The nano mechanical properties of annealed PEEK with PITCH-based and PAN-based carbon fibers: the effect of annealing and indentation tip diameter

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Berkeley

Agenda

1. Introduction
2. Methodology
3. Results
4. Discussion
5. Conclusion

An overview of the microstructure of PEEK composites

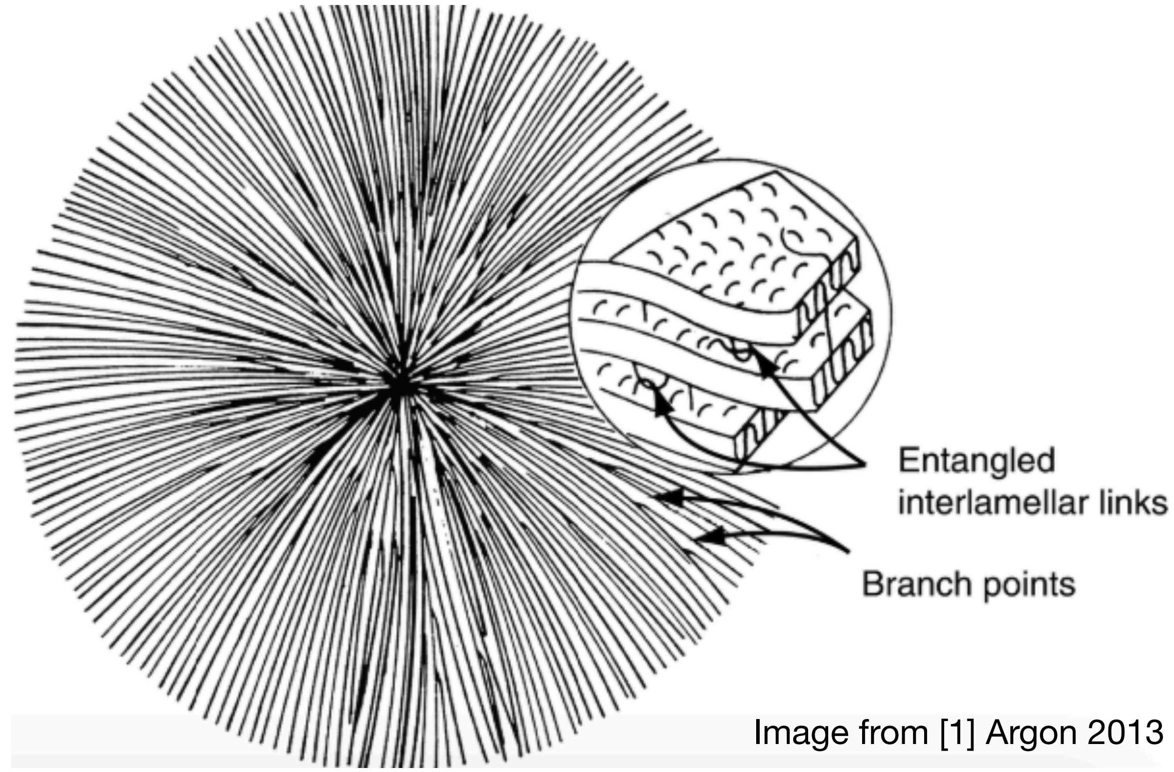
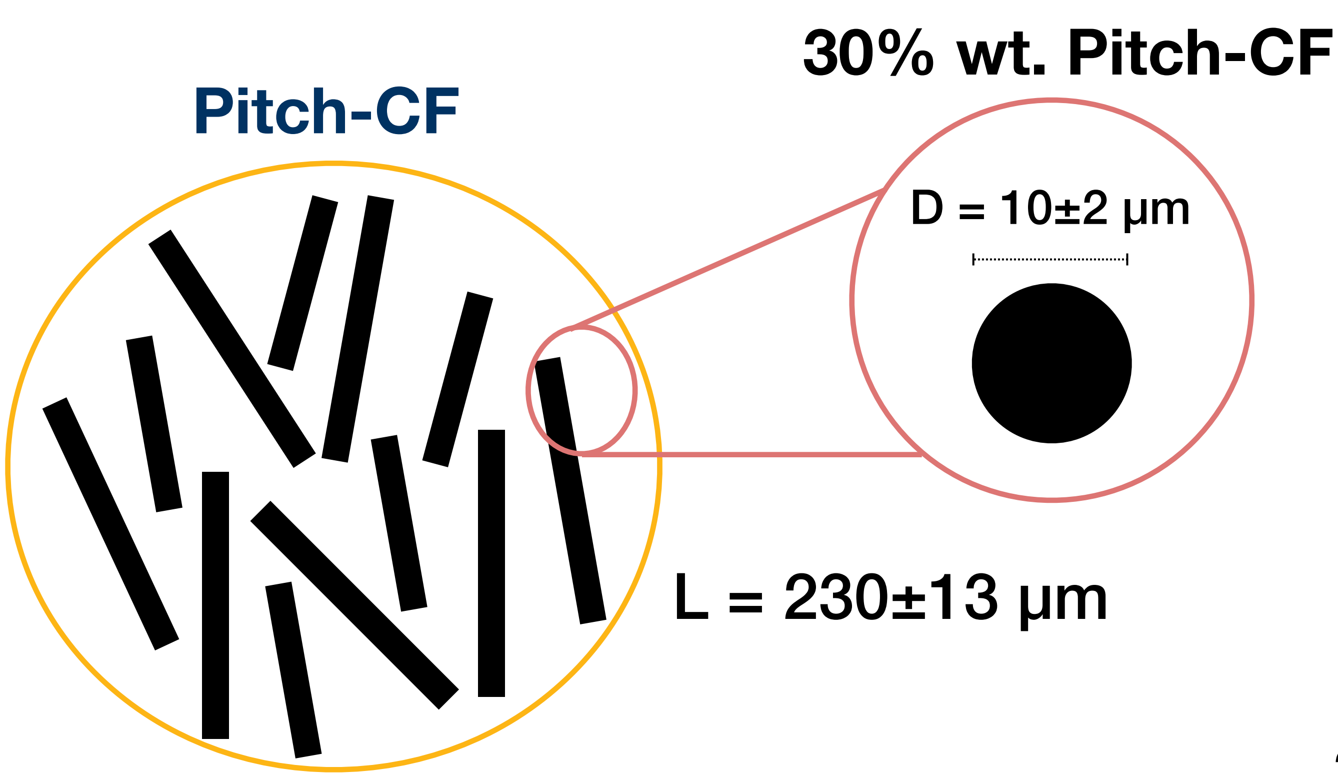
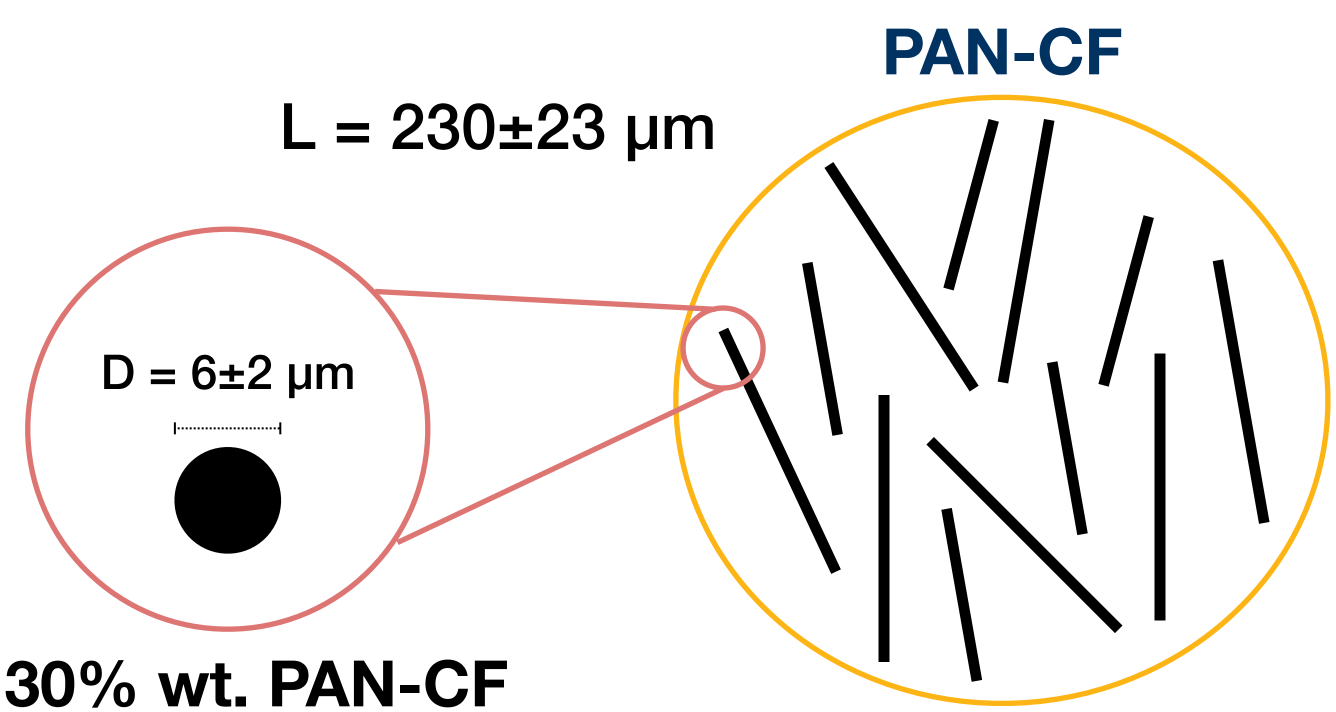


Image from [1] Argon 2013





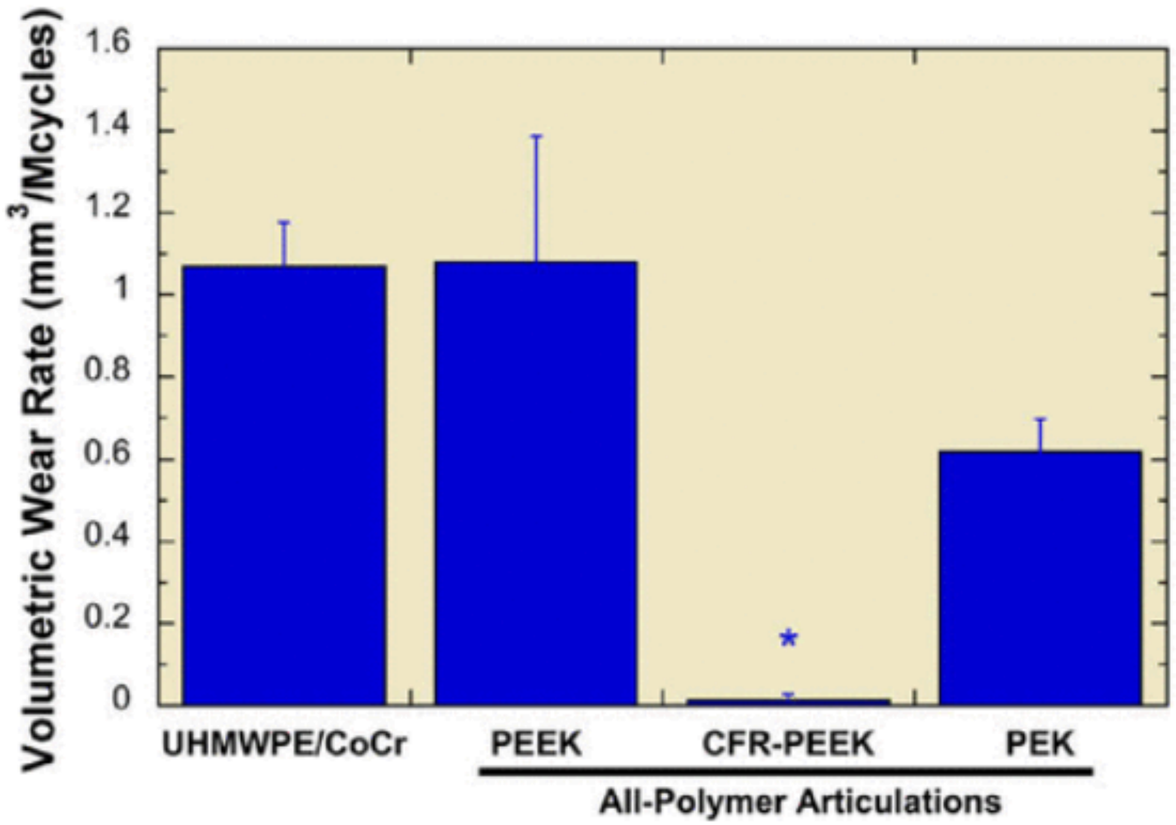
Source: Coal tar pitch

[2] Regis et. al. 2017.

Source: Polyacrilonitrile (PAN)

Mechanical properties and biomedical applications of PEEK

Mechanical Properties



[3] Image obtained from Kurtz et. al. 2013

Tensile modulus of PEEK composites

	Unfilled	Pitch	PAN
E	3.9±0.2	12.5±1.3	18.5±2.3

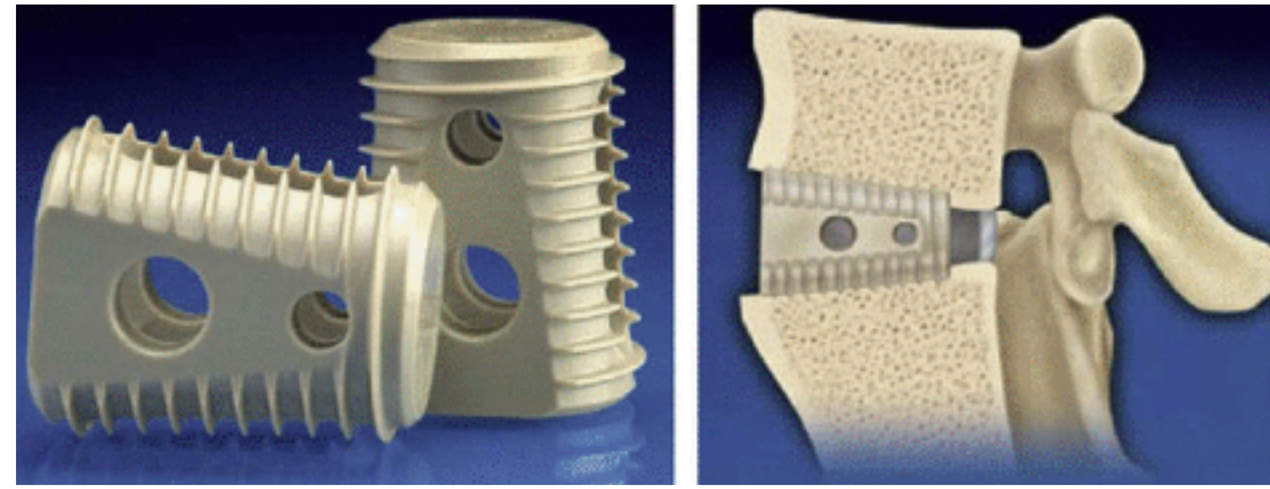
Carbon Fiber Modulus:

PAN: 540 GPa

Pitch: 280 GPa

[4] Bonnheim et. al. 2018

Applications



Tapered PEEK cage for the lumbar spine (LT-CAGE system; medtronic Spinal and Biologics, Memphis, TN)

PEEK rod system for posterior lumbar fusion.

Images obtained from [3] Kurtz et. al. 2013

Benefits of PEEK in biomedical applications:

- Radiolucency and radiative stability
- Sterilization with minimal degradation to mechanical properties.

[3] Kurtz et. al. 2013

Previous Work: The use of Nanoindentation/Microindentation techniques to characterize the mechanical properties of PEEK composites

Surface mechanical properties are influenced by the degree of crystallinity.

[5] Iqbal et. al. 2013

Annealing results in strengthening of surface mechanical properties.

[6] Voyiadjis et. al. 2017

Nanoindentation may provide insight on morphological features of polymeric surfaces.

Exploring microscopic changes in the hardness, and reduced stiffness from different sterilization processes.

[7] Godara et. al. 2007

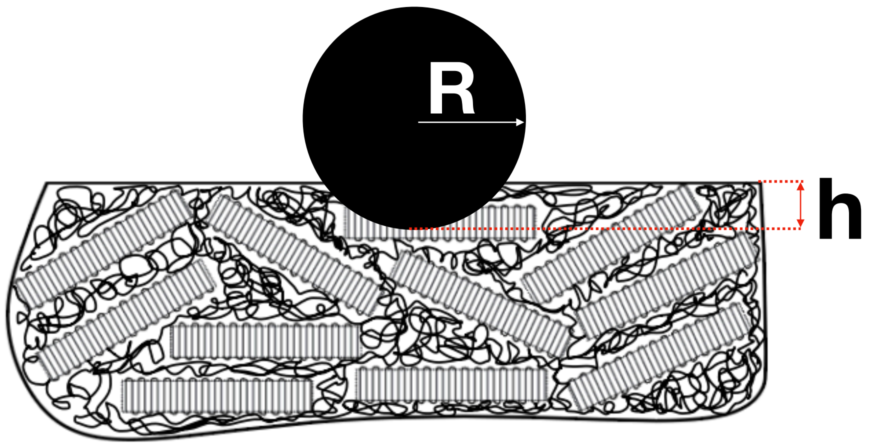
The reduced modulus of all PEEK and CFR PEEK formulations increased with increasing annealing temperature.

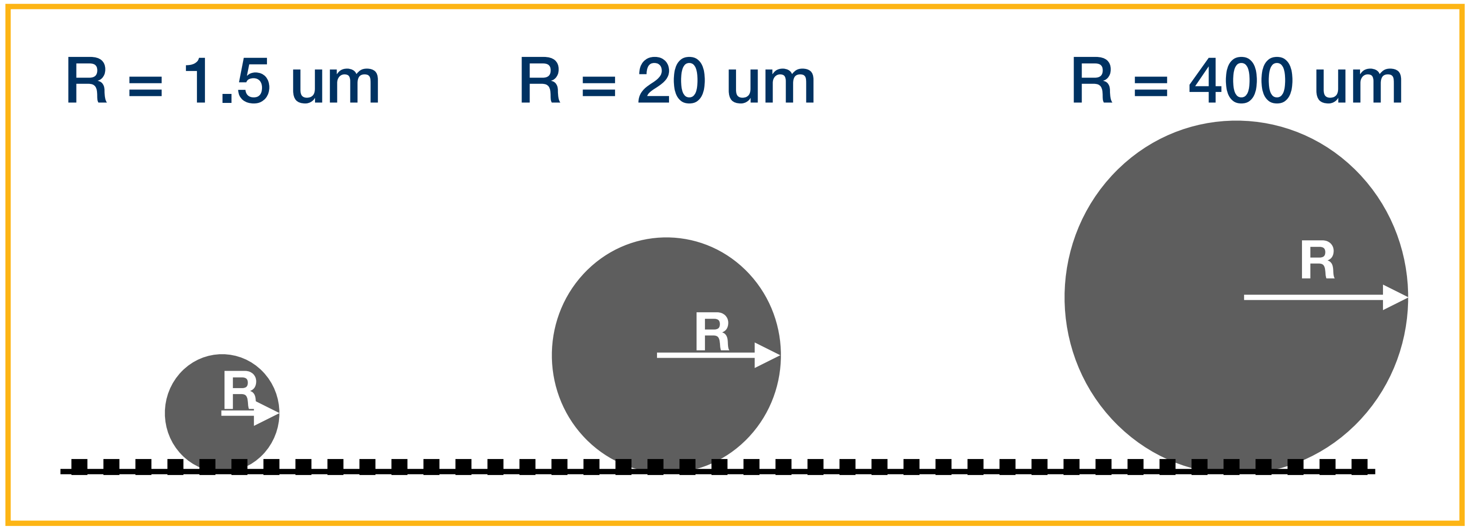
[8] Regis et. al. 2017

Structure-property relations enable development and optimization of PEEK composites

Aim 1: Assessing the effects of using different tip diameters during nano indentation on the nano mechanical measurements.

Nanoindentation





Aim 2: Developing a relationship between nano mechanical modulus and microstructural properties (degree of crystallinity and interlamellar thickness) for PEEK composites of various thermal treatments.

Aim 3: Investigating the effects of heat treatment on nano mechanical properties of PEEK composites.

Polishing of PEEK for improved accuracy and removal of "skin" surface layer induced by manufacturing process.

Step 1: Coarse Grit Polishing → **Step 2: Ultra-fine Polishing** → **Step 3: Lapping Finish**

Step 1: Coarse Grit Polishing	Step 2: Ultra-fine Polishing	Step 3: Lapping Finish
Silicon carbide polishing papers (800, 1200, 2000, 2500)	Silicon carbide polishing papers (3000, 5000, 7000)	Aluminum oxide sand papers (1 um)

Polishing in accordance with [6] Godara et al. 2007 and [7] Voyiadjis et al. 2017

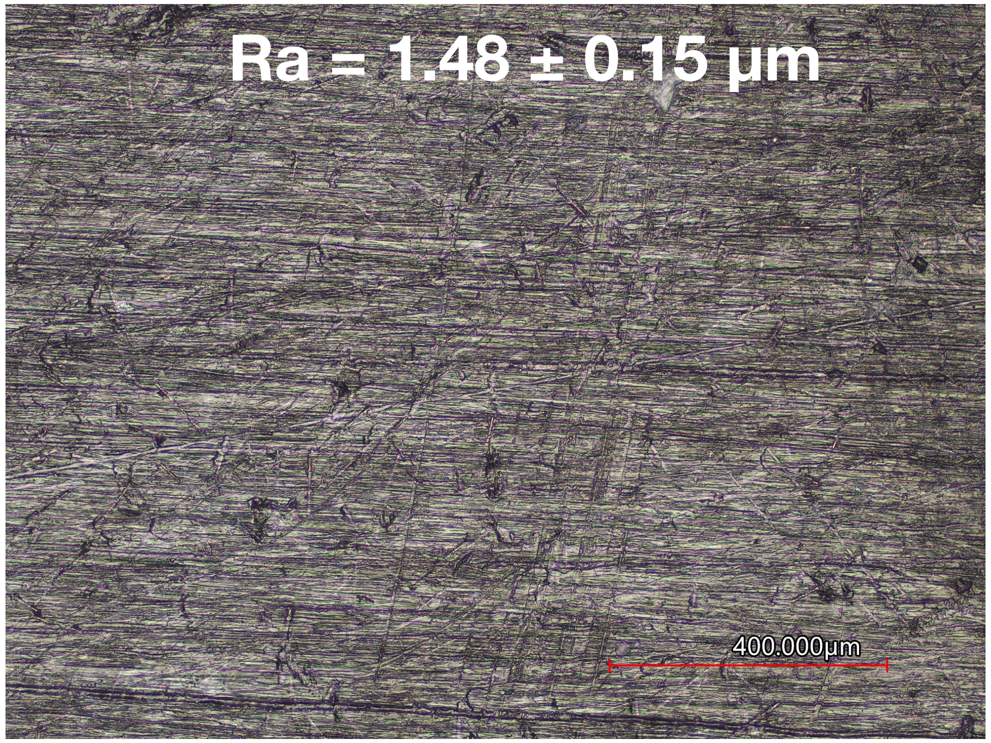
- Voyiadjis et. al. found that polishing reduced the size of standard deviations.
- Recorded modulus does not show significant changes post polishing, suggesting minimal effect of residual fields.

[7] Voyiadjis et al. 2017

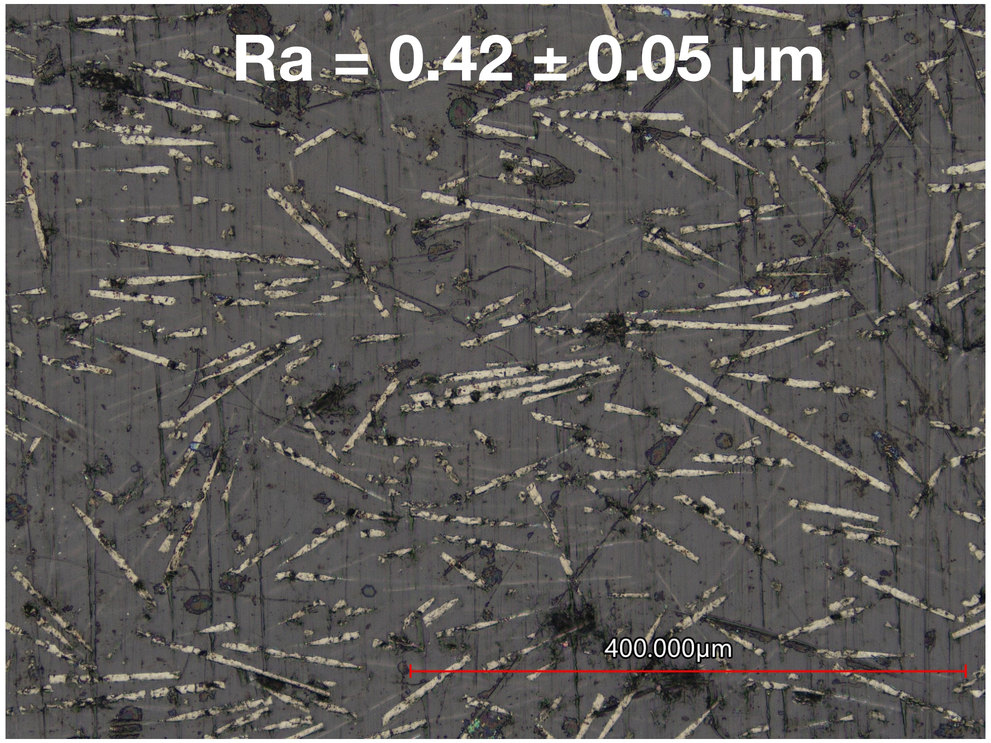
Polishing equipment

http://www.southbaytech.com/shop/920.shtml

Before Polishing

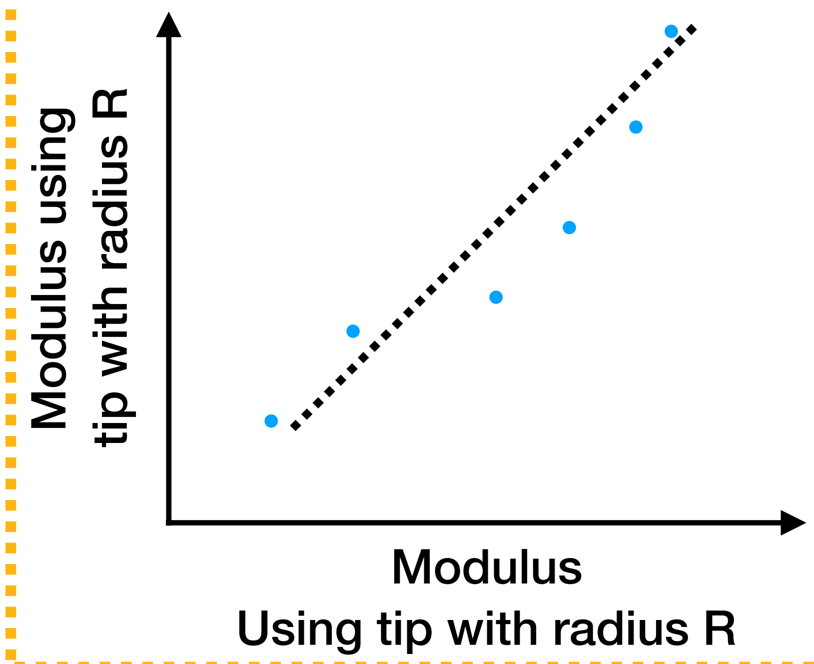


After Polishing



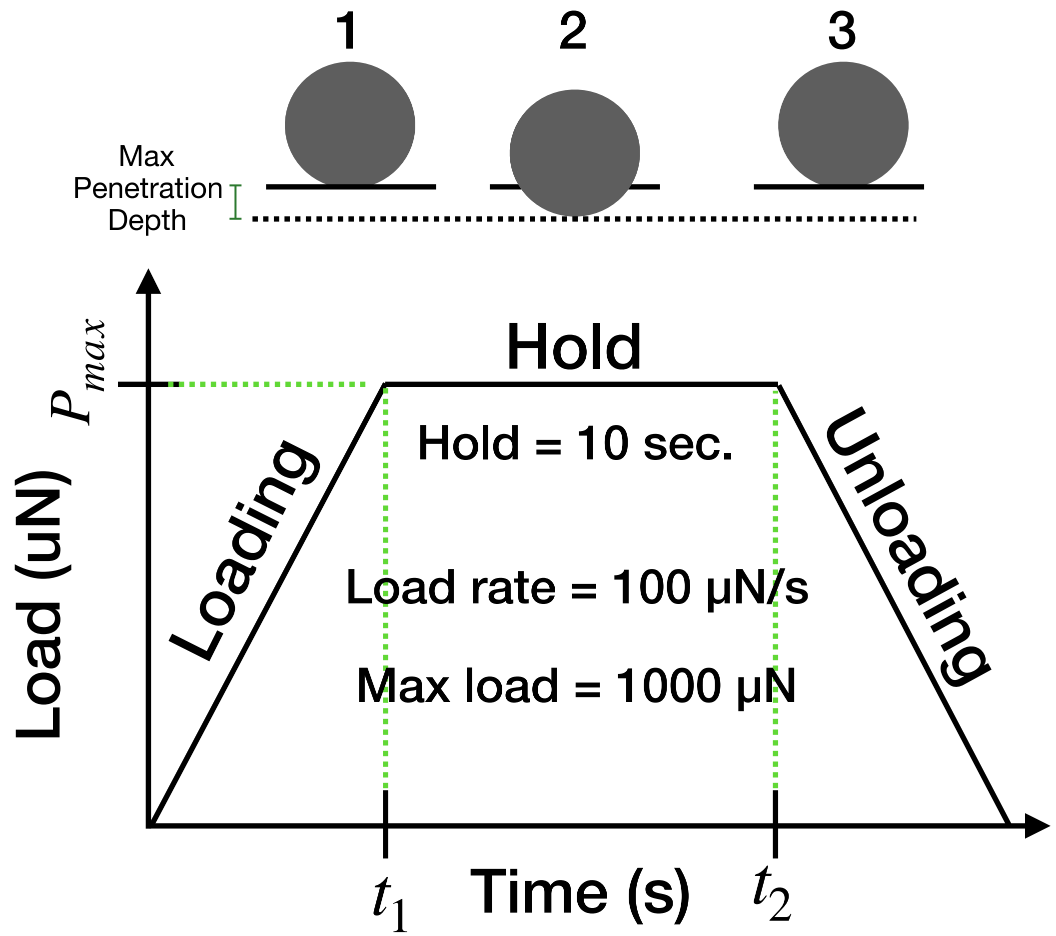
Aim 1: The effects using different diameter nano indentation tips on the nano-mechanical measurements.

Analysis

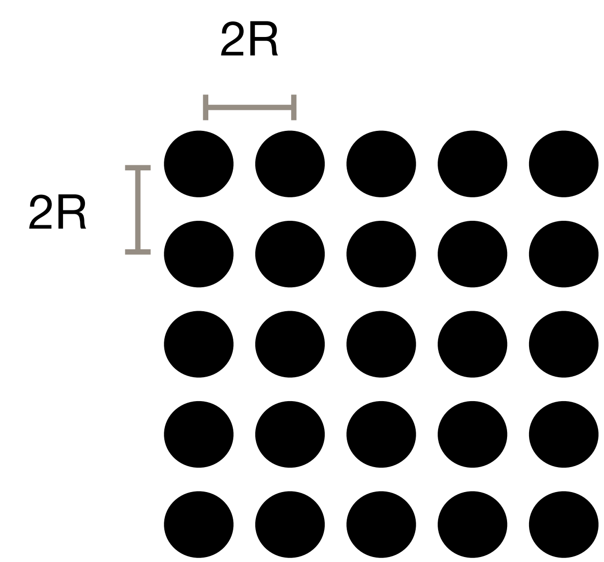


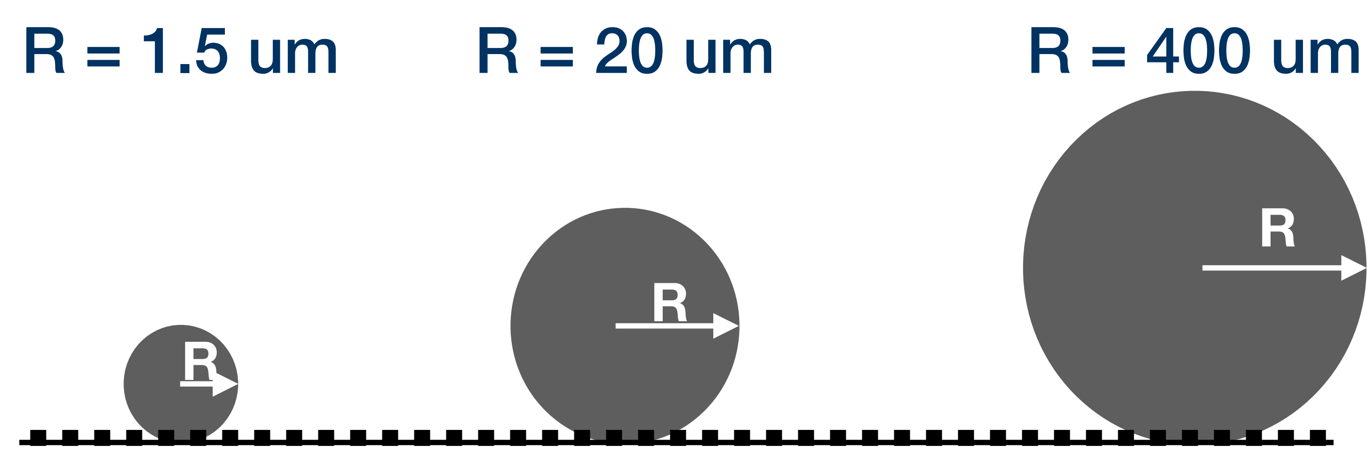
Unfilled	PAN-CF	Pitch-CF
No Heat Treatment	No Heat Treatment	No Heat Treatment
200	200	200
225	225	225
250	250	250
275	275	275
300	300	300
PEEK-OPTIMA™ LT1	PEEK-OPTIMA Reinforced™ 30% wt PAN CF	PEEK-OPTIMA Wear Performance™ 30% wt Pitch CF

Mechanical Testing



Indentation Pattern

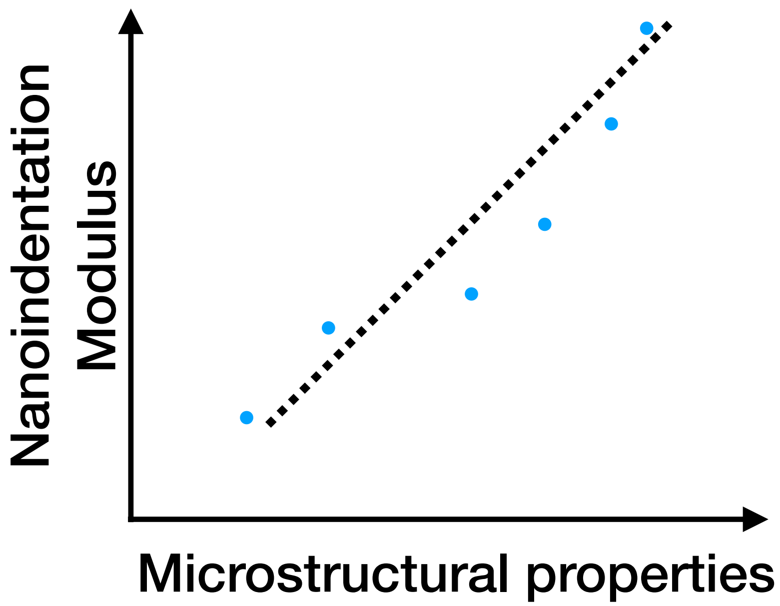




[9] Doerner and Nix 1986; [10] Pharr et. al. 1992; [11] Fischer-Cripps 2000; [12] Klapperich et. al. 2001.

Aim 2: Nanoindentation is a useful tool for developing a relationship between nano indentation modulus and structural properties.

Analysis



[4] Regis et al. 2017

Unfilled	PAN-CF	Pitch-CF
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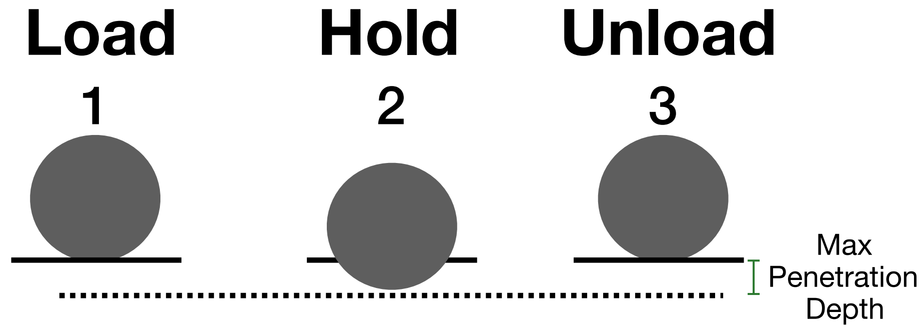
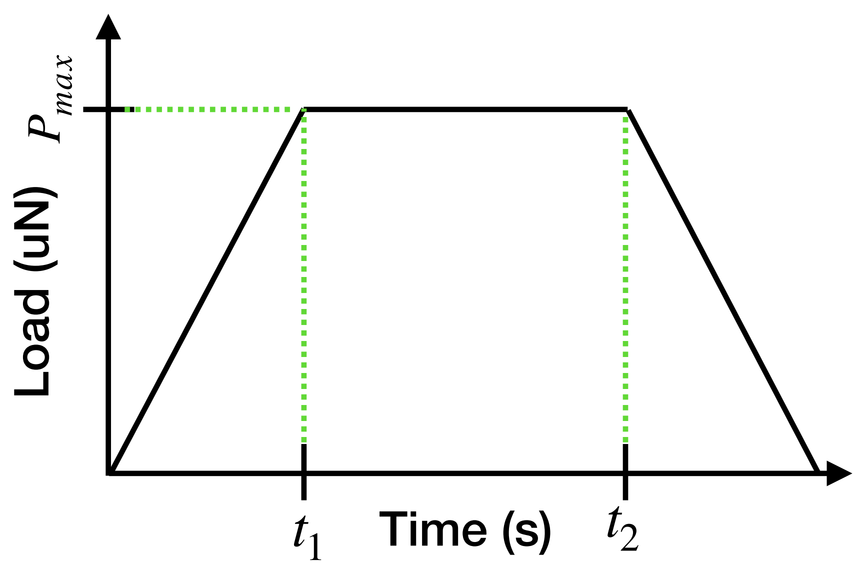
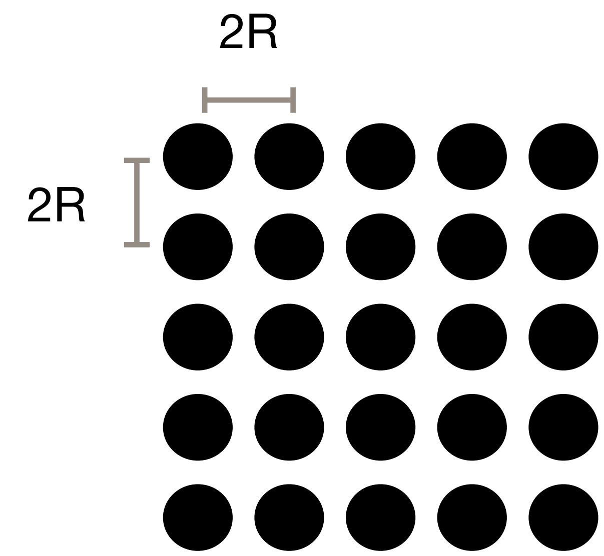
PEEK-OPTIMA™ LT1	PEEK-OPTIMA Reinforced™ 30% wt PAN CF	PEEK-OPTIMA Wear Performance™ 30% wt Pitch CF

Mechanical Testing







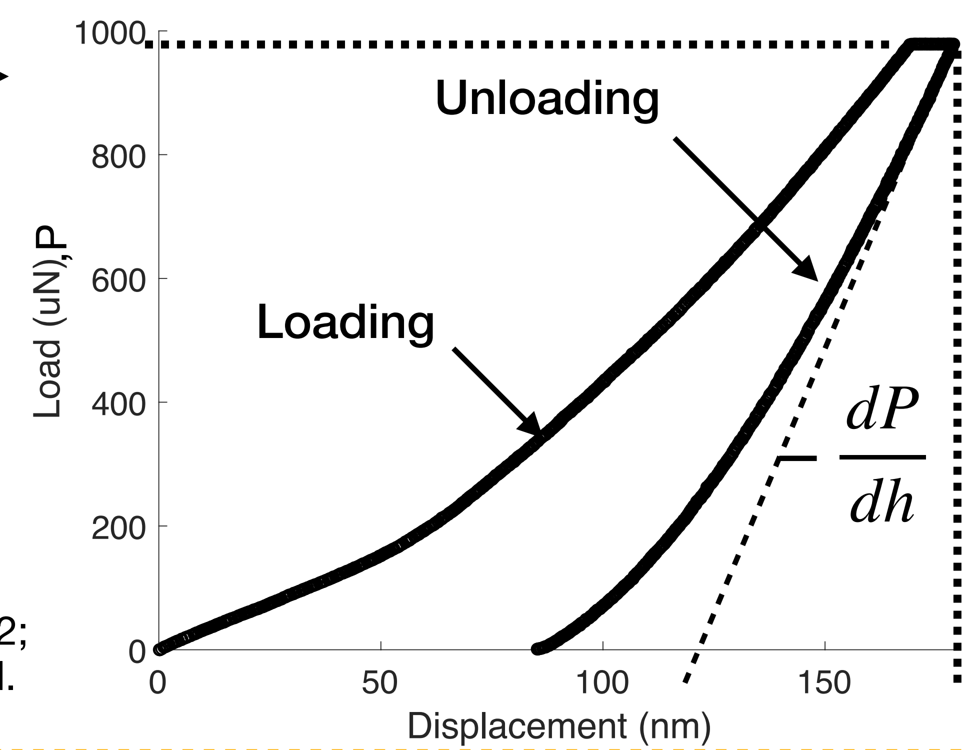
6x5 grids x 6 locations of sample

Max load = 1000 μN

Load rate = 100 μN/s

Hold = 10 sec.

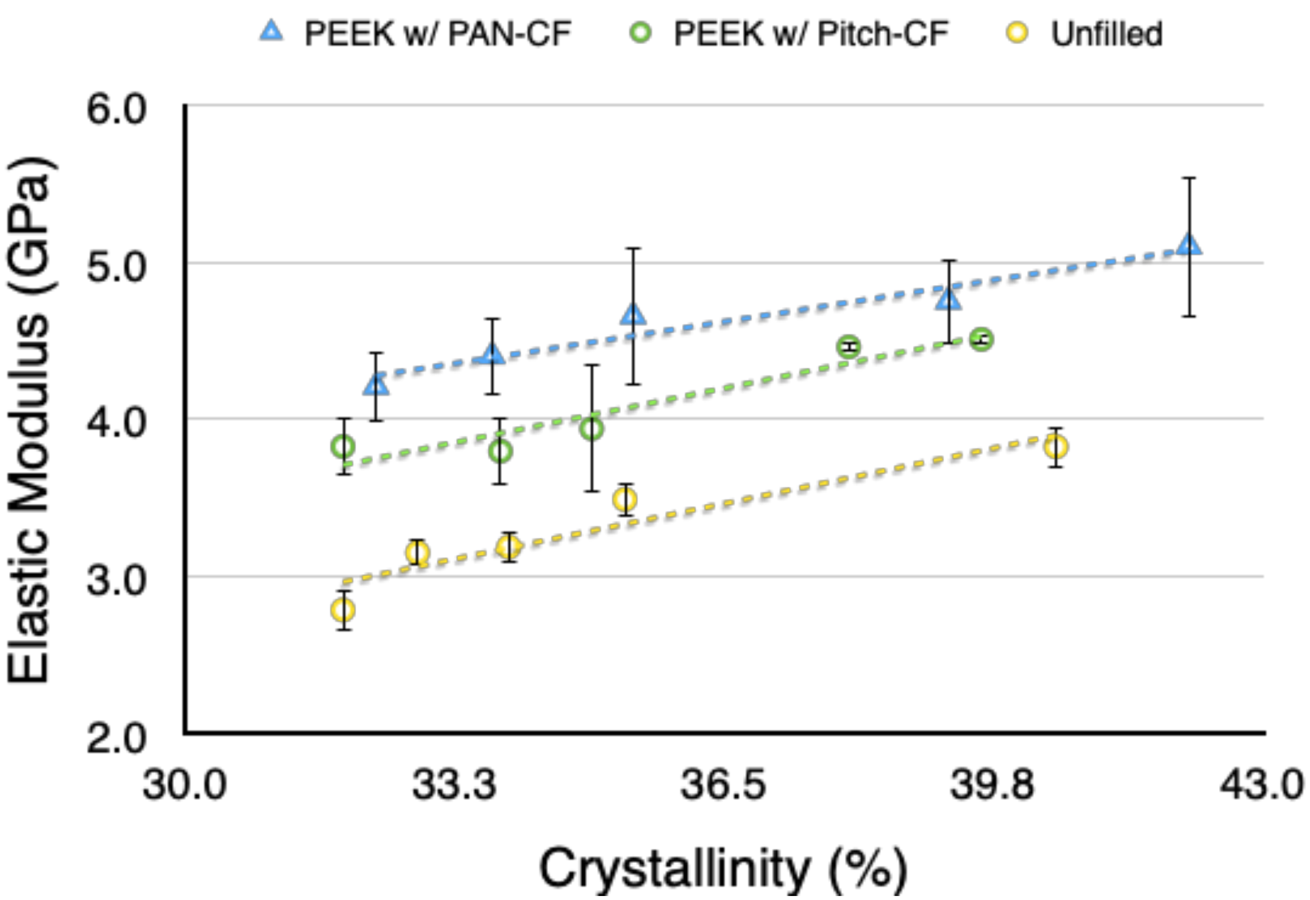
1 indent = 1 load-depth curve



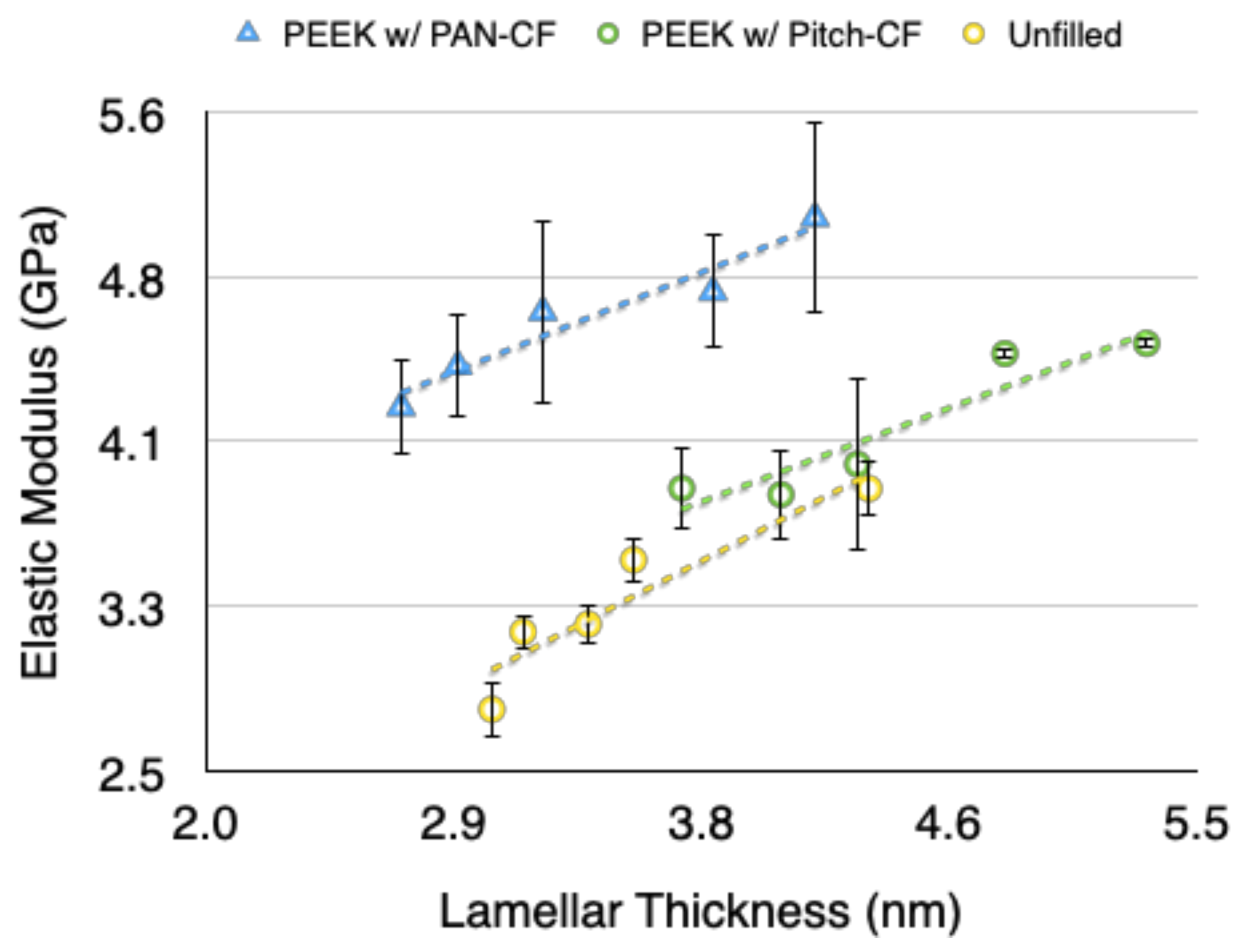
[9] Doerner and Nix 1986; [10] Pharr et. al. 1992; [11] Fischer-Cripps 2000; [12] Klapperich et. al. 2001.

Relationship between crystallinity and nano mechanical modulus

Nanoindentation modulus measured using tip radius R = 20 μm



This figure highlights the relationship between elastic modulus (mean±std. error) and crystallinity for PEEK composites. Crystallinity values were obtained from Regis et. al. 2017.



This figure highlights the relationship between elastic modulus (mean±std. error) and lamellar thickness for PEEK composites. Lamellar thickness values were obtained from Regis et. al. 2017.

	Unfilled	PAN-CF	Pitch-CF
Correlation Strength	0.94	0.97	0.95
P-vals	0.018	0.007	0.012

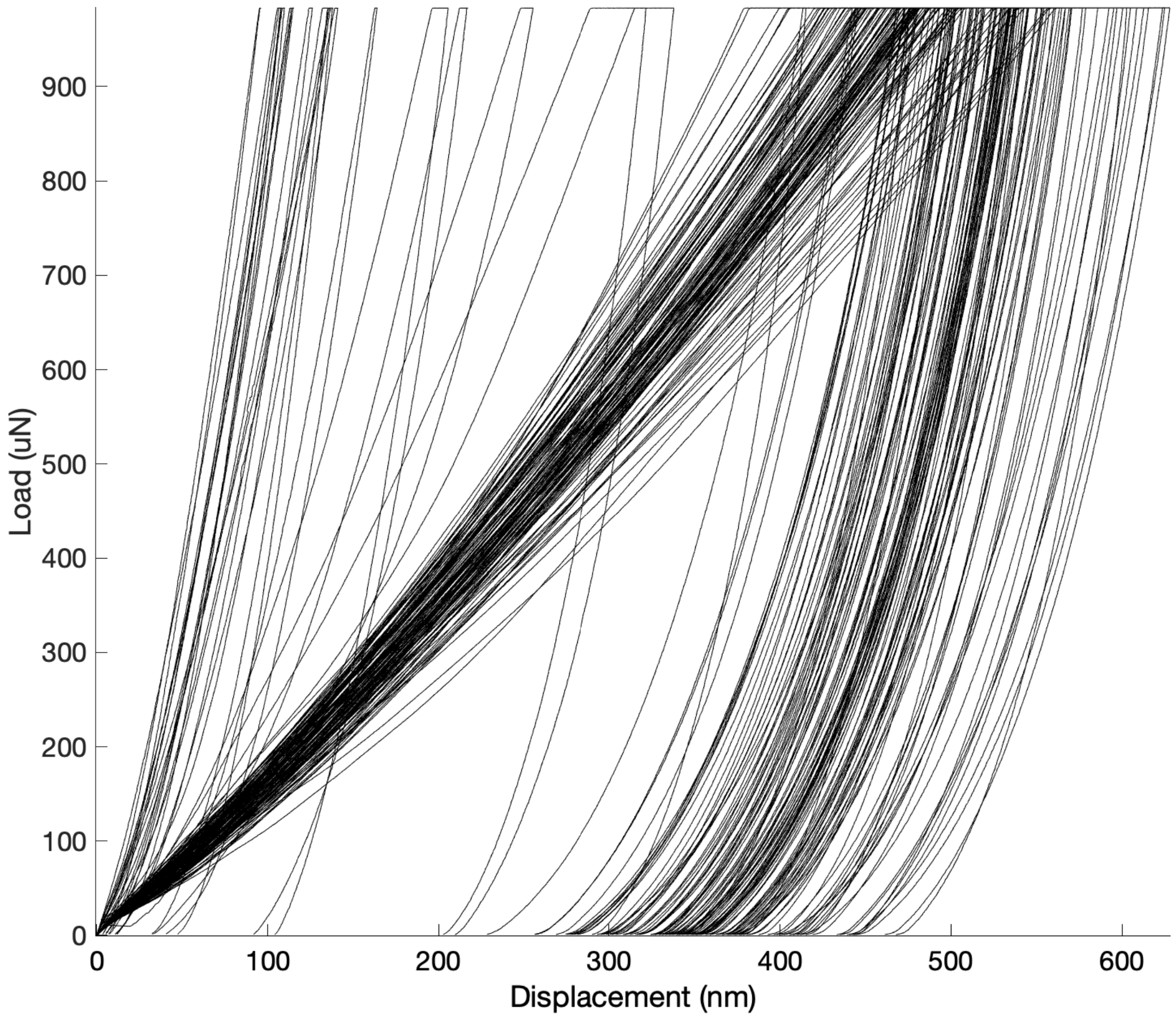
	Unfilled	PAN-CF	Pitch-CF
Correlation Strength	0.93	0.96	0.94
P-vals	0.022	0.008	0.018

Tailoring the microstructure to achieve desired nano-mechanical properties.

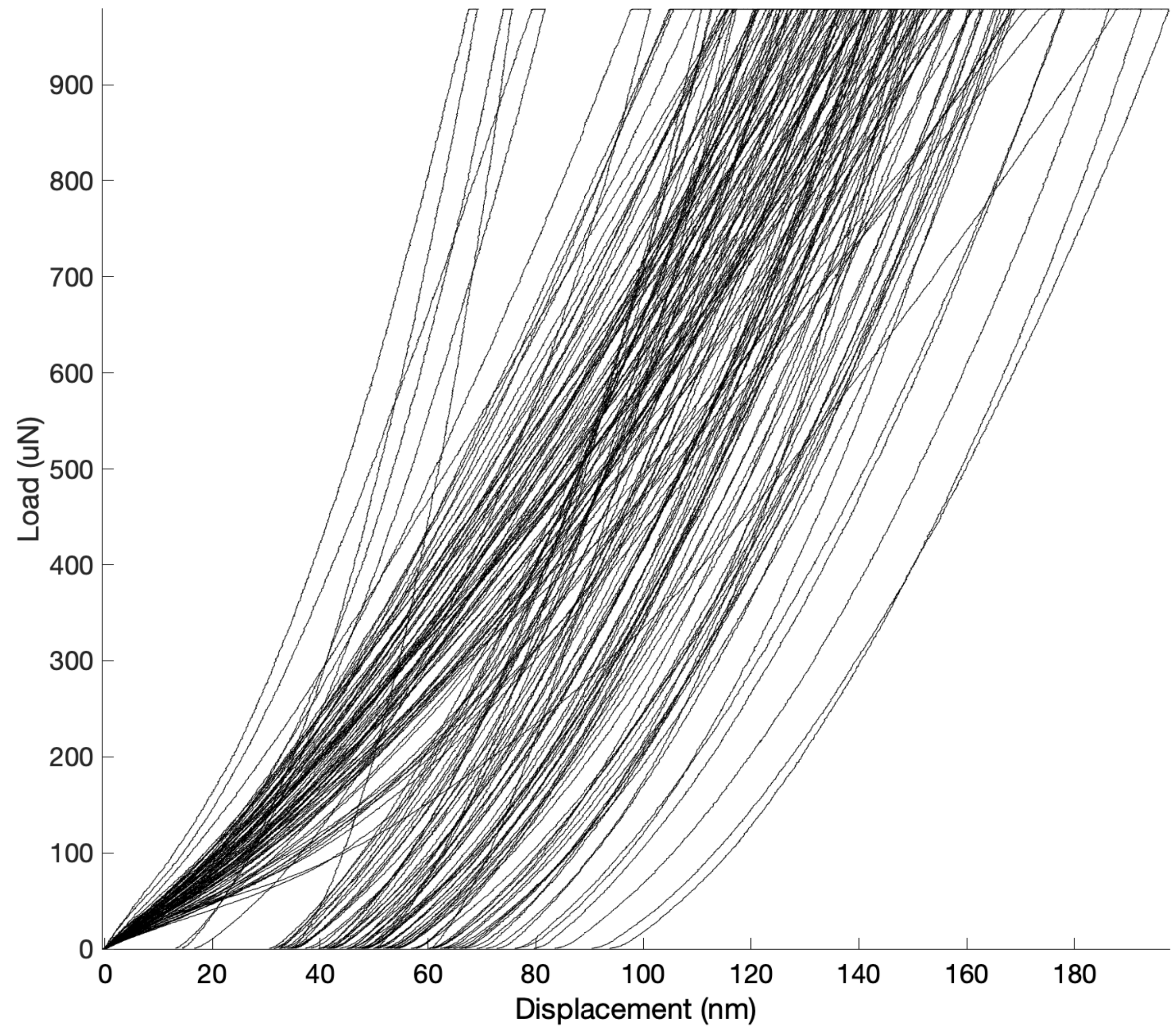
Microstructural differentiation depends on tip diameter

Nanoindentation Load-Depth Curves: PEEK with Pitch-based CF heat treated @ 300 °C

R = 1.5 µm



R = 20 µm



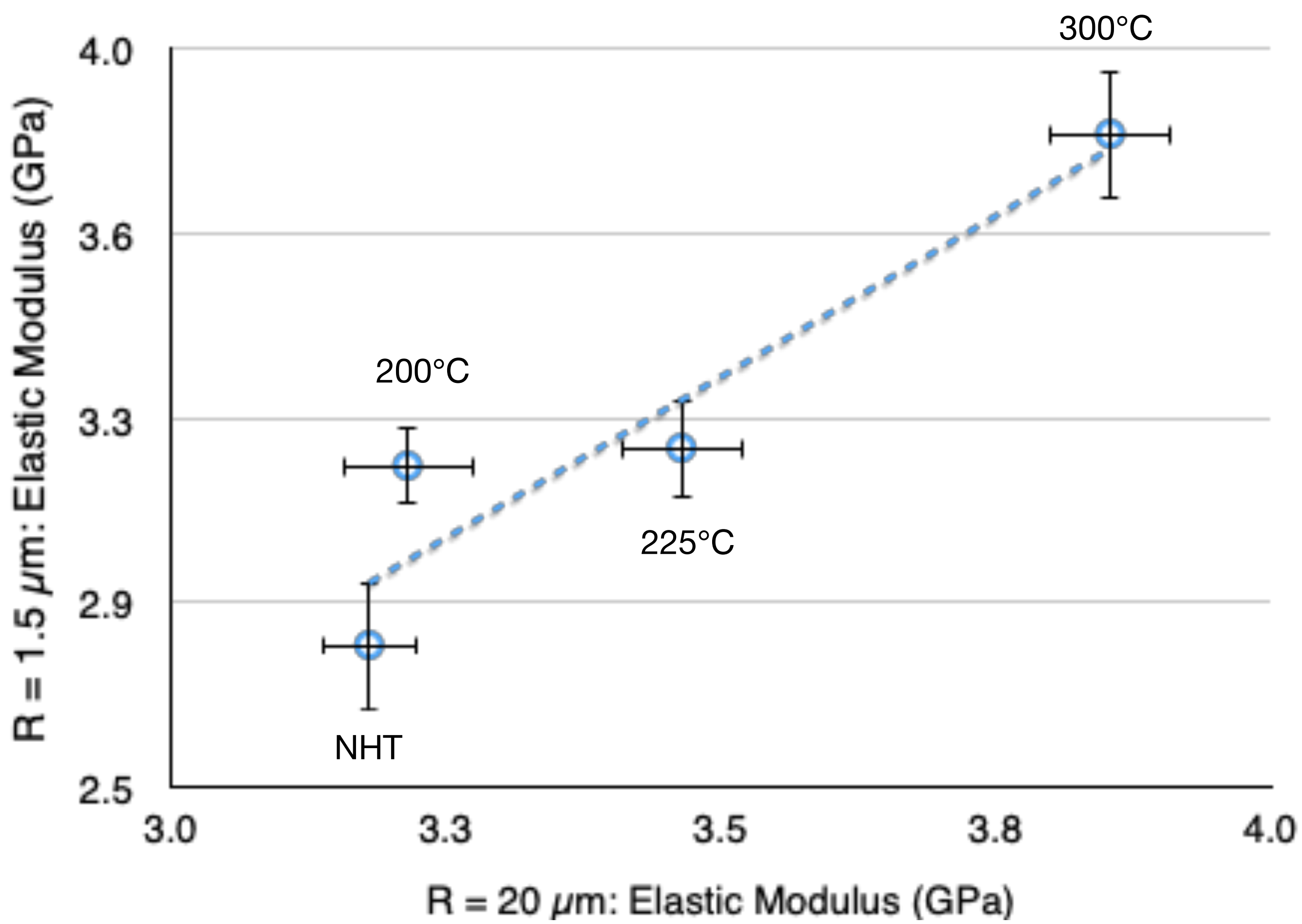
A smaller indentation tip is able to better capture the modulus of the individual component (fiber and the matrix); whereas, larger diameter tips indent over an expanded area containing a mixture of fibers and matrix.

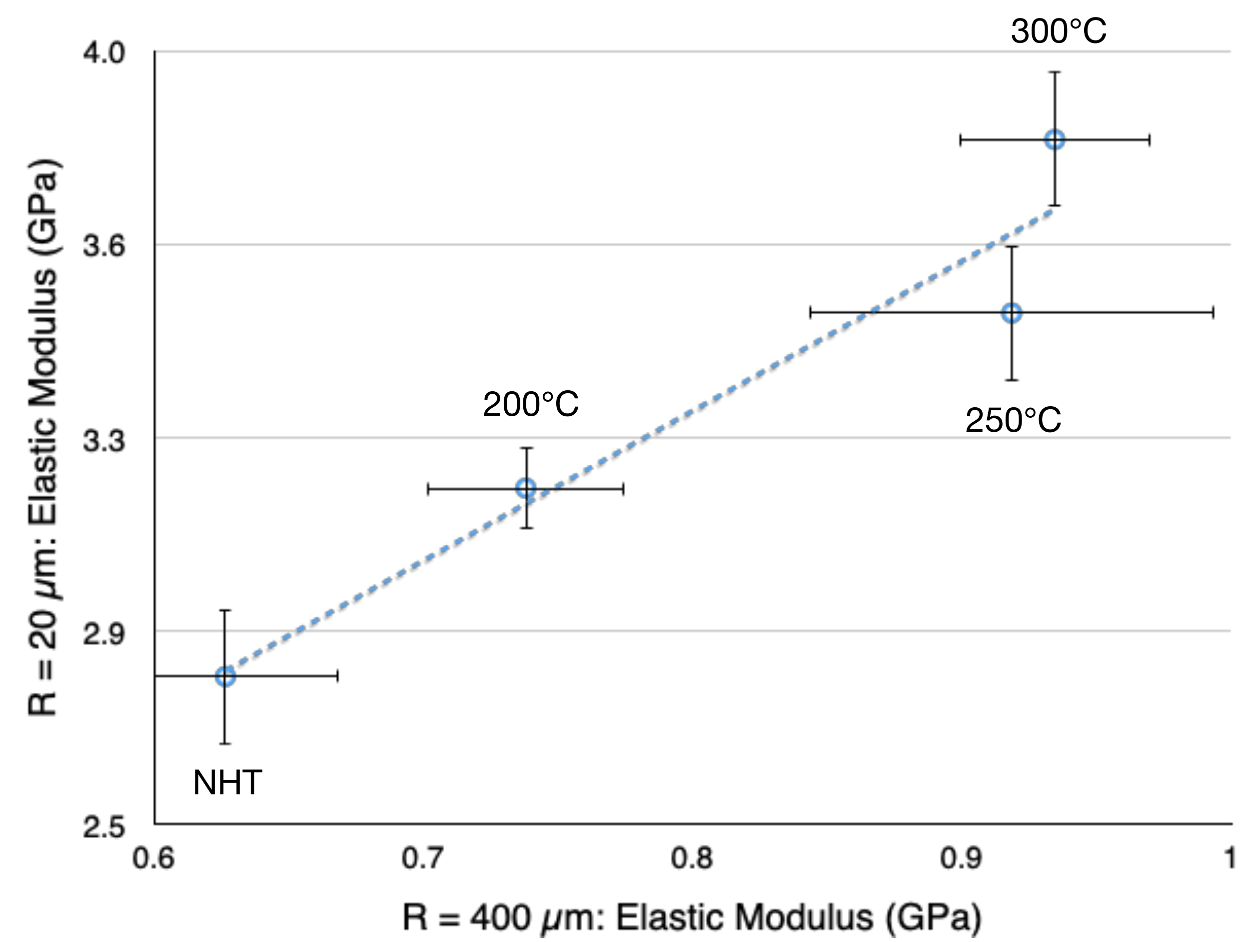
The smaller tip becomes necessary when comparing the behavior of each individual constituent across formulations.

Nanomechanical measurements are dependent on tip diameter

PEEK-Unfilled

Relating modulus across different diameter-sized tips





R = 1.5 μm vs. R = 20 μm

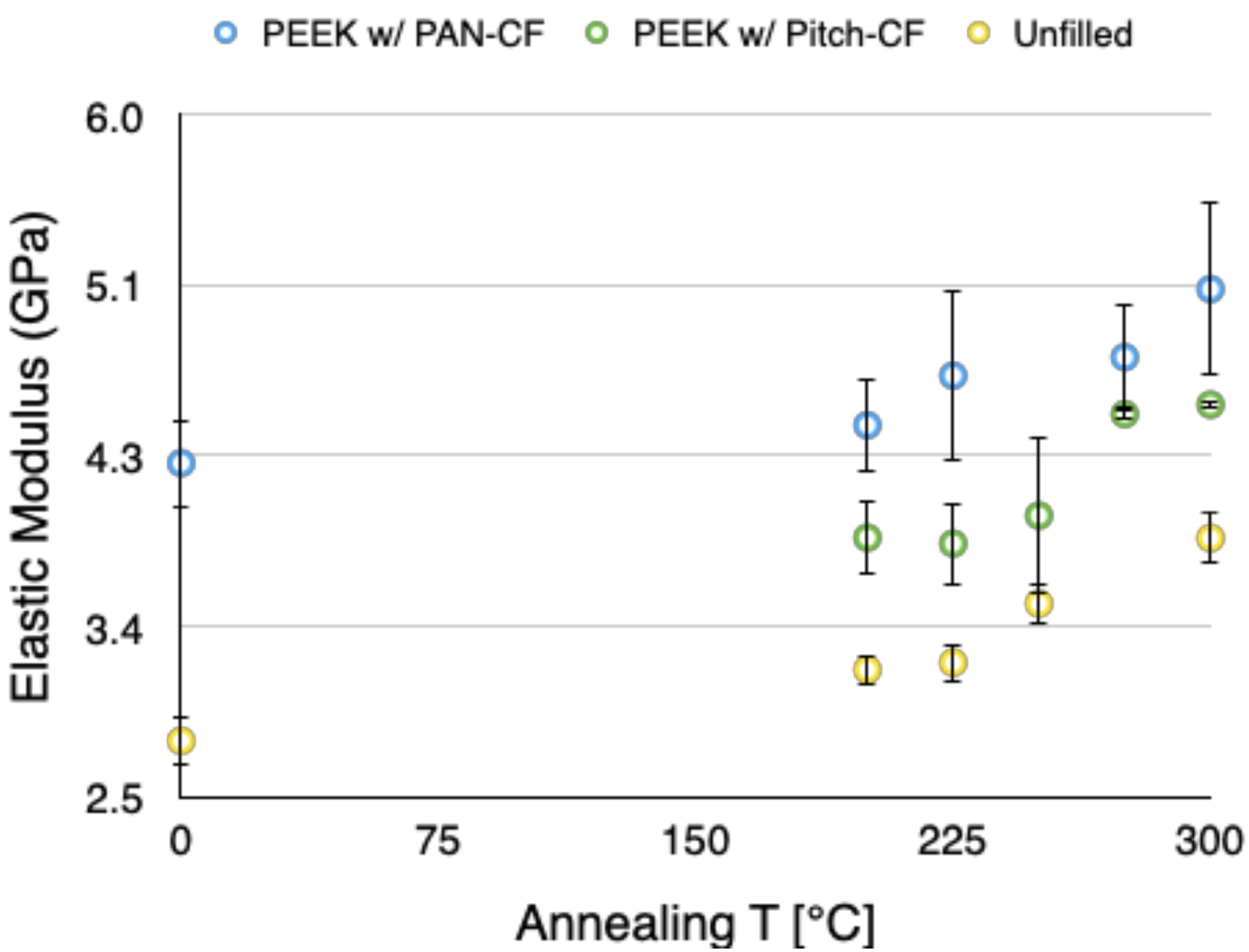
Correlation Strength	0.95
P-vals	0.06

R = 400 μm vs. R = 20 μm

Correlation Strength	0.96
P-vals	0.04

A difference in modulus with increase in tip diameter results from the changes in contact stresses beneath the indenter.

Correlating nano mechanical properties to annealing temperature



Nanoindentation modulus (mean±std. error) using tip radius, R = 20 μm.

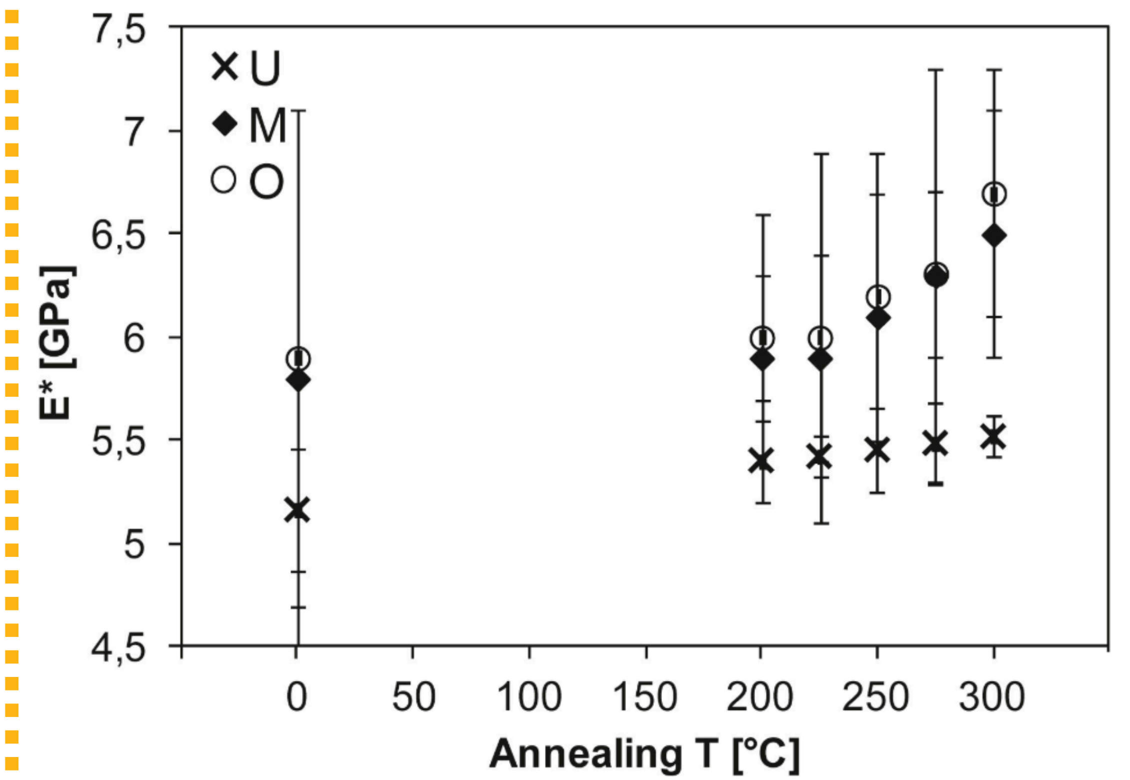


Image obtained from Regis et. al. 2017.

Nanomechanical properties for PEEK composites increase with increase in annealing temperature.

Discussion

- Strong correlations between nano indentation modulus and microstructural properties provide evidence on the utility of nano indentation methods for developing structure-property relations.

- A smaller indentation tip is able to better capture the modulus of the individual component (fiber and the matrix); whereas, larger diameter tips indent over an expanded area containing a mixture of fibers and matrix.

Future Work

- Future work on relating the macro mechanical properties to the micro and nano scale.
- Investigating the nano mechanical property dependency on tip-diameter for Carbon Fiber Reinforced PEEK.
- There is a need for developing a standard nano indentation method that enables comparison of materials across different researchers as nano indentation emerges as a viable characterization tool.

Acknowledgements

- Invibio for supplying PEEK samples.
- Prof. Lisa Pruitt
- Giuliana Davis for profilometry measurements.
- Medical Polymer Group at UC Berkeley

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