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The effects of water on heat-styling damage

PAUL CHRISTIAN, NIGEL WINSEY, MARIE WHATMOUGH, and PAUL A. CORNWELL, *School of Chemistry, The University of Manchester, Oxford Road, Manchester, UK, M13 9PL; Mar-Tech Contract Services Inc., 888 Sussex Boulevard, Broomall, PA 19008; and PZ Cussons (UK) Ltd, Innovation Centre IC-H, Agecroft Commercial Park, Lamplight Way, Manchester, UK, M27 8UJ.*

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Synopsis

Heated styling appliances, such as straightening irons, have grown in popularity in recent years, as have hair products such as heat-protection sprays. In this study we investigate whether the water in a heat-protection spray can affect the level of damage caused by heat styling.

Tryptophan damage from heat styling was measured using fluorescence spectroscopy, and structural damage was investigated using light microscopy and single-fiber tensile testing. Hair samples were heat treated with straightening irons, following treatment with either a water-based, "wet," heat-protection spray or an ethanol-based, "dry," spray.

Results showed that, as expected, tryptophan damage was reduced by repeated applications of both the "wet" and "dry" heat-protection sprays. However, no differences were seen between the "wet" versus the "dry" product. Light microscopy studies showed greater structural damage to hair treated with water and the "wet" spray. Tensile tests confirmed that there was greater damage to hair treated with the "wet" spray. Decreases in Young's modulus were greater in the presence of the "wet" spray.

The results of this study suggest that the *type* of damage caused by heat treatments is different in wet versus dry hair. In dry hair, thermal treatments cause chemical damage and some structural damage. However, in wet hair, thermal treatments cause the same chemical damage, but considerably more structural damage, which causes significant changes in the physical properties of the hair. It is likely that the rapid evaporation of water from the hair is the main causal factor.

Our experiments suggest that the effectiveness of commercial heat-protection sprays can be improved by the removal of water and by the use of volatile ingredients, such as ethanol, as base solvents.

INTRODUCTION

Styling hair with straightening irons or curling tongs to achieve smoother, straighter hair styles, or curls and waves, has grown in popularity. In the UK, for example, over a third of women currently use straighteners every time they wash and style their hair (1). Straightening irons and curling tongs are usually used after blow-drying, and act to drive out any remaining water in the hair. The removal of water encourages the formation of more bonds between hair proteins, helping to set the hair in its new conformation.

The popularity of straightening irons and curling tongs has created a large market for hair products associated with heat styling. These include heat-protection sprays, straightening balms, curl creams, and heat-protection shampoos and conditioners. Heat-protection sprays are very popular. In fact, heat-protection sprays are now the second most frequently used type of styling products used in the UK, second only to hairsprays (1). Heat-protection sprays are usually designed to protect the hair from heat damage, and to give some conditioning and style hold. They are usually sprayed on to the hair after blow-drying and immediately before applying the straightening irons or curling tongs.

The plates of straightening irons and curling tongs reach a range of different temperatures. Ghd IV® straightening irons, for example, claim to reach 185°C, and other irons claim to reach temperatures of up to 230°C. At these temperatures there is always going to be some damage to the hair. It is well known that heat-styling damage from blow-drying and hot irons can be both physical and chemical in nature.

Cycles of wetting and blow-drying hair can result in the formation of multiple, "axial" cracks in the cuticles, aligned parallel to the longitudinal axis of the hair fiber (2). These axial cracks form when the external portions of hair fibers undergo rapid dehydration. Cycles of wetting and blow-drying have also been found to produce deep ovoidal (or bubble) cuticle cracks (3). These cracks are attributed to a combination of cyclic extension actions and the rapid escape of water while drying. Heat treatment with curling irons has also been shown to produce radial and axial cracking along with scale edge fusion (4). Bubbling and buckling of the cuticle was also observed (4).

The chemical effects of thermal treatments (such as treatment with curling tongs) on human hair were investigated by McMullen and Jachowicz (5). Their work demonstrated that heat treatments of between 130° and 164°C result in a decomposition of chromophores, specifically tryptophan and its oxidation products (kynurenines), and an increase in the yellowness of white hair or a simultaneous yellowing and darkening of bleached hair. In other studies, curling irons have also been shown to lower the dynamic contact angle of the hair surface as cuticle lipids are damaged and removed (6).

The effects of structural and chemical damage to the physical properties of the hair include increased hair breakage on combing (7) and, in severe cases, acquired trichorrhexis nodosa (brittle hair) (8). Increases in combing forces are also observed (5), particularly in hair subjected to repeated heat treatments separated by rinsing.

A number of ingredients have been investigated as insulators against heat-styling damage. These include sodium polystyrene sulfonate (6), quaternium-70 and polyquaternium-11 (9), PVP/DMAPA acrylates copolymer (9), sodium PEG-40 maleate/styrene sulfonate copolymer, and silicone quaternium-22 PPG-myrisyl ether. Some other humectant-type ingredients, such as hydrolyzed wheat protein, have also been shown to reduce damage (9).

Most heat-protection sprays on the market at present use these kinds of technologies to protect the hair. However, they all, at present, are formulated as water or water/ethanol-based products. Since some studies (4) have suggested that the structural damage caused by curling irons is greater on wet hair than on dry hair, we have decided to investigate the benefits of using a water-free heat-protection spray made with a volatile solvent such as ethanol. We hypothesize that less chemical and structural degradation should occur at high temperatures in hair treated with a "dry" spray versus hair treated with a "wet" spray.

EXPERIMENTAL

MATERIALS

Fine-density, light-brown, virgin hair (20 cm in length) was purchased from International Hair Importers & Products Inc. (Glendale, New York). Ethanol (96%), laboratory reagent grade, was bought from Fisher Scientific UK Ltd (Loughborough, Leicestershire, UK). Vinylpyrrolidone/vinyl acetate co-polymer (50%) in ethanol (VP/VA E-735®) and quaternium-70 (50%) in propylene glycol (Ceraphyl-70®) were supplied by International Speciality Products (Wayne, NJ). Bis-PEG/PPG-20/20 dimethicone (Abil B 8832®) was supplied by Evonik Industries (Essen, Germany). Methylchloroisothiazolinone and methylisothiazolinone 1.5% (Kathon CG®) were supplied by Rohm and Haas (Morges, Switzerland).

METHODS

Preparation of heat-protection spray formulations. Table I describes the prototype formulations tested in this study. The "wet" spray was adjusted to pH 6 with sodium hydroxide solution.

Hair preparation. Hair was cut into 1.5-cm-wide tresses (approximately 1–2 g in weight, including the bindings). Each tress was clipped at the edge, 41 mm from the bindings, to mark the start of the area to be treated with straightening irons. The hair tresses were dried for two days in a glass dessicator over calcium chloride at room temperature. Blow-drying was always avoided, as this may have caused heat-styling damage and introduced extra variability into our experiments.

Treatment with straightening irons—a comparison of wet versus dry hair. In experiments comparing heat damage in wet and dry hair, tresses were wetted by immersion in tap water for 15 minutes ahead of the heat treatment. Surface water was removed with tissue paper before applying the straightening irons. For tests on dry hair, the tresses were heat treated immediately after removal from the dessicator.

Table I
Prototype Heat-Protection Spray Formulations

Material	% w/w	
	"Dry" spray	"Wet" spray
Vinylpyrrolidone/vinyl acetate co-polymer (50%) in ethanol	8.00	8.00
Quanternium-70 (50%) in propylene glycol	2.40	2.40
Bis-PEG/PPG-20/20 dimethicone	1.00	1.00
Fragrance	1.00	1.00
Methylchloroisothiazolinone and methylisothiazolinone (1.5%) in water	—	0.07
Water	—	87.53
96% Ethanol	87.60	—

The tresses were heat treated with ghd IV® straightening irons with 2-cm-wide ceramic plates at 175°–185°C (ghd UK, Silsden, West Yorkshire, UK). The tresses were wrapped in Post-It® paper at their root end, the lower edge of the Post-It® paper marking the top of the area to be heat treated.

The tresses were treated with straightening irons for five seconds. The irons were held in the same place throughout the treatment. Wet hair was put back into tap water for three minutes before being treated again. Each time, surface water was removed with tissue paper before applying the straightening irons. Dry hair was simply allowed to cool for three minutes before the start of another treatment. Treatments were repeated three times in each session, after which all the hair was put back into the dessicator for two days. In total, each tress was subjected to 4×3 treatments, which equates to a total treatment time of 60 seconds.

Repeated five-second heat treatments were selected for this study, as (a) they were realistic and (b) they made our measurements more sensitive to the effects of water, which evaporates very quickly. In reality, consumers and hair stylists quickly run straightening irons down each section of hair two to three times. Irons are, therefore, never in contact with any one part of the hair for more than a few seconds. A five-second treatment time (without moving the irons down the switch) was selected to represent the heat exposure during one complete styling session.

Long, extended treatment times, of, say, 5–30 minutes, as used by McMullen & Jachowicz (5), were not appropriate for our study. Longer heat treatment times are, perhaps, most suitable for studying protein damage or testing the effectiveness of insulating materials. They are not suitable for investigating the effects of water, since the water evaporates within seconds.

Treatment with straightening irons—single-dose experiments with "wet" and "dry" products. In single-dose experiments, 0.1 ml of product was applied to each tress before heat treatment. The tresses were wrapped with Post-It® paper, as described above, to clearly mark the area for heat treatment. The product was applied, from a syringe, to the top end of the exposed part of each tress (0.05 ml on each side) and spread downwards, just once, with the fingertips. The tresses were left to dry for two minutes before applying the straightening irons. The hair was treated with straightening irons for five seconds. The irons were held in the same place throughout the treatment.

After each heat treatment, the tresses were washed with shampoo (Charles Worthington Brilliant Shine® Shampoo, PZ Cussons (UK) Ltd, Stockport, Cheshire, UK). Shampooing followed a standard protocol. One milliliter of shampoo was applied to each tress. The shampoo was twice massaged into damp hair for 30 seconds, followed, each time, by 30 seconds rinsing under warm tap water. The cleaned tresses were air dried, and then put back into the dessicator. The treatments were repeated 12 times. Each tress, therefore, was heat treated, in total, for 60 seconds.

Treatment with straightening irons—repeat dosing experiments with "wet" and "dry" products. In repeat dosing experiments, tresses were dosed and heat treated as above, but after cooling for one minute, the products were reapplied. This had the effect of building up the protective layer created by the formulations. The tresses were dried for two minutes after the product was applied and then heat treated, again, for five seconds. Product application and heat treatment were repeated three times before washing the tresses with shampoo. The cleaned tresses were air dried and then put back into the dessicator.

The cycle of three repeat doses and associated heat treatments, followed by washing, was repeated four times. Each tress, therefore, was heat treated, in total, for 60 seconds.

Fluorescence spectroscopy. Hair fluorescence measurements were made using a computer-controlled fluorescence spectrophotometer (Varian Cary Eclipse, Varian Inc., Palo Alto, CA). A solid sample holder accessory (Varian Inc.) was used to mount hair tresses in the instrument. The tresses were mounted horizontally at an angle of 30° to the axis perpendicular to the detector, with the root end closest to the detector. The angle at which switches were presented to the beam was found to be critical. Clipped hairs, cut 41 mm from the bindings (see above), were used to help position the beam over the center of the treated section of each tress (note: the treatment effects were invisible to the naked eye). The excitation beam was run at a visible wavelength and a wide-slit setting, to correctly position the hair in front of the beam.

In order to define the optimum excitation wavelength, an excitation spectrum was run on virgin hair at a fixed emission wavelength of 337 nm (Figure 1). The excitation spectrum showed a clear maximum at 285 nm, in good agreement with literature data on pure tryptophan (10). The final settings used on all measurements were an excitation wavelength of 285 nm, a slit width of 2.5 nm, and an emission detector slit width of 10 nm. Spectra were measured from 300 to 550 nm at 4-nm intervals, with two seconds collection time at each point.

For the testing, spectra were taken first from the treated parts of each switch. Control measurements were then made by moving the sample holder horizontally and taking an emission spectrum from untreated hair further towards the root end of each tress. In this way, data were collected as a series of paired comparisons. Between each pair of measurements, the tresses were removed from the sample holder and turned over. This helped to randomize the effects of switch orientation and alignment across replicate measurements.

Typical control and treated-hair measurements from the same switch are shown in Figure 2. The peak in fluorescence at 328 nm, associated with tryptophan (5), is clearly visible in the control spectrum. A broad peak is also seen between 400 and 500 nm. This peak may be associated with keratin disulfide bonds (5). Many spectra also showed a small sharp peak at 392 nm. The origin of this peak is unknown. Figure 3 illustrates how treatment with straightening irons reduces the intensity of the peak at 328 nm. The broad

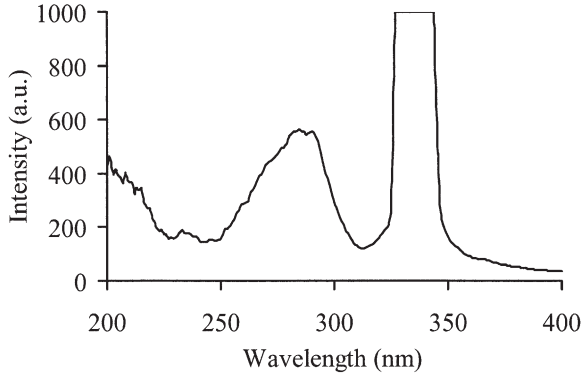

Figure 1. Excitation spectrum at a fixed emission wavelength of 337nm. (Note: The signal at ~340 nm is due to excitation/emission wavelengths coinciding and is not a fluorescence feature of the hair.)

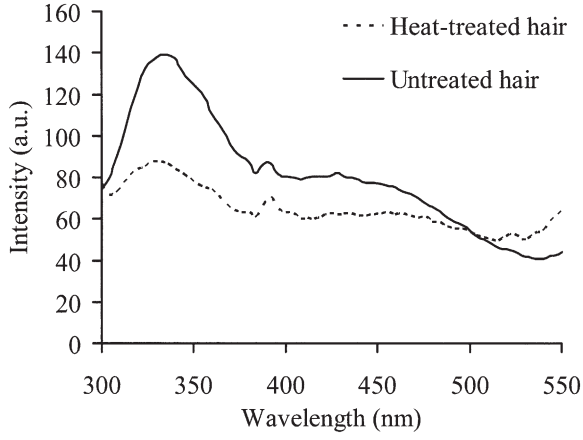

Figure 2. Typical fluorescence spectra from control and treated hair. Excitation wavelength = 285 nm.

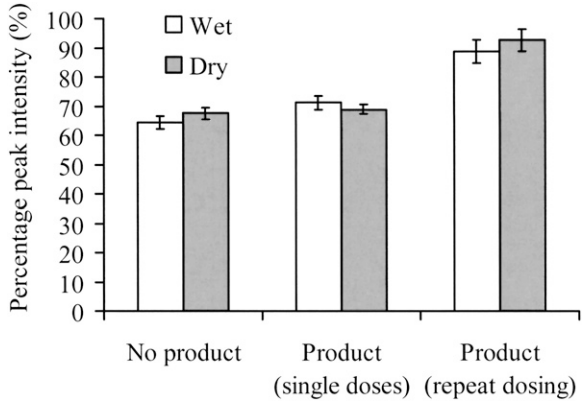

Figure 3. Summary of fluorescence spectroscopy data. Means +/− standard errors, n=29–36.

peak centred at 448 nm was relatively unaffected. The changes in spectra on heat styling damage were in good agreement with literature data (5) and indicate oxidative degradation of tryptophan.

It was noted, early on, that the intensity of the spectra obtained from hair varied according to the alignment of the switch. Better aligned, less frizzy switches tended to give stronger spectra. In order to account for this, the peak in fluorescence at 328 nm due to tryptophan was normalized with the fluorescence intensity at 448 nm. The "normalized" fluorescence intensity used in this work was, therefore, always the intensity at 328 nm divided by the intensity at 448 nm.

Each test usually involved five to six paired comparisons, treated versus control, on six tresses. In total, each test, therefore, involved taking 30–36 pairs of data.

In this study, the "percentage peak intensity" at 328 nm was calculated as follows:

$$\% \text{ Peak intensity} = (\text{normalized } \textit{treated} \text{ peak intensity} / \text{normalized } \textit{control} \text{ peak intensity}) \times 100$$

The percentage peak intensity correlates to the percentage of remaining tryptophan in the hair.

Light microscopy. Hair fibers were mounted on glass slides and observed using a light microscope (Olympus BX50 System Microscope, Olympus Optical Co UK Ltd, London). Images were taken using a digital video camera (SPOT Insight Camera, Diagnostic Instruments Inc., Sterling Heights, MI). Samples were illuminated from underneath. Polarized light was used to improve contrast (U-Pot filter, Olympus Optical Co UK Ltd).

Single-fiber tensile testing. Tensile tests used approximately 60 fibers from each set of six tresses (ten fibers per tress). As paired comparisons improve testing sensitivity, heat-treated and control portions of each fiber were analyzed. Each fiber, therefore, acted as its own control.

The fibers were permanently mounted with a 10-mm gauge length in PVC-lined brass crimps. The shorter 10-mm gauge length ensured that 100% of the heat-treated hair analyzed had actually been in contact with the irons. The ghd IV® straightening irons had 20-mm-wide plates.

The cross-sectional area of each fiber was measured using the Fiber Dimensional Analysis System (FDAS), which incorporates a Mitituyo laser scanner (Dia-Stron Ltd, Andover, Hampshire, UK). The FDAS takes multiple-diameter measurements from the fiber and calculates a cross-sectional area based on an ellipse. The laser micrometer has an accuracy of better than 0.1 microns.

Crimped fibers were loaded into the MTT675 cassette (Dia-Stron Ltd) and then equilibrated at 80% R.H. overnight. The fibers were then extended to break at 12.5 mm/minute (40% strain rate/minute), using the MTT675 Automated Tensile Tester (Dia-Stron Ltd). The range of the load cell was set at 2N, giving a resolution of 1.0×10^{-3} N.

RESULTS

FLUORESCENCE SPECTROSCOPY

Table II and Figure 3 show that there is no statistical difference between the percentage of tryptophan remaining in hair treated when wet versus dry (without product applied). In both cases, a cumulative 60-second treatment with the straightening irons reduced the peak intensity at 328 nm by approximately 35%. Such reductions are in good agreement with previous studies (5) that have shown a 40–50% reduction in tryptophan after five minutes treatment with curling irons at 130°–170°C.

Application of single doses of prototype heat-protection sprays did not significantly reduce tryptophan damage versus either wet or dry unprotected controls, although there was a weak trend towards slightly lower damage. There was also no difference in tryptophan damage in hair treated with a "wet" spray versus a "dry" spray.

Treatment with repeated doses of heat-protection sprays significantly reduced tryptophan damage versus the untreated controls (wet versus dry test) in hair treated with single doses of product (ANOVA, $p<0.05$). There was, however, still no difference between hair treated with a "wet" spray versus a "dry" spray.

Table II
Summary of Fluorescence Spectroscopy Data

		Normalized peak intensity at 328 nm (a.u.)						
		Control		Treated		Percentage peak intensity, treated versus control (%)	+/− Standard error	ANOVA test Homogenous groups
Treatment	Replicates	Mean	+/− Standard error	Mean	+/− Standard error			
Wet hair (no product)	32	2.29	0.07	1.45	0.04	64.37	2.20	
Dry hair (no product)	33	2.12	0.05	1.40	0.02	67.53	2.03	
"Wet" product (single doses)	36	1.72	0.05	1.19	0.03	71.10	2.36	
"Dry" product (single doses)	36	1.99	0.04	1.36	0.03	68.81	1.61	
"Wet" product (repeat dosing)	29	1.71	0.06	1.48	0.07	88.67	3.94	
"Dry" product (repeat dosing)	33	1.76	0.05	1.60	0.05	92.62	3.81	

An ANOVA test was used to compare percentage peak intensity (treated versus control) data. Homogenous groups are those which have data with no significant ($p < 0.05$) difference between them.

The effectiveness of the repeated doses of spray suggests that a buildup of polymers and conditioning agents on the hair helps insulate the hair from heat-styling damage. These protective effects are in good agreement with previous studies (9).

LIGHT MICROSCOPY

In order to investigate structural damage, hair was examined by light microscopy. Figure 4 shows typical images of hair fibers taken by the light microscope. All the images shown have been taken from fibers used in the first wet-versus-dry test, which did not use heat-protection products. Images A, C, and E show no major differences in the cuticle scale patterns.

Images B,D, and F focus on the medulla and cortex. Image B shows how, in untreated fibers with a medulla, light microscopy reveals a smooth dark band running the length of the hair. However, in hair heat treated while wet (image D), the medulla is less intense in "darkness" or contrast and much more broken in structure. It was possible to run along the length of a single fiber and observe the change in the medulla as one moved from an untreated area to a treated area and then back into an untreated area.

The medulla in human hair is comprised of air-filled sacks. It is likely that the medulla fills quickly with water when the hair is wetted, and that rapid heating, boiling, and evaporation of this water causes significant damage. It is this type of damage that is clearly visible under the light microscope.

In addition to changes in the medulla, heat damage was also sometimes observed in the cortex (image D). Dark spots or elongated strips (parallel to the axis of the fiber) were seen. One could speculate that these are due to the separation/cracking apart of cortical cells.

Figure 4 shows that the damage to the medulla and cortex is much less severe in hair that has been heat treated when dry, versus hair that has been heat treated when wet. This was a pattern also seen in the experiments using the heat-protection sprays. Medulla damage was consistently greater on hair that had been treated with the "wet" products versus the "dry" products. Lower structural damage in dry versus wet hair was in good agreement with previous SEM studies on thermal damage to hair (4).

SINGLE-FIBER TENSILE TESTING

Tensile testing was performed on the same fibers used in the fluorescence spectroscopy work and in light microscopy for the single-dose experiments with "wet" and "dry" products.

Figure 5 illustrates the differences in the changes in Young's modulus. Clearly, the reduction in Young's modulus caused by heat treatment is much greater in hair treated in the presence of the "wet" heat-protection spray. No significant change in modulus ($p>0.05$, Student's t-test) was observed in hair treated in the presence of the "dry" heat-protection spray.

Our data are in good agreement with previous work on the effects of repeated thermal treatments on dry hair (4). These previous investigations also showed no significant changes in Young's modulus after treatment. Unfortunately, changes in the mechanical properties of heat-treated wet hair were not reported.

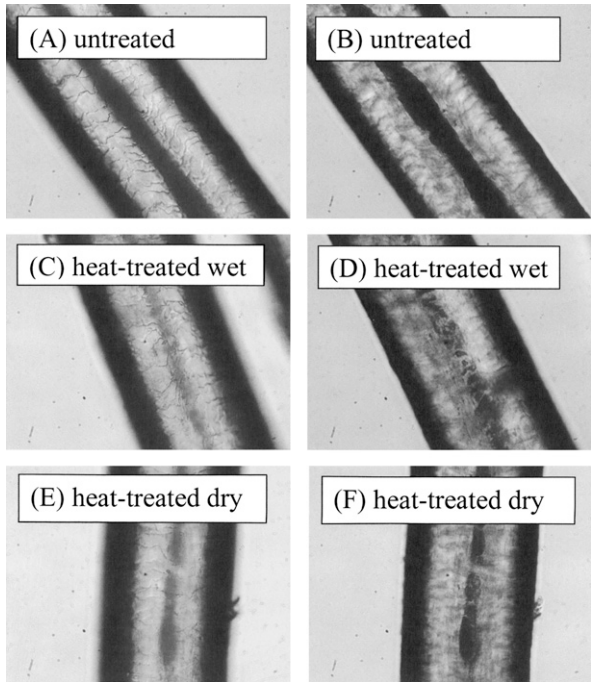

Figure 4. Typical light microscopy images of hair fibers, illustrating the increased structural damage observed in hair treated with straightening irons for 12 × 5 seconds (×60 magnification). A, C, and E are focused on the cuticle and surface. B,D, and F are focused on the cortex and medulla.

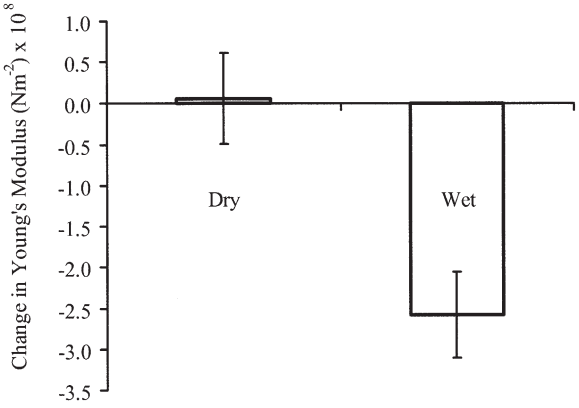

Figure 5. Changes in Young's modulus after heat treatment. Comparison of the effects on hair treated with a "dry" heat-protection spray and a "wet" heat-protection spray.

Table III shows that both the post-yield gradient and the break stress were reduced by heat treatment in the presence of the "dry" spray ($p<0.05$, Student's t-test), but in good agreement with the Young's modulus data, the reductions were significantly greater in the presence of the "wet" spray.

Table III also shows that no significant differences were found in the changes in stress at 15% strain, work at 15% strain, and break extension in hair treated in the presence of "wet" versus "dry" sprays. In the case of work at 15% strain and break extension, this might be explained by the fact that these data are calculated without normalization with fiber cross-sectional areas. It is likely that the greater variability in this data is part of the reason why no statistically significant differences were seen.

DISCUSSION

In this study we have investigated how the presence of water affects the chemical and physical damage to hair caused by thermal treatments with straightening irons.

Fluorescence spectroscopy studies were performed to investigate how heat treatment damaged the hair proteins, specifically the amino acid tryptophan. These experiments showed that, in good agreement with other published data (5), heat treatment at 185°C for a cumulative treatment time of 60 seconds could reduce tryptophan levels by 35%.

In agreement with other fluorescence spectroscopy studies (9), we did see good protective effects from our prototype heat-protection spray containing vinylpyrrolidone/vinyl acetate co-polymer, quaternium-70, and bis-PEG/PPG-20/20 dimethicone. Interestingly, the effects were only seen when quite a thick layer of product had been put on the hair after repeated applications. It is likely that clumping of the fibers and the presence of thick insulating films helped provide extra thermal protection.

Interestingly, in this study we saw no difference in tryptophan damage in wet versus dry hair. Our data, suggest, therefore, that tryptophan oxidation is not sensitive to the presence of water and occurs simply in the presence of oxygen from the air. This conclusion would fit observations made by McMullen and Jachowicz (5). These workers were able to show that thermal degradation of tryptophan at 164°C increases as treatment times

Table III
Effects of Heat Treatment on the Tensile Properties of Hair: Comparison of Hair Treated with a "Wet" Heat-Protection Spray and Hair Treated with a "Dry" Heat-Protection Spray

	"Dry" heat-protection spray			"Wet" heat-protection spray			Mean differences in changes, "wet" spray versus "dry" spray	Statistical significance of the differences (Student's *t*-test)
Measurement	Mean control	Mean treated	Mean change	Mean control	Mean treated	Mean change		
Cross-sectional area (μm^2)	4121	4087	−66	3669	3718	−18	48	0.7766
Young's modulus (Nm^{-2}) $\times 10^9$	1.97	1.98	0.01	2.17	1.96	−0.26	−0.25	0.0007
Stress at 15% strain (gmf μm^{-2}) $\times 10^{-3}$	8.65	7.54	−1.11	8.14	6.92	−1.33	−0.22	0.2437
Work at 15% strain (J) $\times 10^{-4}$	4.72	4.26	−0.49	4.19	3.57	−0.68	−0.19	0.3202
Post-yield gradient (gmf mm^{-1})	10.6	9.50	−1.13	9.96	7.47	−2.61	−1.48	0.0005
Break extension (% strain)	67.3	65.2	−2.14	64.1	63.9	−1.47	0.67	0.7354
Break stress (gmf μm^{-2}) $\times 10^{-2}$	2.04	1.80	−0.23	2.04	1.56	−0.50	−0.27	<0.0001
Total work (J) $\times 10^{-3}$	3.53	3.04	−0.52	3.07	2.31	−0.79	−0.27	0.1581

increase from five minutes to 30 minutes. Clearly, after only a few seconds, water will have been removed from the hair, and the only way that oxidation of the tryptophan could occur would be through oxygen in the air.

Light microscopy studies revealed that the presence of water, delivered from a "wet" heat-protection spray, did cause significant extra structural damage during heat styling. Such damage had not been detected with the fluorescence spectroscopy measurements. Previous SEM studies have shown that the structural damage caused by heat treatment is different on dry versus wet hair (4). On dry hair, repeated heat treatments with curling tongs caused mainly axial cuticle cracking and fusion of scale edges. On wet hair, the same treatments caused bulges or bumps in the cuticle scale faces and ripples or "half-domes" at the scale edges. The authors proposed that these distortions were caused by the hygrothermal "fatiguing" of the wet cuticle. In good agreement with these previous studies, we also saw damage to the fiber medulla in wet hair, which appeared to be related to the rapid boiling and evaporation of water.

Tensile testing was used to get more precise and quantitative measures of structural damage. These experiments confirmed that structural damage to hair caused by heat styling was greater in the presence of a "wet" versus a "dry" heat-protection spray. Decreases in

tensile measures, such as Young's modulus, were clearly greater in samples treated in the presence of the "wet" spray. The lack of any change in Young's modulus on dry hair was in good agreement with similar studies in the literature (4).

It now seems clear that the *type* of damage caused by heat treatments is different in wet versus dry hair. In dry hair, thermal treatments cause chemical damage and some structural damage. However, in wet hair, thermal treatments cause the same chemical damage but considerably more structural damage, which causes significant changes in the physical properties of the hair. It is likely that the rapid evaporation of water from the hair is the main causal factor.

The results of this study raise a number of important issues and opportunities in the area of heat styling:

First, while our data confirm that blends of insulating polymers can help protect hair from chemical damage, they also suggest that heat-protection sprays are best formulated with volatile carrier solvents, such as ethanol, rather than with water. As we have seen, dry hair will be less structurally damaged, and less weakened by the straightening irons. The idea of making "dry" heat-protection sprays has recently been patented (11).

Second, this study suggests that straightening irons are best applied to blow-dried hair to minimize heat-styling damage. It is argued by some stylists that applying irons or tongs to wet hair gives a better straightening effect. Consumers also save time by not first blow-drying their hair before straightening. These habits will, our data suggest, cause greater damage to the hair.

Finally, it is now possible to buy straightening irons that are claimed to allow consumers to straighten wet, towel-dried hair (e.g. Remington Wet2Straight® straighteners; Vidal Sassoon Professional, Wet to Dry® hair straighteners). These appliances typically have steam vents to allow the rapid evaporation of water from the hair. More work needs to be done, our data suggest, to confirm the safety of such appliances in terms of hair damage.

Further work is clearly needed to investigate the effects of water on heat-styling damage. Electron microscopy studies of cross sections of heat-styled hair would identify, with more clarity, the structural damage in hair ironed wet or dry. Differential scanning calorimetry could also be used to better characterize keratin changes (7). One would expect keratin denaturation to occur at lower temperatures in more damaged hair.

Further work is also required to understand what the reactions are in heat-catalyzed tryptophan oxidation, particularly to understand the particular functions of water, oxygen, and free radicals in the reactions. Such studies might suggest new ways of chemically blocking protein damage.

CONCLUSION

This study has confirmed that it is best to use straightening irons on dry hair to reduce structural damage. Furthermore, it is best to use a "dry" heat-protection spray to help keep damage to a minimum.

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REFERENCES

(1) PZ Cussons (UK) Ltd, Internal market research data (2009).
(2) M. Gamez-Garcia, The cracking of human hair cuticles by cyclical thermal stresses, *J.Cosmet. Sci.,* **49,** 141–153 (1998).
(3) C. R. Robbins, *Chemical and Physical Behavior of Human Hair, 4th Ed.* (Springer-Verlag, New York, 2002), pp 268–275.
(4) S. B. Ruetsch and Y. K. Kamanth, Effects of thermal treatments with a curling iron on hair fiber, *J. Cosmet. Sci.,* **55,** 13–27 (2004).
(5) R. McMullen and J. Jachowicz, Thermal degradation of hair. 1. Effect of curling irons, *J. Cosmet. Sci.,* **49,** 223–224 (1998).
(6) B. Schweid and G. Martino, How thermal protection is made possible with sodium polystyrene sulfonate, *S.O.F.W. Journal,* **130,** 36–40 (2004).
(7) R. Rigoletto, J. Karolak, and D. Kolemel, Quantification of fiber fragmentation of hair through combing as a measure of thermal protection, *J. Cosmet. Sci.,* **60,** 578–579 (2009).
(8) P. Mirmirani, Cermanic flat irons: Improper use leading to acquired trichorrhexis nodosa, *J. Am. Acad. Dermatol.,* **62,** 145–147 (2009).
(9) R. McMullen and J. Jachowicz, Thermal degradation of hair. II. Effect of selected polymers and surfactants, *J. Cosmet. Sci.,* **49,** 245–256 (1998).
(10) F. W. J. Teale and G. Weber, Ultraviolet fluorescence of the aromatic amino acids, *Biochem.,* **65,** 476–482 (1957).
(11) P. A. Cornwell and M. Whatmough, Heat protection spray. GB 0906962.6 (2009).