.6	42.3	91/52.5%
VP/DMAPA acrylates Copolymer	138.9	18.5	1.5	2.0	55.5	130/32.6%
PVP K-90	135.0	14.6	5.5	5.9	0.0	192/0%

pretreatments provide about 50% thermal protection to the hair protein in Asian hair subjected to 205°C thermal treatment. In addition, these polymer pretreatments reduce hair breakage from subsequent combing, i.e. by 52% with VP/acrylates/lauryl methacrylate and 31% for PQ-55. However, the homopolymer, PVP which contains no film modifying groups or hydrophobic units shows no protection against protein thermal degradation and no anti-breakage effect.

The thermal protective effect of selected polymer pretreatments was also tested with dark brown European hair. Table II summarizes the results of T_d and ΔH for European hair after thermal exposure at 232°C with and without the protective polymer pretreatment. The DSC results show the thermal degradation of hair keratin, indicated by a 25°C reduction in denaturation temperature T_d and a 17.2 J/g loss of enthalpy ΔH . The protein denaturation enthalpy is associated with the energy required for the helical protein denaturation and, therefore, depends on the amount and structural integrity of the α -helical material in the intermediate filaments of human hair cortex (9). Therefore, the enthalpy reduction after the current thermal treatment corresponds to approximately 90% loss of helical protein compared with the enthalpy reduction of the untreated hair sample. The helix content occupies about 40% of hair cross section, suggesting that the helix protein degradation from the thermal treatment is responsible for at least 36% degradation of overall hair protein. The DSC data in Table II also shows that the polymer pretreatments significantly reduce the protein degradation. The ΔH reduction is especially low for 1% VP/acrylates/lauryl methacrylate copolymer and 2% PEC where it is observed that ΔH losses are than 10% for these polymer pretreated hair. These polymers are made in 0.5% hydroxyethylcellulose (HEC), a thickener to enhance distribution on hair. However, the pretreatment with HEC alone shows only small protein protection (Table II).

Figure 3 shows the hair breakage results of thermally treated European hair with and without polymer pretreatment before heating. Thermally stressing hair led to increased hair breakage from 52 to 214 fragments i.e. when subjected to combing. The pretreatment of hair samples with the polymers tested provides anti-breakage effect on the subsequent combing after heating. Among them, 2% PEC and 1% VP/acrylates lauryl methacrylate copolymer treatments show the highest anti-breakage effect, 76% and 55%, respectively. Although three polymers were formulated with 0.5% HEC, the data clearly show that

Table II
DSC Results of Thermally Treated Hair at 232°C with and without Polymer Pretreatment
(dark brown European hair)

Dark brown European hair, 232°C heating	T_d °C	ΔH (J/g)	T_d Loss	ΔH Loss	% ΔH Loss	% T_d Loss
No thermal treatment	141.6	19.1				
Thermal-treated	116.7	1.9	25	17.2	90.1	17.7
HEC and heat damage	123.6	4.9	18	14.2	74.3	12.7
Polyquaternium-55+ HEC	131.6	12.4	10	6.7	35.1	7.1
VP/DMAc acrylates copolymer+HEC	133.6	13.2	8	5.9	30.9	5.6
VP/acrylates/lauryl methacrylate copolymer+HEC	141.2	18.6	0.4	0.5	2.6	0.3
2% PEC	140.2	17.2	1.36	1.85	9.7	1.0

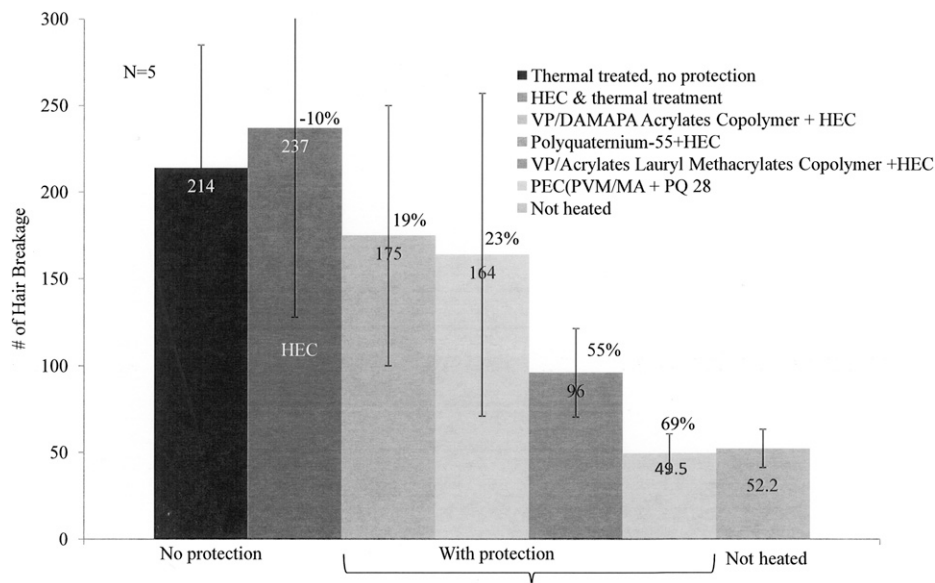


Figure 3. Hair breakage reduction of thermally treated hair at 232°C with polymer pretreatment, 1% polymer solution + 0.5% HEC. European dark brown hair.

the HEC pretreated hair does not have an anti-breakage benefit. The error bars of VP/DMAA acrylates copolymer and polyquaternium-55 pretreated hair indicates that their results are not statistically different, however, the trend of hair breakage numbers shows that these two polymers provide anti-breakage effect, which is supported by the results of DSC and FTIR imaging analysis. The hair breakage results of 2% PEC and 1% VP/acrylates lauryl methacrylate copolymer pretreatment are statistically different. Robbins has studied the pathways of hair breakage and suggests that extending and impacting or compressing hairs with flaws or cracks and/or chemically weakened hair during combing may be one of the possible pathways for hair breakage (10). Alleviation of weakening of the thermally insulted hair through polymer pretreatments allows the hair to withstand these combing stresses and indicates thermal protection through a reduction in fiber fragmentation.

PROTEIN STRUCTURE MODIFICATION FROM THERMAL TREATMENT—FTIR IMAGE ANALYSIS OF HAIR CROSS SECTION

One type of protein denaturation is a change in protein conformation. The undamaged hair has a α -helical coiled coil protein confirmation, a well organized structure in the cortex. Once the protein is damaged, it can unfold and convert into the extended protein chain or beta sheet structure. The protein conformation changes will change the hydrogen bonding structure that stabilizes the helical structure and, therefore, may change the water accessibility to hair.

Further, IR image analysis was conducted on thermally treated hair fibers to examine the hair keratin damage at the molecular level such as protein structural changes due to heat treatment. FTIR image analysis provided the spatially resolved spectroscopic imaging of chemical components over the cross section of hair. It consists of an array of detectors that

collect IR spectra pixel by pixel. By sectioning hair, and collecting spatially resolved infrared spectra of hair samples, spatially resolved images of the changes in hair protein structure as a result of thermal stresses to the hair were generated.

Figures 4a and 4b show the typical IR spectra and the second derivative analysis of a random location in the cortex of undamaged European dark brown hair from 1480-1700 cm^{-1} (Amides I and II) and 3000-3700 cm^{-1} (Amide A) spectral regions. Bands from 1480-1700 cm^{-1} region are sensitive to changes in the protein secondary structural conformation. In order to get the resolutions of the IR bands, secondary derivative analysis was used to locate the different protein peak positions under the curve. The second derivative curve displays the minor component of β -sheet and a major α -helical structure under the curve for undamaged hair. Amide II at 1548 cm^{-1} is assigned to α -helical structure and Amide I at 1656 cm^{-1} is assigned to β -sheet conformation (11.). The ratio of β -sheet peak intensity to the α -helix band intensity was used to quantify the additional conversion of α -helix to β -sheet conformation from thermal treatment. An increase in the ratio indicates an increase in β -sheet composition or a decrease in α -helix content correspondingly, and if the ratio remains the same as the undamaged hair, there will be no change in the two components.

The ratio maps of β -sheet peak intensity to the α -helix band intensity of hair cross sections are shown in Figure 5a. The ratio bar at the right side with higher numbers and corresponding colors indicates the relative β -sheet intensity. It can be seen that the outer layer of hair has a higher β -sheet level than inside the hair as indicated by the brighter color in the outer layer of the hair cross section. Moreover, the β -sheet content becomes more pronounced in the outside layer of thermally treated hair due to the heat of the iron affecting this part of the hair first. Pretreatment with all three tested polymers tested

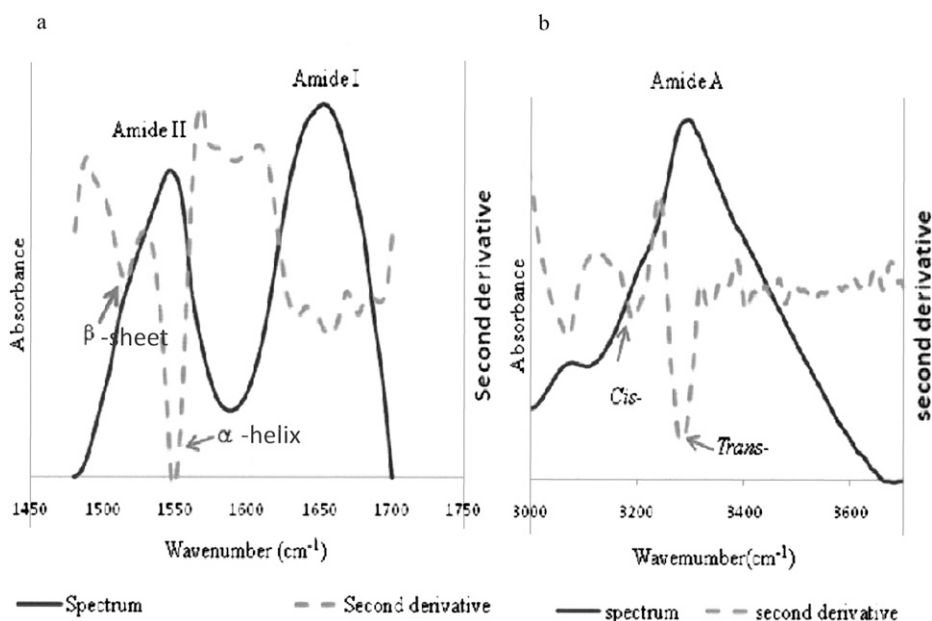


Figure 4. IR spectra and their second derivative curves of undamaged European dark brown hair. a. Amide I & II region (1480–1700 cm^{-1}), b. Amide A region (3000–3700 cm^{-1}).

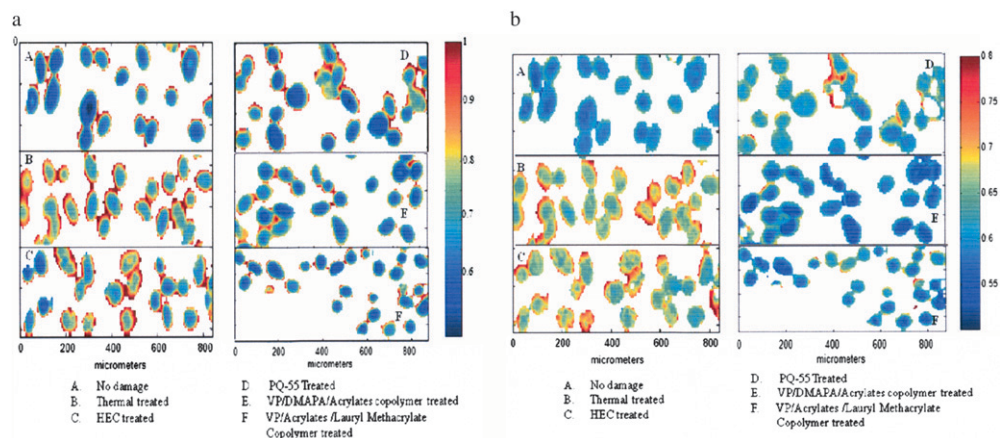


Figure 5. IR images of thermally treated hair cross section at 232°C with and without polymer pretreatment. (a) The ratio maps of b-sheet peak intensity to the a-helix band intensity. (b) The ratio maps of *cis*-bonded Amide A band intensity at 3200 cm^{-1} to that *trans*-bonded Amide A at 3292 cm^{-1} . Dark brown European hair.

effectively prevented the conversion of α -helix structure to the β -sheet conformation. HEC pretreatment provided slight protection to β -sheet conversion.

Protein helices are held together by hydrogen bonds between the carbonyl oxygen of amide bonds in the main chains with the imido hydrogen of amides. The Amide A band (N-H stretching) at $\sim 3290 \text{ cm}^{-1}$ is very sensitive to the disruption of hydrogen bonding. When some of the helix unfolds and changes to the extended protein chain or β -sheet conformation, the hydrogen bonds will break, leading to the shift of the Amide A band. Figure 4b shows the IR spectrum of Amide A region and its second derivative curve. The second derivative curve of the Amide A region shows bands at 3292 cm^{-1} and 3200 cm^{-1} which are assigned to the *trans*-bonded and *cis*-bonded N-H stretching bands, respectively. The *cis*-bonded Amide A band is attributed to the interruption of hydrogen bonding due to helix unfolding. To compare the changes in the *trans*-bonded structure to the *cis*-bonded structure after thermal treatment, the ratio of the peak intensity at 3200 cm^{-1} , which is attributed to the *cis*-bonded structure, to the peak intensity at 3292 cm^{-1} , which is attributed to the *trans*-bonded structure, is used to quantify the additional conversion of *trans*-bonded Amide A to *cis*-bonded Amide A structure due to thermal treatment. An increase of the ratio will indicate the increase of *cis*-bonded component and a decrease of *trans*-bonded structure correspondingly; and if the ratio remains the same as the undamaged hair, there will be no change in the two components. The ratio maps of *cis*-bonded Amide A structure to *trans*-bonded Amide A structure over hair cross sections are shown in Figure 5b. The ratio bar at the right side with higher numbers and corresponding colors indicates the relative *cis*-bonded Amide A content. Consistently, the content of *cis*-bonded amide A for thermally treated hair increases after heat exposure. The increase of *cis*-bonded A content is consistent with the increase of β -sheet formation as stated above. This results confirms the disruption of the hydrogen bonding structure of helical protein and suggests the unfolding of some helical structure. Pretreatment with all three polymers tested effectively prevents the formation of *cis*-bonded amide A protein bands. Therefore the IR image analysis results are consistent with the DSC results on the thermal protection effect of polymers.

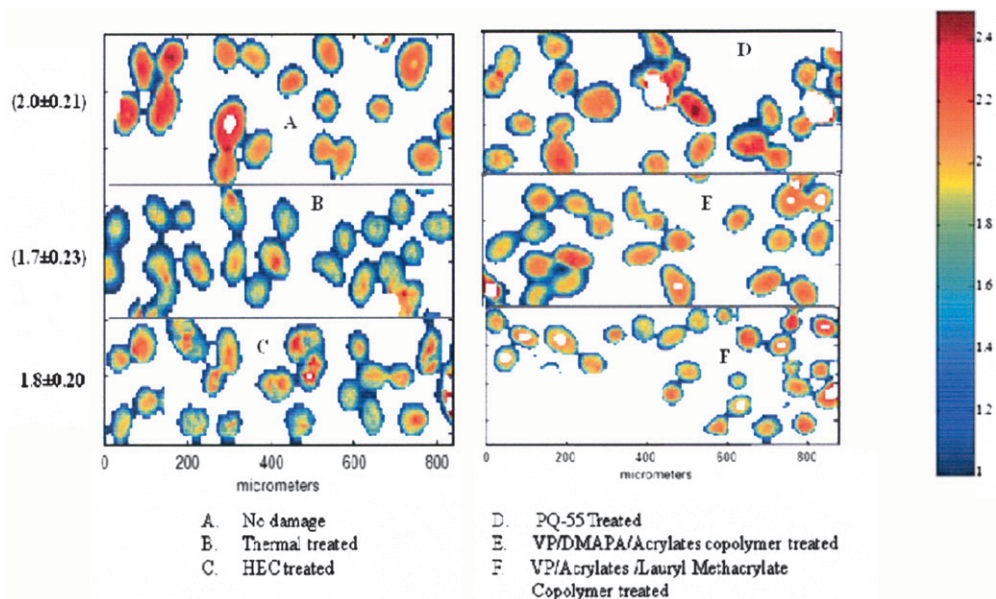


Figure 6. IR images of a thermally treated hair cross section at 232°C with and without polymer pretreatment. Maps were developed from the peak area of 2960 cm^{-1} band, representing the relative protein concentration in the hair cross section. European dark brown hair.

In addition to the protein conformation change, hair protein modification from thermal treatment was further assessed using a band at 2960 cm^{-1} , a C-H asymmetric stretching mode of the CH_3 group. This CH_3 band is mainly attributed to the terminal amino residues of hair proteins with minor lipid contribution. Figure 6 shows the spatial IR images of the hair cross section which depict the concentration profile of hair protein with minor lipid contribution obtained from the CH_3 band area. The intensity color bar at the right side with higher numbers and corresponding colors indicates higher protein concentration. It is observed from the fiber cross sections that there is an overall protein and lipid loss for the thermally treated hair as indicated by a reduction in the integrated area of the bond. Pretreatment with all three polymers tested effectively prevents the overall protein and lipid loss.

FTIR results support the DSC analysis and provide additional insights to the total helical protein degradation. As little is known about the molecular conformational state of other protein components in hair (8), other protein components besides the β -sheet structure, such as other uncoiled, random coil, or denatured cross linking structures that α -helix can transform to but are undetected by this FTIR analysis, may exist.

THERMAL PROTECTION OF THE HAIR SURFACE BY COSMETIC PRETREATMENT

Figure 7 shows atomic force microscopy (AFM) images of the surface of the hair cuticle with and without thermal treatment. The AFM images indicate that thermal treatment at 232°C causes damage on the cuticle surface, including cracks, holes from over-heating, and formation of micropores. These surface damages will increase the hair permeability resulting in faster water loss during drying.

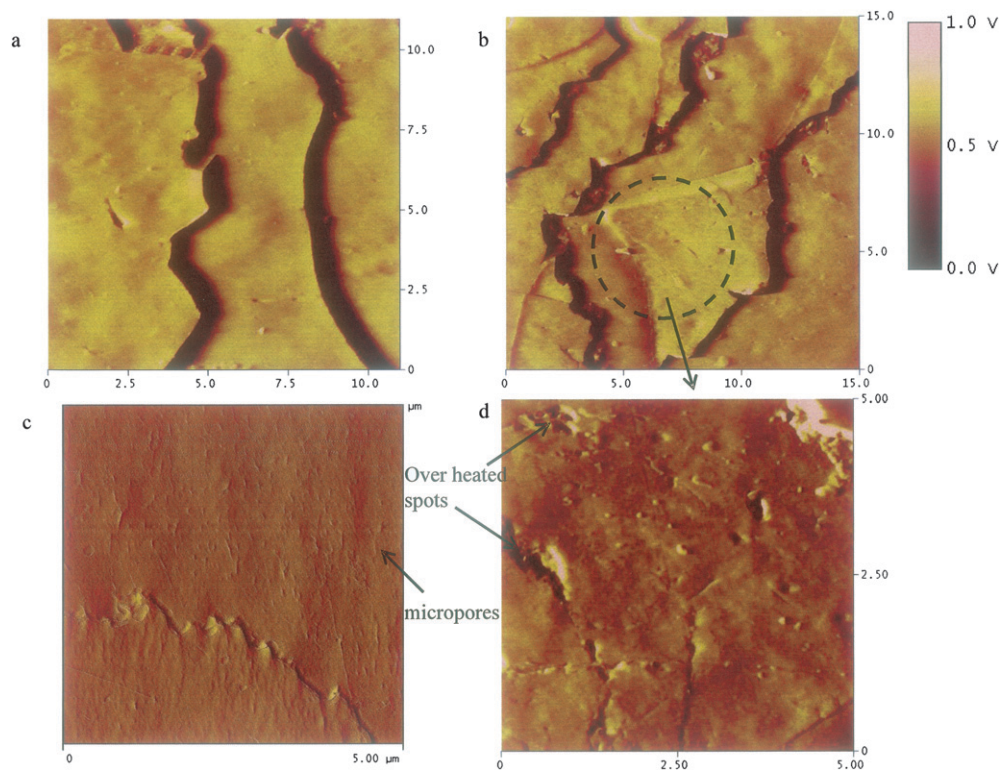


Figure 7. AFM Images of the hair cuticle surface with and without thermal treatment. (a) Not thermally treated. (b, c, d) Thermally treated at 232°C.

Figure 8 shows the scanning electron microscopy (SEM) images of European hair fibers with and without thermal treatment at 232°C and with the pretreatment of the tested polymers. Four to five fibers were examined for each hair sample to ensure reproducibility. Thermal treatment causes severe cuticle damage to the hair fiber surface by showing cuticle disintegration with missing cuticle pieces and jagged cuticle layers. The 0.5% HEC (hydroxyethylcellulose) solution pretreated hair has damage on cuticle layers and shows the fusion of some cuticle cells. Once the cuticle is damaged, hair breaks easily since there is no protection for the cortex. The SEM images also show that polymer pretreatment prevents significant cuticle damage due to thermal treatment. Among them, VP/acrylates/lauryl methacrylate copolymer-treated hair fibers have well defined cuticle layer. This result is consistent with the polymer's high anti-breakage effect, 55%. Therefore, hair surface protection to ensure good cuticle integrity and surface smoothness also plays an important role in their anti-breakage effect besides protecting cortex protein from thermal damage.

WATER VAPOR SORPTION AND DESORPTION OF THERMALLY TREATED HAIR AND THE ROLE OF WATER RESTORATION IN HEAT CONTROL

Water changes the properties of human keratin fibers and, therefore, plays an important role in cosmetic performance. Hot flat irons that lack heat control can destroy the hair

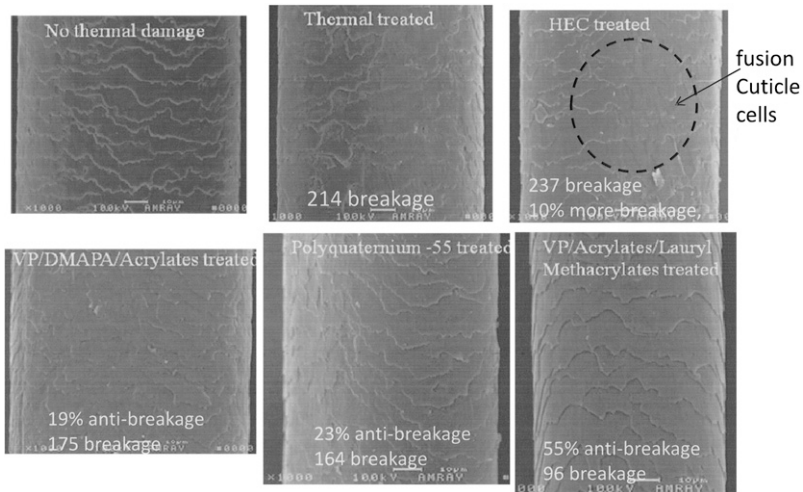


Figure 8. SEM images of the hair fiber surface with and without thermal treatment at 232°C and polymer protection. Dark brown European hair.

protein structure resulting in changes in hair water absorption and desorption profiles. In this work, water sorption/desorption and the kinetics of these processes on thermally treated hair were studied. The effect of polymer pretreatment on the water sorption/desorption performance of hair was evaluated.

Figure 9a shows the water sorption and desorption isotherms of hair fibers with and without thermal treatment and polymer protection. The thermally treated hair has a lower maximum water regain than the unheated hair in each sorption step. The maximum

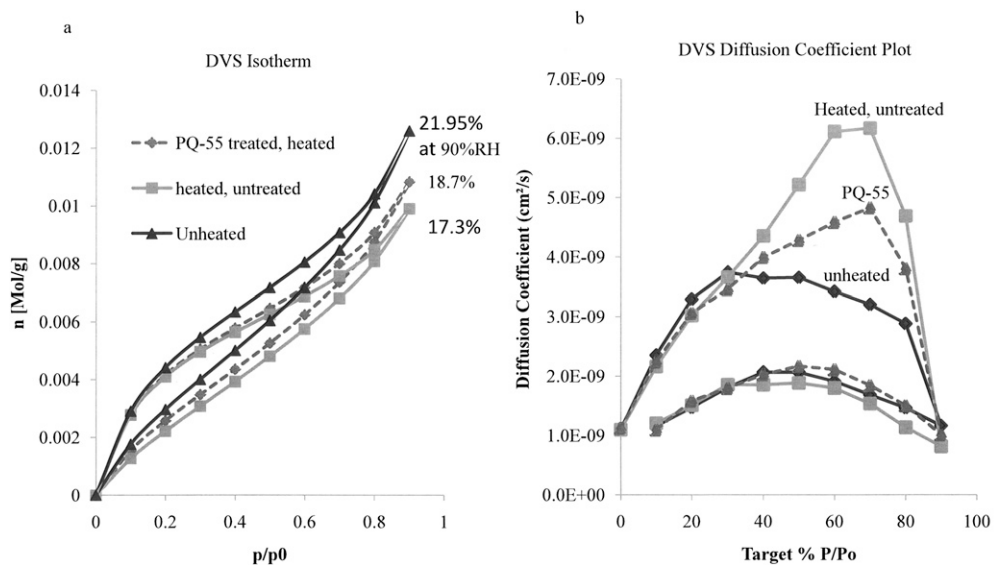


Figure 9. Water sorption and desorption isotherms and apparent diffusion coefficients of hair fibers with and without thermal treatment and polymer protection. Dark brown European hair.

water regain for the unheated hair at 90% RH is 21.95% while the heated hair is 17.27%. To avoid the variation among different hair tresses, the unheated and the heated hair are from the same hair tress split into two halves. One half is heated and the other is not heated. The hysteresis (the difference in net moisture changes between the desorption and sorption processes) is higher for heat-treated hair than unheated hair, indicating a lower water retention of the heated hair on drying. The less water regain and lower retention for thermally treated hair might be attributed to the helical protein conformation change to the beta sheet or other uncoiled denatured cross-linking structure. The new protein conformation may have reduced water accessibility or binding sites. Figure 9a shows that polyquaternium-55 pretreatment increases the water regain of heated hair compared with its untreated control possibly due to the protective effect of the polymer on thermally induced hair protein damage. As shown in the FTIR and DSC studies described previously, polymer pretreatment reduces protein degradation and denaturation, thereby protecting the protein structure and native hydrogen bonding interactions. The data indicates that this has the effect of improving the water sorption of hair, compared with the unprotected thermally damaged hair. The mechanism of increased water restoration of hair via polymer protection of native protein structure is further supported by studying the water sorption and desorption of virgin hair without thermal treatment, both with and without 1% polyquaternium-55 treatment. This is illustrated in Figure 10a. Both isotherms are identical, indicating that the polymer treated and untreated unthermally-stressed hair fibers have the same water sorption and desorption performance. This supports a mechanism in which thermal protection of the native protein structure is a major factor in moisture restoration and, thus, thermal protection.

The apparent diffusion coefficients have been utilized to measure the kinetics of moisture uptake and loss in hair fibers (12,13). Diffusion rates for moisture into and out of the fiber at each relative humidity were calculated from the sorption and desorption data in each

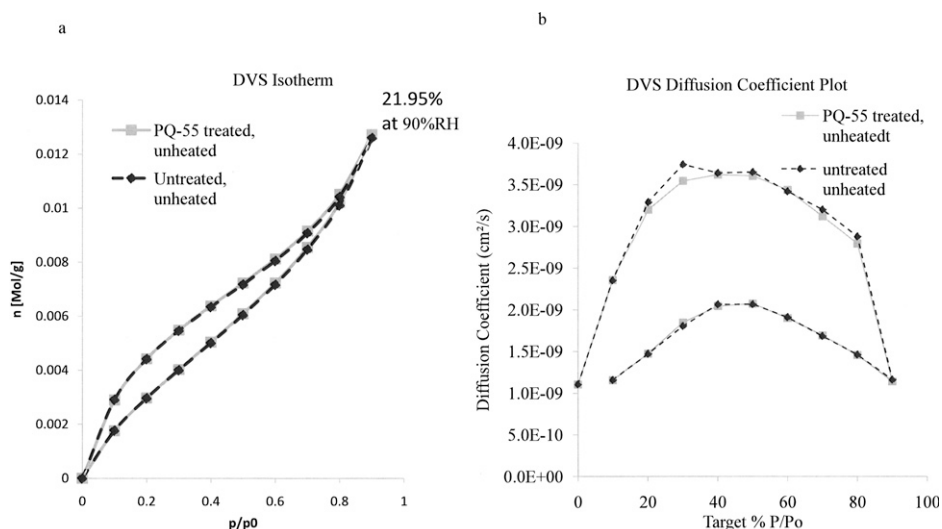


Figure 10. Water sorption and desorption isotherms and apparent diffusion coefficients of virgin hair fibers with and without polymer treatment. Dark brown European hair.

sorption or desorption step. The apparent diffusion coefficients (D) for hair are calculated from Fick's diffusion model applied to a cylindrical geometry:

$$M_t/M_f = 4(Dt/\pi r^2)^{1/2}$$

where D is the apparent diffusion coefficient, M_t is the vapor concentration at time t , M_f is the vapor concentration at equilibrium, and r is the radius of the hair fiber. If the fractional absorbed or desorbed water, M_t/M_f , is plotted against the square root of the absorption or desorption time, the points should form a straight line: $M_t/M_f = 4/\pi^{1/2} r(D)^{1/2} (t)^{1/2}$. The apparent diffusion coefficient of moisture for sorption or desorption can be calculated from the slope as

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

In Figure 9b, the apparent diffusion coefficient plots calculated from the isotherm data show that the thermally damaged hair has a much higher water diffusion coefficient on desorption during drying than the non-thermally-treated hair, i.e. water comes out of the damaged hair fibers much faster than the unheated hair during drying. The difference is more pronounced at the higher humidity at which water is multi-layer absorbed. Therefore the heat damaged hair has increased permeability. On the sorption process, the thermally treated hair or thermally damaged hair has a slower water uptake rate than the unheated hair, though the difference is much smaller, compared with the desorption process. This is because sorption takes place in the dry and un-swollen fibers in which diffusion is more difficult than desorption, which starts from wet and swollen hair fibers experienced from the lengthy sorption process (12). At low humidity less than 30% RH, the water diffusion rate for both thermally treated and untreated hair fibers are similar because at low humidity (relative humidity less than 25%), water molecules are principally bonded water to hair (14).

Figure 9b shows that polymer pretreatment of hair by polyquaternium-55 reduces the water diffusion coefficient on desorption compared with untreated and heated control samples, indicating that the polymer pretreatment slows down the loss of moisture from hair during drying. In Figure 10b, the diffusion coefficient plots of virgin hair with and without PQ-55 treatment are almost identical, again, suggesting that the reduced water diffusion coefficient on desorption by PQ-55 pretreatment for the thermally treated hair in Figure 9b is due to the protective effect of the polymer on hair protein structure. Figure 11 shows the water sorption and desorption isotherm of thermally treated hair fibers pretreated with PEC versus untreated control sample. The PEC-treated hair and the untreated hair are the two split halves from the same tress to avoid variation among different hair samples. The PEC-pretreated hair after heating has a much higher water regain than the untreated control samples.

The increased water regain on sorption, faster vapor sorption rate and slower vapor desorption of hair from the polymer pretreatment will, in turn, help to provide heat control to hair during repeated hot flat ironing. This will have the effect of reducing further thermal damage.

In order to evaluate the heat control effect of polymer pretreatment, the hair temperature during hot flat ironing was measured in three different heating schedules. Figure 12 shows the hair temperature of hair samples during hot flat ironing at 232°C with and without polymeric pretreatments. The lowest temperatures are seen after the first

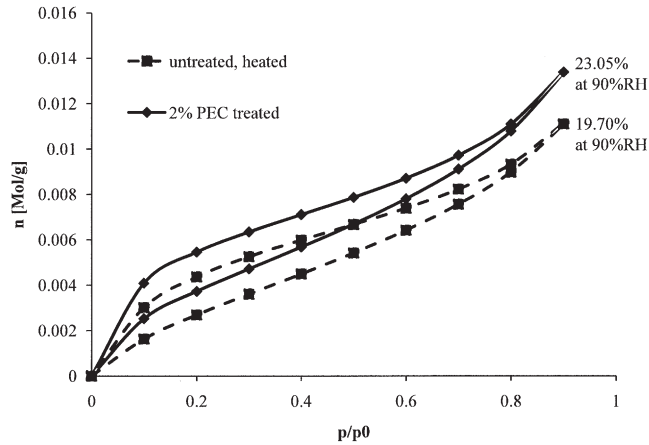


Figure 11. Water sorption and desorption isotherms of thermally treated hair fibers pretreated with PEC. Dark brown European hair.

heating cycle (each cycle is three 5-second strokes). Seven cycles of continuously repeated heating result in much higher measured temperatures. However, another seven cycles of heating with an overnight interval between cycles at 60% RH, to allow the hair samples to have a chance to rehydrate, show much lower temperatures as expected. These results indicate that the water restoration of hair contributes to heat control on hot flat ironing. The thermal protective polymers tested in this study shown in the shaded box reduce hair temperatures significantly. The temperature reduction of hair pretreated with PEC increases significantly with the increasing level of PEC used from 1% to 4%, supporting the critical role of the polymer barrier in protecting the hair from thermal damage.

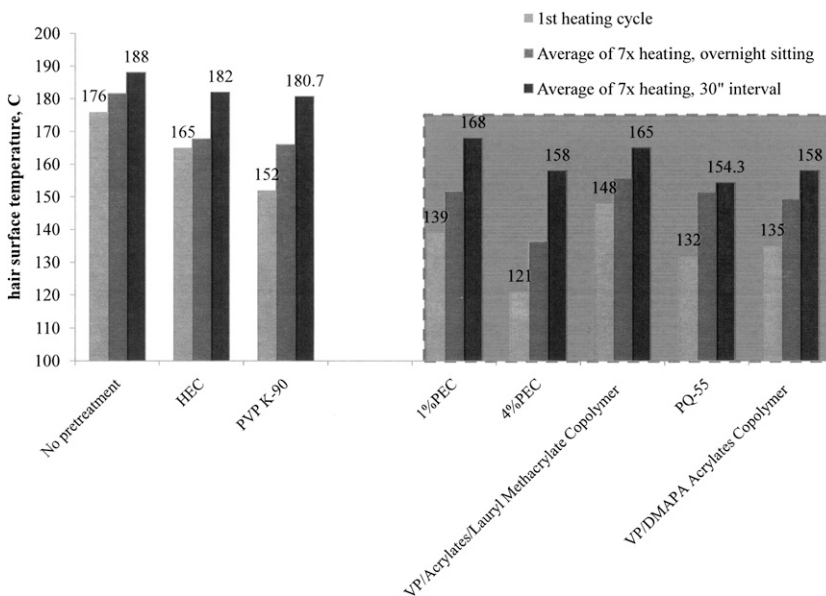


Figure 12. Hair temperatures of hair samples during hot flat ironing at 232°C with and without cosmetic pretreatment.

CONCLUSIONS

This study has shown through the use of various instrumental techniques that the thermal insult of hair from hot flat ironing appliances causes damage to the hair surface and the structural proteins in the cortex. One measure of this damage is the conversion of proteins from the α helical to the β -sheet conformation, as well as a measurable loss of protein. Also evident is damage to the hair cuticle including micropore formation and cuticle cell disintegration. The internal and surface damage resulting from thermal treatment increases hair breakage especially with the additional stress of hair combing. Dynamic vapor sorption (DVS) data indicate that thermally damaged hair has reduced water regain and lower water retention possibly resulting from the thermally induced changes in protein structure. Pretreatment of hair with selected high molecular weight polymers containing film-modifying groups or hydrophobic units such as VP/acrylates/lauryl methacrylate copolymer, PEC, and polyquaternium-55 clearly provide thermal protection to the hair surface and cortex resulting in reduced hair breakage during combing. The pretreatment of hair with selected polymers also improve moisture restoration and water retention of thermally treated hair. The studies continue to improve our understanding of the many changes that occur on, and in, the hair fiber with thermal stress and provide insights into the mechanisms whereby polymer pretreatments can provide significant protection to the hair fiber as it is exposed to repeated thermal stress.

ACKNOWLEDGMENTS

The authors to thank William Thompson for providing SEM analysis of hair samples used in this work, Grisel Tumalle for her assistance in measuring hair temperature, Jean Karolak for her contribution to some of the anti-breakage data used in this work, Larry Senak for his support in obtaining FTIR image analysis data, and Roger McMullen for his help in the thermal imaging and AFM techniques.

REFERENCES

- (1) S. B. Ruetsch and Y. K. Kamath, Effect of thermal treatment with a curling iron on hair fiber, *J. Cosmet. Sci.*, **55**, 13–27 (2004).
- (2) R. McMullen and J. Jachowicz, Thermal degradation of hair. I. Effect of curling ironing, *J. Cosmet. Sci.*, **49**, 223–244 (1998).
- (3) R. McMullen and J. Jachowicz, Thermal degradation of hair. I. Effect of selected polymers and surfactant, *J. Cosmet. Sci.*, **49**, 245–256 (1998).
- (4) P. Milczarek, M. Zielinski, and M. Garcia, The mechanism and stability of thermal transition in hair keratin, *Colloid Polym. Sci.*, **270**, 1106 (1992).
- (5) C. R. Robbins and K. Chesney, Hysteresis in heat dried hair, *J. Cosmet. Sci.*, **32**, 27 (1981).
- (6) R. Rigoletto, Y. Zhou, and L. Foltis, Semi-permanent split end mending with a polyelectrolyte complex, *J. Cosmet. Sci.*, **58**, 451–476 (2007).
- (7) R. Rigoletto, Y. Zhou, and L. Foltis, Mending hair damage with polyelectrolyte complexes, *US Patent* 7,837,983.
- (8) J. A. Swift, “Fundamentals of Human Hair Science,” in *Cosmetic Science Monographs*, No.1, Hilda Butler, Series Ed. (Micelle Press, Weymouth, Dorset, England, 1997), pp. 25.
- (9) F.-J. Wortmann, C. Springob, and G. Sendelbach, Investigations of cosmetically treated human hair by differential scanning calorimetry in water, *J. Cosmet. Sci.*, **53**, 219–228 (2002).
- (10) C. R. Robbins, Hair breakage during combing. I. Pathways of breakage, *J. Cosmet. Sci.*, **57**, 233–243 (2006).

- (11) R. Medelsohn and H. H. Mantsch, "Fourier Transform Infrared Studies of Lipid-Protein Interaction," in *Progress in Protein-Lipid Interaction, Vol 2*, A. Watts and J. J. H. M. de Pont, Eds. (Elsevier, Amsterdam, 1986), pp. 103–146.
- (12) K. Keis, C. L. Huemmer, and Y. K. Kamath, Effect of oil films on moisture vapor absorption on human hair, *J. Cosmet. Sci.*, **58**, 135–143 (2007).
- (13) C. Barba, M. Marti, A. M. Manich, J. Carilla, J. L. Parra, and L. Coderch, Water absorption/desorption of human hair and nails, *Thermochimica Acta*, **503/504**, 33–39 (2010).
- (14) C. R. Robbins, *Chemical and Physical Behavior of Human Hair, 3rd ed.* (Springer-Verlag, New York, 1994), pp.78.