

# Reactive Silicone Flexible Hardeners for Epoxy Resins

Bob Ruckle, Tom Seung-Tong Cheung  
Siltech Corporation



# Epoxy Resins

## ▶ Myriad Applications

- Adhesives
- Aerospace
- Coatings
- Composites
- Construction
- Electronics
- Specialty Applications
- Transportation



# Epoxy Resins

- ▶ Thermoset
- ▶ Often 2k
- ▶ Diverse Base Resins
- ▶ Cure Mechanisms
  - Amine
  - Mercapto
  - Anhydride
  - UV Initiated Acid
- ▶ Modifiers



# Epoxy Resin Properties

- ▶ Few Compromises
- ▶ Solvent Resistance
- ▶ Low Shrinkage
- ▶ Processability
- ▶ Insulative
- ▶ Adhesion
- ▶ Strength
- ▶ Relatively Brittle



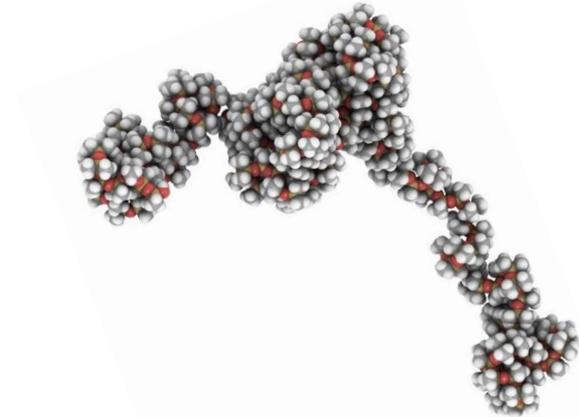
# Need for Flexible Epoxies

- ▶ Adhesives
- ▶ Composites
- ▶ Electronics
- ▶ Floors
- ▶ Marine
- ▶ Plastics
- ▶ Wood



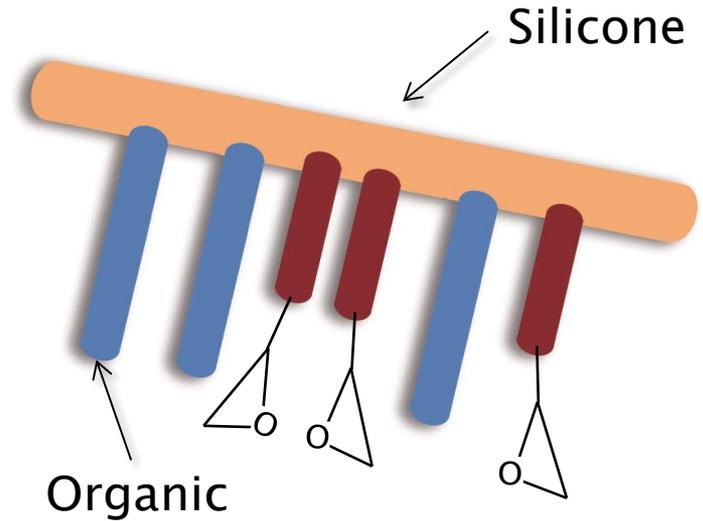
# Silicones

- ▶ Incompatible
- ▶ Gas Permeable
- ▶ Low Tg:  $-120^{\circ}\text{C}$
- ▶ Low Order of Toxicity
- ▶ Flexible, Compressible
- ▶ Low Surface Energy (ST, COF)
- ▶ Very Good Thermal Flexibility
- ▶ Excellent Spreading and Wetting
- ▶ Insulative (Electrical and Thermal)
- ▶ Thermally and Radical Stable ( $\text{O}_2$ ,  $\text{O}_3$ , Sunlight)
- ▶ Good Chemical and Very Good Water Resistance



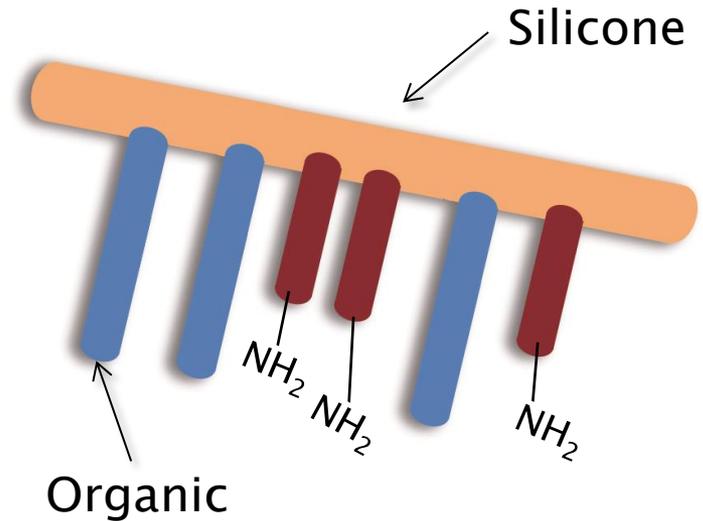
# Reactive Silicones

- ▶ Silicones can be synthesized with a variety of reactive groups including cycloaliphatic or glycidyl epoxy moieties.
- ▶ These can be reacted as homopolymers or copolymers with other epoxy resins



# Reactive Silicones as Hardeners

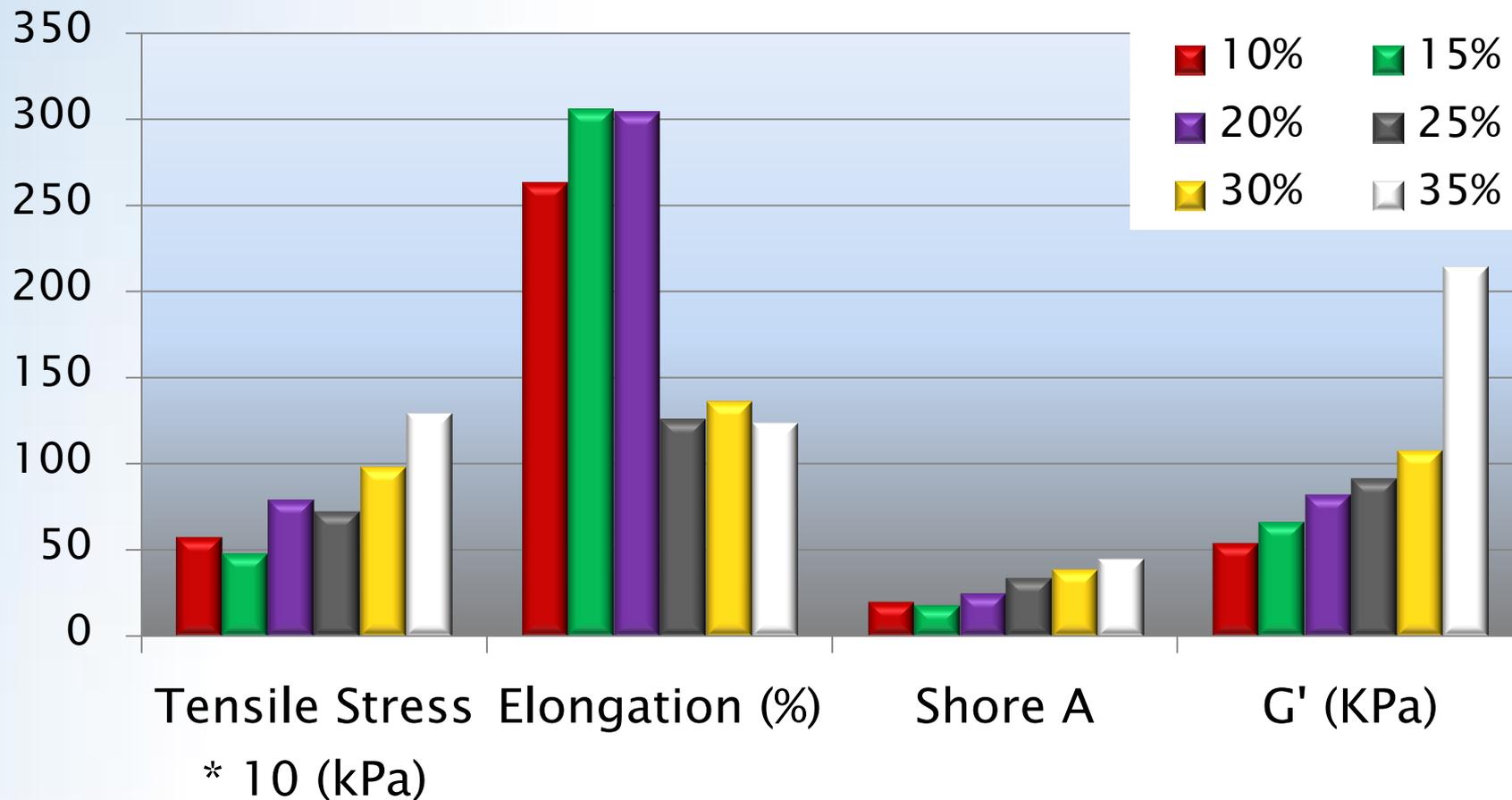
- ▶ ...or amine functionality
- ▶ These reactive silicones can be used as “flexible hardeners.”
- ▶ The organic groups provide solubility.



# Concept Proof: Epoxy Silicone Resins

- ▶ Three cycloaliphatic epoxy silicones are reacted in various ratios.
- ▶ Blends of High / Low MW di-functional epoxy silicones and a high X-link epoxy silicone.
- ▶ Cross-linking epoxy silicone kept at 8%
- ▶ MHPA and Imicure AM-1 used to affect cure.
- ▶ Cured at 100°C for 4 hours.
- ▶ Properties are followed with Brookfield DV-III Rheometer AR-G2 or measured with Instron #1122.

# Cycloaliphatic Epoxy Silicones



Percent of low MW Linear

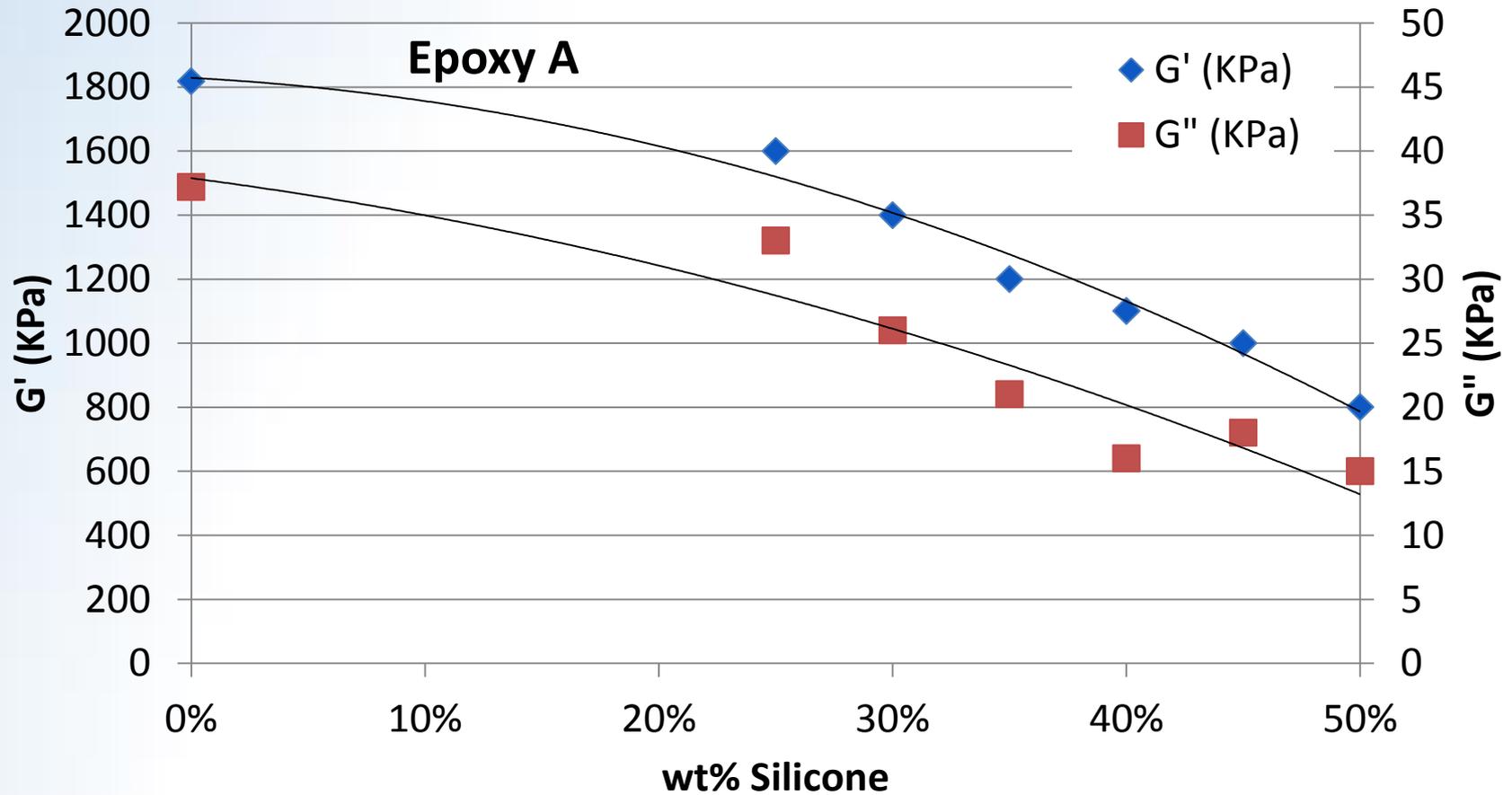
# Silicones Used

Silicone	# Reactive Sites	Equivalent Weight	Organic Group
Epoxy A	1 EP/3 OH	2400	Polyether
Epoxy B	1 EP/5 OH	8200	Polyether
Hydroxyl A	3 OH	3800	None
Hydroxyl B	2 OH	1980	None
Hydroxyl C	4 OH	360	None
Hydroxyl D	4 OH	3000	Polyether
Amine A	4 NH <sub>2</sub>	300	None
Amine B	1 NH <sub>2</sub> /3 OH	2550	Polyether
Amine C	2 NH <sub>2</sub>	450	None

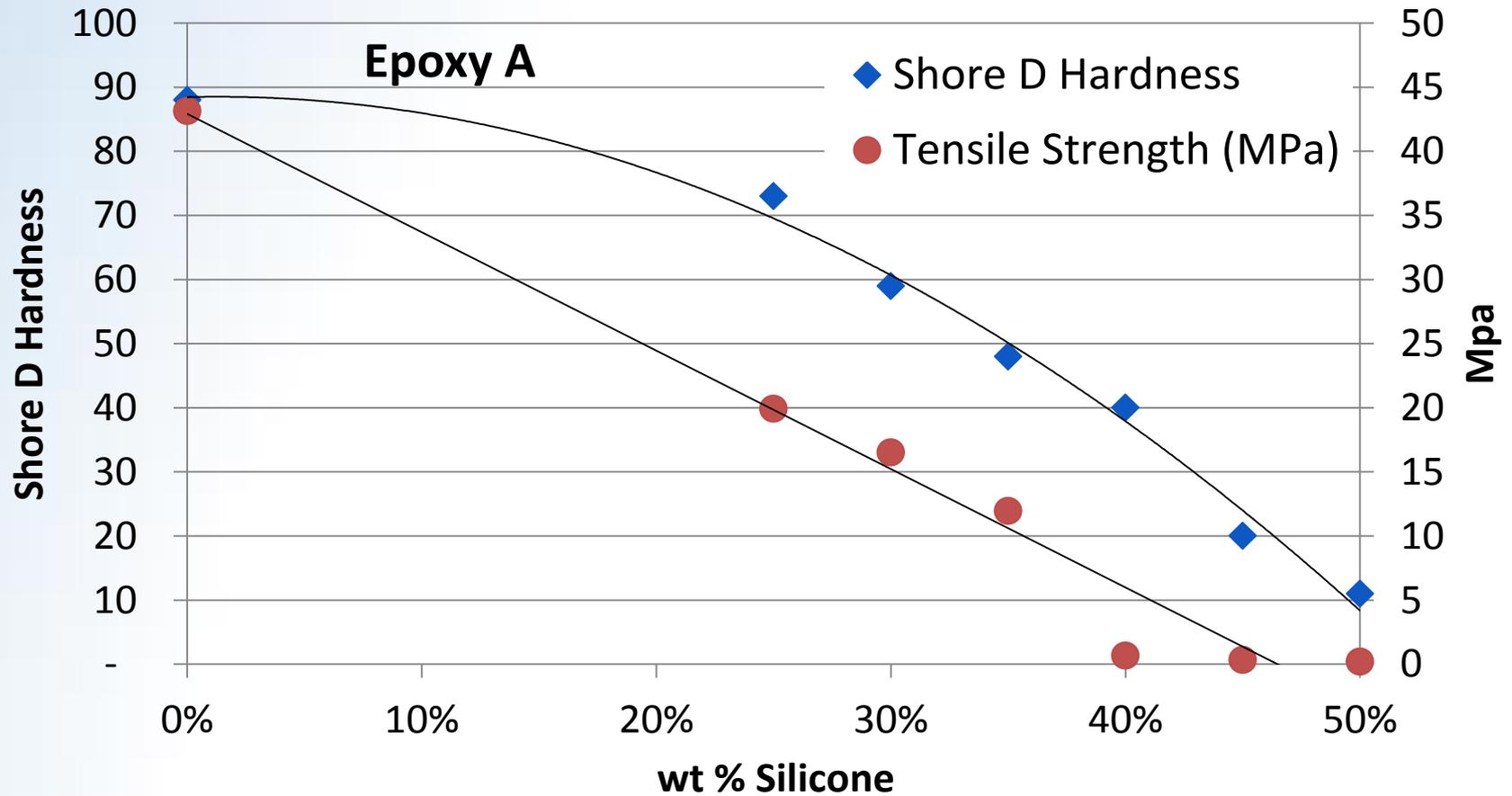
# DER 671–X75 Epoxy with Epoxy A

- ▶ Dow DER 671–X75, a commercial low MW, Epichlorohydrin/ bisphenol A system is reacted with epoxy silicone A.
- ▶ MHPA and Imicure AM–1 used to affect cure.
- ▶ Cured at 100°C for 4 hours.
- ▶ Properties are followed with Brookfield DV–III Rheometer AR–G2 or measured with Instron #1122.

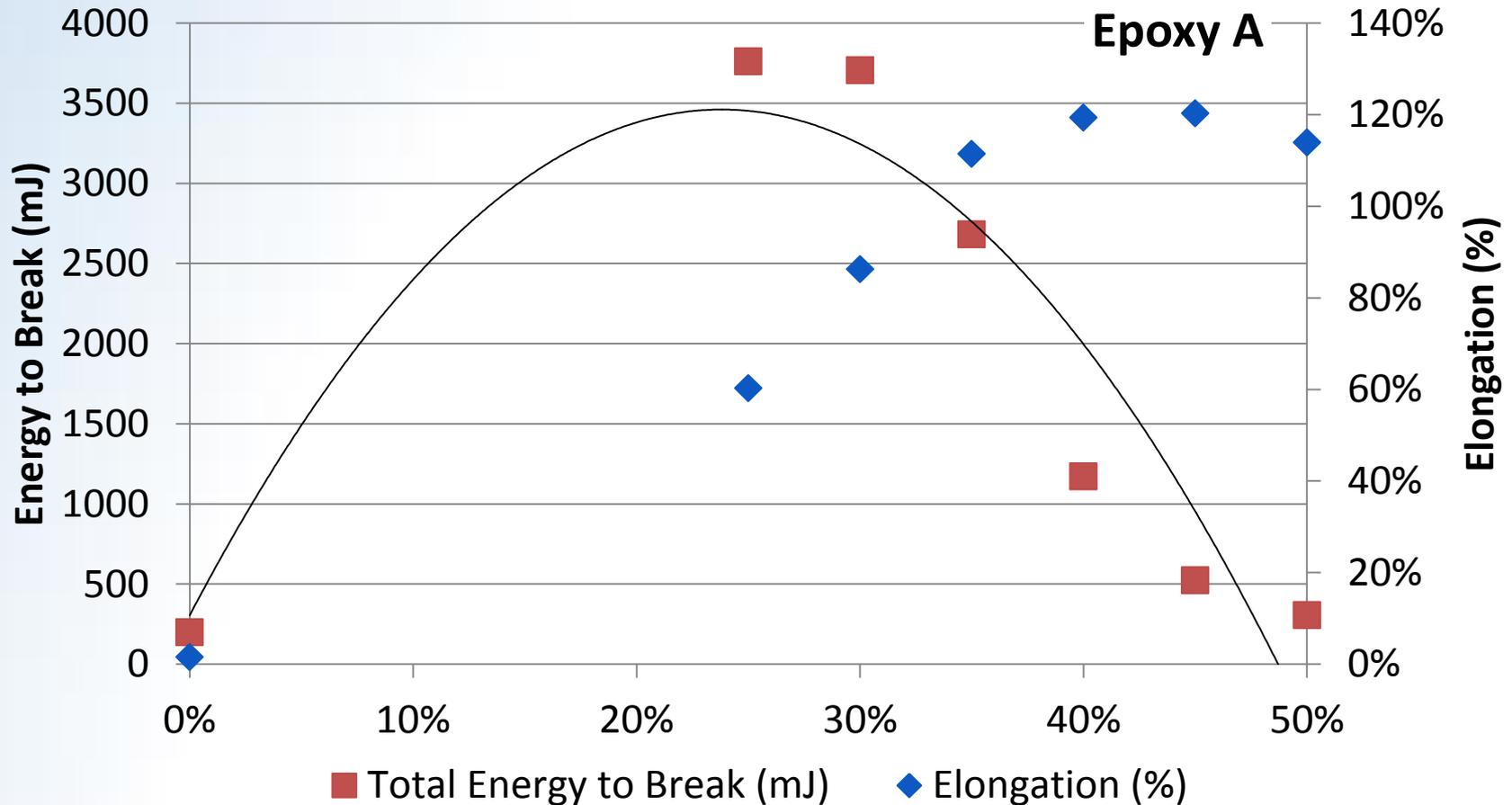
# Moduli



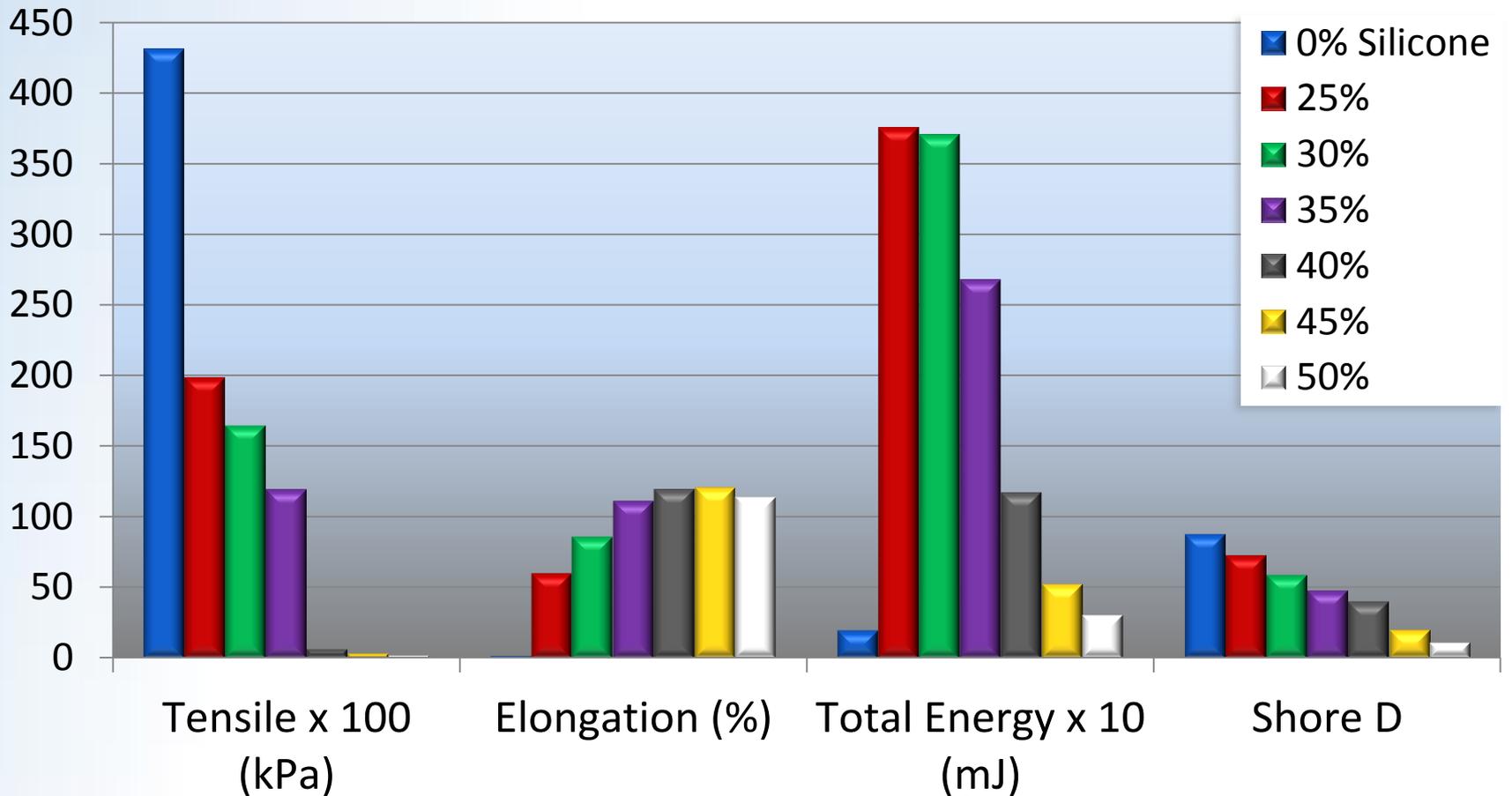
# Hardness and Strength



# Total Energy to Break/ Elongation



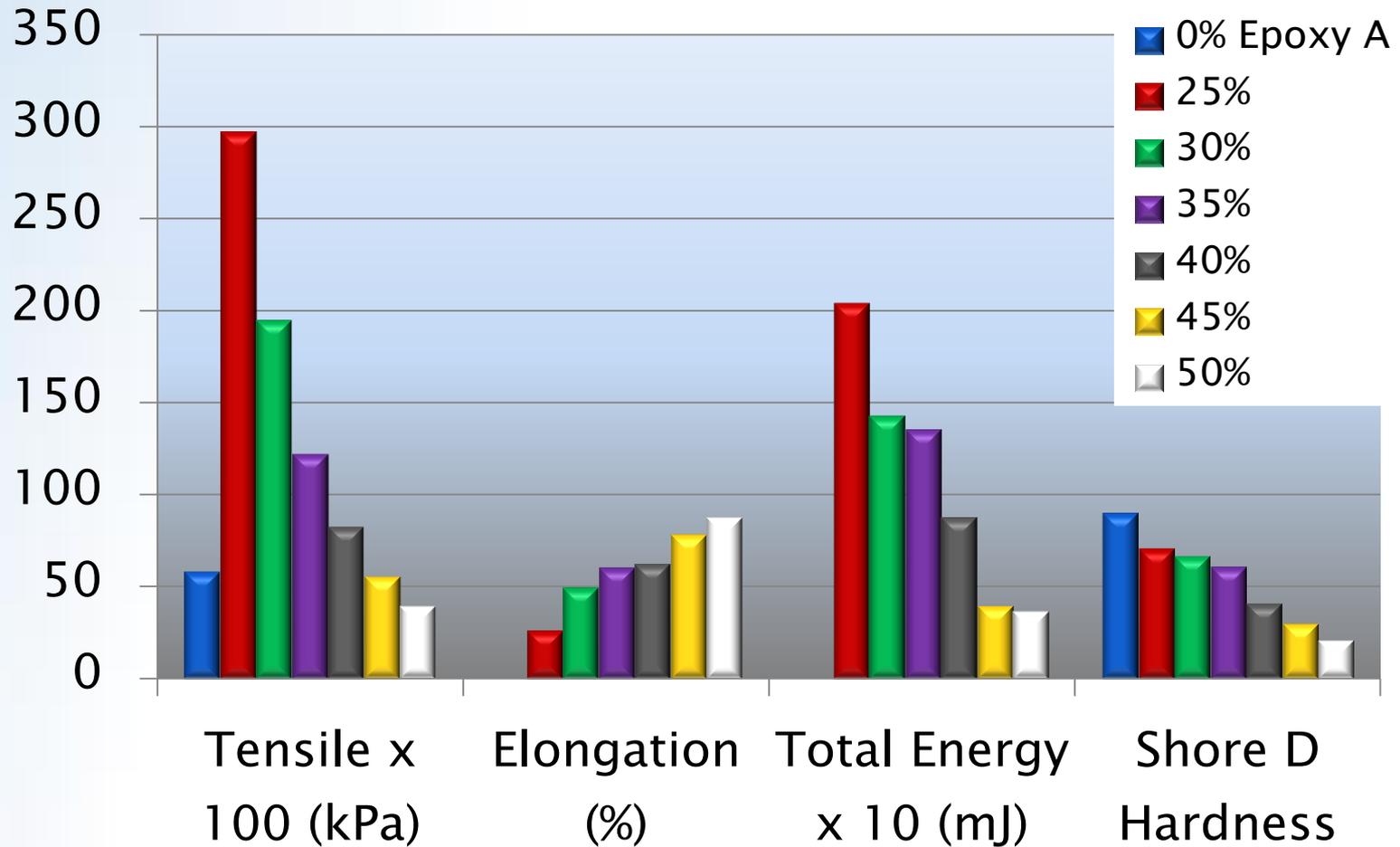
# Summary DER 671-X75 / Epoxy A



# DER 331 with Epoxy A

- ▶ Dow DER 331, a commercial faster and softer, Epichlorohydrin/ bisphenol A system is reacted with epoxy silicone A.
- ▶ MHHPA and Imicure AM-1 used to affect cure.
- ▶ Cured at 100°C for 4 hours.
- ▶ Properties are followed with Brookfield DV-III Rheometer AR-G2 or measured with Instron #1122.

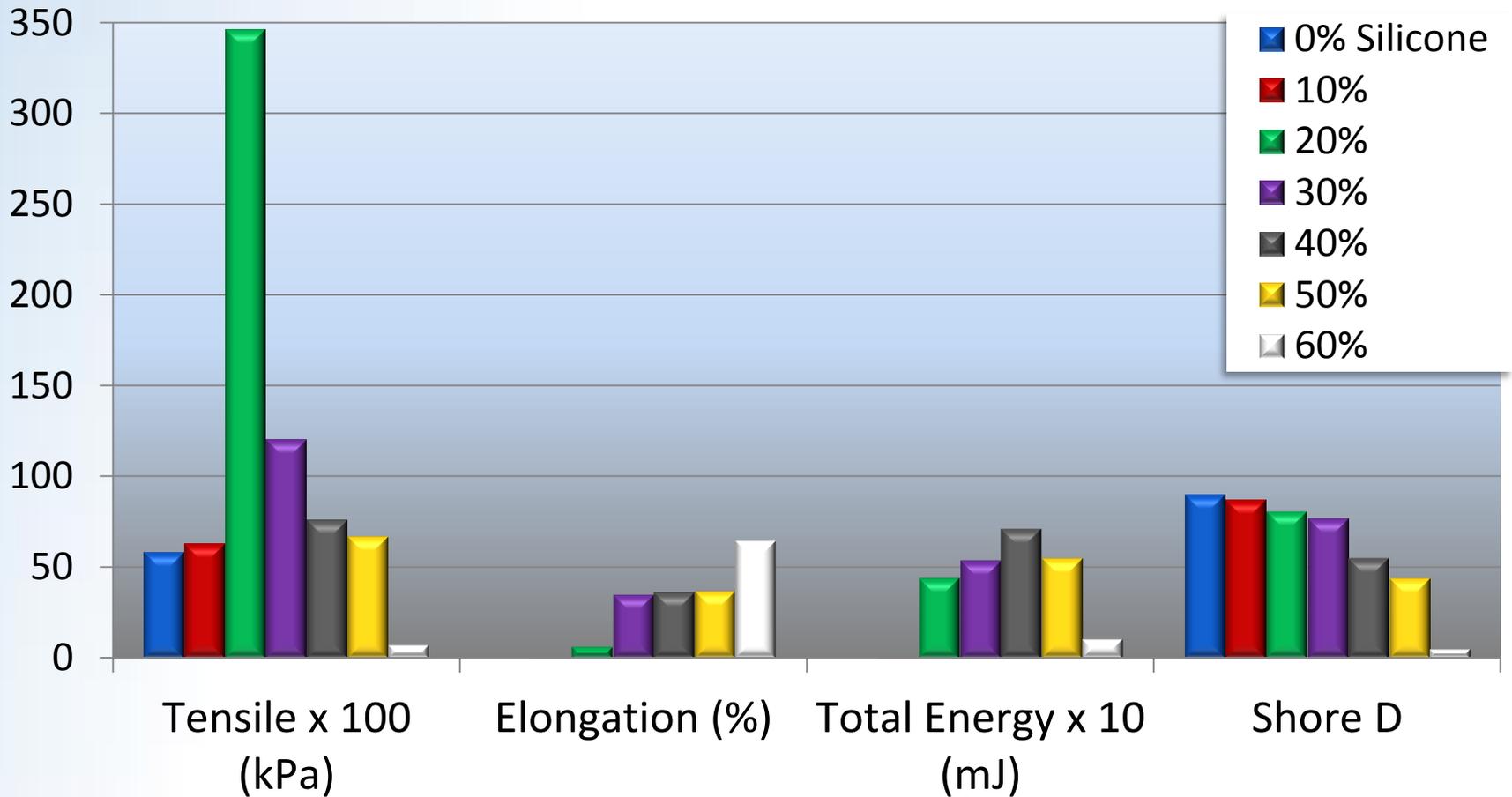
# DER 331 with Epoxy A



# Cycloaliphatic with Epoxy B

- ▶ UVACure 1500, a commercial cycloaliphatic epoxy system is reacted with epoxy silicone B
- ▶ MHPA and Imicure AM-1 used to affect cure.
- ▶ Cured at 100°C for 4 hours.
- ▶ Properties are followed with Brookfield DV-III Rheometer AR-G2 or measured with Instron #1122.

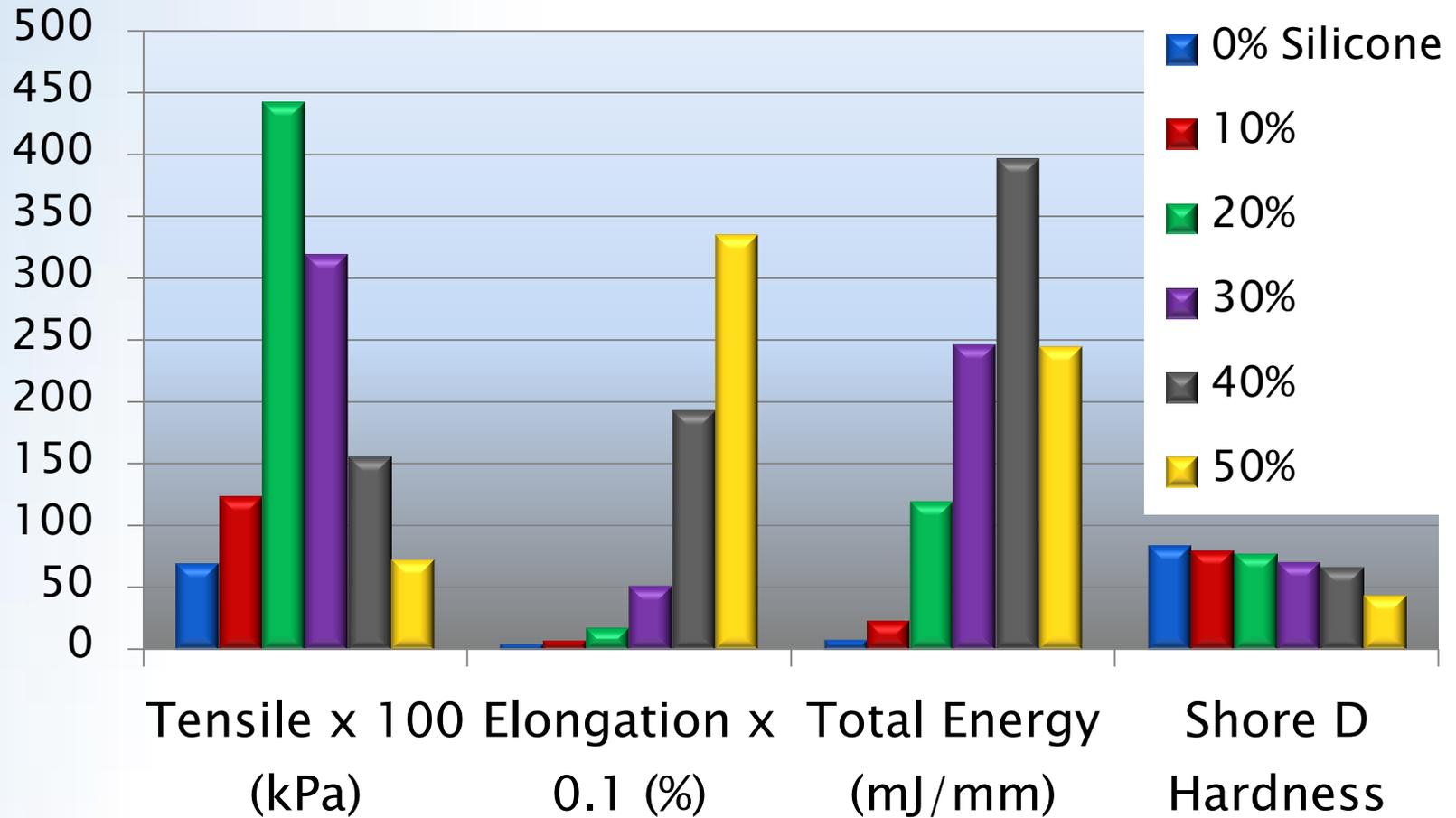
# UVACure 1500 with Epoxy B



# Cycloaliphatic / Epoxy B (UV)

- ▶ UVACure 1500, a commercial cycloaliphatic epoxy system is reacted with epoxy silicone B
- ▶ UV 9380 Photoinitiator used.
- ▶ Cured at RT under UV light.
- ▶ Properties are followed with Brookfield DV-III Rheometer AR-G2 or measured with Instron #1122.

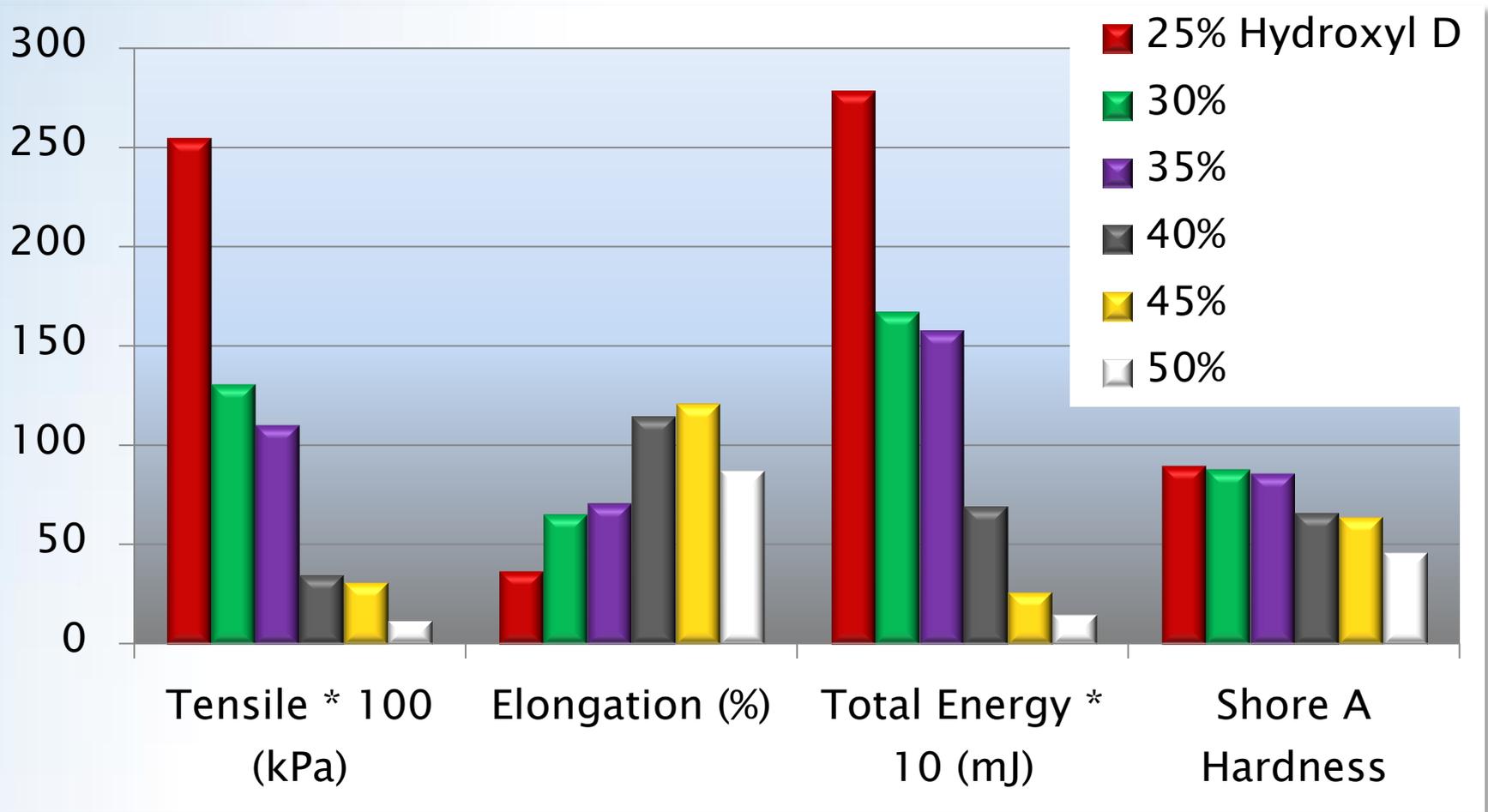
# UVACure 1500 / Epoxy B (UV)



# DER 331 / Hydroxyl Silicone D

- ▶ Dow DER 331, Epichlorohydrin/ bisphenol A system is reacted with Hydroxyl silicone D.
- ▶ MHPA and Imicure AM-1 used to affect cure.
- ▶ Cured at 100°C for 4 hours.
- ▶ Properties are followed with Brookfield DV-III Rheometer AR-G2 or measured with Instron #1122.

# DER 331 with Hydroxyl D



# Amine Hardened Epoxy/ Silicones

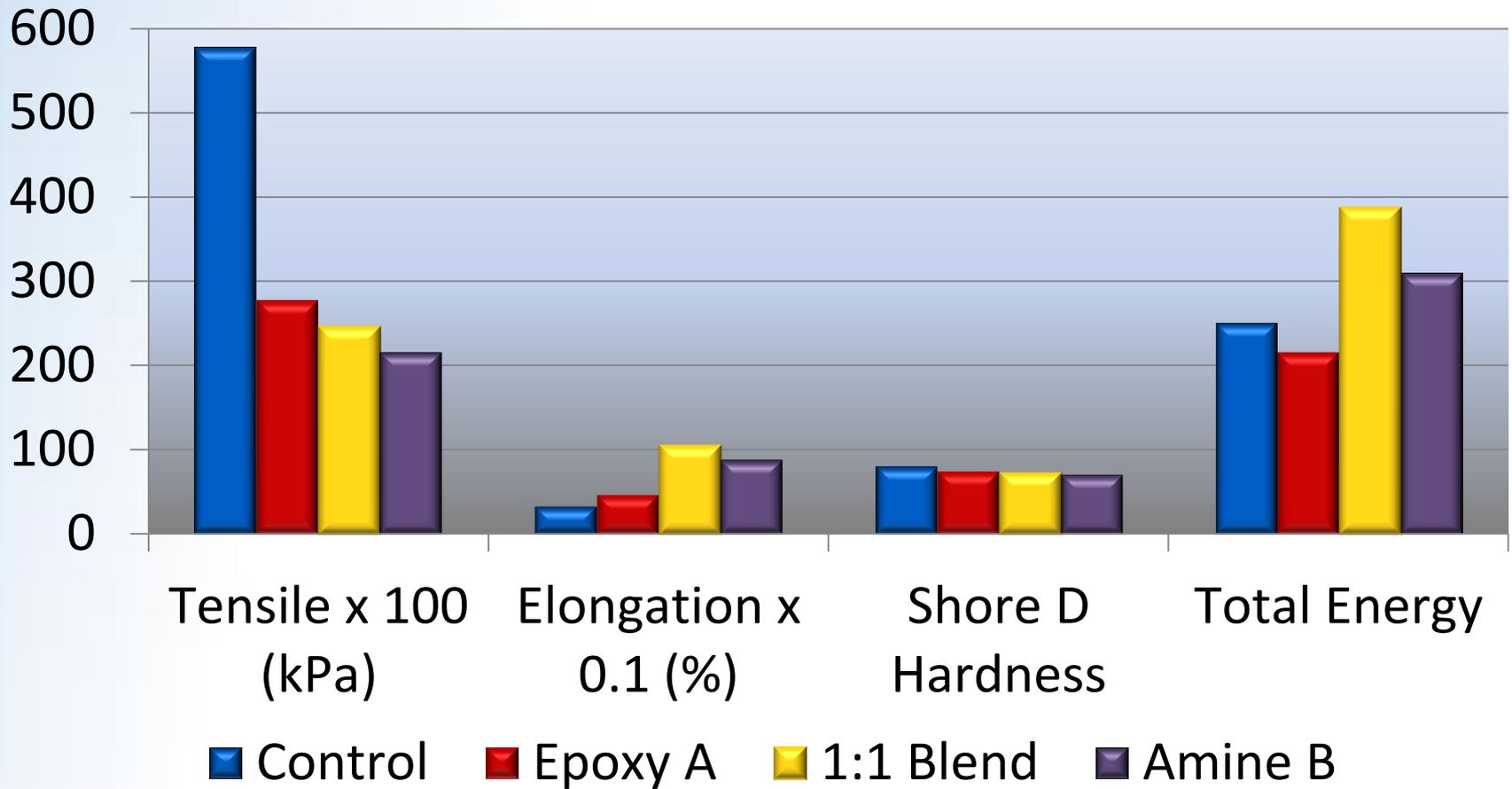
- ▶ Dow DER 331 Epichlorohydrin/ bisphenol A commercial system is reacted with reactive silicones
- ▶ MHPA and Imicure AM-1 used to affect cure.
- ▶ Cured at ambient for 24 hours.
- ▶ Ancamine 1618 is found to be best for hardening over Ancamine 1483 or TEPA.
- ▶ Properties are followed with Brookfield DV-III Rheometer AR-G2 or measured with Instron #1122

# Silicone Hardeners

Replace 20% of Ancamine 1618 (hardener):

- ▶ Silicone Amine B
- ▶ Silicone Epoxy A
- ▶ 1:1 blend of Amine B/ Epoxy A

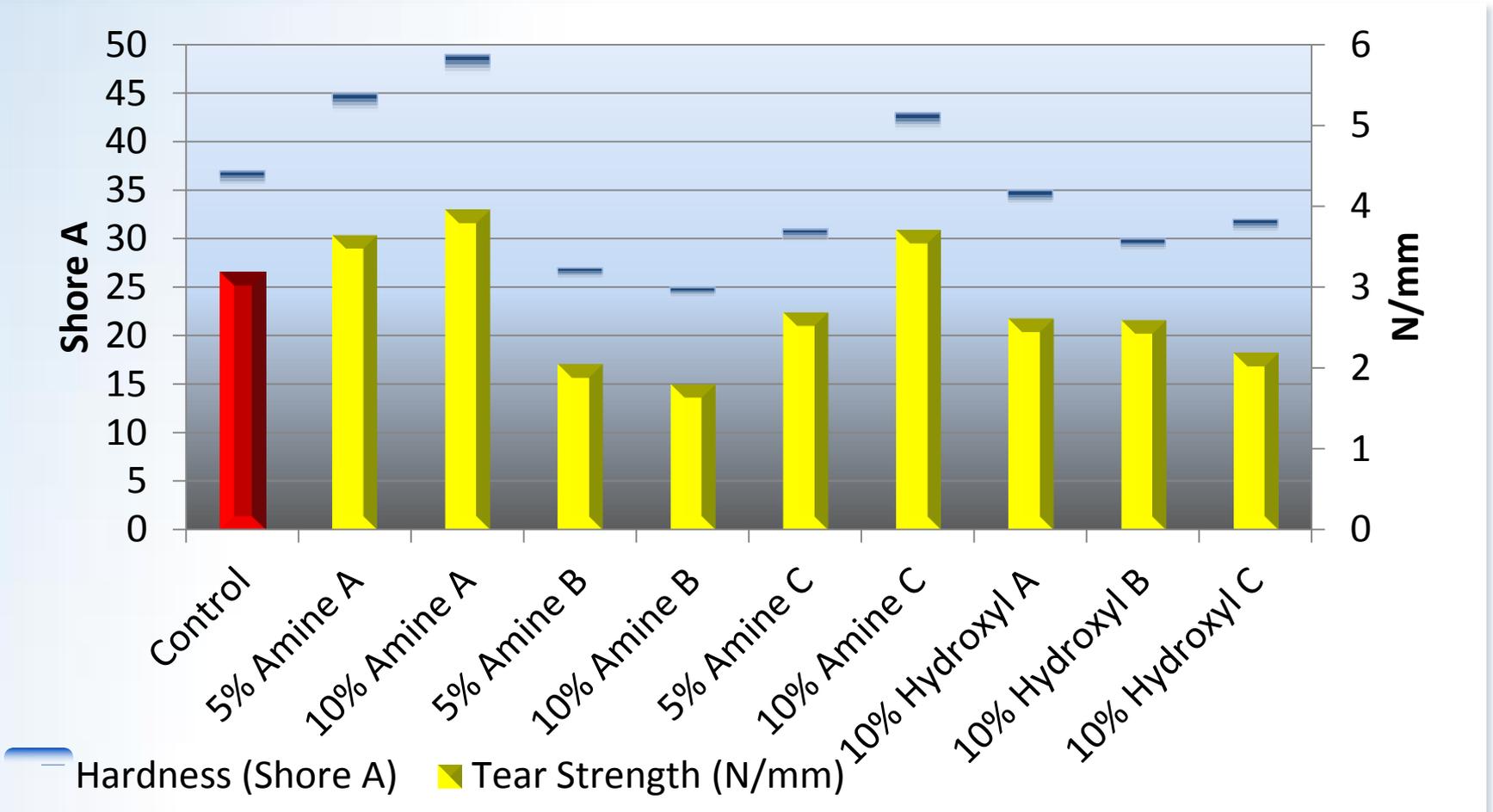
# DER 331 with Hardener



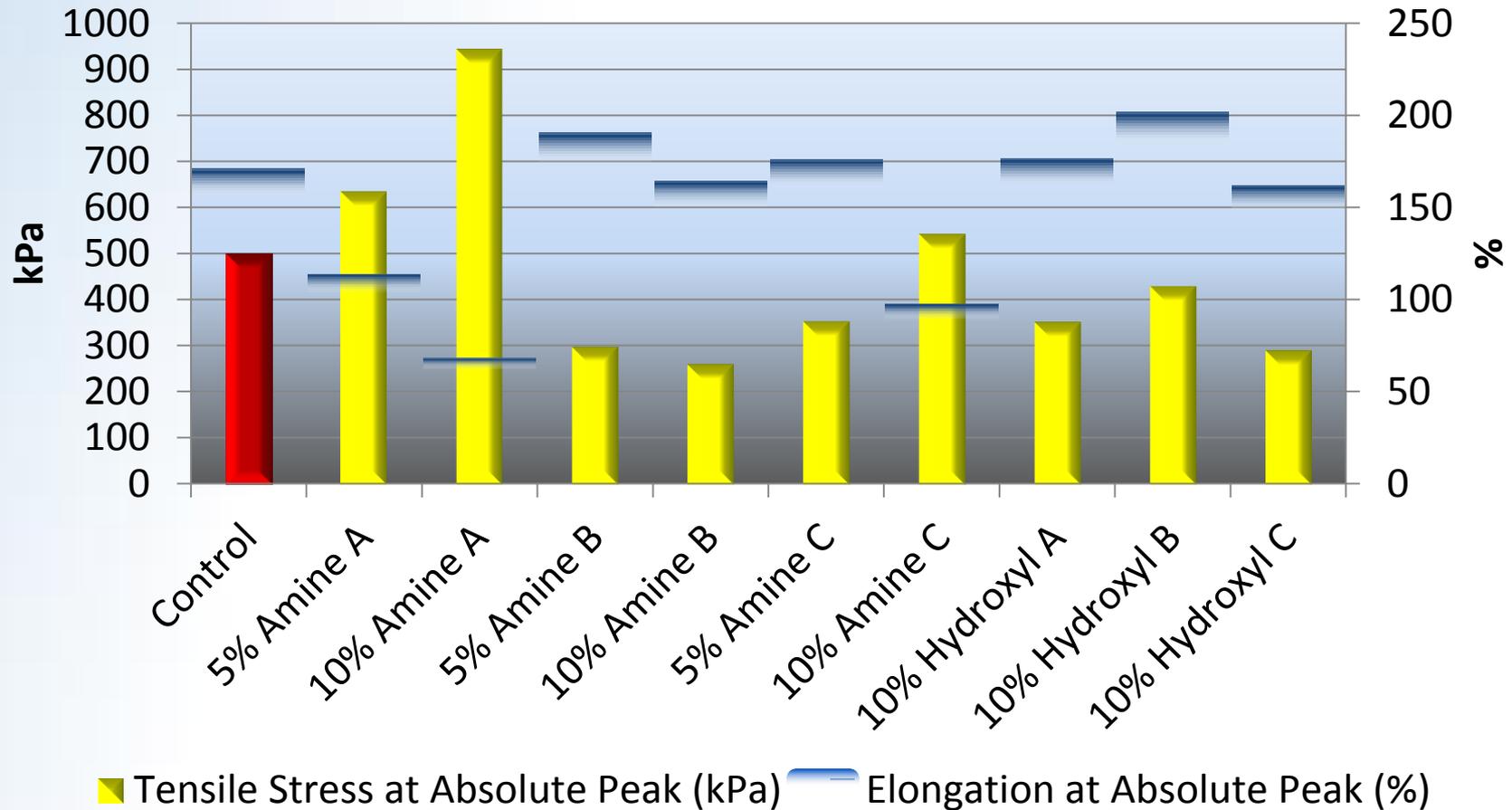
# Rubber Filled Epoxy with Silicone Hardener

- ▶ Proprietary epoxy with 5–10% reactive silicones and rubber crumbs
- ▶ Mold and cure at ambient for 7 days
- ▶  $-15^{\circ}\text{C}$  and  $-30^{\circ}\text{C}$  impact resistance
- ▶ Severity of fracture rated 1–10 (best)

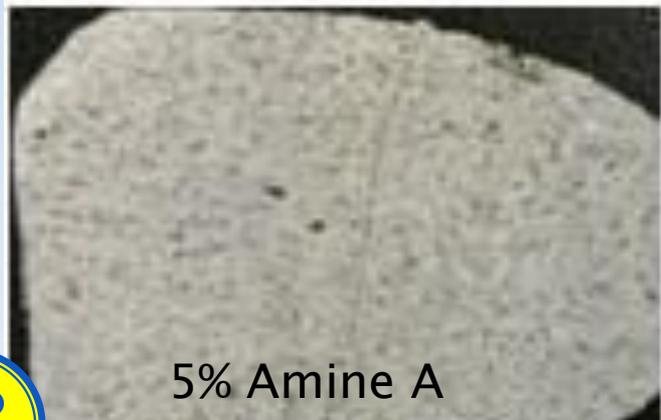
# Hardness and Strength



# Tensile Stress and Elongation



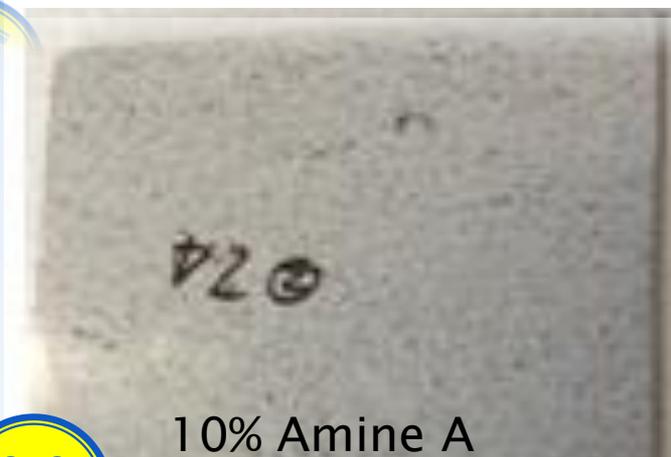
-15°C  
Fracture



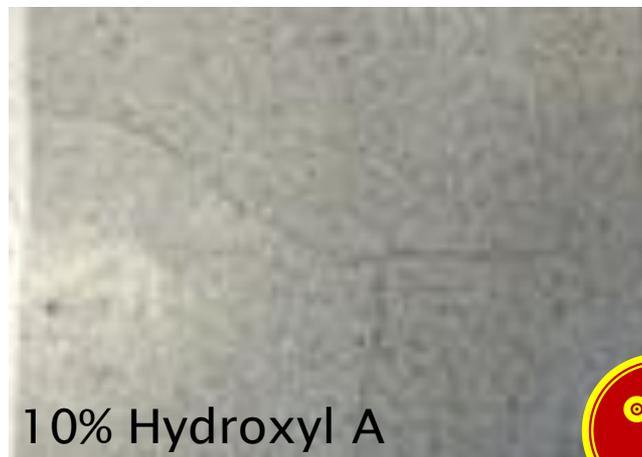
5% Amine A



Control



10% Amine A

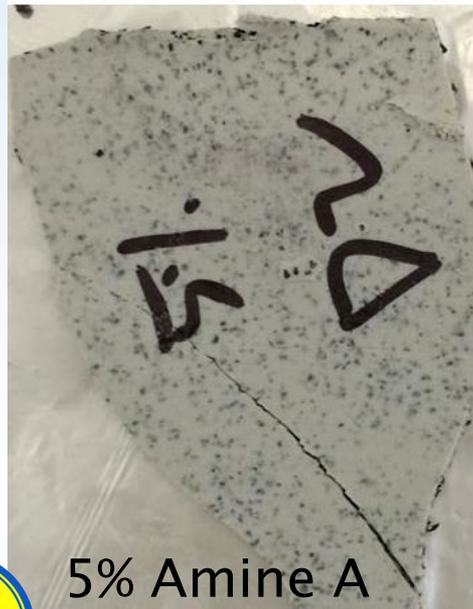


10% Hydroxyl A

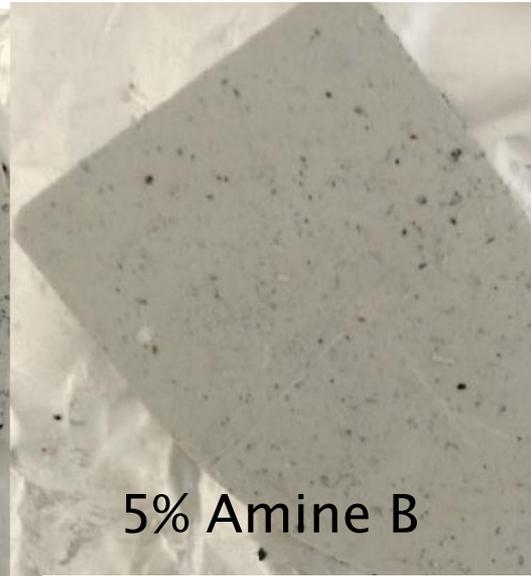




Control

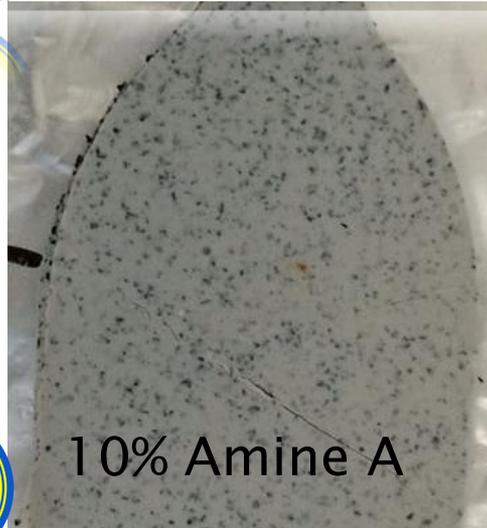


5% Amine A

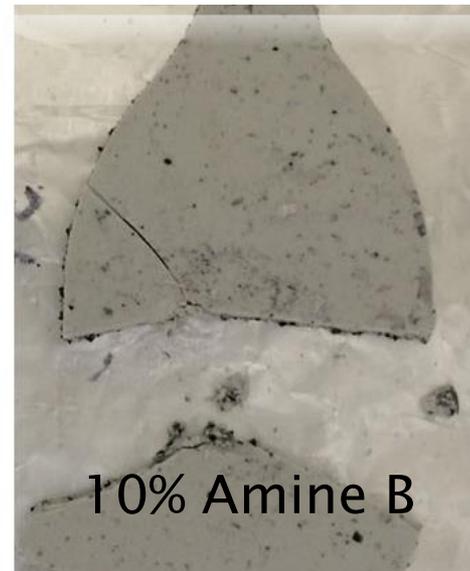


5% Amine B

-30°C  
Fracture



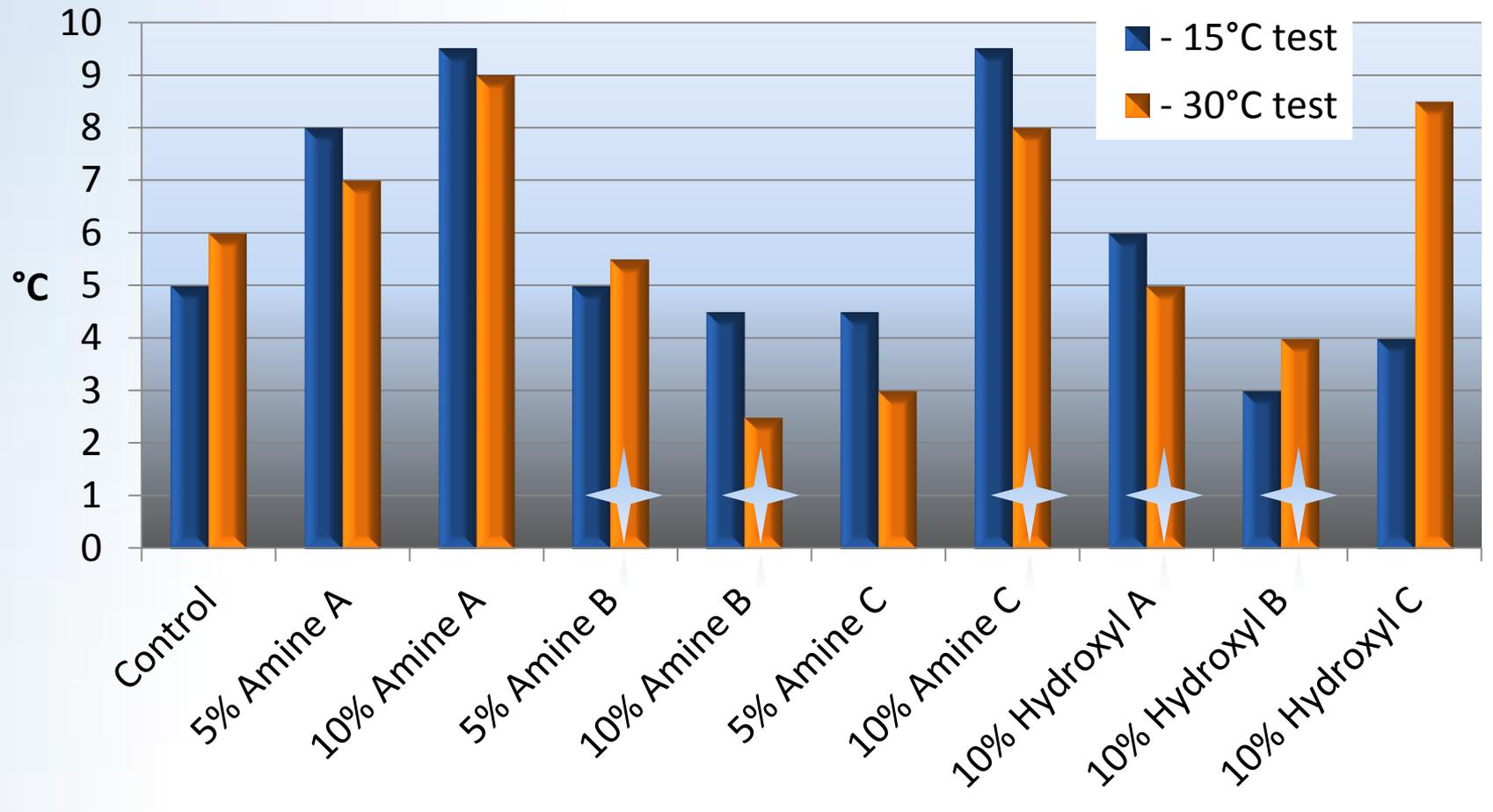
10% Amine A



10% Amine B



# Low Temperature Impact



★ Fractured on first of two impacts

# Conclusions

- ▶ In the Shore D systems, silicone reduces hardness.
  - Slowly up to 20%
- ▶ Strength and elongation improve and maximize at ~10–20% silicone.
- ▶ Amine more effective than epoxy
- ▶ In the Shore A system, with tetra-functional Amine A, hardness is increased.
- ▶ Impact resistance is also increased.
- ▶ OH is not as effective for this.

# Thank You

