Aqueous MEA and Ammonia Sorption-Induced Damage in Keratin Fibers

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ABSTRACT: The sorption of aqueous monoethanolamine (MEA) and ammonia solutions in keratin fibers and its subsequent effect on their mechanical performance has been investigated. The diffusion kinetics of MEA into keratin fibers for 0.1, 1.0, and 5 v/v % MEA in water at 30 and 50 °C were found to exhibit two clear regimes of absorption behavior: a linear Fickian diffusion regime for initial times up to 100 min, after which a second slower uptake process was observed. Single fiber tensile tests showed that the Young’s modulus and the tensile failure stress for 5% MEA-treated fibers, compared to untreated fibers, were 25% lower after 1 h of treatment and 50% lower after 9 h of treatment. Aqueous treatments of 0.1 and 1% MEA, as well as 0.6 and 3% aqueous ammonia, had no measurable effect on either Young’s modulus or tensile failure stress for the fibers. Scanning electron microscopy images and protein content analysis confirmed that keratin fibers exposed to 5% MEA solution exhibited significant surface damage as well as high levels of protein loss. This study confirms for the first time the important damage hair treatments containing 5% aqueous MEA can cause on keratin fibers.

INTRODUCTION

Because of an increase in the aging population, and changes in the perception of hairstyles, permanent artificial hair coloring has become increasingly common for all ages and genders. It is therefore not surprising that manufacturers of hair care products are evaluating new dyes and alternative chemical technologies for permanent hair dyeing, often with stronger and more chemically active treatments. However, these active treatments are known to cause “damage” to human hair fibers. These treatments can also lead to irreversible hair loss and dermatitis in mice hair.

In the last three decades, there has been a significant growth in our understanding of the chemical and physical properties of hair. Hair is mainly composed of keratinous protein which is “65−95% of the hair weight”, followed by water, lipids, pigments, and trace elements. A fully grown hair consists of the cuticle (10% of the fiber), cortex (88%), and medulla (2%). However, the latter zone is sometimes absent in fibers with smaller diameters. The complex morphology and structure of hair are thought to be similar to other animal fibers such as wool and is represented in Figure 1.

The three-dimensional long chains of keratin fibers are held together by covalent bonding, hydrogen bonding, van der Waals forces, and hydrophobic interactions as well as significant levels of cross-linking based on cystine groups. When these bonds are chemically altered, the structure of the fiber, and therefore its stability, changes. Both monoethanol-
A majority of the keratin proteins are found in the cortex region of hair, specifically the cortical cells. Attempts to disrupt hair proteins, which are insoluble because of their cross-linked nature, will necessitate the breaking of these cross-linked disulfide bonds by either reduction or oxidation to form keratins or keratosis accordingly.

A typical hair dye contains tint and developer components. The dye reaction process involves the slow oxidation of primary coloring intermediates and the subsequent reaction with the coloring couplers, such as m-aminophenol or resorcinol. The tinting component is composed of alkalizing agents, coloring intermediates, and couplers. Alkalizing agents such as ammonia or MEA neutralize coloring primaries and swell the hair cuticle to facilitate the penetration of the color pigments deeper into hair oxidizing composition. Both aqueous ammonia and MEA are preferred hair-swelling agents for adjusting the pH of peroxide hair oxidizing compositions. Reducing agents prevent the premature oxidation of coloring intermediates and thereby stabilize the hair dye product until use. The developer component is made up of an oxidant, usually hydrogen peroxide (H₂O₂).

There is a solid understanding of the macroscopic structure of keratin fibers and there has also been some progress in our understanding of the mechanisms involved in the hair dyeing process. A recent review highlights the current understanding of permanent hair dyeing and natural hair color pigmentation processes. Yet despite the general understanding of active hair dye chemistry, the detailed impact of many of the commonly used chemicals on the physical properties of hair is poorly understood.

The main interest of this study is to develop an analytical method to measure the uptake of MEA and aqueous ammonia by keratin fibers, common active ingredients in many industrial applications, and to understand their subsequent impact on the physical and mechanical properties of hair. MEA is increasingly being used for setting and coloring hair, and it is currently being used as a replacement for ammonia because of ammonia’s unpleasant odor. One of the key challenges in replacing ammonia with MEA is the higher percentage of MEA (in comparison to ammonia) required to deliver the same bleaching effect, commonly referred to as the lightening intensity. However, high levels of MEA have been observed to cause a significant surface damage to fibers. Comparing equimolar amounts of MEA and ammonia (aq), scanning electron microscopy (SEM) images revealed cuticle loss and further investigations on protein loss indicated a higher level of damage caused by MEA than ammonia. This study did not investigate diffusion behavior and kinetics of uptake for the active species, which is critical for a detailed mechanistic understanding. It is therefore crucial to understand the impact of damage caused by MEA and ammonia, including the effects of concentration and temperature for specific alkalizer treatment times.

The general chemical and physical damages to the cuticles caused by chemical treatments have been established by several researchers. Although there is an emerging understanding of dye diffusion pathways and the factors influencing the process kinetics, published research into the kinetics of diffusion of molecules from aqueous solutions into hair for experimental times greater than 3 h is very limited. A few studies have investigated diffusion behavior for experimental times less than 100 min. Diffusion studies of different solutes in both wool and hair fibers have reported the following diffusion coefficients as summarized in Table 1.

Table 1. Diffusion Coefficients of Different Solutes in Aqueous Solution into Keratin Fibers

| fibre          | $D$ (cm$^2$/s) ($\times 10^{-9}$) | temperature (°C) | solute reference       | references |
|----------------|----------------------------------|-------------------|------------------------|------------|
| hair           | 5.67                             | room              | commercial hair dye    | 17         |
| bleached hair  | 0.82−1.0                         | 50                | rhodamine              | 18         |
| bleached cortex | 0.40−0.42                        |                   |                        |            |
| hair           | 1.83                             | 22                | feric acid             | 19         |
|                | 1.84                             |                   | caffeic acid           |            |
|                | 1.21                             |                   | gallic acid            |            |
|                | 1.21                             |                   | chlorogenic acid       |            |
|                | 2.57                             |                   | catechin               |            |
| hair           | 0.09                             | 25                | acid alizarin black    | 20         |
|                | 2.6                              |                   | azobenzene p-sulfonic acid |        |
|                | 4.8                              |                   | 4-amino-2-nitrophenol  |            |
|                | 3.2                              |                   | phenol                 |            |
| hair           | 1.0                              | 25                | water vapor            | 31         |
| wool           | 0.07                             | 25                | acid orange            | 21         |
| wool           | 0.14                             | 35                | acid orange            | 21         |
| wool           | 0.25                             | 50                | Cu$^{2+}$(II)          | 22         |
|                | 1.2                              |                   | Zn$^{2+}$(II)          |            |
|                | 1.0                              |                   | Ni(II)                 |            |

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impact of these active chemicals on the mechanical properties of the keratin fibers and provides supporting evidence on fiber damage as visualized using SEM and as detected via protein levels.

**MATERIALS AND METHODS**

**Materials.** MEA (Sigma >98%), aqueous ammonia (5.0 N, Fluka Analytical), European human head hair (International Hair Imports), and deionized water were used in this study. The hair has not been chemically altered prior to this experiment and is commonly referred to as "virgin hair".

**Instrumentation: GC–MS.** GC–MS analyses were performed with Shimadzu GC–MS QP2010. The carrier gas was He with a total flow rate of 43.4 mL/min, a column flow rate of 1.91 mL/min, a linear velocity of 50.0 cm/s, a purge flow rate of 3.0 mL/min at a pressure of 110.4 kPa, and a nominal split ratio of 20:1. Separation of the solute was achieved using a Restek RTx5 amine capillary column (30 m long, 0.25 mm diameter, and 1 μm thickness) (Restek Corporation, Bellefonte, PA) at temperatures of 250 °C, for both injector and interface, and 200 °C, for the ion source at a solvent cut time of 0.2 min. The initial oven temperature was 40 °C and set to increase at a rate of 6.5 °C/min until 75 °C. The final temperature of the oven was held at this temperature for a further 1 min. Before starting the main uptake experiment, background experiments were performed to establish the optimum GC–MS operational configuration as described below.

**Method: GC–MS.** The GC–MS detector sensitivity test was carried out to check if the detector is sensitive enough to detect low concentrations of MEA. The MEA concentration calibration curve was then obtained between 0.1 and 2.5 v/v % of MEA. Once this calibration has been established, the aliquots were diluted to ensure that the samples remained within the linear calibration range.

Once confidence was established on the GC–MS, the samples were prepared for the analysis. Careful and systematic sample preparation and preconditioning were required prior to the experiment for accurate sample analysis. Hair fibers were rinsed with deionized water, and any excess water from the hair was removed by gentle squeezing. Deionized water (200 ± 0.16 mL) and the hair samples were prepared 12 h before usage (n = 3). Hair, 2.5 g, was added to three different Erlenmeyer glass flasks and left to soak in the deionized water; the fourth flask was left as a control, that is, no hair. The solution temperature was maintained at the required temperature for each experiment. After 12 h when the hair was fully hydrated, a stock solution of MEA was added to each vessel to make up the required concentration (0.1, 1, and 5 v/v %). These flasks were maintained at either 30 or 50 °C. From the time at which MEA is initially added to each vessel, 0.5 mL of aliquots was taken from the solution every 10 min for the first hour and then at each hour for further 8 h and analyzed for the MEA content by using GC–MS. Before taking liquid samples (n = 3) to determine the MEA concentrations, the vessels were gently shaken.

**Instrumentation: GC-TCD.** A GC-TCD (6890N Agilent, UK) with a maximum oven temperature of 450 °C, a capillary column, and an automated injector (7683 series) were used. Although the purpose of this study is to make a direct comparison on the diffusion behavior of MEA and aqueous ammonia, because of the volatile nature of ammonia, extra precautions had to be implemented during sample preparation.

Virgin hair (three samples, ~1.5 g dry) was left to soak in deionized water (10 min) and then added to Erlenmeyer flasks (100 mL) which were capped with Suba-Seals (37 mm). The three flasks were filled with deionized water (109.5 g). A fourth reference flask was capped with a Suba-Seal and filled with deionized water (114.5 g). All flasks were left in an oven overnight at the required temperature. Ammonium hydroxide solution was added to the vials, and aliquots were taken in the same manner as the GC–MS method. However, because of the volatility of ammonia, a few modifications had to be made to the sample collection method. Aliquots were taken using a syringe. Once the liquid sample was taken, it was replaced with equal volume of deionized water. The collected samples with ammonia were kept in the fridge (5 °C), to prevent further evaporation, prior to the analysis on the GC-TCD equipment. Data were collected from Agilent 6890N with a TCD. To ensure the reliability of the data collected, the water peak was used as a reference and the concentration for ammonia in each sample was calculated by comparing the ratio of the NH3 peak to H2O peak areas.

**Instrumentation: Dia-Stron.** In order to determine whether the chemical treatment methods used affected the tensile properties of the hair, the wet tensile stress–strain curves were determined for treated hair samples and compared to virgin hair samples (Figure 1). To measure the diameters of dry hair fibers, a Dia-Stron automated diameter/tensile tester MTT600 (Dia-Stron Limited, UK) was used. The diameter measurements were carried out at 20 °C and 65% relative humidity. Hair fibers (25 per sample and 30 mm long) were attached with two crimping ferrules at both ends. The diameter measurement was carried out at several planes along the fiber axis as the fiber is rotated. The elliptic cross section of the fiber is calculated from short and long diameter at each plane (averaged). To carry out these wet tensile measurements, the fiber is soaked in water during the fiber testing at 25 °C. Each fiber is slowly stained until it breaks at a constant crosshead speed of 10 mm/min.

**Instrumentation: SEM.** A Hitachi S-3000N scanning electron microscope was used at 5 kV voltage. Hair samples were sputter-coated prior to the measurement with 15 nm of gold.

**METHOD: PROTEIN LOSS**

Approximately 0.5–0.56 g of hair tresses was prepared and distilled water was added (10× the mass of hair samples). The samples were then shaken at 2500 rpm for 60 min. At the end of 60 min, the aqueous hair tress extract was then separated leaving the hair samples behind. A working reagent was prepared by weighing 25 mL of bicinchoninic acid (BCA) reagent A with 0.5 mL of BCA reagent B. The working reagent solution prepared was bright green. Then nine standard solutions were prepared. The first standard solution was prepared by adding 1800 μL of distilled water and 1200 μL of albumin standard solution. Seven other standard solutions were prepared by adding 1000 μL of distilled water and 1000 μL of the albumin standard. The last solution was blank containing only 1000 μL of distilled water. A total of 25 μL of the standard, 25 μL of the hair tress extract, and 200 μL of the green working reagent solution were then mixed for 15 s and kept at 37 °C for 60 min. The solutions were analyzed for their protein content by using a NanoDrop 2000 spectrometer.
RESULTS AND DISCUSSION

For glassy biopolymers such as hair, both the solute concentration gradient and swelling/relaxation of the biopolymers contribute to the solute diffusion process. In this experiment, preswollen fibers are used to negate the effect of swelling/relaxation of the fibers on the diffusion rate of the penetrant molecules. The concentration of MEA was recorded using GC−MS from aliquots taken in vials containing hair, and the resultant fiber uptakes have been calculated. A decrease in the concentration of MEA in solution is observed for all samples because of MEA uptake by the fibers. The dimensionless uptake of solutes has been presented as a function of the square root of time in Figure 2 for 30 °C. These dimensionless data are not dependent on the actual MEA concentration.

Fickian diffusion is observed in Figure 2, with a constant initial slope in the initial uptake. All three concentrations exhibit a linear increase in the first hour with the fibers taking up 70% of the solutes within the first hour, followed by a gradual uptake in the remaining time for 30 °C at a second much lower slope, indicating a slower secondary diffusion.

The dimensionless uptake data for the solutes shown in Figure 3 for 50 °C show a much more complex behavior. However, all four data sets exhibit a common series of behavioral traits:

- For times <1 h, linear or initially linear Fickian diffusion data are observed
- For times of 1−5 h, uptake is constant or quasi-constant
- For times >5 h, some samples exhibited a second slower uptake kinetic

For 1 and 5 v/v % MEA solutions at 30 and 50 °C, a quasi-equilibrium was reached after an hour where almost no uptake was observed for further 2−4 h. In the 5% MEA experiment, the second step of the diffusion process is more pronounced for 50 °C, as shown in Figure 4. Although solution samples of the GC−MS analysis were collected over 9 h, a change in the concentration of MEA beyond the first hour was not detected in the GC−MS for 0.1% MEA solutions. For the rest of the concentration samples, the uptake at this second phase of diffusion is linear where 20% of the solutes are taken up in a quarter of an hour at 50 °C. The maximum absorption of MEA at this temperature was found to be 0.78% mass MEA per gram of virgin hair.

Further uptake of solute molecules by amorphous keratin domains after the initial quasi-equilibrium has been reached is shown to be an indicator of a possible relaxation-controlled diffusion.23 Given sufficient time and a range of temperatures, a behavior deviating from ideal Fickian diffusion to a relaxation-/swelling-controlled sorption process is expected for a given penetrant.23 However, in this work, preswollen hair fibers (hair hydrated overnight before adding MEA) have been used to minimize the impact of swelling on the diffusion behavior. Further uptake of solutes by the fibers over a long period of time shows that the experimental time scales given, 9 h, were not long enough to reach the absolute equilibrium.

For direct comparison with the data set for 5 v/v % MEA, the equimolar amount of aqueous ammonia was tested (3 v/v %). For aqueous ammonia, the maximum solute absorption occurs at 240 min and following this, the system begins to equilibrate (Figure 3). This is a similar time frame for the second-stage uptake of MEA. Comparison of the diffusion behavior of aqueous ammonia with that of MEA shows that under similar conditions, aqueous ammonia solutions exhibit only one distinctive mode of absorption into the studied hair samples. It can therefore be concluded that a one-stage absorption mechanism is the most likely contender for aqueous

Figure 2. Aqueous MEA uptake kinetics for 0.1, 1, and 5 v/v % at 30 °C over 9 h.

Figure 3. Aqueous uptake kinetics for 0.1, 1, and 5 v/v % MEA and 3 v/v % ammonia at 50 °C over 9 h.

Figure 4. Primary and secondary diffusion steps observed for the MEA uptake for 5 v/v % at 50 °C over 9 h fitted to a Fickian diffusion model in an infinite cylinder (solid line).
ammonia uptake for this experimental setup. Ammonia also shows a faster diffusion rate than MEA at the same temperature compared with 5% MEA. This however could also be due to the high volatility of ammonia from the solution. Because of the difficulty of the experimental setup for ammonia, we only present results for 3 v/v % at 50 °C.

Assuming the fiber to be an infinitely large cylinder in an infinitely large solute bath, the solute uptake process is controlled by the rate of diffusion into the fiber and can be described by Wilson's equation:

\[
\frac{C_t}{C_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(a + 1) \exp(-a^2q_n^2)}{4 + 4\alpha + a^2q_n^2} \tag{1}
\]

\(C_t/C_\infty\): ratios of the amount of diffusant at time \(t\) and at equilibrium, \(r\): the radius of the fiber (35 μm), \(D\): the diffusion coefficient, \(\alpha\): the ratio of the diffusant in the solution and in the fiber at equilibrium, \(q_n\): values for the roots \(q_n = \left(n + \frac{1}{4}\right)\pi - \tan^{-1} 8q_n\).

Using eq 1, and the experimental values for \(C_t/C_\infty\) the corresponding values for the diffusion coefficients can be determined.

The diffusion coefficients calculated in Table 2 are all of a magnitude similar to those found for cationic diffusion in wool at 50 °C and for acid diffusion in hair at 32 °C, as listed in Table 1. At an elevated temperature, 50 °C, a larger diffusion coefficient was observed for the initial step than for the secondary uptake step at high MEA concentrations.

The amorphous keratin found in the cuticle allows water and other dyes to diffuse through, but it is more resistant to diffusion than the cortex. However, in a short time period, it is possible to observe the diffusion behavior of small molecules penetrating through the fibers into the cortex. During the diffusion process, the active molecules first penetrate the cuticle and subsequently the cortex, which are chemically and morphologically different. Table 3 shows the distance of penetration for MEA molecules calculated using the Einstein–Smoluchowski equation, \(D = L^2/2t\), where \(L\) represents the average distance travelled by the MEA molecules at a given time \(t\).

Examining the results reported in Table 3 with an average fiber diameter of 70 μm illustrates that the molecules have started to penetrate into the cortex of the material within the first few minutes, and even faster at higher temperatures.

Overall, increasing the initial concentration of solutes in the solution results in an increase in the final concentration of MEA in the fibers as expected.

From Figure 4, it can be seen that when the experimental temperature is raised to 50 °C, the apparent equilibrium uptake increases again introducing a second stage of solute sorption into the fibers. Although there is no reported explanation for the two-stage behavior observed here, three possible explanations for the two-step diffusion/sorption of MEA are suggested below. However, a detailed examination of these factors is not considered in this current work.

i. Diffusion of MEA into elements of the substructure, for example, crystalline fibrils

ii. Hydrolysis of the proteins. The thioester linkage between the F-layer (18-methyleicosanoic acid) and the A-layer protein is hydrolyzed

iii. Additional protein degradation at the second stage

For scenario (i), the initial uptake is due to penetrants diffusing through the cuticle layer, followed by a second step where molecules diffuse into the crystalline domains. However, as hair fibers have a low surface area (less than 0.2 m²/g), adsorption on the fiber surface will not be a dominant process for the observed 100 min.

For scenario (ii), at high MEA concentrations and temperatures, as well as for long experimental times, a phenomenon is observed similar to what was observed in relaxation chemistry: hydrolysis of peptide bonds, lanthionine formation, and breakdown of S–S bonds, resulting in a loss in tensile strength. This scenario anticipates that the thioester linkage between the F-layer (18-methyleicosanoic acid) and the A-layer protein has been hydrolyzed, removing the hydrophobic surface barrier and creating sulfonate groups. Such reactions are likely to take place in the experiments carried out in this study using solutions with a very high pH, a chemistry well understood in the detergent industry where high pHs are used to remove fats and greases. Possible reaction mechanisms that could take place in keratin fibers due to the action of alkalinity have been discussed in more detail.

Scenario (iii) anticipates that more protein degradation occurs at high MEA concentration and for longer time. For this scenario to be accepted a potential hypothesis for a two-step diffusion, a difference in protein loss for different experimental times is expected.

### Table 2. Diffusion Coefficients Calculated Using Eq 1

| Concentration (%) | Initial Uptake Step | Secondary Uptake Step | Initial Uptake Step | Secondary Uptake Step |
|-------------------|---------------------|-----------------------|---------------------|-----------------------|
| 0.10              | 4.0 × 10⁻¹⁰        | 0.5 × 10⁻¹⁰           | 16.0 × 10⁻¹⁰        | N/A                   |
| 1                 | 4.0 × 10⁻¹⁰        | 0.5 × 10⁻¹⁰           | 5.3 × 10⁻¹⁰         | N/A                   |
| 5                 | 4.0 × 10⁻¹⁰        | 0.5 × 10⁻¹⁰           | 4.5 × 10⁻¹⁰         | 1.4 × 10⁻¹⁰           |
| Ammonia (aq)      | 3                   | N/A                   | 13.0 × 10⁻¹⁰        | N/A                   |

### Table 3. Theoretical Penetration Distance of MEA Molecules Using the Einstein–Smoluchowski Equation

| Concentration (%) | Penetration Distance (μm) for a Given Concentration at 30 °C | Penetration Distance (μm) for a Given Concentration at 50 °C |
|-------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| 0.10%             | 1%                                                            | 5%                                                            |
| 5                 | 5.2                                                           | 4.9                                                           | 9.6                                                           | 5.6                                                           | 5.2                                                           |
| 20                | 10.4                                                          | 9.7                                                           | 8.8                                                           | 19.3                                                          | 11.3                                                          | 10.4                                                          |
| 30                | 12.7                                                          | 11.9                                                          | 10.5                                                          | 23.6                                                          | 13.8                                                          | 12.7                                                          |
| 60                | 18.0                                                          | 16.8                                                          | 14.8                                                          | 33.4                                                          | 19.5                                                          | 18.0                                                          |
| 120               | 25.5                                                          | 23.8                                                          | 21.0                                                          | 47.2                                                          | 27.6                                                          | 25.4                                                          |
| 240               | 36.0                                                          | 33.7                                                          | 29.7                                                          | 66.8                                                          | 39.0                                                          | 36.0                                                          |
Tensile Properties. Hair damage is one of the major consumer worries, and its property is often related to breakage, which hinders hair growth. In order to determine whether the treatment methods used in previous experiments affect the tensile properties of the hair, the load–elongation curves of the chemically treated fibers have been measured and compared to virgin hair samples. Figures 5 and 6 show a clear difference in tensile properties between “as received” virgin hair and “treated” hair samples. The largest change in mechanical property is observed for hair treated with 5 v/v % MEA, indicating the significance of damage to the keratin fibers at high MEA concentrations. The data of tensile properties correlate with the two-phase behavior observed. There is no significant change with time for the hair treated with ammonia, but for MEA-treated hair, the change is visible.

Figure 5 shows that a steep increase in stress is observed up to 2.5% fiber extension where yields commence, and then the fiber continues to yield until it reaches ~25% strain with minimal change in the yield stress of 40–50 MPa. Both virgin hair and ammonia (aq)-treated hair exhibit a similar stress–strain behavior. For MEA-treated fibers, the yield region is observed at a lower stress, 20–30 MPa. After 25% extension, the fiber stresses continue to increase until a failure condition is reached. Both the yield and post-yield regions indicate a typical viscoelastic behavior.

It has been previously reported that the tensile properties of hair are mostly related to the cortex, not the cuticle. For a wet virgin hair, the Young modulus has been reported to be in the regions of 1.5–2.0 GPa with a break/failure stress of 192 MPa for a Caucasian hair. The wet tensile properties of keratin fibers are related to the disulfide bonds and higher concentrations of alkalizers that are known to cause tensile damage. A study by Arai and co-workers reported on the mechanical stability with a high number of cross-links. This presents a potential explanation for a reduction in tensile strength when fibers are treated at high MEA concentration. The mechanical properties reported here indicate that even when used alone, MEA has a significant impact on the tensile property of hair. This observation is no surprise as chemical treatments are known to cause damage on hair, which can be reflected in keratin fiber tensile properties.

Further analysis to investigate the impact of both MEA and ammonia (aq) was carried out by comparing the protein loss of the samples. The samples were taken both after 1 and 9 h immersion in the solutions. The measurement was only carried out for the samples treated at 50 °C.
Figure 7 shows the highest protein loss for the hair treated with MEA, which is fully consistent with the chemical damage to the keratin structures which might include hydrolysis. More interestingly, the hair treated with MEA even for 1 h shows more protein loss than aqueous ammonia for 9 h. For long treatment times, the data show a linear increase in protein loss for both types of treatments. Overall, these data show more protein damage for MEA versus ammonia, which increases with time. However, this increase in time is the same with both alkalisers.

There is visibly more damage (Figure 8) caused to the cuticle, where the highest cystine content is found, because of MEA than ammonia, and higher concentrations of alkalisers exacerbate this damage.

The SEM figures (Figure 8) correlate with the protein loss, showing a more visible cuticle loss for MEA versus ammonia. When the hair is subjected to oxidative conditions and inevitably prone to damage, cysteic acid levels are often measured to quantify the amount of damage to the fibers. However, this method alone is not sufficient enough to quantify the amount of damage caused to the fibers as it might not take account of the different pathways hair damage can be measured. In this report, further work has been done to quantify protein loss because of the different hair treatments. Protein loss enables us to quantify the oxidative damage.

The SEM images presented in Figure 8 and the protein loss data in Figure 7, in addition to the tensile test measurements provided, confirm the significance of oxidative damage by both MEA and aqueous ammonia at different concentrations and experiment time frames.

CONCLUSIONS

Experimental studies on hair have indicated a significant change in mechanical properties when exposed to a high aqueous concentration of MEA. A GC–MS technique has revealed a new key insight into the diffusion behavior of MEA, with a two-step diffusion/sorption process being observed that has not been reported before. Diffusion coefficients have been calculated to be a magnitude of $10^{-10}$ cm$^2$/s. A comparison with aqueous ammonia uptake showed a smaller uptake than MEA. MEA-treated hair (5%) has shown the largest decreases in tensile properties compared to other treatments as well as untreated hair samples. It is however possible to use MEA at low concentrations without causing measurable damage. However, high concentrations such as 5% MEA will result in keratin fibers that exhibit significant damage, lower tensile mechanical properties, and visual surface damage.

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REFERENCES
(1) Seo, J.-A.; et al. Hydrogen peroxide and monoethanolamine are the key causative ingredients for hair dye-induced dermatitis and hair loss. J. Dermatol. Sci. 2012, 66, 12–19.
(2) Bailey, A. D.; Zhang, G.; Murphy, B. P. Comparison of damage to human hair fibers caused by monoethanolamine and ammonia-based hair colorants. J. Cosmet. Sci. 2014, 65, 1–9.
(3) Dawber, R. Hair: its structure and response to cosmetic preparations. Clin. Dermatol. 1996, 14, 105–112.
(4) Leon, N. H. Structural aspects of keratin fibres. J. Soc. Cosmet. Chem. 1972, 23, 427–445.
(5) Roe, H. Z.; Lipson, B. The Structure of a Merino Wool Fibre in Textile and Fibre Technology Program; CSIRO: Materials Science & Engineering, 1992–2006.
(6) Feughelman, M. Mechanical Properties and Structure of Alpha-Keratin Fibres: Wool, Human Hair and Related Fibres, 2nd ed.; Australia UNSW Press: Sydney, 1997.
(7) Murphy, B. P. Hair colourants. Poucher’s Perfumes, Cosmetics and Soaps; Springer, 2000; pp 307–324.
(8) Menkart, J.; Wolfram, L. J.; Mao, I. Caucasian Hair, Negro Hair, and Wool—Similarities and Differences. J. Soc. Cosmet. Chem. 1966, 17, 769–787.
(9) Rastogi, S. C.; et al. Unconsumed precursors and couplers after formation of oxidative hair dyes. Contact Dermatitis 2006, 55, 95–100.
(10) Boswell, H. D.; et al. Compositions Suitable for the Treatment of Hair Comprising Chelants and Methods for Reducing Oxidative Hair Damage. PCT/US2002/008477, 2002.
(11) Prem, P.; et al. New insights into the physicochemical effects of ammonia/peroxide bleaching of hair and Sepia melanos. J. Cosmet. Sci. 2003, 54, 395–409.
(12) Morel, O. J. X.; Christie, R. M. Current trends in the chemistry of permanent hair dyeing. Chem. Rev. 2011, 111, 2537–2561.
(13) Sigrid, B. R.; Binhua, Y.; Yash, K. MEA Possess Characteristics of Both Alcohols and Amines Acting Readily as a Nucleophilic and Hygroscopic Molecule in IFSCC Magazine, 2008; pp 131–137.
(14) Xing, X.; et al. Structural change of human hair induced by mercury exposure. Environ. Sci. Technol. 2013, 47, 11214–11220.
(15) Im, K. M.; Kim, T.-W.; Jeon, J.-R. Metal-Chelation-Assisted Deposition of Polydopamine on Human Hair: A Ready-to-Use Eumelanin-Based Hair Dyeing Methodology. ACS Biomater. Sci. Eng. 2017, 3, 628–636.
(16) Güney, K. A.; et al. Selective Peptide-Mediated Enhanced Deposition of Polymer Fragrance Delivery Systems on Human Hair. ACS Appl. Mater. Interfaces 2017, 9, 24238–24249.
(17) Chandrashekar, M. N.; Ranganathiah, C. Diffusion of permanent liquid dye molecules in human hair investigated by positron lifetime spectroscopy. Colloids Surf., B, 2009, 69, 129–134.
(18) dos Santos Silva, A. L.; Joekes, I. Rhodamine B diffusion in hair as a probe for structural integrity. Colloids Surf., B, 2005, 40, 19–24.
(19) Wang, L.; et al. Kinetics and equilibrium of solute diffusion into human hair. Ann. Biomed. Eng. 2012, 40, 2719–2726.
(20) Holmes, A. W. Diffusion Processes in Human Hair. J. Soc. Cosmet. Chem. 1964, 15, 15595–15608.
(21) Hudson, R. F. The Kinetics of Acid Absorption on Wool Fibre; Royal Society of Chemistry, 1953.
(22) Balko, D.; Baltacioglu, H. Adsorption of Heavy Metal Cations from Aqueous Solutions by Wool Fibers. J. Chem. Technol. Biotechnol. 1992, 54, 393–397.
(23) Berens, A. R.; Hopfenberg, H. B. Diffusion and relaxation in glassy polymer powders: 2. Separation of diffusion and relaxation parameters. Polymer 1978, 19, 489–496.
(24) Etters, J. N.; Urbanik, A. An automated computation of diffusion equation solutions. Text. Res. J. 1983, 53, 598–605.
(25) Robbins, C. R.; Crawford, R. J. Cuticle damage and the tensile properties of human hair. J. Soc. Cosmet. Chem. 1991, 42, 59–67.
(26) Robbins, C. R. Chemical & Physical Behaviour of Human Hair, 5th ed.; Springer: New York, 2012.
(27) Chapman, B. M. IS-A REVIEW OF THE MECHANICAL PROPERTIES OF KERATIN FIBRES. J. Text. Inst. 1969, 60, 201–207.
(28) Barel, A. O.; Paye, M.; Mailbach, H. I. Handbook of Cosmetic Science and Technology; CRC Press, 2014.
(29) Arai, K.; et al. Crosslinking structure of keratin. I. Determination of the number of crosslinks in hair and wool keratins from mechanical properties of the swollen fiber. J. Appl. Polym. Sci. 1989, 38, 1159–1172.
(30) Evans, T. Measuring hair strength, part II: Fiber breakage. Cosmet. Toilet. 2013, 28, 854–859.
(31) Wortmann, F.-J.; Hullmann, A.; Popescu, C. Water Management of Human Hair. Int. J. Cosmet. Sci. 2008, 30, 386–389.