Comparison of macro-, micro- and nanomechanical properties

of clinically relevant UHMWPE formulations

- **Miroslav Slouf, Helena Vlkova, Veronika Gajdosova**
  Institute of Macromolecular Chemistry, Prague, Czech Republic
  (micromechanical properties, infrared microspectroscopy
- **Sofia Arevalo, Lisa Pruitt**
  University of California, Berkeley, CA, USA
  (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].

Sample series	Sample ID	Full sample name	Manufacturer
Series 1	PE-1a	GUR 1050	Orthoplastic
	PE-1b	GUR 1050 75kGy RM	Quadrant
Series 2	PE-2a	GUR 1020	Orthoplastic
	PE-2b	GUR 1020 35kGy	Orthoplastic
	PE-2c	GUR 1020 75kGy RM	Orthoplastic
Series 3	PE-3a	GUR 1020 VE	Orthoplastic
	PE-3b	GUR 1020 VE 50kGy	Orthoplastic
	PE-3c	GUR 1020 VE 75kGy	Orthoplastic
	PE-3d	GUR 1020 VE 125kGy	Orthoplastic
Series 4	PE-4a	GUR 1020 AO	De Puy
	PE-4b	GUR 1020 AO 80kGy	De Puy

→ non-crosslinked

→ crosslinked
and remelted

→ gamma-sterilized

→ vitamin E
stabilized

→ ...and crosslinked

→ new bio-stabilizer
...and crosslinked

What was known before we started?

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

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

What we wanted to study ⇒ 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).

[1] Malito et al.: JMBBM 83 (2018) 9-19.

[2] Balta-Calleja: Microhardness of polymers, Cambridge (2000).

Experimental

What mechanical properties did we measure?

Method	Modulus	Yield stress/Hardness *
MACROscopic compression	E	Y
Non-instrumented MICROindentation	-	MH/H_V
Instrumented MICROindentation	MHI/E_{IT}	MHI/H_{IT}
Instrumented NANOindentation	NHI/E_{IT}	NHI/H_{IT}

* 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 thicknes (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:

$$
\begin{aligned}
H &= \textstyle\sum_i v_i H_i \\
H &= v_a H_a + v_c H_c
\end{aligned}
$$

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

a) for T(measurement) >> $T_g \Rightarrow H_a \approx 0$:

$$H \approx v_c H_c$$

b) for T(measurement) $\leq T_g \Rightarrow H_a > 0$:

$$
\begin{aligned}
H &= v_a H_a + v_c H_c \\
H &= (1 - v_c) H_a + v_c H_c \\
H &= H_a + v_c \left(H_c - H_a\right)
\end{aligned}
$$

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

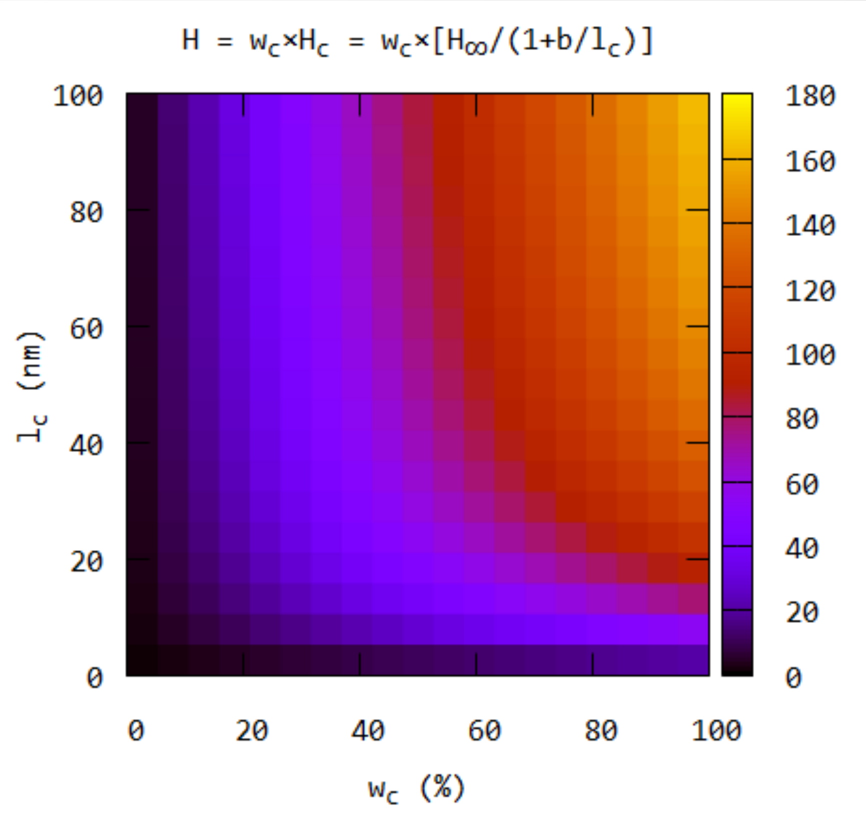
$$H_c = \frac{H_c^{\infty}}{1 + b/l_c}$$

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

- Full justification of $H = f(w_c, l_c)$ & (H_∞, b):
  Calleja: Microhardness of polymers, 2000.

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):

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

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):

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

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]:

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

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

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

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]).

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. →

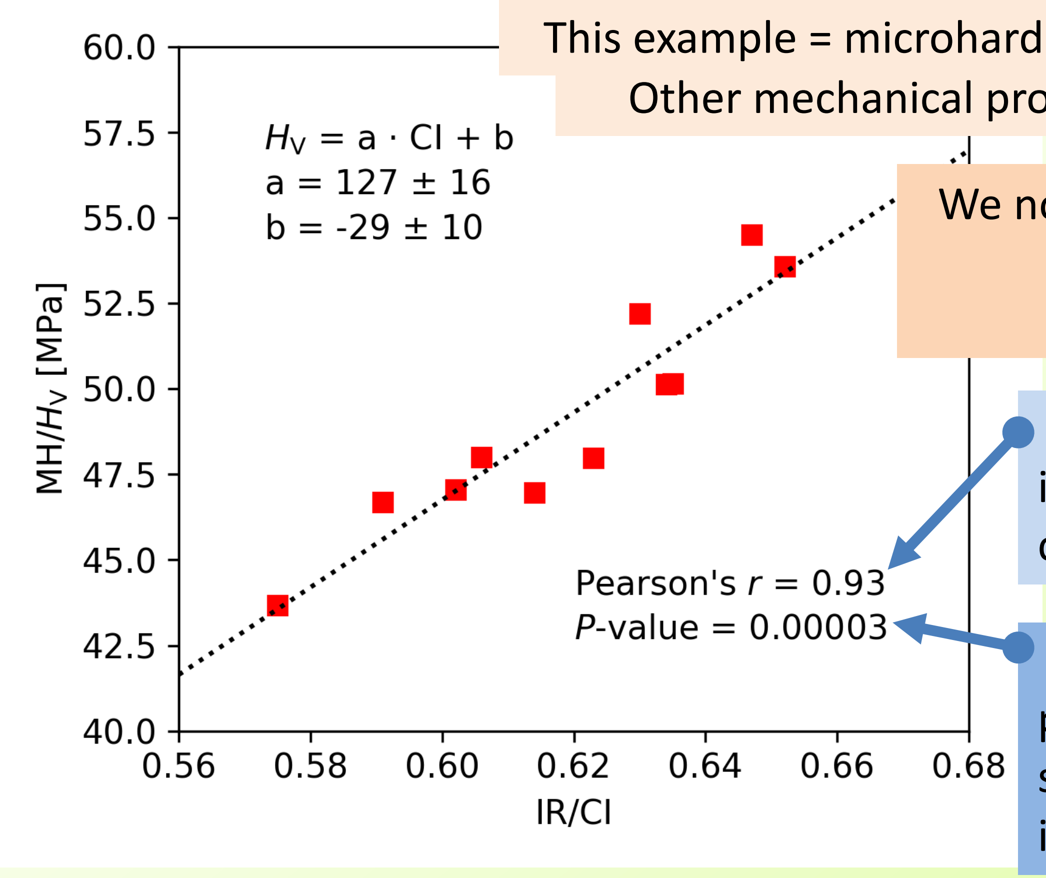
$$\frac{H}{Y} = \frac{2}{3}\left[2 + \ln\left(\frac{E \tan\beta}{3Y}\right)\right]$$

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?



This example = microhardness (H_V) as a function of crystallinity (CI)
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 %.

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

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

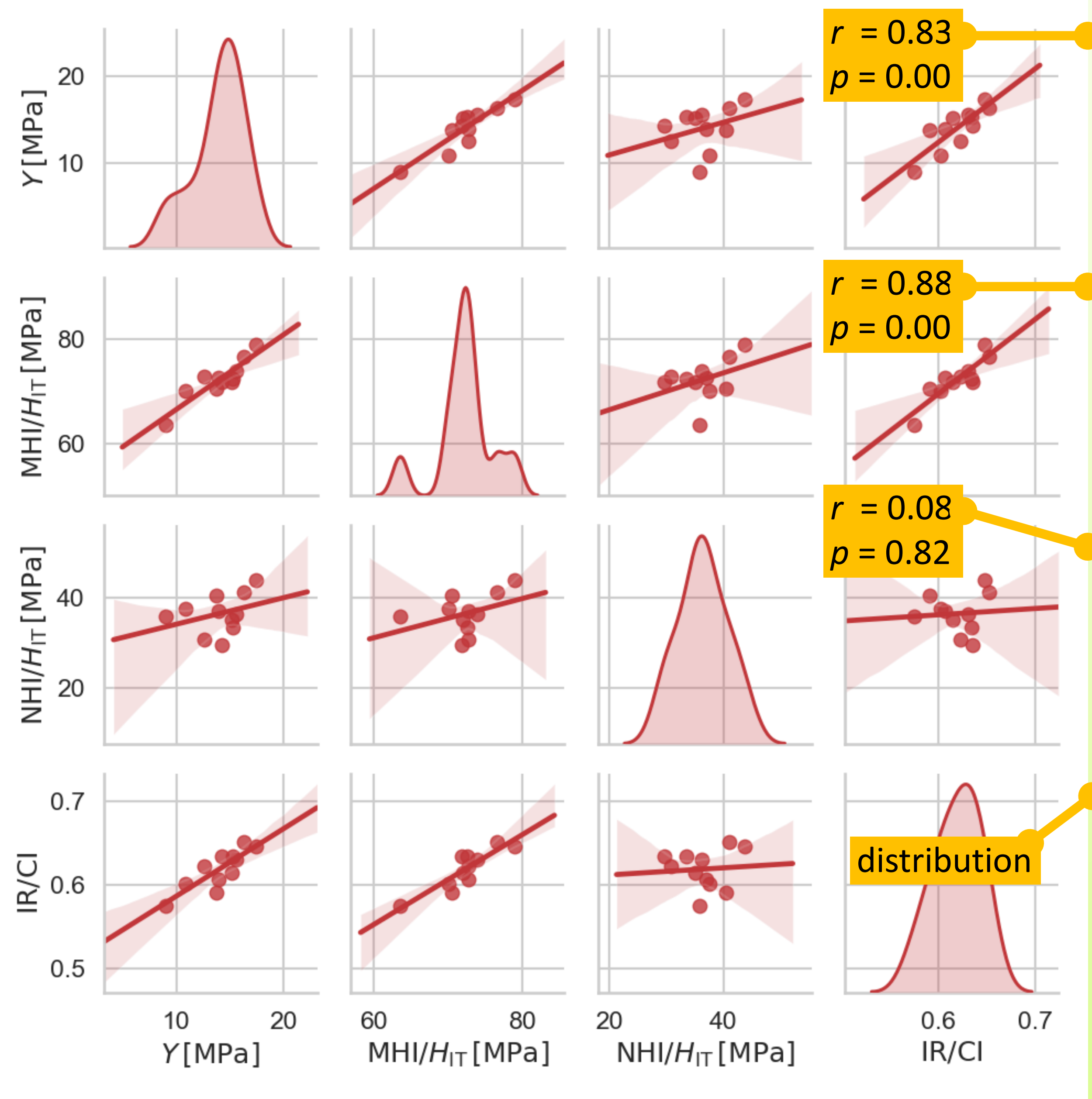
Q2: UHMWPE properties correlate with crystallinity – in agreement with theory.

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 ↑

Results :: Crystallinity × yield stress and hardness

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



$r = 0.83$
$p = 0.00$

Macroscopic compression yield stress = Y:
⇒ strong correlation with crystallinity

$r = 0.88$
$p = 0.00$

Instrumented micro-hardness = MHI/H_{IT}:
⇒ even stronger correlation with crystallinity

$r = 0.08$
$p = 0.82$

Instrumented nano-hardness = NHI/H_{IT}:
⇒ almost no correlation with crystallinity

distribution

Crystallinity: IR/CI $\approx v_c \approx w_c$

Scatterplot matrix graph:
main diagonal = distributions
off-diagonals = correlations
*produced by Python/Seaborn

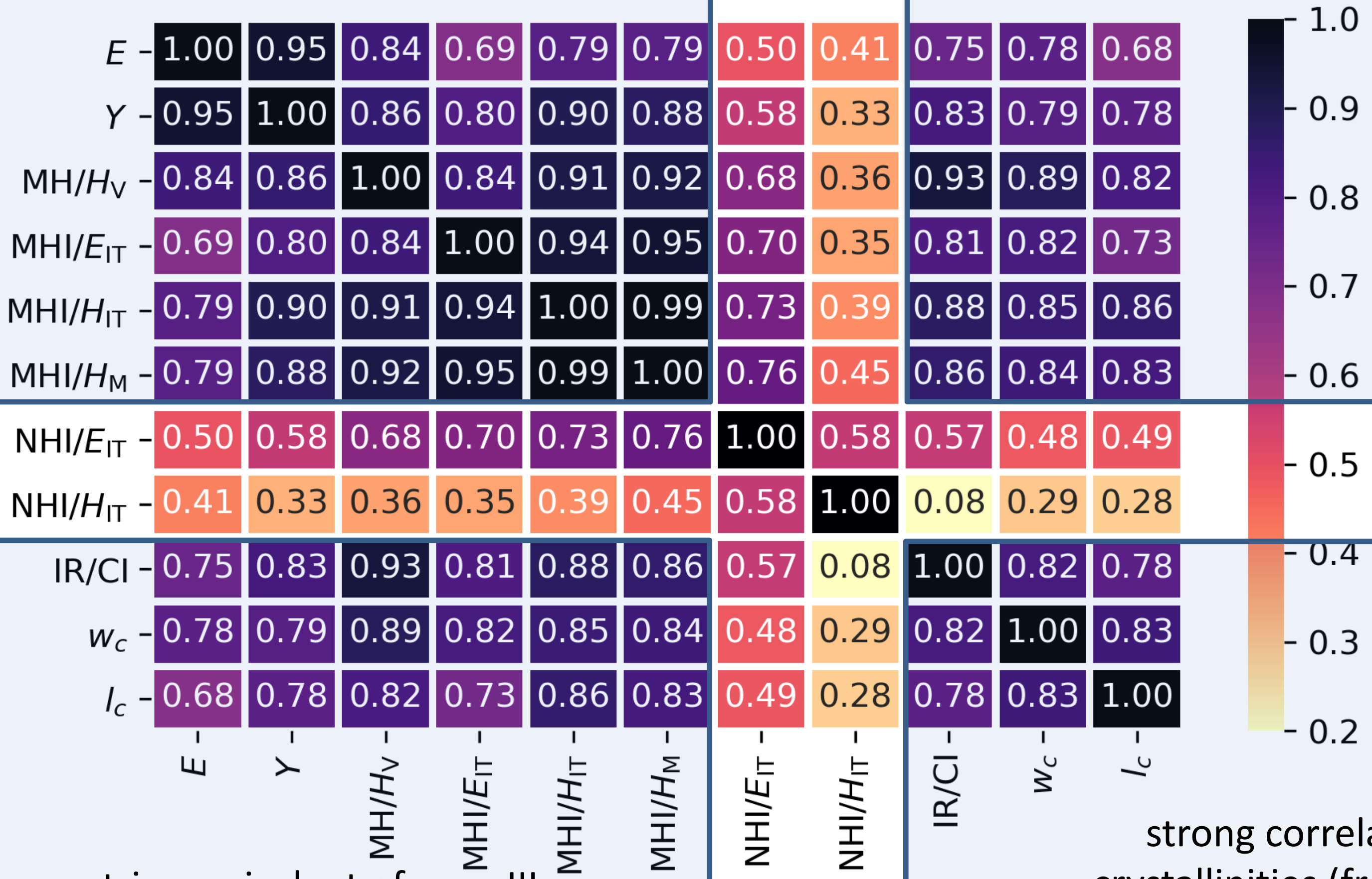
Results :: Statistical evaluation of ALL correlations

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

Note: total positive linear correlation ⇒ *r* = 1 (dark), no correlation ⇒ *r* = 0 (bright)

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

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



	E	Y	MH/H_V	MHI/E_{IT}	MHI/H_{IT}	MHI/H_M	NHI/E_{IT}	NHI/H_{IT}	IR/CI	w_c	l_c
E	1.00	0.95	0.84	0.69	0.79	0.79	0.50	0.41	0.75	0.78	0.68
Y	0.95	1.00	0.86	0.80	0.90	0.88	0.58	0.33	0.83	0.79	0.78
MH/H_V	0.84	0.86	1.00	0.84	0.91	0.92	0.68	0.36	0.93	0.89	0.82
MHI/E_{IT}	0.69	0.80	0.84	1.00	0.94	0.95	0.70	0.35	0.81	0.82	0.73
MHI/H_{IT}	0.79	0.90	0.91	0.94	1.00	0.99	0.73	0.39	0.88	0.85	0.86
MHI/H_M	0.79	0.88	0.92	0.95	0.99	1.00	0.76	0.45	0.86	0.84	0.83
NHI/E_{IT}	0.50	0.58	0.68	0.70	0.73	0.76	1.00	0.58	0.57	0.48	0.49
NHI/H_{IT}	0.41	0.33	0.36	0.35	0.39	0.45	0.58	1.00	0.08	0.29	0.28
IR/CI	0.75	0.83	0.93	0.81	0.88	0.86	0.57	0.08	1.00	0.82	0.78
w_c	0.78	0.79	0.89	0.82	0.85	0.84	0.48	0.29	0.82	1.00	0.83
l_c	0.68	0.78	0.82	0.73	0.86	0.83	0.49	0.28	0.78	0.83	1.00

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

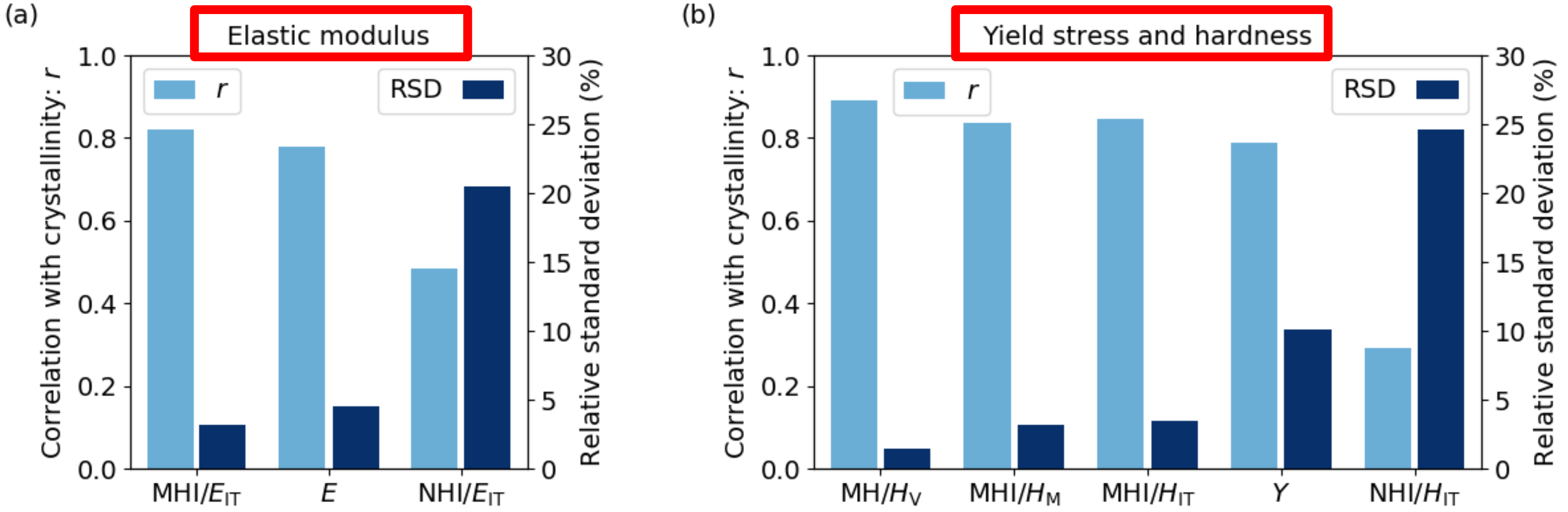
Zone II: strong correlations between crystallinities (from IR and DSC) and average lamellar thickness (SAXS)

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%)



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...
...**MACRO**scopic compression, **MICRO**indentation , and **NANO**indentation

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

$$\boxed{E_{IT} \propto E \propto 30Y \propto 10H_{IT} \propto 10H \propto w_c}$$

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

MICROindentation ≥ **MACRO**scale compression >> **NANO**indentation

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)

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

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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.

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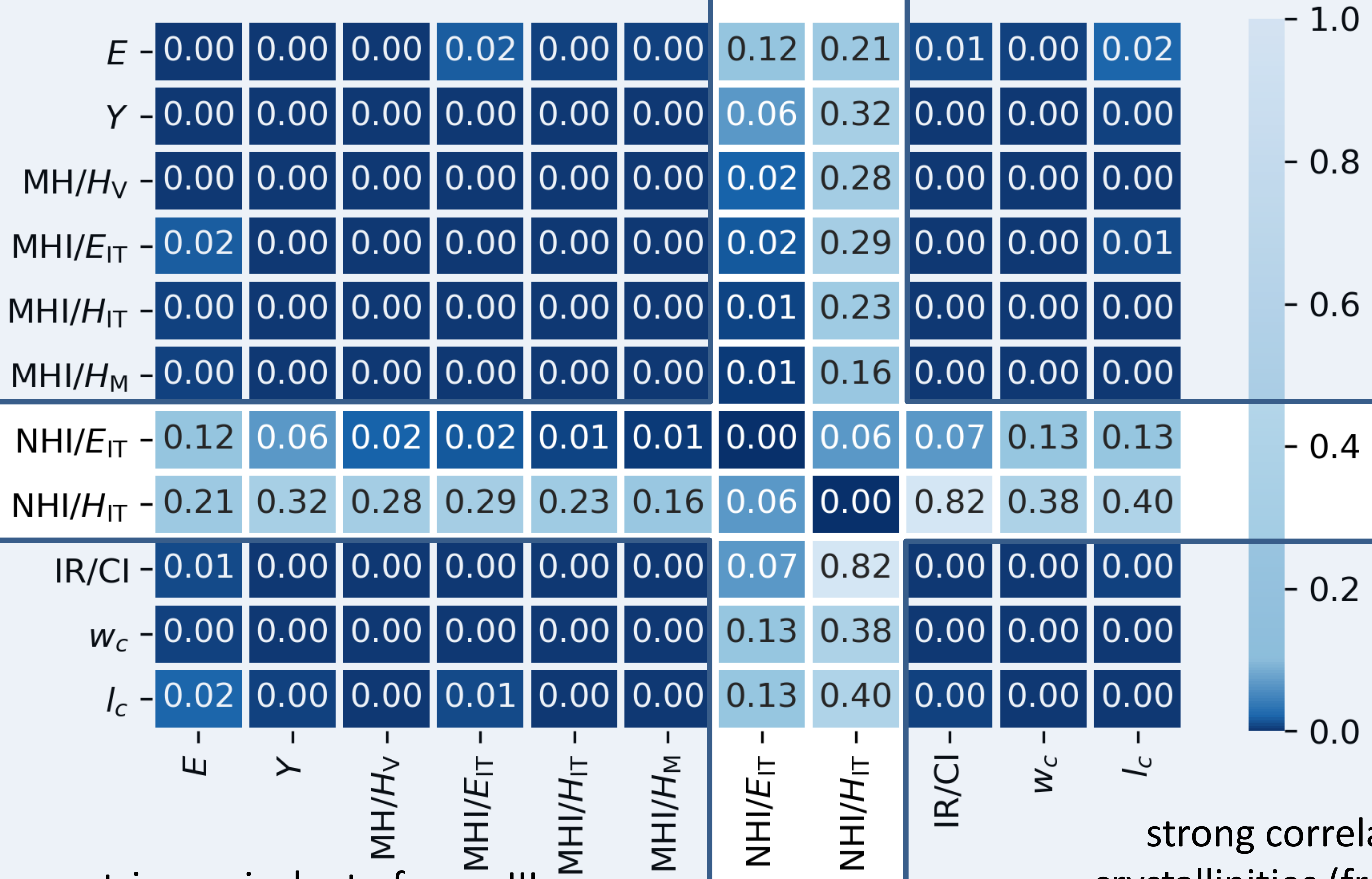

	E	Y	MH/H_V	MHI/E_{IT}	MHI/H_{IT}	MHI/H_M	NHI/E_{IT}	NHI/H_{IT}	IR/CI	w_c	l_c
E	0.00	0.00	0.00	0.02	0.00	0.00	0.12	0.21	0.01	0.00	0.02
Y	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.32	0.00	0.00	0.00
MH/H_V	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.28	0.00	0.00	0.00
MHI/E_{IT}	0.02	0.00	0.00	0.00	0.00	0.00	0.02	0.29	0.00	0.00	0.01
MHI/H_{IT}	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.23	0.00	0.00	0.00
MHI/H_M	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.16	0.00	0.00	0.00
NHI/E_{IT}	0.12	0.06	0.02	0.02	0.01	0.01	0.00	0.06	0.07	0.13	0.13
NHI/H_{IT}	0.21	0.32	0.28	0.29	0.23	0.16	0.06	0.00	0.82	0.38	0.40
IR/CI	0.01	0.00	0.00	0.00	0.00	0.00	0.07	0.82	0.00	0.00	0.00
w_c	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.38	0.00	0.00	0.00
l_c	0.02	0.00	0.00	0.01	0.00	0.00	0.13	0.40	0.00	0.00	0.00

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

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.