Influencing Absorption and Desorption of Ions in Human Hair

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Changing the Absorption and Desorption Properties of Human Hair by Ion-Induced Matrix Modification

Erik Schulze zur Wiesche (Henkel)
Rene Krohn (Henkel)
Stefanie Freye (University Manchester)
Franz Josef Wortmann (University Manchester)
Content

- Keratin composition of hair
- Chemical oxidation of hair
- Effects of pH adjustments on the hair matrix
- Modification of absorption and desorption properties of hair
- Conclusions
Morphological Structure of Human Hair

- Semi-crystalline intermediate filaments (IFs) are embedded in an amorphous matrix
Morphological Structure of Human Hair

“Simplified Models”

**Two-phase model (2PM)**
*Feughelman 1959*

- C: crystalline filaments
- M: amorphous matrix

**“Three-phase” model (3PM)**
*Popescu 2012*

- Amorphous Matrix (IFAP)
- Crystalline Interface
- Rod (IF) (Side chains)

- 2PM: IFs and amorphous matrix are mainly responsible for the hair strength
- 3PM: The interface contributes significantly to the fiber stability
Composite structure of Human Hair

Fiber reinforced composite

- Semi crystalline IFs are embedded in the amorphous protein matrix

SEM of transverse section of sheep’s wool: IFs (approx. 8 nm diameter) by Parry 1997
Composite Structure of Human Hair

Matrix

- KAP – keratin associated proteins with high content of cystine
- Matrix stabilizes the embedded semi crystalline IFs
- Formation of cysteic acid due to chemical treatments
- Penetrable by water and the swelling component in hair
- Area for oxidative dye reactions
Bleaching Stress on Hair
Materials and formulation

• **Hair Samples:**
  Kerling European Hair 7.0

• **“Ultra Bleaching”** (commercial product):
  potassium persulphate mixed with a hydrogen peroxide solution (9%) in a ratio of 1:2, pH-value of 10.2-10.5 for 45 minutes
Bleaching Stress on Hair
Cleavage of S-S bonds in the KAP-Matrix

- Bleaching leads to cleavage of cystine and the formation of cysteic acid (pKa1.3)
Bleaching Stress on Hair
Formation of cysteic acid

R-S-S-R → ... → 2 x R-SO$_3^-$
Cystine Cysteic acid
Bleaching Stress on Hair
Effects on the swelling behavior

- Bleached hair swells approx. 50% more than virgin hair
Bleaching Stress on Hair  
Effects on color retention

- Bleached hair losses approx. 50% more color than virgin hair
Bleaching Stress on Hair
Effects on the thermal stability

- The denaturation temperature decreases strongly with bleaching
The “Self Recovery Phenomenon”

Tensile and DSC measurements on ultra bleached hair

- $T_D$ increases and break extension decreases over a period of 6 months
Time-Related Inner Structural Changes

Hypothesis

- Formed cysteic acid dives a reorganization process of the secondary protein structure within the amorphous matrix
Ionic-Modification of Matrix
Influence on the uptake of Cu$^{2+}$ ions

- EDX analysis of Cu atoms on 2 x bleached hair with and without pretreatment of 1 % EDTA before applying 1 % Cu(II)SO$_4$

\[
\begin{align*}
\text{Cu [At%]} & \\
\text{bleached/ untreated} & \quad 1.1 \pm 0.06 \\
\text{bleached / treated} & \quad 0.4 \pm 0.02
\end{align*}
\]

- EDTA and acetic acid pretreatments at pH 4.4 reduces the Cu uptake of hair up to 65 %
Ionic-Modification of Matrix
Hypothesis

- Adjustment of an isoionic pH value and the presence of multivalent ions stabilizes the hair matrix by the formation of ionic bonds.
Determination of Color Retention
Method

**Hair Color:** Schwarzkopf Igora Royal
**Shades:**
- 6-88 (dark red)
- 6-99 (violet)
- 9-98 (violet red)
- 7-77 (copper)
- 4-88 (dark red)
- 5-88 (dark red)
- 6-68 (red brown)
- 0-88 (light red)

**Shampoo:** 2% cocoyl amphoacetate, 4% cocoamidopropyl betain, 8.8 % LES

**Beaker Screening test:**
20 % shampoo solution for 4 hours stirring

**Ultra sonic washing simulation:** 2,5 % shampoo solution 5 min ultra sonic bath (3 hand washes)

**Hand washes on strands:** 0,05 g shampoo/g hair, 30 sec shampooing, 30 sec application, 1 min rinse off
Color Retention and Color Shift
CIE-L-a-b Color Analysis

\[ \Delta E = \sqrt{ \left( L_C - L_s \right)^2 + \left( a_c - a_s \right)^2 + \left( b_c - b_s \right)^2 } \]
Color Retention and Color Shift
CIE-L-a-b Color Analysis

Color Retention: \( \Delta E_{CR} = \Delta E_{01} - \Delta E_{02} \)
Color Shift: \( \Delta E_{CS} \)
Ionic-Modification of Matrix

Influence of pH on color shift $\Delta E_{CS}$ and color retention $\Delta E_{CR}$

- Strong differences between $\Delta E_{CS}$ and $\Delta E_{CR}$
- Highest color stability at pH 4.5 in the range of the isoionic point of hair
Ionic-Modification of Matrix

Influence of pH on color $\Delta E_{CS}$ and denaturation $T_D$

<table>
<thead>
<tr>
<th>pH</th>
<th>$\Delta E_{CS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.75</td>
<td>13.0</td>
</tr>
<tr>
<td>4.0</td>
<td>13.5</td>
</tr>
<tr>
<td>4.25</td>
<td>14.0</td>
</tr>
<tr>
<td>4.5</td>
<td>14.5</td>
</tr>
<tr>
<td>4.75</td>
<td>15.0</td>
</tr>
<tr>
<td>5.0</td>
<td>15.5</td>
</tr>
</tbody>
</table>

- Thermal stability and color stability show maxima at pH 4.5

DSC measurement of 2 x bleached hair 24 h in pH controlled aqueous solution
Ionic-Modification of Matrix
Influence of organic acids on the color shift $\Delta E_{CS}$

- Significant differences between organic acids
- Ca lactate shampoo shows the strongest effect

![Graph showing the influence of organic acids on the color shift $\Delta E_{CS}$](image-url)
**Ionic-Modification of Matrix**

Influence of organic acids on the color shift $\Delta E_{CS}$

<table>
<thead>
<tr>
<th>sham. pH 5.5</th>
<th>sham. pH 4.5 tartaric acid 2%</th>
<th>sham. pH 4.5 malic acid 2%</th>
<th>sham. pH 4.5 lactic acid 2%</th>
</tr>
</thead>
</table>

[Image showing different hair samples under varying conditions]
Ionic-Modification of Matrix
Influence of oxidative hair color

- Effects based on pH depend strongly on the hair color
- Ca lactate shows an increase of color retention on all tested shades
Ionic-Modification of Matrix
Hand washes with commercial shampoos

- hair strands after 12 hand washes with commercial shampoos without Ca lactate at pH 4.75 with Ca lactate at pH 4.5
Conclusion

- The amorphous matrix is the key target of the inner hair structure for cosmetic treatments
- Oxidative treatments lead to unstable matrix conditions
- Ionic induced matrix modification can re-stabilize the inner hair structure and improve the retention of oxidative colors at the same time
- Hair treatments of pH 4.5 show a maximum effect on bleached hair
- The color retention strongly depends on the choice of organic acid and the ions
- Strong effects could be found for Ca lactate