Comparison of macro-, micro- and nanomechanical properties of clinically relevant UHMWPE formulations

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  (micromechanical properties, infrared microspectroscopy)

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  (macro- and nanomechanical properties, DSC, SAXS)

Background of the slides in this presentation:

- **Yellow slides**: Intro, Conclusion
- **Gray slides**: Theory, Models
- **Green slides**: Reality, Results

Goethe JW, Faust: *All theory is gray, my friend. But forever green is the tree of life.*
Introduction

There are many different UHMWPE formulations on the market...

This study: 11 clinically relevant UHMWPE formulations, coming from USA [1].

<table>
<thead>
<tr>
<th>Sample series</th>
<th>Sample ID</th>
<th>Full sample name</th>
<th>Manufacturer</th>
</tr>
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<tbody>
<tr>
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<td>Quadrant</td>
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<tr>
<td></td>
<td>PE-4b</td>
<td>GUR 1020 AO 80kGy</td>
<td>De Puy</td>
</tr>
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</table>

What was known before we started?

Experiments [1]: macro- and nano-mechanical properties → somewhat different behavior

Theory [2]: micro-hardness of UHMWPE \( \propto \) macro-yield/modulus \( \propto \) crystallinity

What we wanted to study \( \Rightarrow \) correlations of macro-micro-nano-properties

In other words: Are micro/nanoindentation suitable for UHMWPE characterization?

References (detailed list of references is given at the end of this presentation).

### Experimental

**What mechanical properties did we measure?**

<table>
<thead>
<tr>
<th>Method</th>
<th>Modulus</th>
<th>Yield stress/Hardness *</th>
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</thead>
<tbody>
<tr>
<td>MACROscopic compression</td>
<td>$E$</td>
<td>$Y$</td>
</tr>
<tr>
<td>Non-instrumented MICROindentation</td>
<td>-</td>
<td>$MH/H_V$</td>
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<tr>
<td>Instrumented MICROindentation</td>
<td>$MHI/E_{IT}$</td>
<td>$MHI/H_{IT}$</td>
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<tr>
<td>Instrumented NANOindentation</td>
<td>$NHI/E_{IT}$</td>
<td>$NHI/H_{IT}$</td>
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</table>

* Yield stress and hardness of semicrystalline polymers are proportional: $H \approx 3Y$

**How did we characterize UHMWPE morphology?**

- IR: oxidation index (IR/OI), trans-vinylene index (IR/VI), and crystallinity index (IR/CI)
- DSC: heating up to 200 °C, determination of crystallinity ($w_c$)
- SAXS: average lamellar thickness ($l_c$)

**What specific questions did we ask?**

Q1: Are the macro/micro/nano-properties ($E$, $Y$, $H$) of UHMWPE’s different?
Q2: Do the macro/micro/nano-properties correlate with crystallinity?
Q3: If yes, which properties show the best correlation – macro, micro or nano?
Theory :: Morphology and microhardness in UHMWPE

(1) Additivity law for a semicryst. polymer:

\[ H = \sum_i v_i H_i \]
\[ H = v_a H_a + v_c H_c \]

(2) Microhardness of a semicrystalline polymer is proportional to crystallinity \( v_c \):

a) for \( T(\text{measurement}) \gg T_g \Rightarrow H_a \approx 0 \):

\[ H \approx v_c H_c \]

b) for \( T(\text{measurement}) \leq T_g \Rightarrow H_a > 0 \):

\[ H = v_a H_a + v_c H_c \]
\[ H = (1 - v_c) H_a + v_c H_c \]
\[ H = H_a + v_c (H_c - H_a) \]

(3) Microhardness of crystalline phase grows with increasing lamellar thickness \( l_c \):

\[ H_c = \frac{H_c^\infty}{1 + b/l_c} \]

Derivation by Balta-Calleja [2]

(4) Final relation for microhardness of semicrystalline polymers (from Eq. 1-3):

\[ H = v_c \times \frac{H_c^\infty}{1 + b/l_c} \]

\( v_c \) dominates \( l_c \) = correction

• Final result for a typical (UHMW)PE graphically:

\[ \Rightarrow H_v(PE) \text{ grows with } (v_c, l_c) \rightarrow \text{ for all semicryst.} \]
\[ \rightarrow \text{ constants for PE: } H_\infty = 200 \text{ MPa, } b = 20 \text{ nm} \]
\[ \rightarrow \text{ DSC and SWAXS: } w_c \approx v_c \sim 0.6; l_c \sim 10 \text{ nm} \]
\[ \Rightarrow H_v(PE) = f(v_c, l_c) \approx 40-80 \text{ MPa } \rightarrow \text{ Ok} \]

• Full justification of \( H = f(w_c, l_c) \) & \((H_\infty, b)\):

Theory :: Micro/nanoindentation × macroscale properties

Basic relations between macro and micro/nano-properties of (semicrystalline) polymers.

(1) Indentation hardness ($H_{IT}$) is proportional to macroscopic yield stress ($Y$):

$$H_{IT} \approx 3Y \quad \text{(Eq. 1)}$$

Tabor's relation [2,3], derived for metals and alloys (plastic), but holds quite well also for polymers (elasto-visco-plastic).

(2) Indentation modulus ($E_{IT}$) is proportional to macroscopic modulus ($E$):

$$E_{IT} \approx E \quad \text{(Eq. 2)}$$

Oliver & Pharr theory [4], supported by numerous experiments, including the MHI measurements on polymer systems.

Note #1: All type of micro/nanohardness are (in principle) proportional ($H \propto H_V \propto H_M \propto H_{IT}$).

(3) Modulus and yield stress of amorphous and many semicrystalline polymers are roughly proportional, as derived and verified by Struik [5]:

$$E \approx 30Y \quad \text{(Eq. 3)}$$

Note #2: More precise models relating [$H - Y - E$] exist, but they are not important here, because the simple equations (Eq.1-4) work for UHMWPE very well.

(4) Combination of (Eq. 1 + Eq. 2 + Eq. 3) + Calleja's relation ($H \propto w_c \rightarrow$ previous slide) suggests that modulus, yield stress, hardness and crystallinity of semicrystalline polymers are proportional:

$$E_{IT} \propto E \propto 30Y \propto 10H_{IT} \propto 10H \propto w_c \quad \text{(Eq. 4)}$$

The constants in Eq.4 are very approximate, but the linearity usually holds for given polymer and experimental conditions as proved experimentally in many previous studies (refs. [2,6,7]).

ECM, derived by Johnson [2]
Results :: **Structure vs. properties of various UHMWPE’s**

Q1: Are the macro/micro/nano-properties ($E$, $Y$, $H$) of UHMWPE’s different?

Q2: Do the macro/micro/nano-properties correlate with crystallinity?

**Conclusions (for stiffness-related macro/micro/nanomechanical properties = $H$-$Y$-$E$):**

Q1: UHMWPE properties are significantly different, if their crystallinities are different.

Q2: UHMWPE properties correlate with crystallinity – in agreement with theory.

The correlation with crystallinity is applicable as a criterion of $H$-$Y$-$E$ measurement correctness!

Reasons: theoretically predicted, established in literature & verified here for our UHMWPE’s

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**This example = microhardness ($H_V$) as a function of crystallinity ($Cl$)**

Other mechanical properties show similar trends → next slides

We note linear increase in microhardness with crystallinity, which in agreement with theory → previous slides

Pearson’s correlation coefficient $r = 0.93$ is close to +1, which evidences that the correlation is strong and positive.

$P$-value = 0.00003, which means that the probability of getting the same or stronger correlation just by coincidence is below 0.003 %.
Results :: **Crystallinity × yield stress and hardness**

Q3: How do the macro/micro/nano-properties correlate with crystallinity?

- **Macroscopic compression yield stress = Y:**
  - $r = 0.83$
  - $p = 0.00$
  - ⇒ strong correlation with crystallinity

- **Instrumented micro-hardness = MHI/$H_{IT}$:**
  - $r = 0.88$
  - $p = 0.00$
  - ⇒ even stronger correlation with crystallinity

- **Instrumented nano-hardness = NHI/$H_{IT}$:**
  - $r = 0.08$
  - $p = 0.82$
  - ⇒ almost no correlation with crystallinity

**Crystallinity:** $IR/Cl \approx \nu_c \approx \omega_c$

Scatterplot matrix graph:
main diagonal = distributions
off-diagonals = correlations
*produced by Python/Seaborn
Results :: **Statistical evaluation of ALL correlations**

Correlation matrix table (in the form of heatmap) showing Pearson’s correlation coefficients $r$.

Note: total positive linear correlation $\Rightarrow r = 1$ (dark), no correlation $\Rightarrow r = 0$ (bright)

<table>
<thead>
<tr>
<th>Zone I: strong correlations between macro- and micromechanical properties.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
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<tr>
<td>$Y$</td>
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<tr>
<td>MH/HV</td>
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<tr>
<td>MHI/EIT</td>
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<td>MHI/HIT</td>
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<td>MHI/HM</td>
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<tr>
<td>NHI/EIT</td>
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<td>NHI/HIT</td>
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</table>

<table>
<thead>
<tr>
<th>Zone III: Strong correlations between macro- and micromechanical properties and crystallinity</th>
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<tbody>
<tr>
<td>$E$</td>
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<tr>
<th>Zone IV: symmetric equivalent of zone III; strong correlation macro-micro and crystallinity</th>
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<tr>
<td>Zone IV: symmetric equivalent of zone III; strong correlation macro-micro and crystallinity</td>
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</table>

**Bright cross in the middle = weak correlations of NANO-properties with all other quantities.**
Supplement :: Precision and accuracy of our methods
Macro/micro/nanomechanical measurements from the point of view of precision and accuracy.

- **Accuracy** (≈ correctness) = strength of correlation with crystallinity (Pearson’s $r$)
- **Precision** (≈ scatter of the data) = relative standard deviation (RSD = sd/mean × 100%)

(a) Elastic modulus

(b) Yield stress and hardness

**Accuracy ≈ Pearson’s $r$:**
MHI ≥ MACRO >> NHI.

**Precision ≈ RSD:**
MHI ≥ MACRO >> NHI.

**Conclusion:** Nanoindentation is the least precise and the least accurate.

**Accuracy ≈ Pearson’s $r$:**
MH ≥ MHI ≥ MACRO >> NHI.

**Precision ≈ RSD:**
MH > MNI > MACRO >> NHI.

**Conclusions:** The most precise and accurate is non-instrumented (!) microindentation.
Summary and conclusions

0) Eleven clinically relevant UHMWPE formulations were collected.

1) Their mechanical properties were characterized at multiple length scales by...
   ...MACROscopic compression, MICROindentation, and NANOindentation

2) Theoretical predictions suggested that crystallinity should be the decisive parameter
determining the stiffness-related properties ($E$, $Y$, $H$ = modulus, yield stress, hardness):

   \[
   E_{IT} \propto E \propto 30Y \propto 10H_{IT} \propto 10H \propto w_c
   \]

3) Experimental results showed that the strength of
crystallinity-properties correlations decreased in the following order:

   MICROindentation $\geq$ MACROscale compression $>>$ NANOindentation

4) This confirms that MICROindentation is reliable tool for characterization of polymers...
   ...which somehow corrects the conclusions about indentation in UHMWPE handbook
   ...and confirms the conclusions in the key book in the field: Microhardness of polymers [2]

5) This does not mean that NANOindentation is bad...
   ...BUT it seems to be extremely sensitive to surface preparation, properties and/or artifacts

6) Stiffness-related macro- and micromechanical properties ($E$, $Y$, $H$) of various UHMWPE’s
   are significantly different ON CONDITION that their crystallinities are different.
   (other parameters like crosslinking density, sterilization etc., play minor role)
Acknowledgement

Helena Vlkova, Veronika Gajdosova
Institute of Macromolecular Chemistry, Prague, Czech Republic
(non-instrumented + instrumented microindentation, IR microspectroscopy)

Sofia Arevalo, Lisa Pruitt
University of California, Berkeley, CA, USA
(materials, macroscale compression tests, nanoindentation, DSC, SAXS)

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TE01020118: Technology Agency of the Czech Republic

Thank you for your attention!
Supplement :: **Statistical evaluation of ALL correlations**

Correlation matrix table (in the form of heatmap) showing *P*-values.

Here: *P*-value = probability that we get so strong or stronger correlation just by coincidence.

**Zone I:** strong correlations between macro- and micromechanical properties.

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>Y</th>
<th>MH/HV</th>
<th>MHI/EIT</th>
<th>MHI/HIT</th>
<th>MHI/HM</th>
<th>NHI/EIT</th>
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<td>0.82</td>
<td>0.38</td>
<td>0.40</td>
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</tbody>
</table>

**Zone II:** Strong correlations between crystallinities (from IR and DSC) and average lamellar thickness (SAXS)

**Zone III:** Strong correlations between macro- and micromechanical properties and crystallinity

**Zone IV:** symmetric equivalent of zone III; strong correlation macro-micro-nano-crystallinity

Bright cross in the middle = weak correlations of NANO-properties with all other quantities.