

## **Thermal degradation of hair. II. Effect of selected polymers and surfactants**

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### **Synopsis**

Fluorescence spectroscopy, combing analysis, and texture analysis with a dual-cantilever bending accessory have been employed to study the effect of pretreatments on the thermal damage of hair. The pretreatments, applied to hair as 1% aqueous solutions, included a cationic polymer (PVP/DMAPA acrylates copolymer), a protein hydrolyzate (hydrolyzed wheat protein), and a cationic surfactant (quaternium 70). Fluorescence spectroscopy was used to probe the content of tryptophan (Trp) in hair, which is gradually destroyed by the application of curling irons at 132°C and 152°C. All pretreatment materials were found to reduce the extent of Trp decomposition by 10–20% as a result of 4–12 min of thermal exposure. Surface damage has been quantified by combing analysis and has shown that the use of PVP/DMAPA acrylates copolymers or a cationic surfactant can suppress an increase in combing forces, which is observed in unmodified hair subjected to thermal exposure. The variation in stiffness of hair tresses has been studied by texture analysis with a dual-cantilever bending accessory. From the texture analysis, an increase in the stiffness ratio of the fiber assemblies was evident for polymer-modified and intact (unmodified) hair.

### **INTRODUCTION**

The thermal degradation of hair has been discussed in several publications (1–5) that have demonstrated various aspects of hair damage. Changes in hair coloration, decomposition of hair chromophores, and damage to the fiber surface were found to be typical manifestations of hair damage after exposure to temperatures greater than 130°C. The changes in fiber structure and properties, as a result of the use of milder thermal conditions (<100°C) that accompany drying by hair dryers, have also been discussed (6). On the other hand, the thermal protection of hair keratin has not been a topic of scientific inquiry, with only patent literature reflecting several studies pertaining to this subject.

Currently, there are several commercial products sold on the retail market that claim to protect hair from thermal styling appliances. These formulations often contain a wide range of actives, including protein hydrolyzates, enzyme cofactors, fatty acids, saccharides, surfactants, and various polymers. It has been suggested that hydrolyzed wheat protein, wheat oligosaccharides, wheat amino acids, and panthenol, formulated together, increase the strength and moisture retention of hair fibers when used in conjunction with

a thermal styling appliance (7). Several patents specifically identify the compound or formulation as a protectant against thermal hair dryers or hot irons. For hair dryer protection, the following systems were identified as effective: high-molecular-weight silicone and fatty acid alkanolamide(s) (8); mono-N-acyl basic amino acid lower-alkyl-ester salt and/or cationic surfactant, liquid oil, and heme iron compound (9); quaternary ammonium salt(s), fruit extracts, and a water-soluble cationic polymer (10); and conditioners containing stearyltrimethyl-ammonium chloride and polyethylene-polypropylene glycol butyl ether as its actives (11). For patents that strictly apply to protecting hair from hot irons, one formulation includes a two-phase system and a surfactant in which the oil phase contains hydrocarbon or silicone oils, an aqueous phase comprised of glycerol, propylene glycol, and polyethylene glycol, and a surfactant possessing nonionic or ionic character (12). Another composition, consisting of polyoxyethylene sorbitol tetraoleate, polyoxyethylene castor oils, fatty acids (from animal or vegetable sources), and a nonionic surfactant, has also been suggested to protect hair from hot irons (13). Several compounds have also been used as thermal setting agents, in which the active is applied to hair prior to or during thermal treatment. Specifically, the application of a thermoplastic polyester fixative resin used in conjunction with a thermal styling appliance has been described in the patent literature (14).

The objective of this study was to compare the thermally induced interactions of hair with selected materials including a cationic polymer, cationic surfactant, and a protein hydrolyzate. The thermal protection potential of these materials has been evaluated by previously developed methodology, i.e., combing analysis to detect hair surface modification, fluorescence spectroscopy to analyze the decomposition of tryptophan (Trp), and texture analysis to provide information about the mechanical properties of the fiber assemblies.

## EXPERIMENTAL

### INSTRUMENTATION

The instrumentation used to quantify thermally induced changes of hair, in terms of combing forces and fluorescence, has been described in the first publication of this series (5). Additionally, we have conducted experiments in which the mechanical properties of hair tresses, before and after thermal treatment, could be quantified. This was achieved using a texture analyzer (Model TA-XT2, Texture Technologies Corp.) equipped with a custom-made attachment in order to perform dual-cantilever bending measurements (15). The texture analyzer had a load sensitivity of 0.1 g and was operated using XTRA dimension software 3.7 from Stable Micro Systems. The bending measurements were performed by placing a hair tress on cantilevers separated by a distance of 1.25 in. and fastening it to a clamp from one side. During the test, a blade-shaped probe attached to the texture analyzer produces a deformation in the hair tress of 3.0 mm after detection of a 2.0 G trigger force. The ratio of the forces recorded at the 3.0-mm deformation, for modified and unmodified hair, is defined as the stiffness ratio and is discussed further in the context of various treatments in this paper.

### MATERIALS AND METHODS

The thermal treatment of hair was performed using a Soft Sheen, Optimum Styling

Tools, curling iron (Model SOC125S) manufactured by Continental Hair Products, Glendale, AZ. This curling iron model was chosen for the analyses since its temperature profile was the most representative of the commercially available curling irons. As indicated by our previous studies (5), thermal treatment to each hair tress was administered in the same position in order to maintain experimental uniformity. The thermal treatment of hair was administered for a duration of 1 min, at which time the samples were thoroughly rinsed and pretreated with the indicated compound. The sum of all heating cycles constitutes a total treatment time, normally 12 min in duration. After each 2-min cycle, the samples were thoroughly rinsed, followed by shampooing. After each 4-min cycle, all instrumental measurements were performed. These consisted of combing analysis and texture analysis after thoroughly rinsing the samples and, again, after shampooing the samples. Once the mechanical measurements were completed, we obtained fluorescence spectra in order to monitor the Trp degradation. For each fluorescence measurement, readings were obtained from the thermally exposed and unexposed regions of the hair tress.

The hair tress treatments were administered with 1% solutions of the indicated active. The fibers were wetted prior to treatment, followed by towel drying. Then the damp hair was saturated with a solution of active (2.5 g), with the excess amount of treatment removed by paper towel blotting, resulting in a 0.55-g application of the 1% solution (3.46 mg of active/1 g of hair). The treated tress was then air-dried (23°C) with an Elchim Professional hair dryer (model EC 35227), distributed by Elchim-USA, Inc., Union, NJ. After drying, the hair tresses were subjected to thermal treatment as described above. Experiments were performed on light-brown hair purchased from International Hair Importers & Products, Inc., Valhalla, NY, and Piedmont hair, purchased from DeMeo Brothers, Inc., New York, NY.

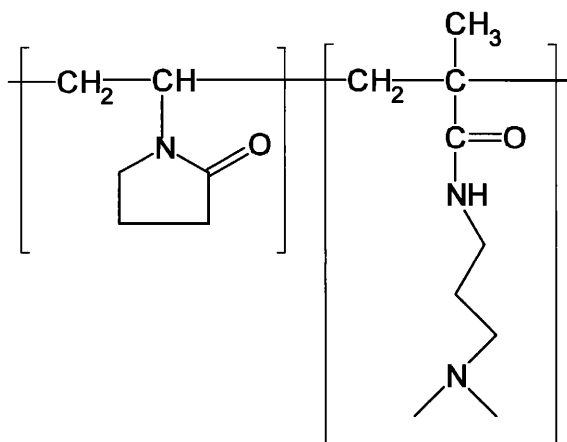
#### POLYMERS AND SURFACTANTS

PVP/DMAPA acrylates copolymer, quaternium 70, and hydrolyzed wheat protein are commercial products sold under the trade names of Styleze CC-10 (ISP), Ceraphyl 70 (ISP), and Hydrotriticum 2000 (Croda), respectively. Additionally, we examined sodium bisulfite (Aldrich), which was used for studies on Piedmont hair. The structures of PVP/DMAPA acrylates copolymer and quaternium 70 are presented in Figure 1.

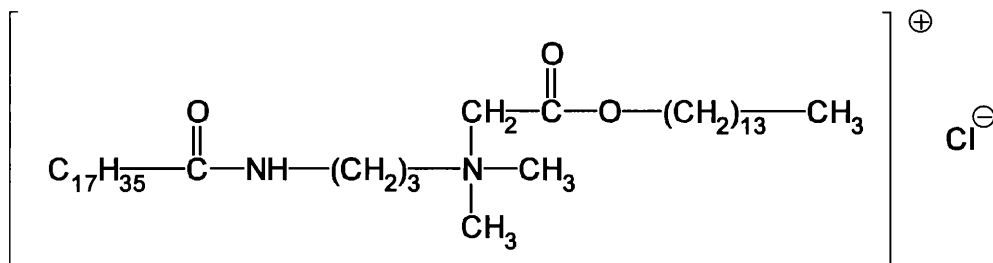
## RESULTS AND DISCUSSION

#### SPECTROSCOPIC ANALYSIS

The effect of polymers and surfactants on the thermal decomposition of Trp in hair was investigated at 132°C and 152°C, with intermittent heating periods of 1 min, for a total treatment time of either 10 min or 12 min. We also explored other temperatures and treatment schedules in which the observed effects were generally similar to those reported for the conditions specified above. The data analysis suggests that the thermal decomposition of Trp may be impeded by pretreating the fibers with a polymer or surfactant. Figures 2 and 3 demonstrate the progression of Trp damage, on light-brown hair at 132°C and 152°C, as a function of thermal treatment time for an untreated control, and for hair modified with PVP/DMAPA acrylates copolymer, quaternium 70,



### PVP/DMAA Acrylates Copolymer



### Quaternium 70

Figure 1. Chemical structures of PVP/DMAA acrylates copolymer and quaternium 70.

and hydrolyzed wheat protein. At these temperatures, 12 min exposure of intact hair results in a 27.5% (132°C) and 50.0% (152°C) loss of Trp. The data in Figures 2 and 3 indicate that modified hair undergoes a slower Trp decomposition as compared to untreated hair. For example, hair modified with quaternium 70 and subjected to 12 min of curling iron exposure at 132°C undergoes a Trp loss of approximately 22%, providing  $(27.5\% - 22\% / 27.5\% \times 100\% = 20\%)$  a 20% thermal protection factor. The effect of all treatments was similar, with the protective effect ranging from 10% to 20% and evident even after the shortest exposure times (4 min). We conducted similar experi-

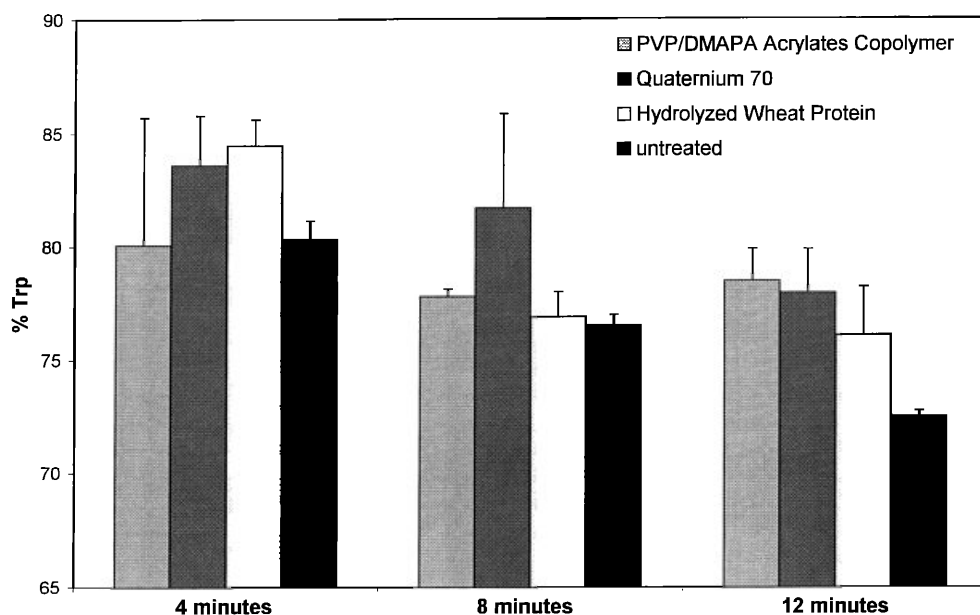


Figure 2. Trp degradation as a function of time for light-brown hair treated with the indicated compounds and subjected to a curling iron temperature of 132°C.

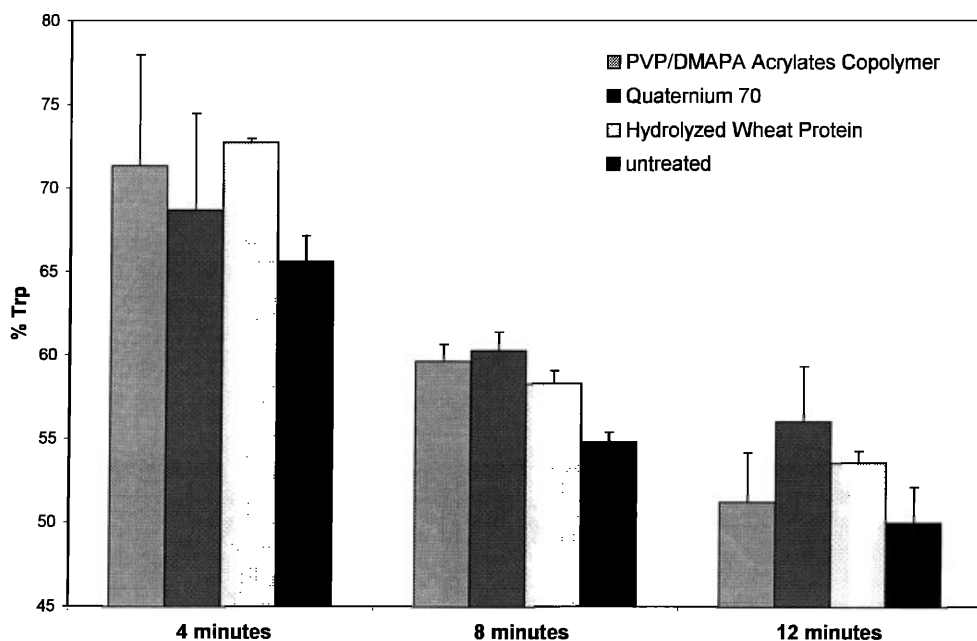


Figure 3. Trp degradation as a function of time for light-brown hair treated with the indicated compounds and subjected to a curling iron temperature of 152°C.

ments on Piedmont hair, which resulted in 40% and 65% Trp decomposition after 10 min of exposure at 132°C and 152°C, respectively. In addition to polymers, which provided a 10–20% thermal protection effect, we also administered pretreatment with

sodium bisulfite, a strong reducing agent and antioxidant. The use of this reagent resulted in 15% and 23% protection of Trp after 10 min of hair exposure to hot irons at 132°C and 152°C, respectively.

The mechanism for the thermal decomposition of Trp most likely involves oxidation, which could be inhibited by using sodium bisulfite. Similarly, it has previously been reported that the photodecomposition of Trp in hair can be affected by reducing agents such as ascorbic acid. In contrast to this, the thermal-protective effect of such chemically diverse materials as a cationic polymer, cationic surfactant, or protein hydrolyzate cannot be explained by an oxidation-prevention mechanism. The retardation of heat conduction is a possibility, although our earlier calculations suggest that heat propagation through a fiber assembly is so fast that steady-state conditions are attained within a fraction of a second (5). A very thin layer of surface treatment, with a thickness on the order of a fraction of a micron, could result in a multilayer heat barrier in a bundle of hair possibly affecting the temperature distribution and consequently the rate of Trp decomposition. Conceivably, another factor could be that an intervening layer of surface treatment prevents direct contact between the hot surface of an appliance and the fiber surface, thus eliminating local overheating effects.

#### COMBING ANALYSIS

In order to monitor the surface damage or surface modification induced by thermal exposure, we have performed combing analysis on thermally treated hair. This technique, which measures frictional forces corresponding to the combing process, has previously been found to be a very sensitive tool for detecting changes in the fiber surface as a result of thermal treatment (5), photo-irradiation (16), and reactive chemical treatments (17). Figure 4 contains combing curves, representing force difference as a function of distance (or tress length), for modified and unmodified hair that was thermally exposed to a curling iron at 152°C for a total of 12 min. The values of force difference were obtained by subtracting untreated control traces from the curves obtained after the treatment. In agreement with our previous publication (5), untreated hair exhibits an increase in combing force values in the thermally exposed region of the tress, resulting in a peak (maximum) on the force-vs-distance curve presented in Figure 4. This may be attributed to the thermal-oxidative damage of the lipid layer present on the fiber surface. For fibers treated with hydrolyzed wheat protein, there is an even greater increase in fiber friction than in untreated hair. This result has been obtained not only for neat solutions of protein hydrolyzates, but also for commercial formulations based on this raw material. This effect, perhaps caused by heat-activated grafting of wheat protein fragments to hair keratin, could lead to an increase in the hydrophilicity and surface energy of hair, resulting in increased combing forces. In contrast, hair treated with PVP/DMAPA acrylates copolymer exhibits a depression (minimum) in the combing curve, corresponding to the thermally exposed region of the tress. This suggests preferential binding of the cationic polymer to the thermally treated section of the fiber assembly and either an actual reduction in surface damage or its masking by a deposited layer of polymer capable of reducing the combing forces. Finally, with a cationic surfactant (quaternium 70), the changes in the combing curve as compared to the untreated control are minimal and provide evidence of only a slight increase in the region where thermal treatment was administered.

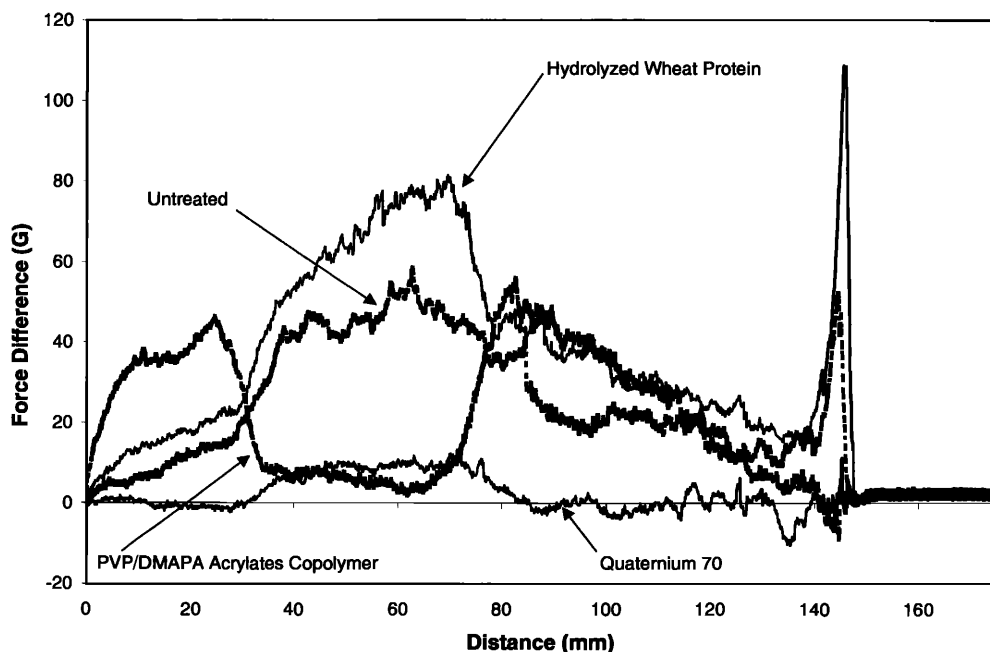


Figure 4. Combing curve differences for light-brown fibers treated with the indicated compounds and subjected to 12 min of thermal treatment at 152°C.

It should also be mentioned that the thermal treatment of Piedmont hair, pretreated with sodium bisulfite, yielded very high increases in combing forces and combing work values. After 10 min of thermal exposure at 152°C, the combing work values for sodium bisulfite-treated hair were in the range of 900–1100 G · cm as compared to 180–200 G · cm for untreated samples of Piedmont hair. The damaging effect of sodium bisulfite may be attributed to the ability of this compound to break disulfide linkages with the formation of thiol and Bunte salt groups (18), reactions that could also affect the structural elements of the hair surface.

In order to provide further evidence for the surface effects illustrated by the data presented in Figure 4, we have carried out the kinetic studies of combing analysis for curling iron application at two temperatures. Figures 5 and 6 display combing work difference (calculated by integrating combing force curves in the thermally affected section of a tress) as a function of thermal treatment time for curling iron temperatures of 132°C and 152°C. It should be stressed that, as in Figures 2 and 3, the combing data were obtained after each 4-min period of thermal exposure, consisting of 1-min heating cycles, in which the tresses were shampooed after each 2-min cycle. The data illustrate a gradual increase in combing work for the untreated control, and an even more pronounced increase for protein-treated hair at both temperatures. The use of both cationic polymer and cationic surfactant resulted in low combing work values and no combing force increases as a function of time.

#### TEXTURAL PROPERTIES

Throughout the course of our experiments, we have observed changes in the textural

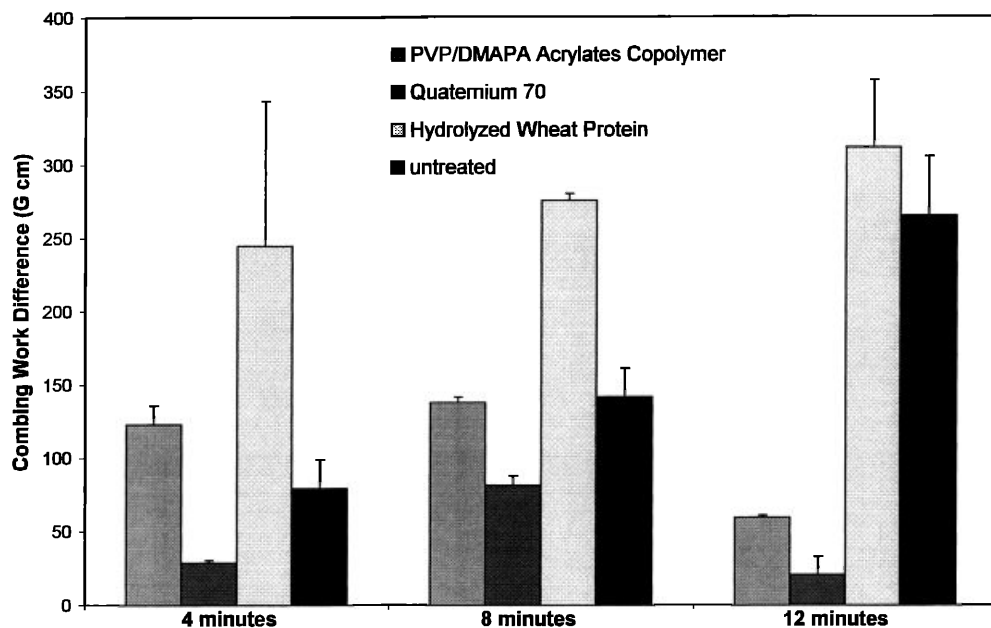


Figure 5. Combing work difference as a function of thermal treatment time for light-brown fibers treated with the indicated compounds and subjected to a curling iron temperature of 132°C.

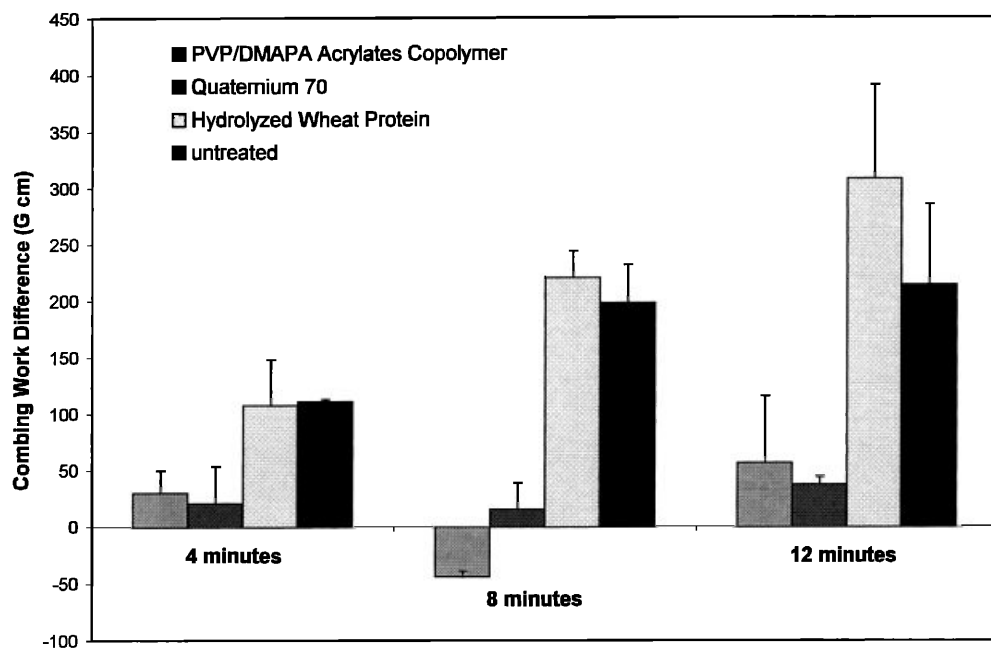


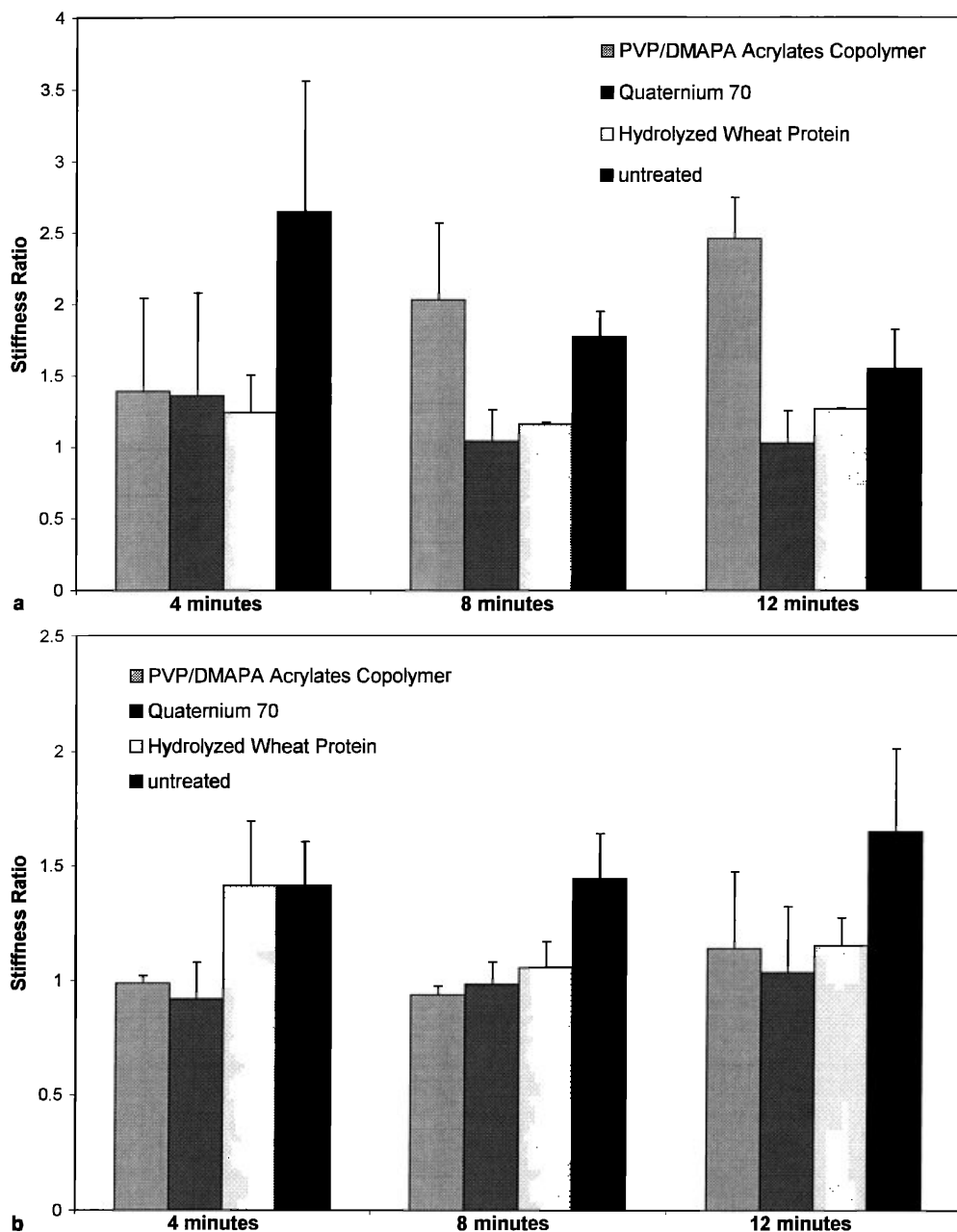
Figure 6. Combing work difference as a function of thermal treatment time for light-brown fibers treated with the indicated compounds and subjected to a curling iron temperature of 152°C.



properties of the hair fiber assemblies as a result of polymer or surfactant pretreatments prior to curling iron application. The most perceptible effect was increased binding between fibers, evident after allowing them to dry undisturbed while in close contact with each other. This was most evident after pretreatment with a polymer, such as PVP/DMAPA acrylates copolymer, at high-temperature conditions ( $>152^{\circ}\text{C}$ ). The condition of hair after such a procedure resembles that commonly observed after application of a leave-in styling product in which the fibers are linked together and the stiffness of the fiber assembly is significantly increased. The bonds between fibers are produced by a residual amount of polymer, whose affinity to hair was enhanced by thermal treatment and could not be removed by rinsing. This effect can often be diminished by a single shampooing, although we observed that certain experimental polymers, not discussed in this paper, were able to resist several shampooings. We should also mention that the thermally induced interfiber bonds can easily be broken by dry combing, which leaves individual hair fibers separated from each other. However, subsequent hydration and drying results in reformation of bonds between fibers and increased stiffness of the hair tress. As described in the Experimental section, we have employed a texture analyzer and a dual-cantilever bending apparatus to measure the variation in mechanical properties of thermally treated hair. Figure 7 presents the variation in stiffness ratio as a function of treatment time at  $152^{\circ}\text{C}$  for intact hair and hair pretreated with a polymer, a protein hydrolyzate, and a surfactant. The data in Figure 7 were obtained for hair subjected to thermal treatment followed by rinsing (a) and shampooing (b). After rinsing, an increase in the stiffness ratio of hair pretreated with PVP/DMAPA acrylates copolymer is evident, reaching a value of approximately 2.5 after 12 min of exposure. The values obtained for untreated hair are also elevated, especially at shorter treatment times. On the other hand, fibers treated with protein and surfactant are characterized by values that are only slightly higher than 1.0. After shampooing, the binding effect of the polymer disappears, presumably due to removal of the polymer by a detergent. Differently, the stiffness ratio values for unmodified fibers remain elevated, ranging from 1.4 to 1.7. The increase in hair stiffness, observed after thermal treatment, could be related to the previously reported toughening transition observed at  $140^{\circ}\text{--}170^{\circ}\text{C}$  by differential scanning calorimetry (1). The reason for this transition, appearing as a decrease in sample heat capacity (opposite to glass transition), is the removal of tightly bound water and an increase in the content of the crystalline  $\alpha$ -helical phase in hair. It has also been demonstrated by Milczarek *et al.* (1), in agreement with the results of the present work, that an increase in hair crystallinity as a result of high temperatures ( $>150^{\circ}\text{C}$ ) is stable and remains unchanged even after fiber exposure to high humidity or liquid water. The increased stiffness effects are not evident in all of the data obtained for hair thermally exposed at  $132^{\circ}\text{C}$ . For example, the stiffness ratios for untreated and polymer- or protein-treated hair fall within the range of 1.0–1.4 (Figure 8). However, fibers pretreated with quaternium 70 are generally characterized by the lowest stiffness ratios, suggesting that the surfactant may play the role of a plasticizer within the keratin structure.

## CONCLUSIONS

The use of a cationic polymer, protein hydrolyzate, and a cationic surfactant as a hair pretreatment (i.e., prior to the use of curling irons) was found to affect the processes that lead to (a) damage of hair amino acid (e.g. Trp), (b) damage of the fiber surface, and (c)



**Figure 7.** Stiffness ratio as function of time for light-brown fibers treated with the indicated compounds and subjected to a curling iron temperature of 152°C after rinsing (a) and after shampooing (b).

modification of the fiber mechanical properties reflected by a change in the stiffness of hair assemblies. All analyzed materials, which were employed as leave-in treatments, were found to reduce the extent of thermal decomposition of Trp by 10–20% as a result of 4–12 min of curling iron application at 132°C and 152°C. Combing measurements have demonstrated that the use of PVP/DMAPA acrylates copolymer or a cationic

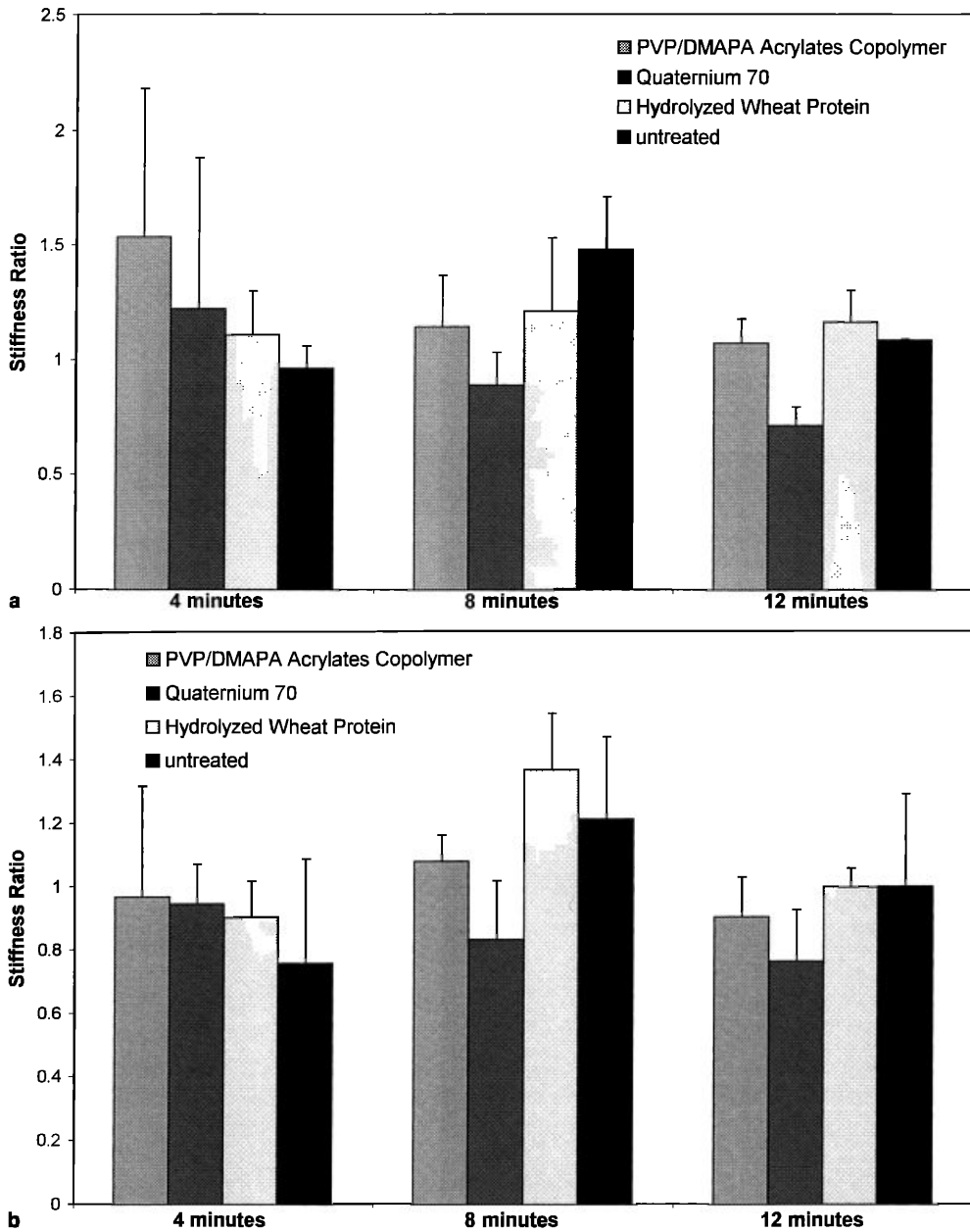


Figure 8. Stiffness ratio as function of time for light-brown fibers treated with the indicated compounds and subjected to a curling iron temperature of 132°C after rinsing (a) and after shampooing (b).

surfactant will suppress an increase in combing forces. Untreated hair, on the other hand, will provide increased combing forces after curling iron exposure, which is most likely associated with the thermal decomposition of the surface lipid layer. Finally, dual-cantilever bending experiments have been employed to probe the variation in the stiffness of hair tresses after thermal exposure. The stiffness of the fiber assemblies for both

unmodified and polymer-treated hair was found to increase as a result of thermal exposure. This may be a result of structural rearrangements in hair, consisting of (a) an increase in the content of the crystalline phase for intact hair, and (b) the addition of adsorbed amounts of polymer, which produce linkages between fibers.

## REFERENCES

- (1) P. Milczarek, M. Zielinski, and M. Garcia, The mechanism and stability of thermal transitions in hair keratin, *Colloid Polym. Sci.*, **270**, 1106 (1992).
- (2) L. Rebenfeld, H. Weigmann, and C. Dansizer, Temperature dependence of the mechanical properties of human hair in relation to structure, *J. Soc. Cosmet. Chem.*, **17**, 525 (1966).
- (3) W. Humphries, D. Miller, and R. Wildnauer, The thermomechanical analysis of natural and chemically modified human hair, *J. Soc. Cosmet. Chem.*, **23**, 359 (1972).
- (4) R. Arnaud, G. Perbet, A. DeFlandre, and G. Lang, ESR study of hair and melanin-keratin mixtures—The effects of temperature and light, *Int. J. Cosmet. Sci.*, **6**, 71 (1984).
- (5) R. McMullen and J. Jachowicz, Thermal degradation of hair. I. Effect of curling irons, *J. Cosmet. Sci.*, **49**, 223–244.
- (6) R. Crawford, C. Robbins, and K. Chesney, A hysteresis in heat dried hair, *J. Soc. Cosmet. Chem.*, **32**, 27 (1981).
- (7) S. Shah, *EP 0 681 826 A2*, 1995.
- (8) Kobayashi Kose KK, *JP 3 135 909 A*, 1991.
- (9) Lion Corp., *JP 3 291 211 A*, 1991.
- (10) Sunstar KK, *JP 3 157 316 A*, 1991.
- (11) Lion Corp., *JP 57 206 605 A*, 1982; *Chem. Abstr.*, **98**, 362 (1983).
- (12) KAO Corp., *JP 6 206 808 A*, 1994.
- (13) Sunstar KK, *JP 60 116 624 A*, 1983.
- (14) R. Galleguillos and D. Bhatt, *US Patent 5 639 448*, 1997.
- (15) A detailed description of the cantilever bending assembly is included in a manuscript which will be submitted for publication (1998).
- (16) J. Jachowicz, M. Heliouff, C. Rocafort, A. Alexander, and R. Chaudhuri, Photodegradation of hair and its photoprotection by a substantive photofilter, *DCI*, **157**, 28 (1995).
- (17) M. Garcia and J. Diaz, Combability measurements on human hair, *J. Soc. Cosmet. Chem.*, **27**, 379 (1976).
- (18) L. Wolfram and D. Underwood, The equilibrium between the disulfide linkage in hair keratin and sulfite or mercaptan, *Textile Res. J.*, **36**, 947 (1966).