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Assessing the Properties of Thermally Treated Human Hair by Tensile Testing and DSC: Are They Complementary or Equivalent Methods?

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α-Keratin: General Morphology of a Fiber and relevant model approaches
Background & Research Question

Two important methods for R&D as well as marketing claim support in the hair cosmetic industry are:

**Tensile Testing (wet): Young’s Modulus**

**Differential Scanning Calorimetry of human hair in water (DSC\textsubscript{w}): Denaturation temperature & enthalpy**

Both of these aspects of the methods are in special ways related to a specific 2-phase model.

Do the methods lead to independent, synergistic results or is there an inherent connection/correlation?

Or are things a bit more complicated ???

The investigation requires a set of samples, which have been tested by tensile testing as well as by DSC.

The samples should differ substantially in their physical and chemical history due to systematic and well defined treatments.

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**Background of Study: Thermal Hair Straightening**

The established practice of treating slightly curly or frizzy European hair with flat, heated devices provides an effective grooming tool to achieve straight hair.

The effect is reasonably stable until exposure to humid conditions or washing.

Due to the relevance of this grooming practice, the expert working group ‘Hair Care Products’ of the German Association for Scientific and Applied Cosmetics (DGK) conducts a comprehensive study to contribute to our understanding of the changes of European hair through thermal straightening.

This part of the investigation focuses on the analytical determination and quantification of such changes & the potential synergisms of bleaching.
Treatment Schedule & Methods: DWI, Aachen, D

Modeling 2 month, 6 month, 1.5 years of hair care cycles (less washing)

Virgin hair → Bleaching, 2x → Damaged hair

N11 N12 N21 N22 N31
100°/200°C dynamic Zymat
300°/200°C dynamic Zymat
800°/200°C dynamic Zymat

B11 B12 B21 B22 B31

Tensile Testing
HP-DSC
Knot Test/SEM & further methods

N01 N02
Reference, virgin
B01 B02
Reference, bleached

Keratin Stress/Strain Curve (wet)

E_w = 2.1 GPa
E_IW = 1.7 GPa
E_M = 0.4 GPa

The stress/strain-curve of a keratin fibre in the wet state shows three distinct regions.
The specific behaviour in the regions is essentially associated with the strain-induced transformation of α-helical into β-sheet material in the IFs. The matrix behaves as a low modulus, thixotropic gel.

The Young’s modulus (wet) is a composite parameter. It contains a large contribution by the IFs and a small one by the matrix.

http://www.diastron.com/
Water depresses the denaturation temperatures of keratins compared to the dry state by approx. 80°C and removes the peak(s) out of the range of pyrolysis (>220°C).

As a first approximation, the peak area (denaturation enthalpy, $\Delta H_D$) is associated with the thermal stability of the filaments, while the peak location (denaturation temperature, $T_D$) is related to the properties of the matrix and, namely, its viscosity.

DSC is a large number fibre test.
For bleached hair, apparent linearity is limited to a treatment time of about 300 s. Beyond this, modulus and temperature approach limiting values, while enthalpy continues towards zero.

Overall apparent linearity is observed for untreated hair within the experimental time range of heating (200 °C, 0 - 800 s).

Consideration of Matrix Properties: $E_w$ vs $T_D$

- The relationships between $E_w$ and $T_D$ appear to be largely linear and are attributed to a net decrease of cross-link density in the matrix.
- The lines meet at the point where the linear relationships break down. This is assumed to indicate that hair starts to turn into an amorphous, brittle polymer, in line with practical observations.
- The bleaching pre-treatment decreases the initial cross-link density and sensitizes the matrix for the change into a thermoset polymer.
- The limiting modulus (wet) is estimated as $\approx 0.9$ GPa.

D Istrate, Diss RWTH Aachen, D, 2011
Consideration of IF properties: $E_w$ vs $\Delta H_D$

- The relationships between $E_w$ and $\Delta H_D$ appear (again) as largely linear.
- The intercept of the line for untreated hair ($\Delta H_D = 0$ : no $\alpha$-helix) coincides with the limiting modulus.
- For bleached hair, the denaturation of helical material continues, while the matrix has already been turned into a thermoset polymer.
- This confirms that the chemical pre-damage sensitizes the matrix in a specific way, which can be linked to the thermal instability of the disulphide cross-links.
- The limiting lower modulus (wet) is (again) consistently estimated as $\approx 0.9$ GPa

Considerations of Effects Underlying the Correlations

- Observations from the correlations are consistent.
  - $E_w$ represents a composite parameter.
  - DSC$_w$ distinguishes between effects on IFs and matrix.

However,

- The differences for the correlations for IFs ($\Delta H_D$) and matrix ($T_D$) indicate that individual kinetics of the changes – as a hidden dimension of the correlations - can be expected to be quite different.
Matrix: Heat Damage Kinetics

- The matrix shows a fast damage development with heat and intermittent wetting. This is attributed to the specific sensitivity of the disulphide bonds.
- By bleaching the matrix is further sensitized.

\[ T_D = T_D^\infty + (T_D^0 - T_D^\infty) \exp(-k_H t) \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Natural Hair</th>
<th>Oxidized Hair</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_D^0 ), °C</td>
<td>154.9 ± 0.37</td>
<td>140.6 ± 0.60</td>
</tr>
<tr>
<td>( T_D^\infty ), °C</td>
<td>145.6 ± 1.07</td>
<td>134.1 ± 0.54</td>
</tr>
<tr>
<td>( k_H ), 200°C ± SE, 10^{-4} s^{-1}</td>
<td>2.4 ± 0.64</td>
<td>10.3 ± 3.33</td>
</tr>
<tr>
<td>( t_{1/2}, \text{min} )</td>
<td>4.8</td>
<td>1.1</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.981</td>
<td>0.939</td>
</tr>
</tbody>
</table>

The half-time for the matrix to turn into a brittle thermoset polymer is decreased for bleached hair from ≈5 to ≈1 min.

\( T_D^\infty \) for natural hair is higher than predicted from the correlation (≈135 °C). However, a nearly equally good fit can be achieved by including the limiting, lower temperature as a restriction. This increases \( t_{1/2} \).


IFs: 1st Order Heat Damage Kinetics

\[ \Delta H_D = \Delta H_D^0 \exp(-k_H t) \]
\[ \ln \Delta H_D = \ln \Delta H_D^0 - k_H t \]

- The decrease of \( \Delta H_D \) follows pure 1st order kinetics. The amount of α-helical material in the IFs goes to zero, when hair turns into an amorphous duroplast.
- The reaction rate constants and thus the half-times are not significantly different: \( t_{1/2} \approx 20-25 \) min
- Apart from the initial drop in \( \Delta H_D \) there is no specific sensitization of the IFs by bleaching
- The half-time for the IF heat damage is much longer than for the matrix (20-25 min vs 1-5 min)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Natural Hair</th>
<th>Oxidized Hair</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ln \Delta H_D^0 ) ± SE</td>
<td>2.83 ± 0.016</td>
<td>2.55 ± 0.027</td>
</tr>
<tr>
<td>( k_H ), 200°C ± SE, 10^{-4} s^{-1}</td>
<td>5.2 ± 0.37</td>
<td>4.4 ± 0.67</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.902</td>
<td>0.676</td>
</tr>
</tbody>
</table>

For natural and bleached hair changes of $E_w$ follow different kinetical paths.

- There is a tendency towards $m < 1$, taken as indication for two underlying processes.
- $t_{1/2}$-values indicate that, for natural hair the kinetics are controlled by the IFs, while for bleached hair they are controlled by the matrix.
- This discrepancy is attributed to increased sensitivity of the matrix in bleached hair to turn into a brittle, amorphous polymer.

### Table

<table>
<thead>
<tr>
<th></th>
<th>Natural</th>
<th>Bleached</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$, GPa</td>
<td>1.84</td>
<td>1.60</td>
</tr>
<tr>
<td>$E_\infty$, GPa</td>
<td>0.9 (fixed)</td>
<td>0.79</td>
</tr>
<tr>
<td>$m$</td>
<td>0.965</td>
<td>0.895</td>
</tr>
<tr>
<td>$t_{1/2}$, min</td>
<td>22.7</td>
<td>4.36</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.965</td>
<td>0.988</td>
</tr>
</tbody>
</table>

$E(t) = E_\infty + (E_0 - E_\infty) \exp (-t/\tau)^m$

$
\begin{align*}
\frac{1}{2} & \Delta H (N & B) = 20 \text{ – } 25 \text{ min} \\
\frac{1}{2} & \Delta t_D (N \approx 5 \text{ min}, \ B \approx 1 \text{ min})
\end{align*}
$

**Conclusion - 1**

**DSC vs Modulus Testing (wet): Are They Complementary or Equivalent Methods?**

**Both !**

**It depends!**

http://study-aids.co.uk/dissertation-blog/research-methods/

https://www.15five.com/blog/4-scientifically-proven-methods-increase-productivity/
Conclusions - 2

DSC vs Modulus Testing (wet): Are They Complementary or Equivalent Methods?

• While $E_w$ represents a composite parameter, DSC$_w$ distinguishes between effects on IFs and matrix.
• However, considerations only apply where a model-based approach suggest an overlap of analytical concepts.

Thus

• Potential correlations between further TT- & DSC- parameters have still to be analysed.
• The general approach is suggested to apply for irreversible changes/damage to hair structure (bleaching, waving, radiation) and may give some novel insights (synergisms).
• Validity of the approach for reversible changes (e.g. pH) is expected to be more complicated

Acknowledgements

The authors are grateful to the working group ‘Hair Treatments’ (Chairman: Dr.J.Wood) of the DGK (Deutsche Gesellschaft fuer Wissenschaftliche und Angewandte Kosmetik e.V.) for the opportunity to use data, which were generated by DWI (Aachen) as part of a group project on the effects of thermal treatments on human hair. In this context, the authors wish to specifically acknowledge the contribution of Dr. P Augustin (DWI) for sample treatment and data acquisition.
Thank you for your attention!