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 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 sheeps 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

\[ R-S-S-R \rightarrow \ldots \rightarrow 2 \times R-SO_3^- \]

Cystine \hspace{5mm} Cysteic acid

![Bar chart showing the formation of cysteic acid in different bleaching conditions.](chart.png)
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

\[
y = -0.0216x + 15.356 \\
R^2 = 0.8161; p = 0.00
\]

\[
y = 0.0245x + 140.44 \\
R^2 = 0.9272; p = 0.00
\]
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$_4$

- 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 amphotacetate, 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

\[ dE = \sqrt{\left( (L_C - L_s)^2 + (a_c - a_s)^2 + (b_c - b_s)^2 \right)} \]
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 isionic point of hair
Ionic-Modification of Matrix

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

- 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
Ionic-Modification of Matrix

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

<table>
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<th>Condition</th>
<th>pH</th>
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<td></td>
<td>malic acid 2%</td>
<td></td>
<td>lactic acid 2%</td>
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</tr>
</tbody>
</table>

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*Henkel*
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**.