Replacement of carbon black with biochar in rubber composite materials

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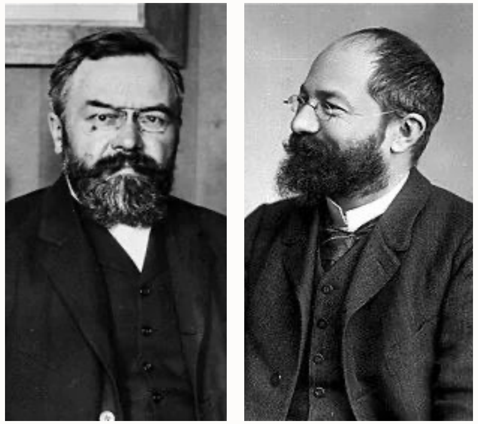
February 14, 2024

Tires and war: the catalysts for the carbon black industry

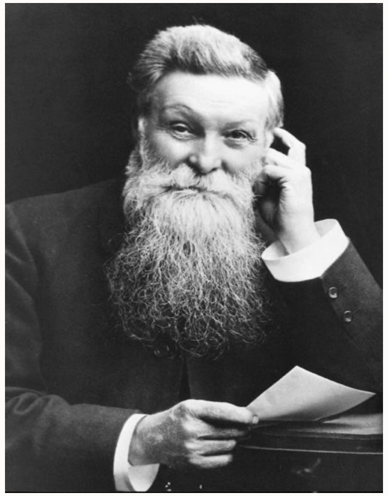
- 1830: Hancock and Goodyear obtain patent for mixing carbon black into rubber, but mainly for coloring
- 1845: Robert W. Thompson obtains 1st patent on pneumatic rubber tire
- 1888: John Dunlop develops first commercial tire for bicycles
- 1895: Michelin brothers introduce tires to “horseless carriage”

Goodyear

Thompson



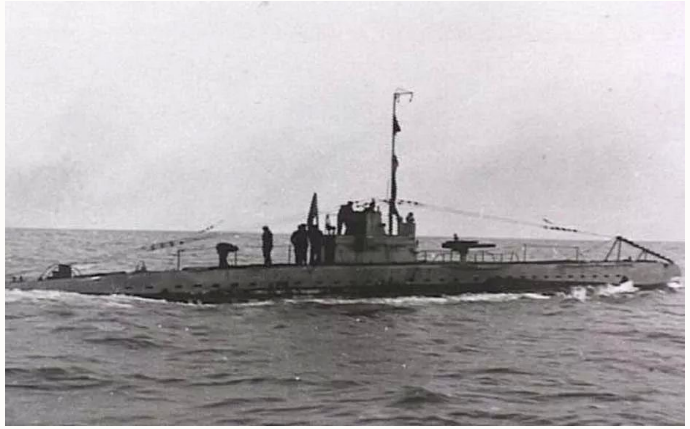
Michelin brothers



Dunlop

Tires and war: the catalysts for the carbon black industry

- 1904: S.C. Mote discovers reinforcement qualities of carbon black; in 1912 the Diamond Rubber Company of Akron, OH, acquired the rights to use carbon black from Mote’s company
- WWI initiated a high demand for rubber products, and carbon black’s advantages were shown in improved wear and lower failure rates – Germany pioneered synthetic rubber



Tires and war: the catalysts for the carbon black industry

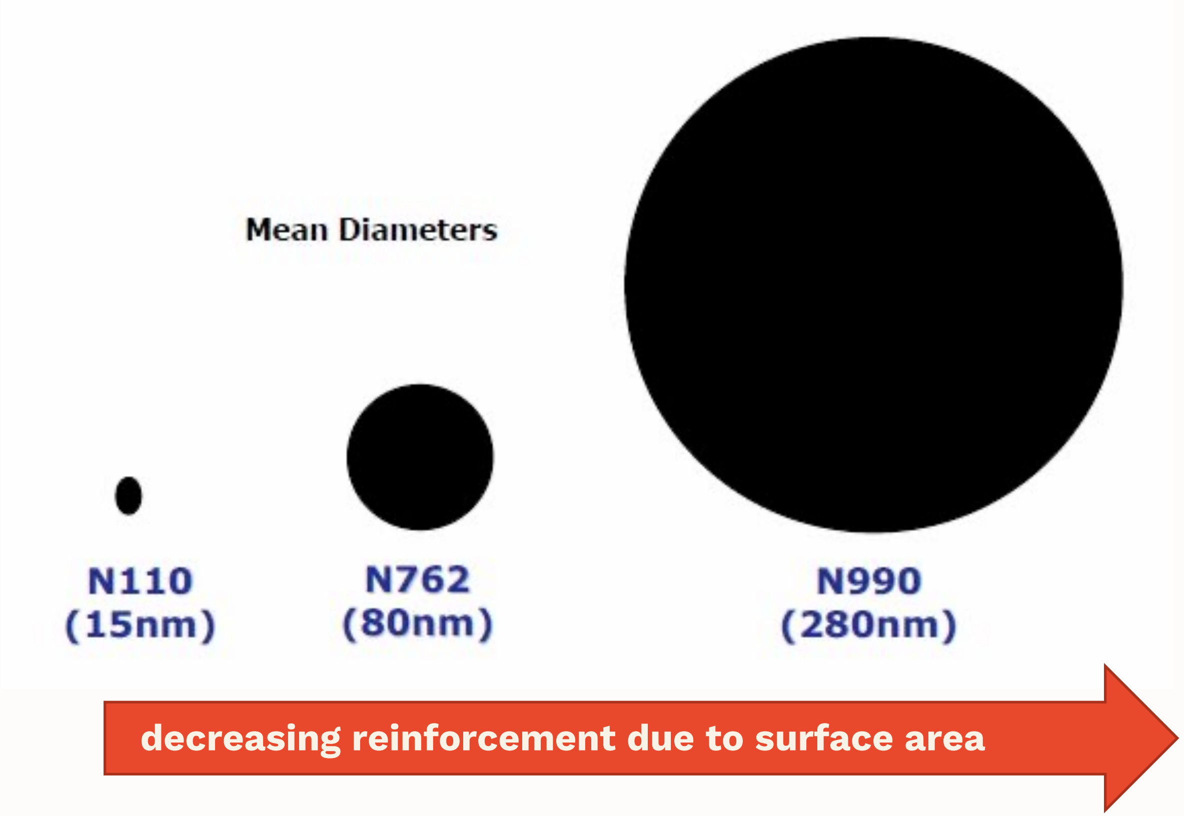
- WWII brought about the Synthetic Rubber Research Program since natural rubber was cut off by the Japanese

Military airplane: ½ ton	Battleship: 75 tons
Tank: 1 ton	Each soldier: 32 pounds

- Today 70% of rubber used in manufacturing is a descendant of GR-S

Modern carbon black advantages

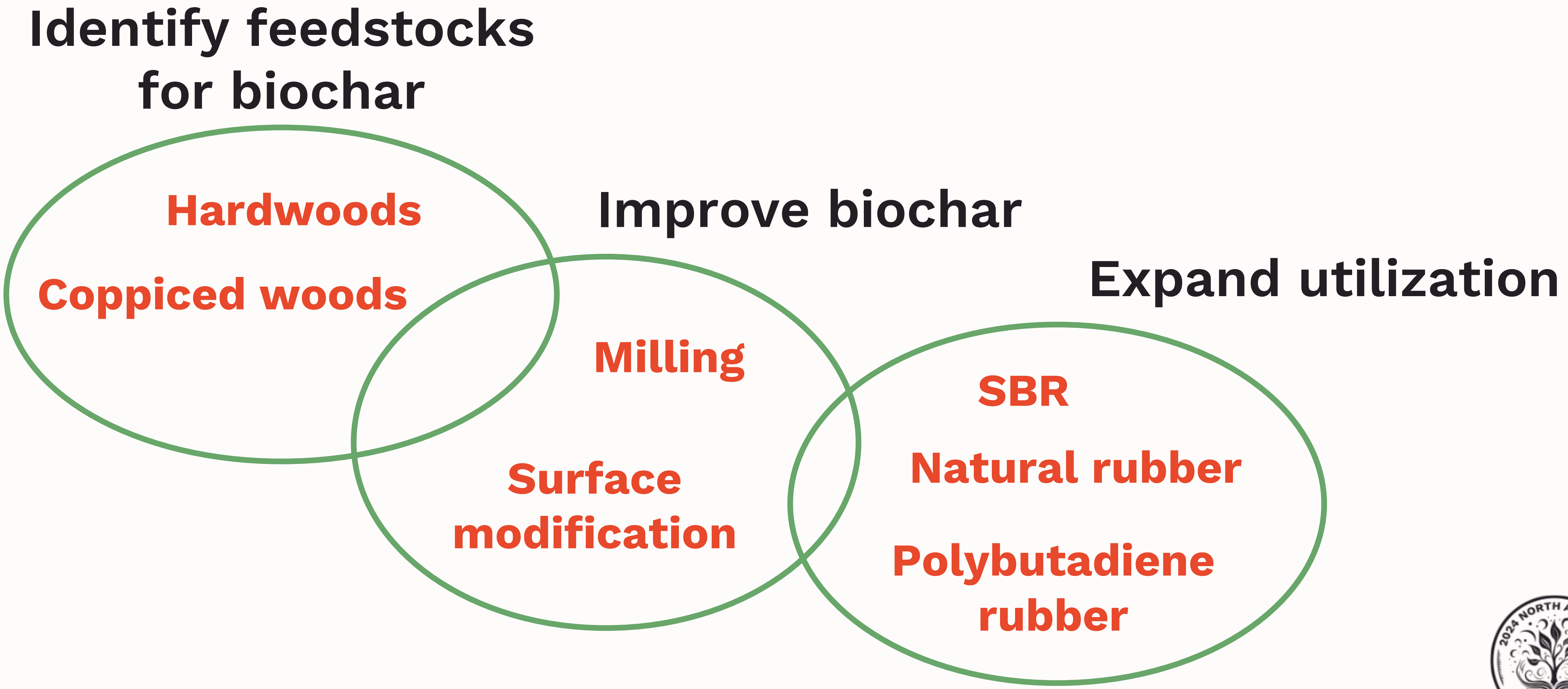
- Carbon black (CB)
  - today CB can be made in a range of sizes and structures
  - has excellent purity (>99% carbon)



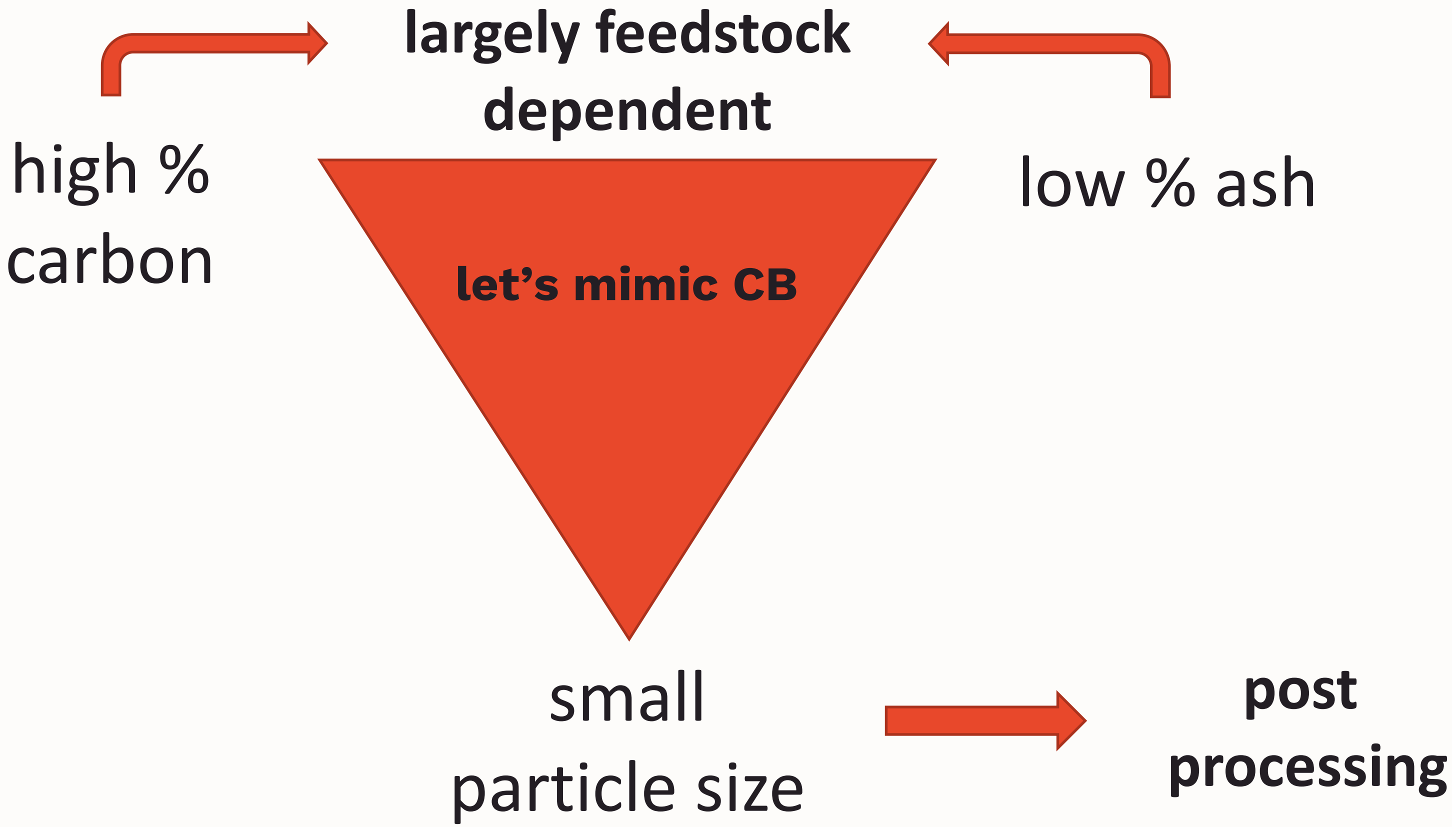
Replacing carbon black with biochar

- Renewable source of carbon; reduces petroleum dependence
- Energy capture during production
- Feedstocks are low-value non-foods
- Sequesters carbon

Project plan for utilizing biochar as rubber composite filler

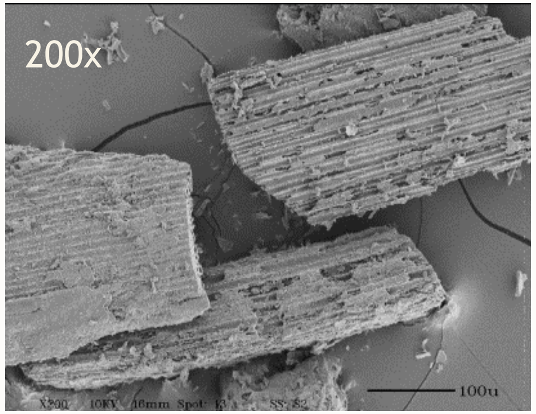


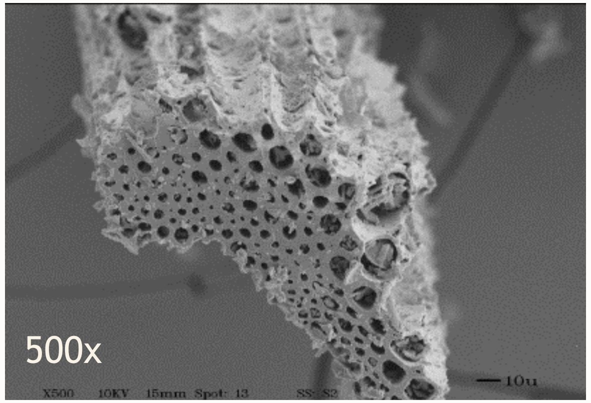
Desirable biochar feedstock targets



Early research: biochar feedstocks

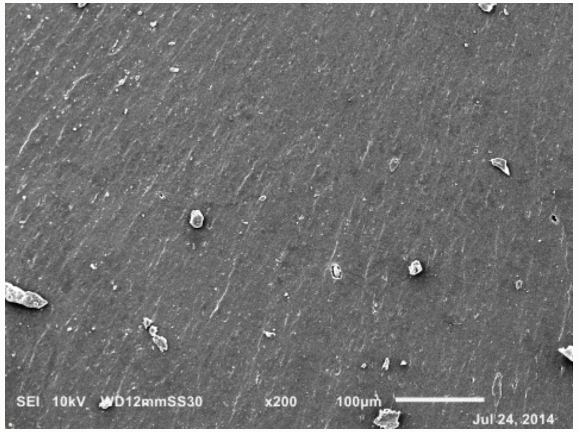
- Began by looking at corn stover biochar
  - agricultural waste product
  - 45% carbon, 40% ash 😬
  - at 10% total filler, composite had decent strength but was softer (low modulus)
  - takeaway: increase carbon content and decrease ash content of biochar



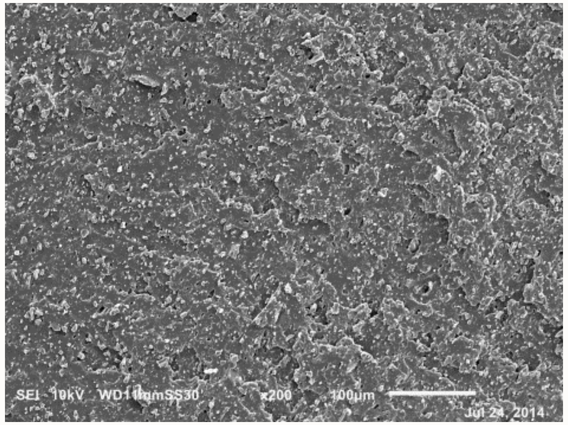


Improving carbon:ash ratio with hardwood feedstocks

- Lab produced birch wood char
  - 89% carbon, 1.8% ash
  - at <u>30%</u> total filler, this biochar can replace up to 50% of the CB and tensile properties were close to the CB control
  - similarly, at <u>40%</u> total filler, could replace 25% CB and tensile strength still close to CB control
  - low modulus still a problem



CB control composite@200x



birchwood composite@200x

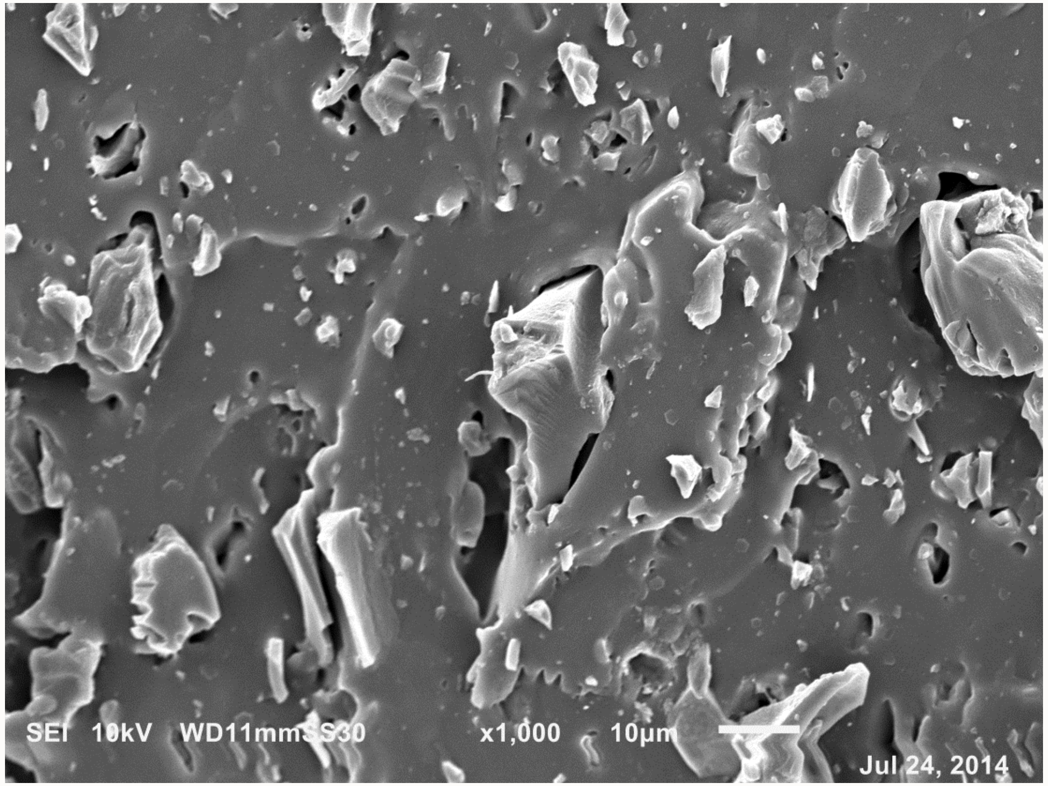
Coppiced woods

6” diameter in
4 years growth

- Poplar and *Paulownia elongata* biochar
  - 89-95% carbon, 1.9-2.5% ash
  - at 10% total filler, replaced 25-50% of the CB with biochar; had improved tensile strength and elongation but lower modulus
  - biochar had small population of very large particles ~3-10 microns, suspect this weakened the composites

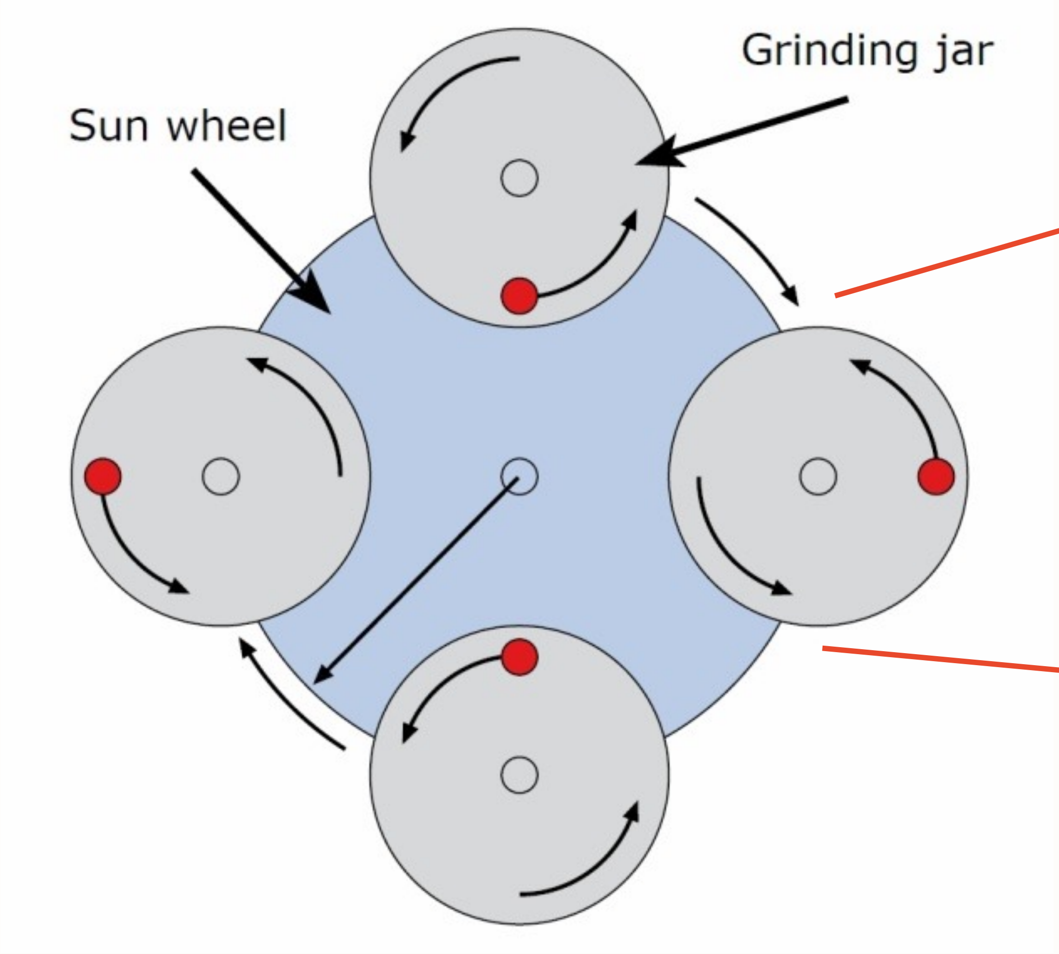
Large particles problematic

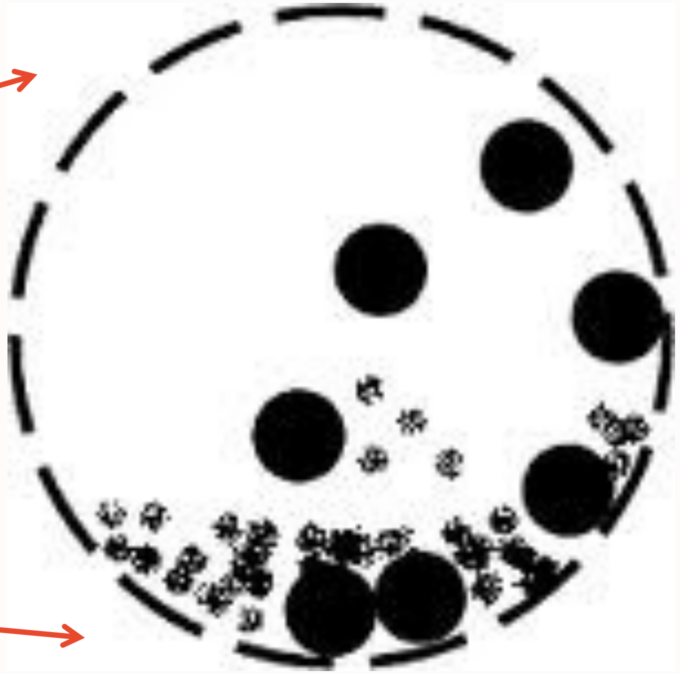
- smaller is better with fillers to aid dispersion and maximize surface area
- “large” particles > 3 microns can drastically reduce composite tensile strength, even at low concentrations (volume effect)
- localize stress in the composite



Particle size reduction via milling

planetary
ball
mill

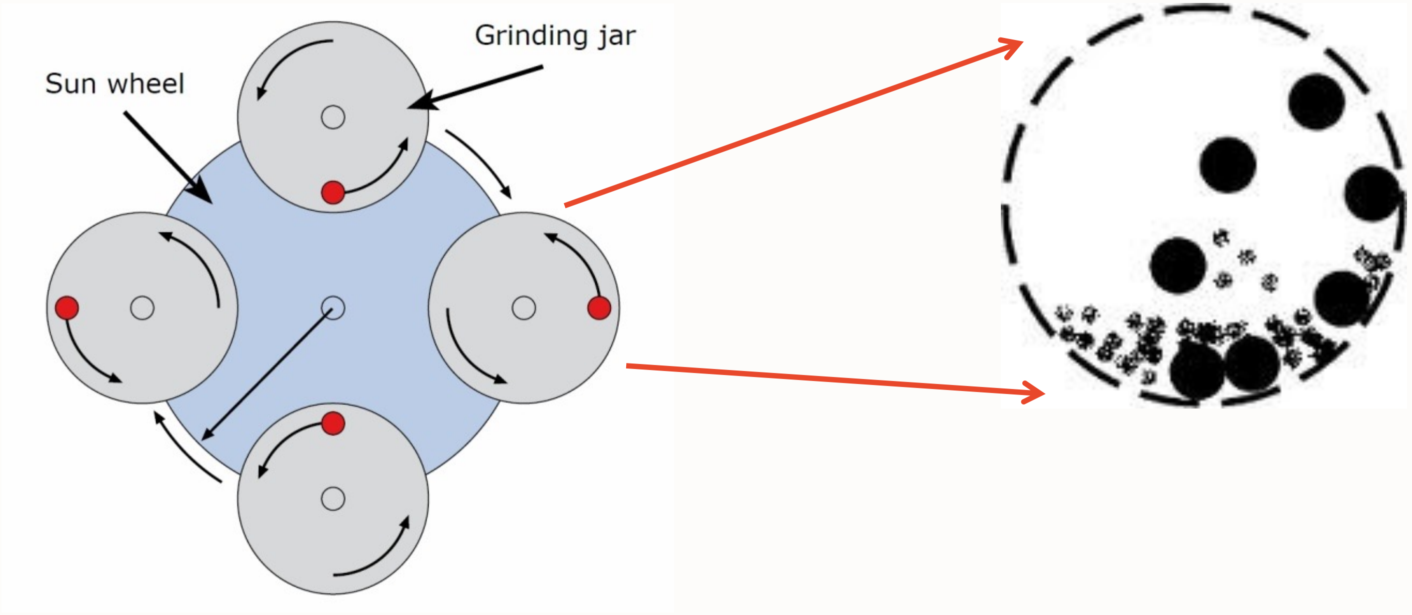




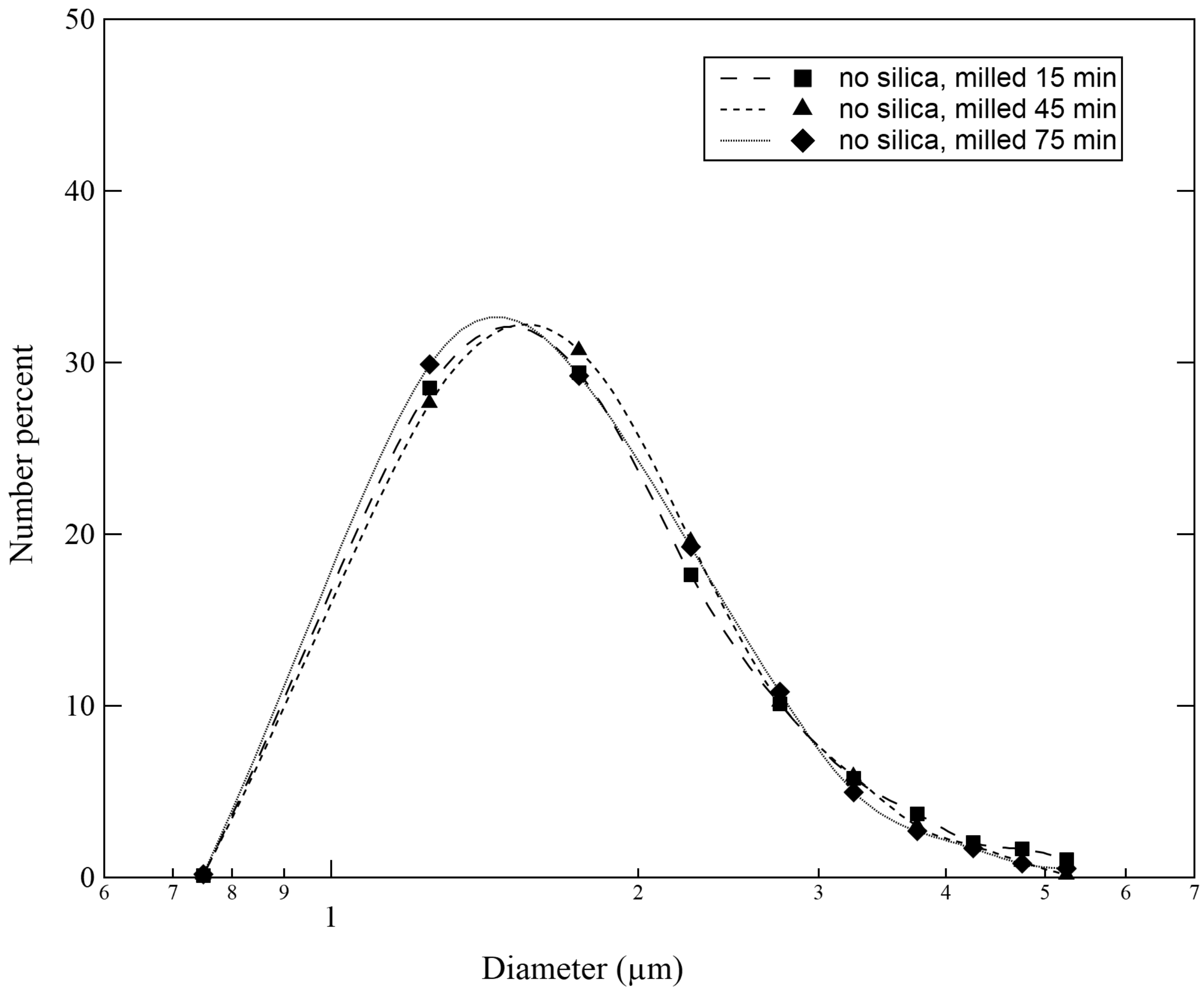
Particle size reduction via milling

- **Ball-milling biochar with nanosilica**
  - SiO_2 spheres ~ 12 nm in diameter
  - Hardness is ~ 6-7 GPa
  - Big advantage: SiO_2 is already a good composite filler so there is no need to remove it post-milling

planetary
ball
mill

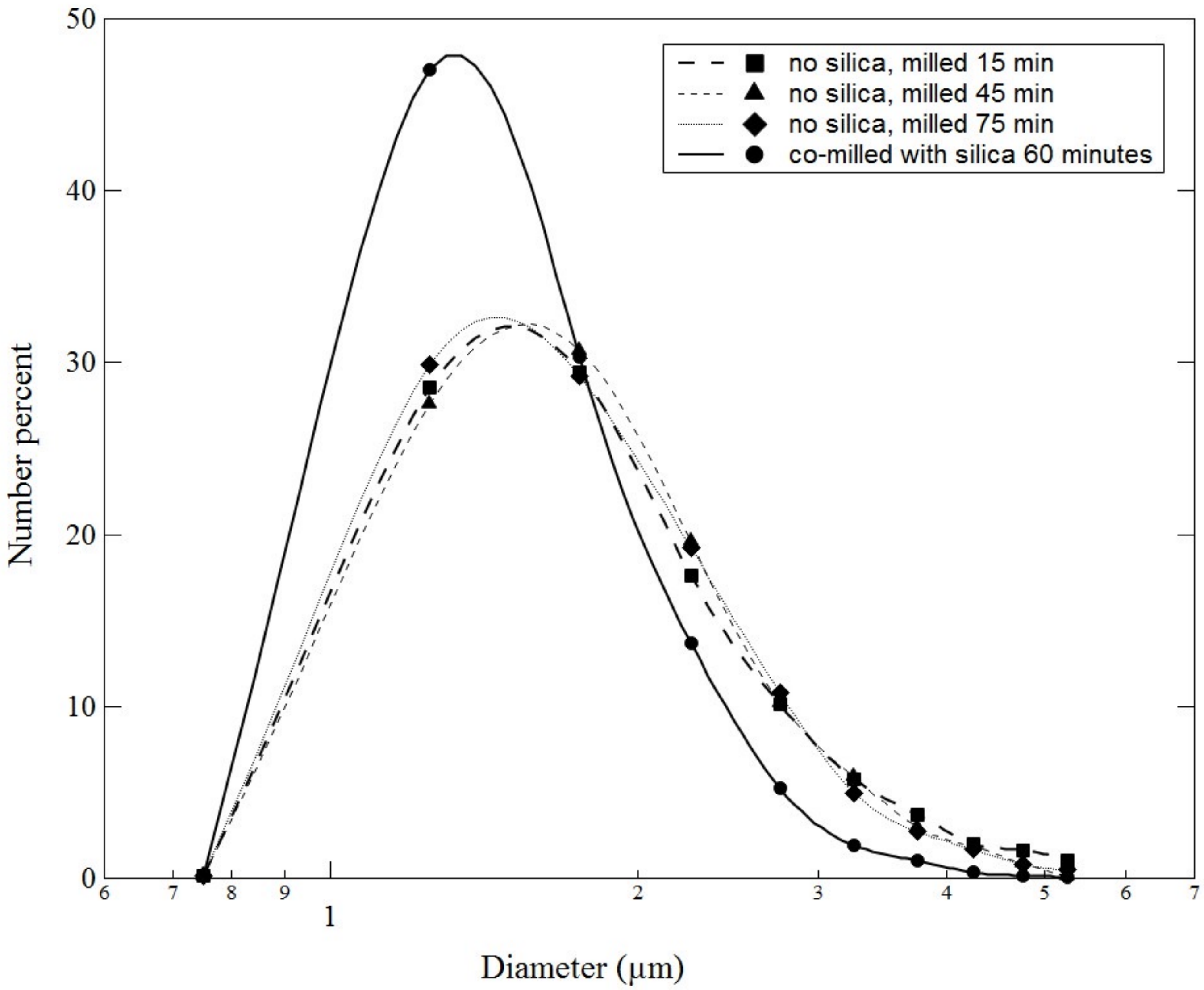


Effect of ball milling



Peterson, S.C.; Kim, S. Reducing Biochar Particle Size with Nanosilica and Its Effect on Rubber Composite Reinforcement. *J. Polym. Environ.* ***2020**, 28, 317-322, doi:10.1007/s10924-019-01604-x.*

Effect of ball milling + nanosilica



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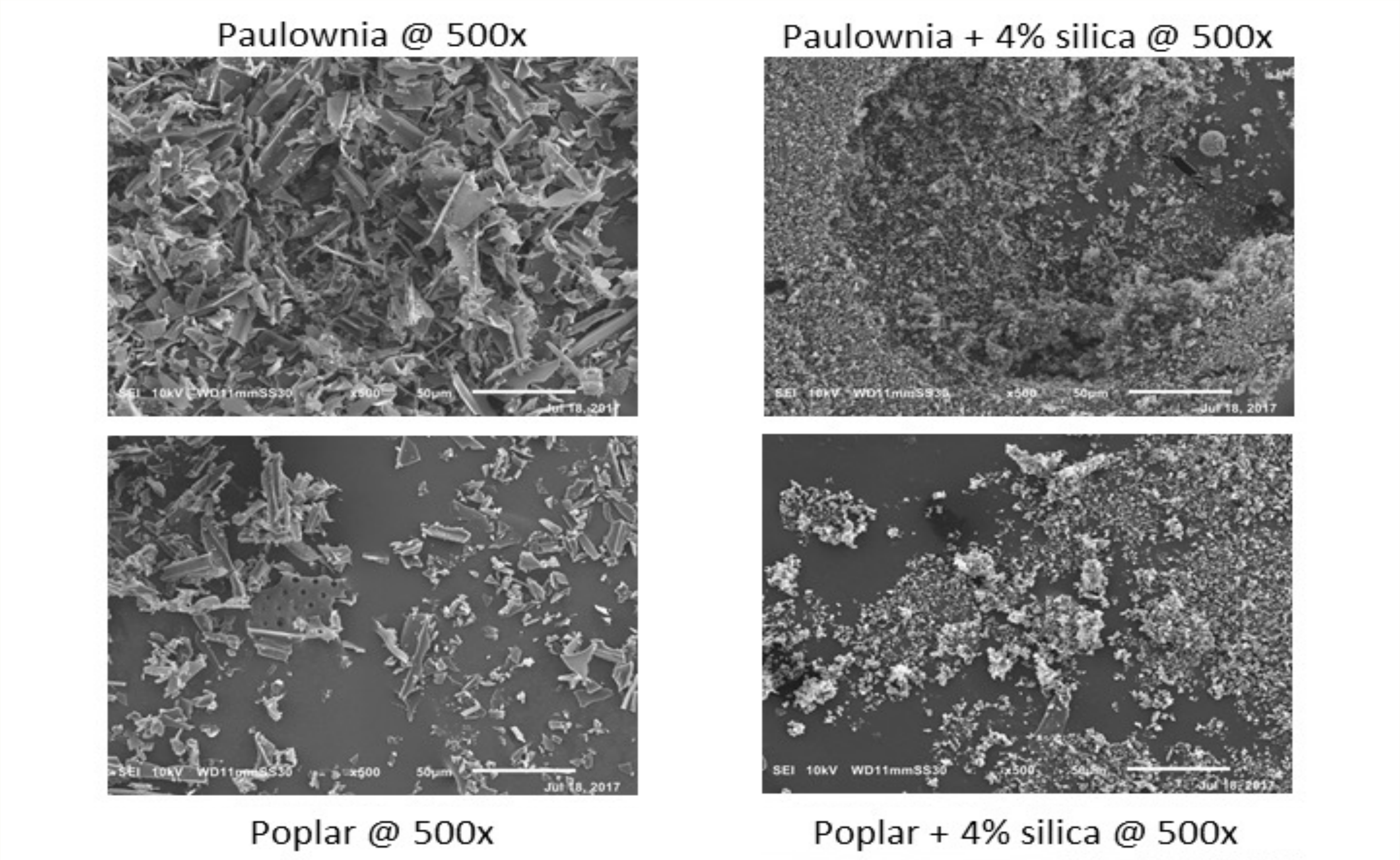
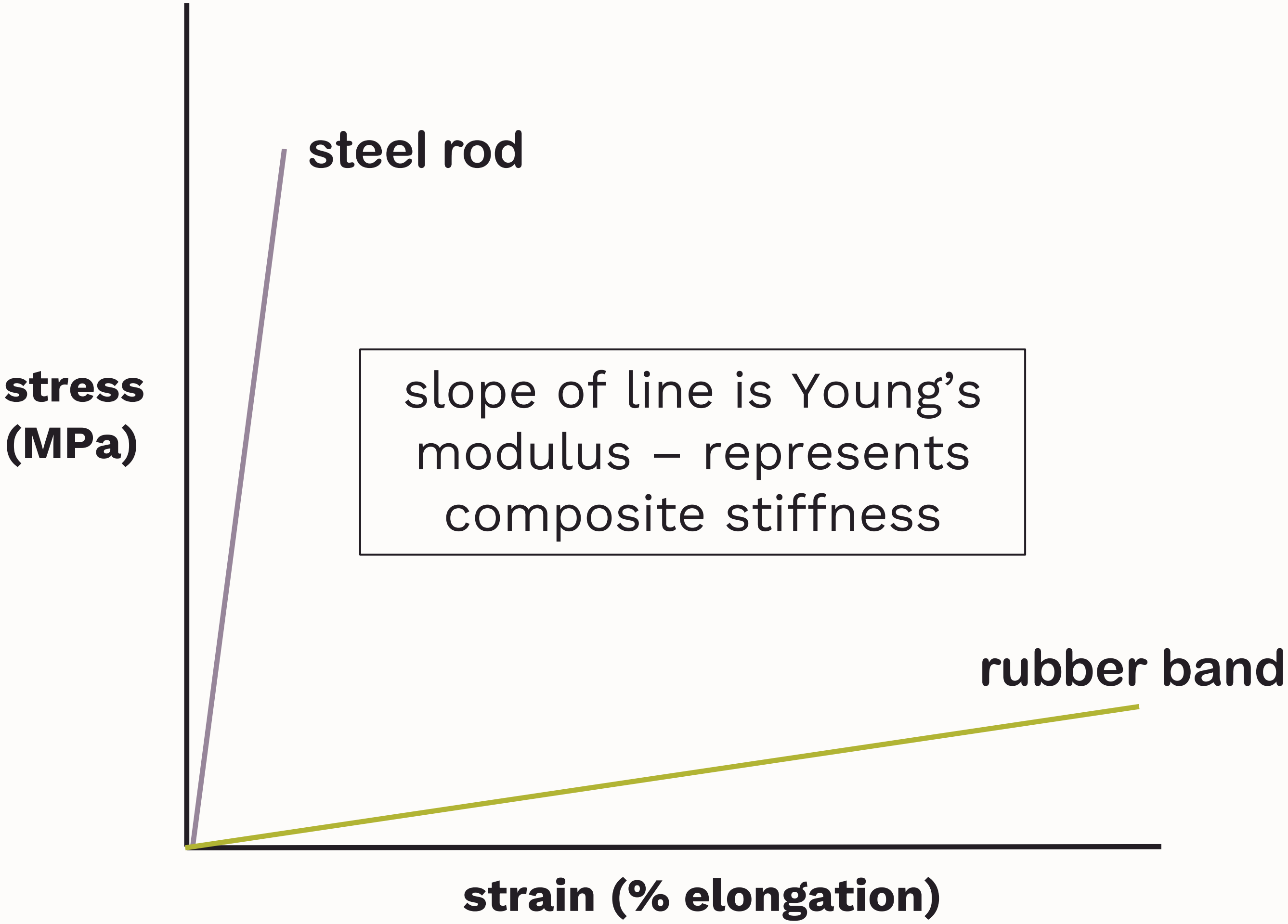
Effect of nanosilica milling



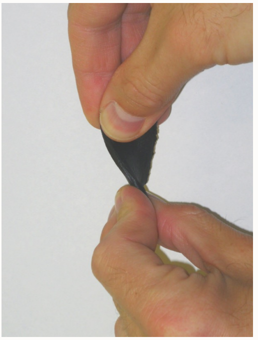
later found out that 1% nanosilica is sufficient & effective

Peterson, S.C.; Joshee, N. Co-milled silica and coppiced wood biochars improve elongation and toughness in styrene-butadiene elastomeric composites while replacing carbon black. *J. Elastomers Plast. 2018, 50(8), 667-676*, doi:10.1177/0095244317753653.

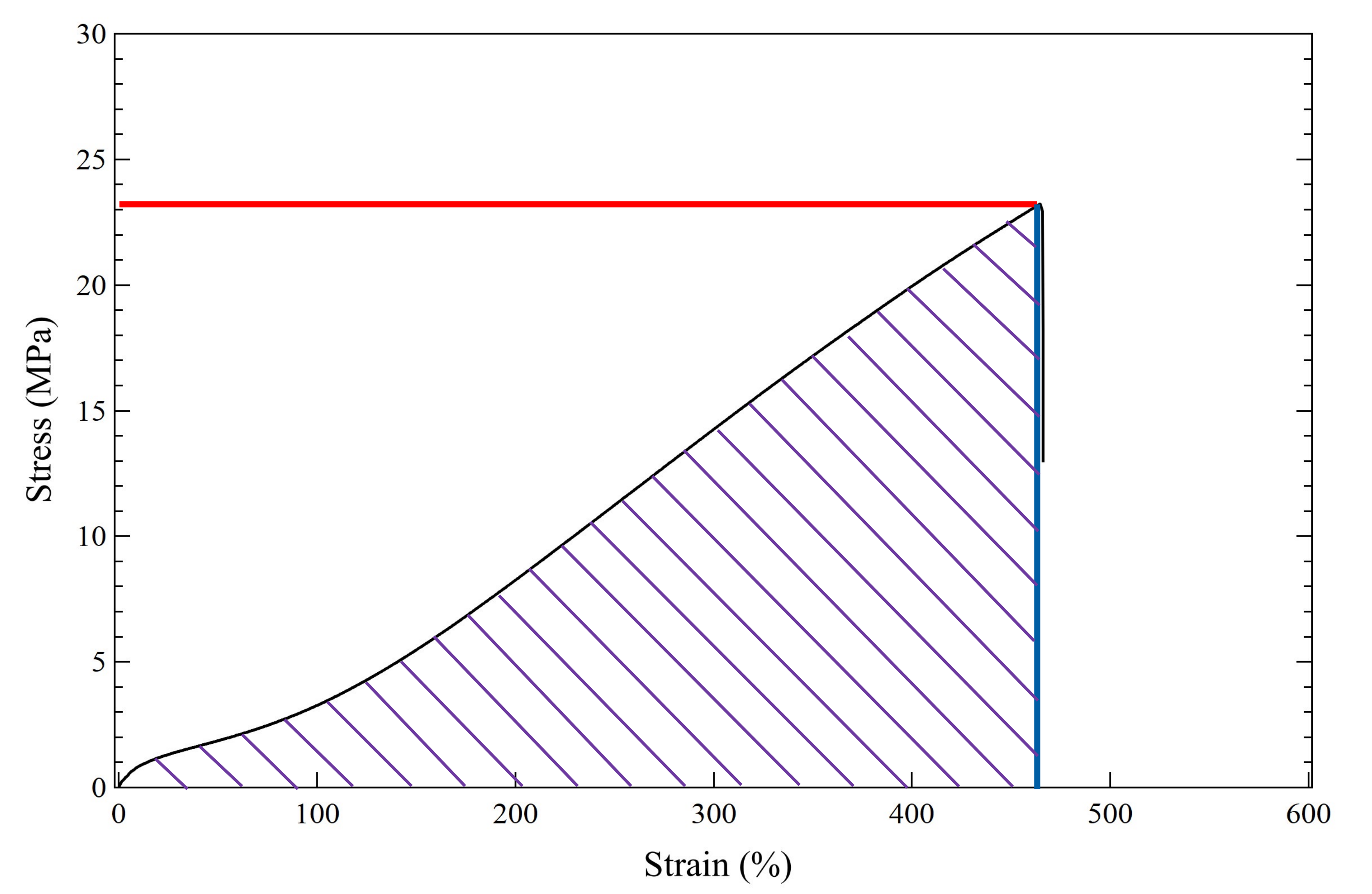
Tensile properties; our measuring stick



Instron UTM

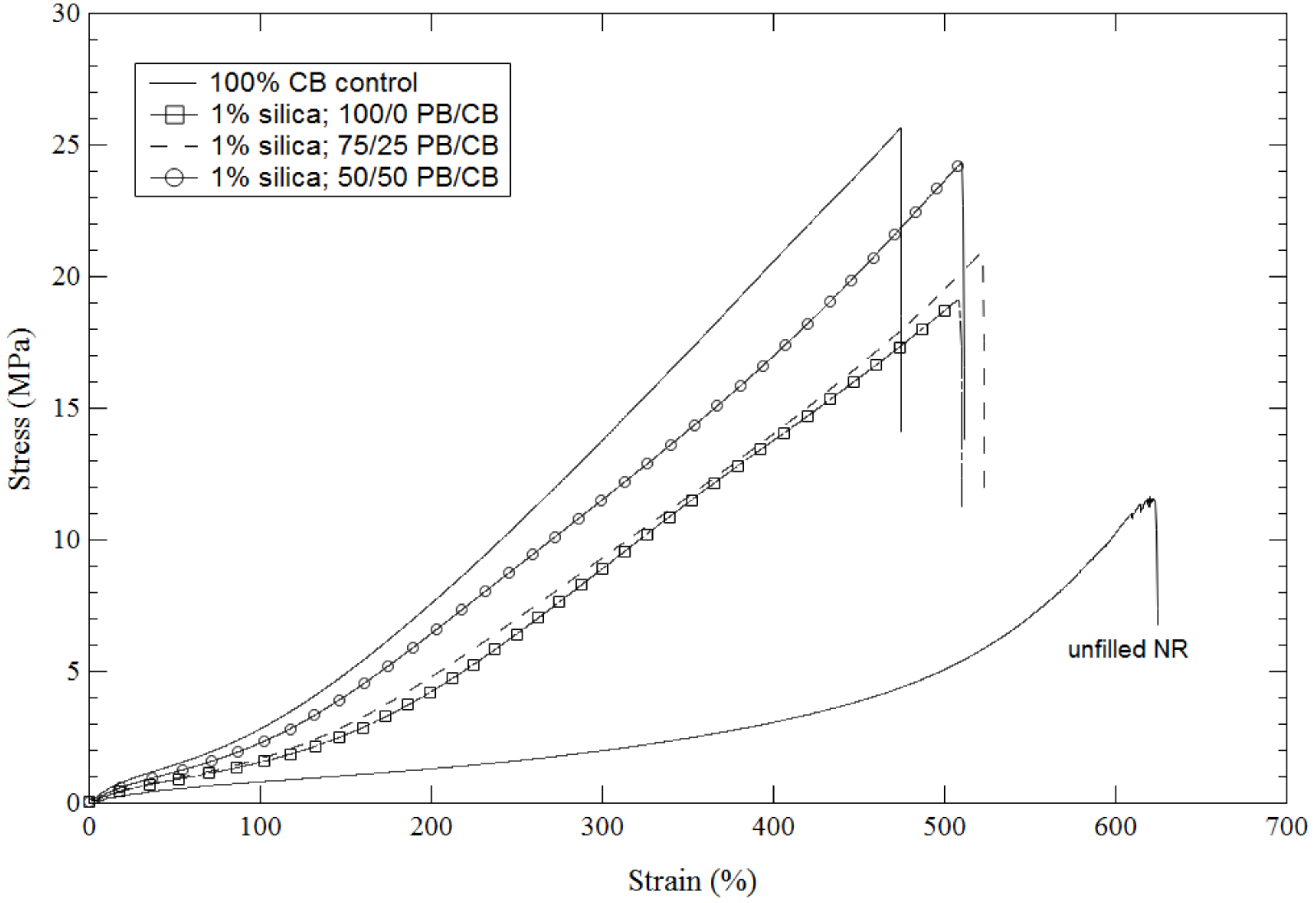


Tensile properties, our measuring stick



Tensile strength – stress needed to break a sample
% Elongation – strain on sample at break point
Toughness – area under the curve

Measuring strength via tensile properties



Results: CB replacement

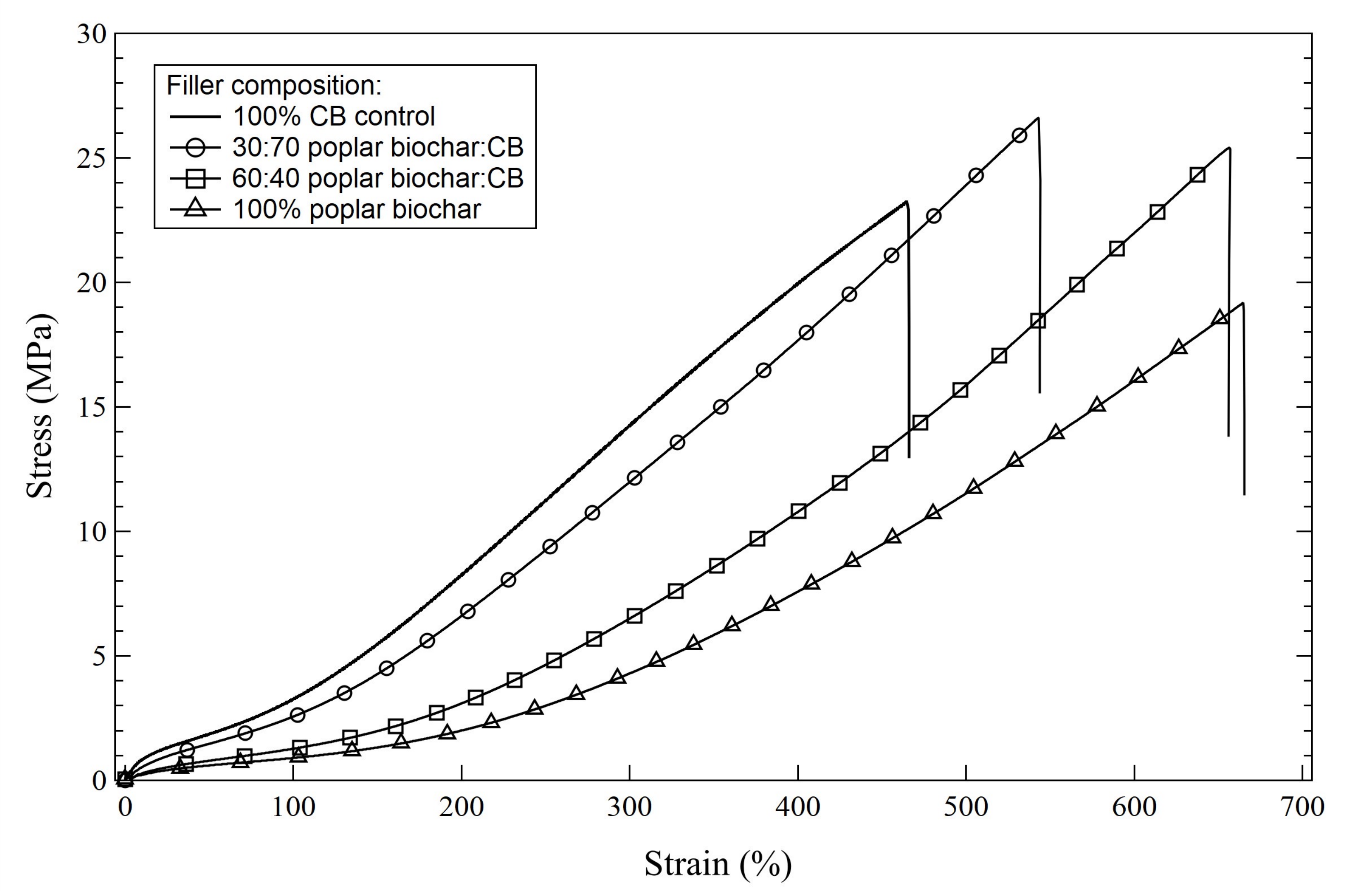
Rubber matrix	Feedstock	Total filler (%)	Carbon black replaced (%)
SBR	Birch wood	40	25
SBR	Wood waste	40	40
SBR	Poplar	40	40
SBR	Paulownia	40	40
NR	Paulownia	30	50
PBD/NR	Poplar	33	30
PBD/NR	Paulownia	33	30

Towards more sustainable natural rubber

- Natural rubber essential to US economy & military
- Over 90% of natural rubber from SE Asia
- USDA-OSEC prioritizing domestic natural rubber production
  - guayule – primarily in bark, typically whole plant homogenized
  - sunflower - leaves
  - Taraxacum kok-saghyz (TKS) “Russian dandelion” - root



Poplar biochar/CB/guayule rubber



Superior tensile strength with both 30 & 60% poplar biochar replacement

Peterson, S.C.; McMahan, C.M. Replacement of Carbon Black with Coppiced Biochar in Guayule Rubber Composites Improves Tensile Properties. *J. Compos. Sci. 2023, 7, 499,* doi:10.3390/jcs7120499.

Conclusions

- Coppiced hardwoods have been best performing feedstocks for composite filler
- For most rubber matrices, can replace ~40-50% CB with biochar for composites with similar or better strength and elongation
- Composite stiffness relative to CB filled composites still needs improvement; this is a current research focus
- Guayule composites show promising interactions with biochar filler & improve tensile strength relative to CB

Acknowledgements

- USDA/ARS
  - A.J. Thomas
  - Colleen McMahan
  - Chen Dong
  - Sanghoon Kim
  - Kelly Utt
  - Jason Adkins
- Non-USDA/ARS
  - Steve Nichols (Green Carbon Nanostructures)
  - Sriraam Chandrasekaran (ISTC/Eastman)
  - B.K. Sharma (ISTC/ERRC)
  - Nirmal Joshee (Fort Valley State University)

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