Features of a Dual-Curing Strategy for Making Highly Biobased Thermosets from Plant-Derived Ingredients

Mariia Usiichuk

PhD student at Coatings and Polymeric Materials Department

Dr. Voronov's research group

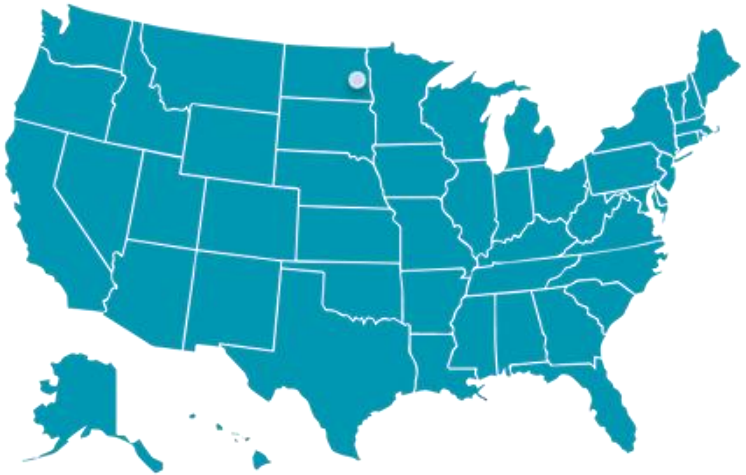
North Dakota State University, Fargo, ND



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Department of Coatings & Polymeric Materials

is an interdisciplinary department covering a broad range of polymer and coatings research



Dr. Dean Webster

- Marine Fouling
- Ice Adhesion
- Biobased Materials
- Non-Isocyanate Chemistry



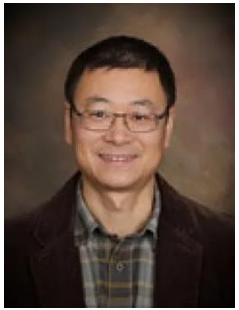
Dr. Andriy Voronov

- Plant oil-based monomers & polymers
- Self-assembly
- Polymer interfaces



Dr. Bakhtiyor Rasulev

- Computational polymer science
- Molecular modeling & simulation
- Machine learning



Dr. Xiaoning Qi

- Corrosion Prevention
- High Temperature Coatings



Dr. Eugene B. Caldona

- Electrochemistry & Surface Chemistry
- 3D printing
- Fluoropolymers
- Nanocomposites



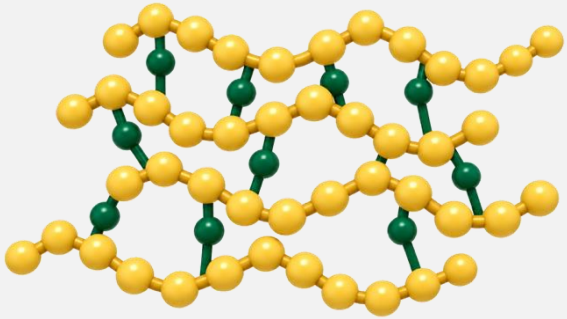
Dr. Ivan Hevus

- Sustainable polymers
- UV- resins
- Stimuli-responsive polymers

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Thermosets: high-performance polymeric materials



Thermoset

- Heat and flame resistance
- High strength and durability
- Chemical resistance
- Dimensional stability



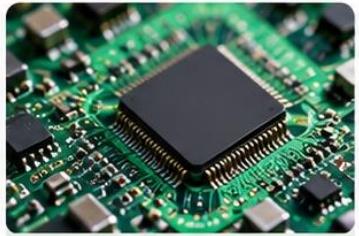
Automotive



Aerospace



Construction



Electronics



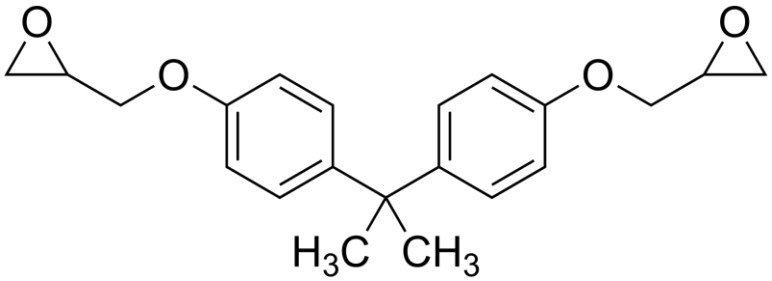
Healthcare

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Goodman, S.; Dodiuk, H. *Handbook of Thermoset Plastics*; Elsevier/William Andrew: Amsterdam, 2014.
Qipeng Guo. Thermosets : Structure, Properties, and Applications; Elsevier: Amsterdam, 2018.

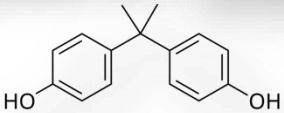
Epoxy thermosets





Diglycidyl ether of bisphenol A (DGEBA)



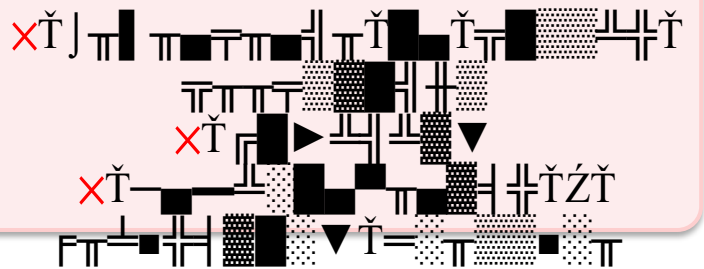


Bisphenol A (BPA)

Key advantages

- Processability
- Tunability
- No volatile emissions
- Predictable performance

Key challenges



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https://www.sciencedirect.com/topics/chemistry/bisphenol-a-diglycidyl-ether

Our approach

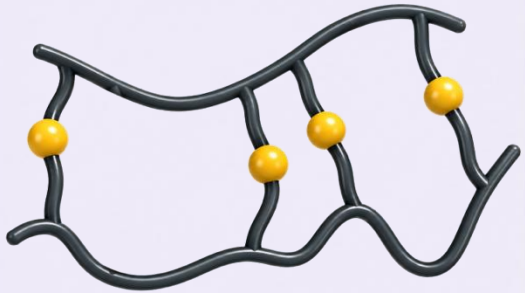
Biomass as a feedstock



Renewable and abundant

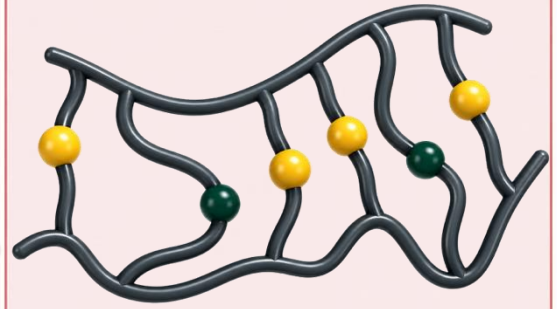
Reduced reliance on fossil resources.

Single curing chemistry



Challenges in balancing thermoset properties

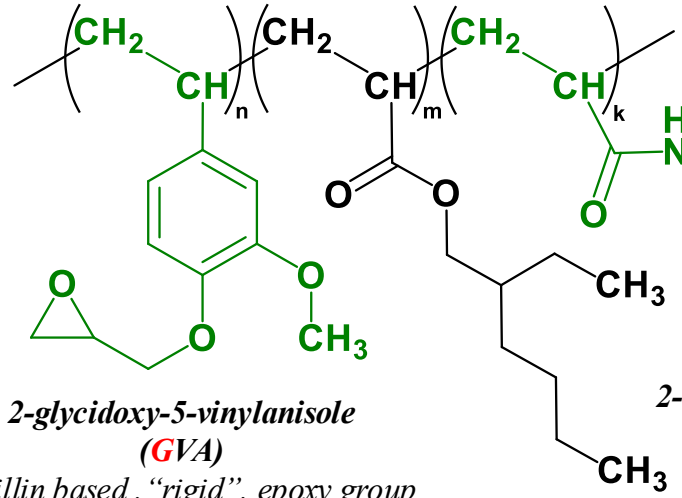
Multicuring concept



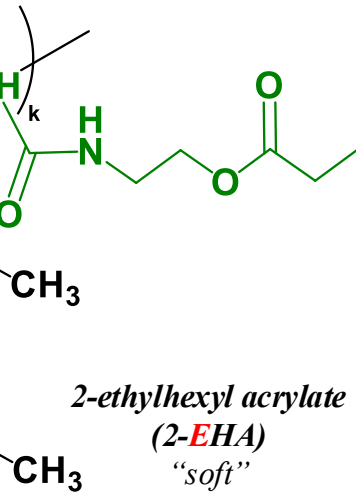
Tailored network structure and performance

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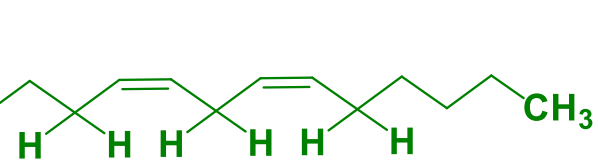
Biobased dual-cured thermosets



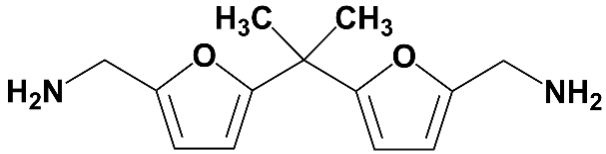
2-glycidoxy-5-vinylanisole
(GVA)
vanillin based , "rigid", epoxy group



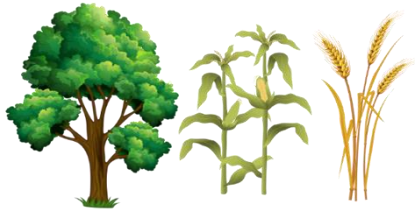
2-ethylhexyl acrylate
(2-EHA)
"soft"



Soybean oil-based monomer
(SBM)
"soft", allyl groups



5,5'-(1-Methylethylidene)bis[2-furanmethanamine]

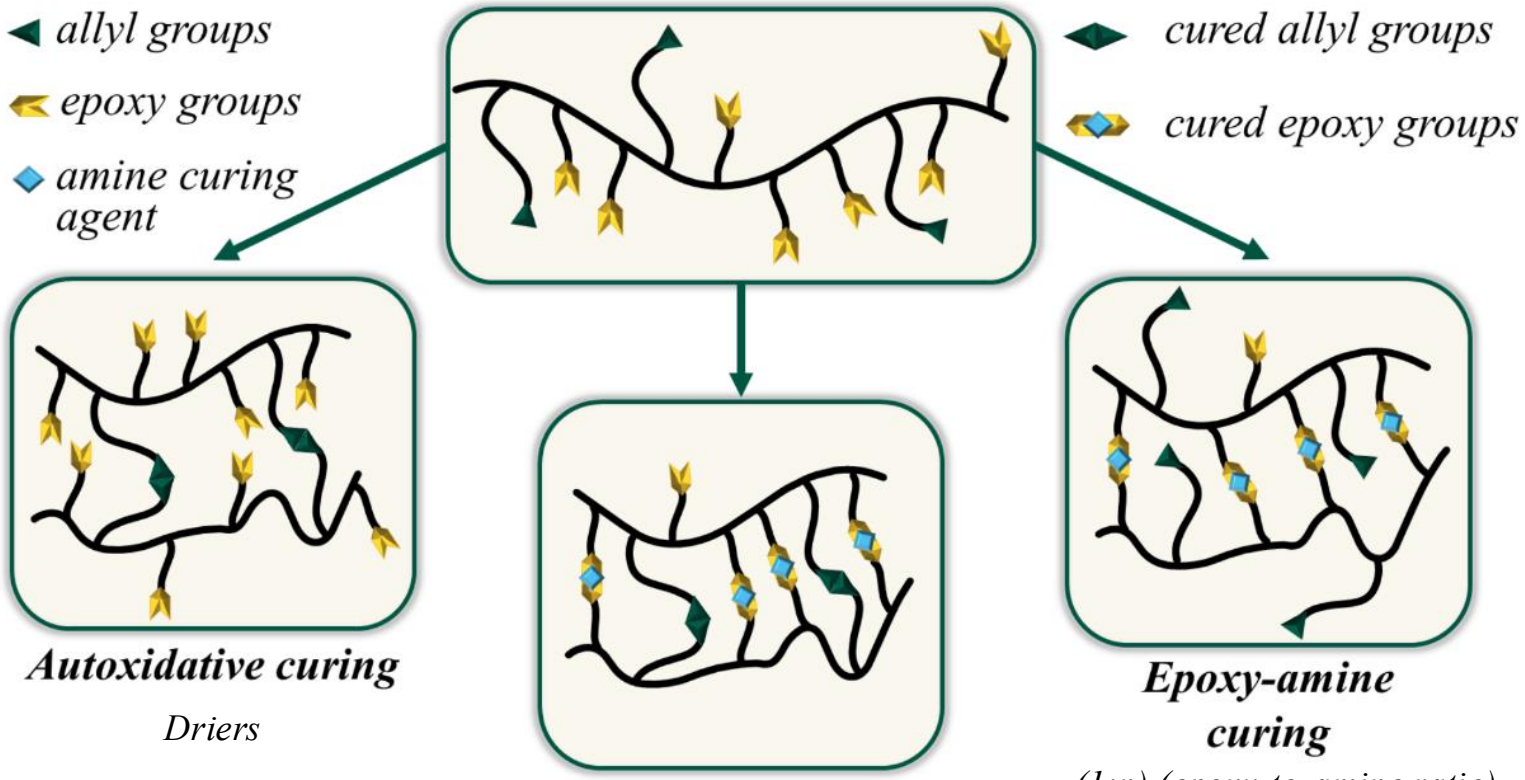


Biomass

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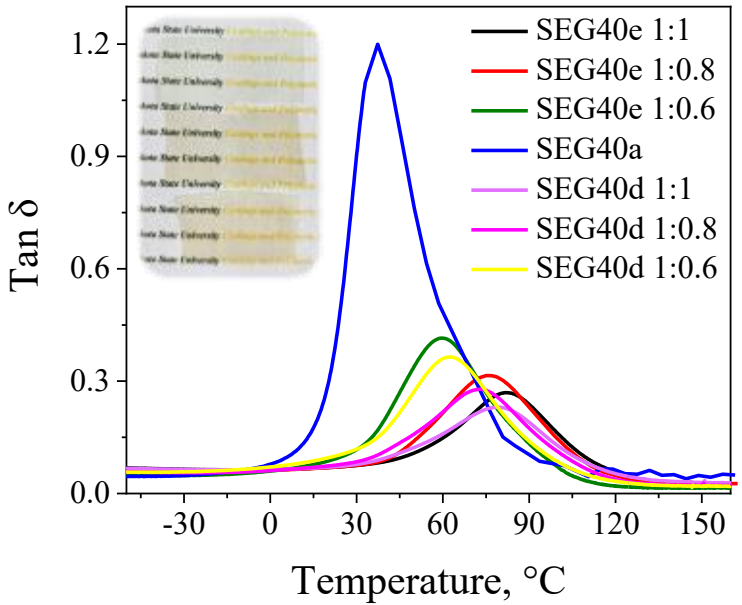
Dual crosslinking mechanism

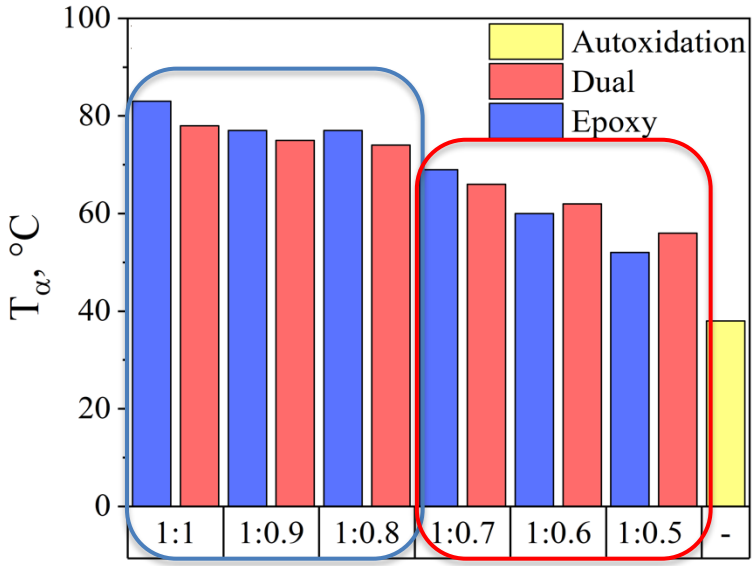


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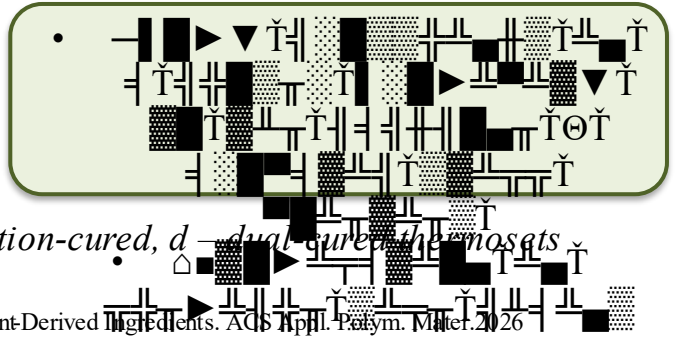
Usiichuk, M. et al. Features of a Dual-Curing Strategy for Making Highly Biobased Thermosets from Plant-Derived Ingredients. ACS Appl. Polym. Mater.2026

Characterization of cured thermoset films





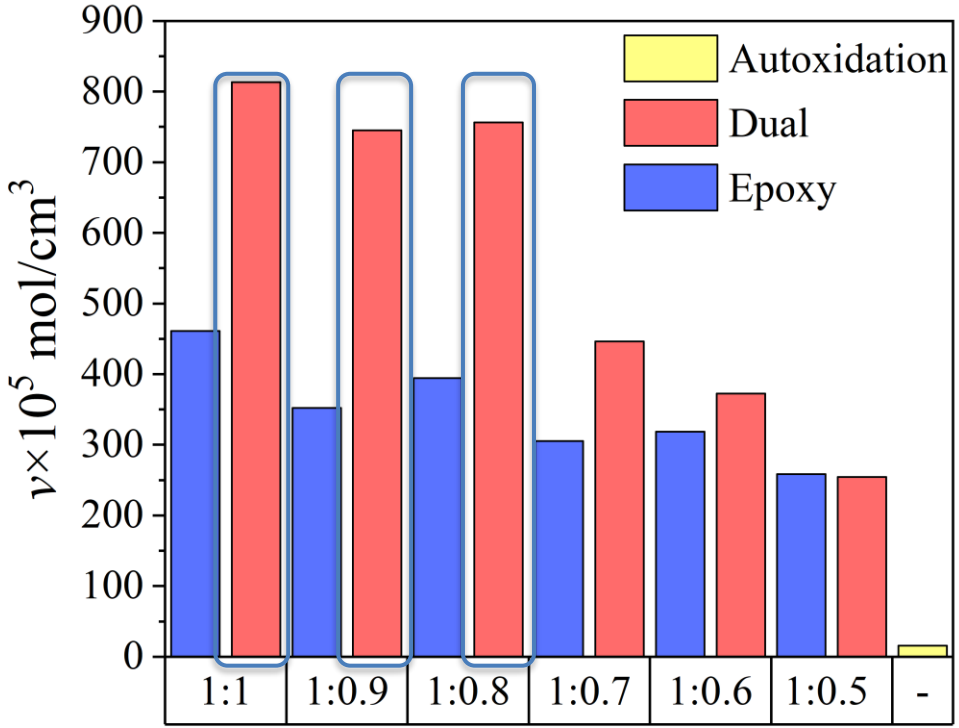
- Autoxidation: tan δ > 1 → flexible, energy-dissipating behavior
- Epoxy & dual: tan δ < 0.5 → rigid, highly crosslinked network



e – epoxy-cured, a – autoxidation-cured, d – dual-cured thermosets (1:n) (epoxy-to-amine ratio)

Usiichuk, M. et al. Features of a Dual-Curing Strategy for Making Highly Biobased Thermosets from Plant-Derived Ingredients. ACS Appl. Polym. Mater. 2026

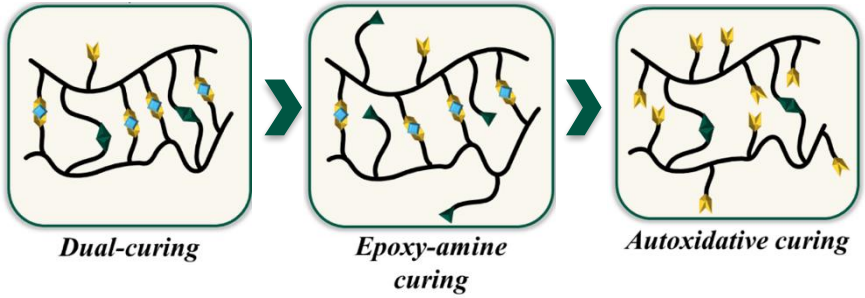
Characterization of cured thermoset films



(1:n) (epoxy-to-amine ratio)

$$\nu = \frac{E'}{3RT}$$

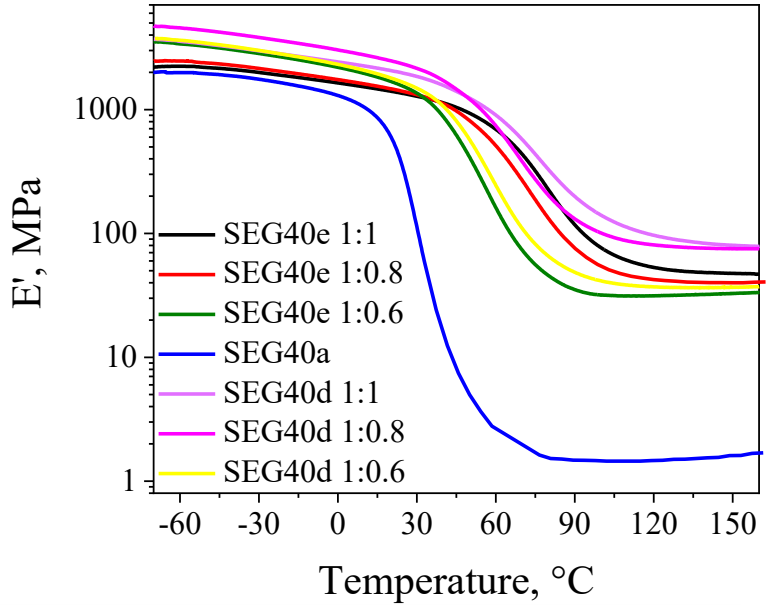
where R is the gas constant and T is the absolute temperature (K) at which E′ is recorded, taken as T_α + 60 °C.

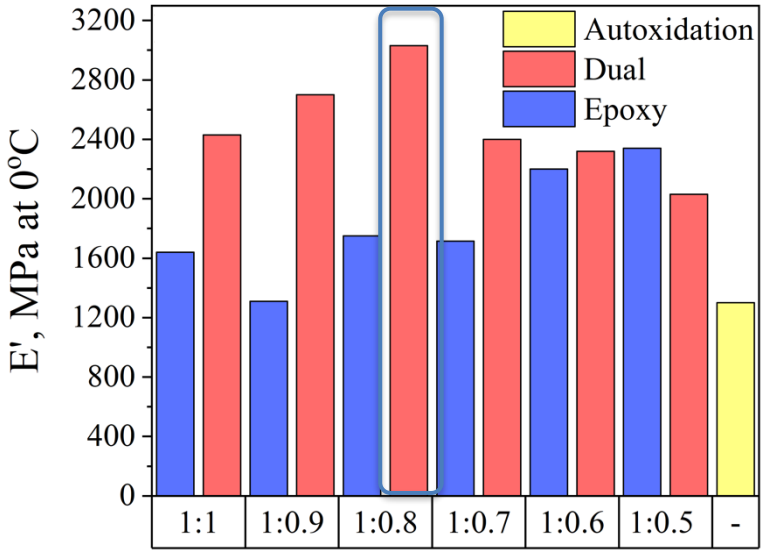


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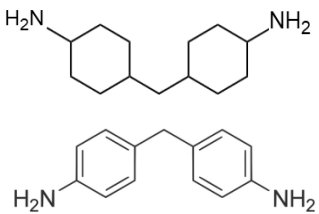
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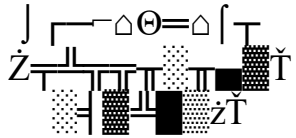
Characterization of cured thermoset films





Highest modulus at non-stoichiometric ratio due to "antiplasticization" effect and improved network packing





E'_g = 1200-2500 MPa

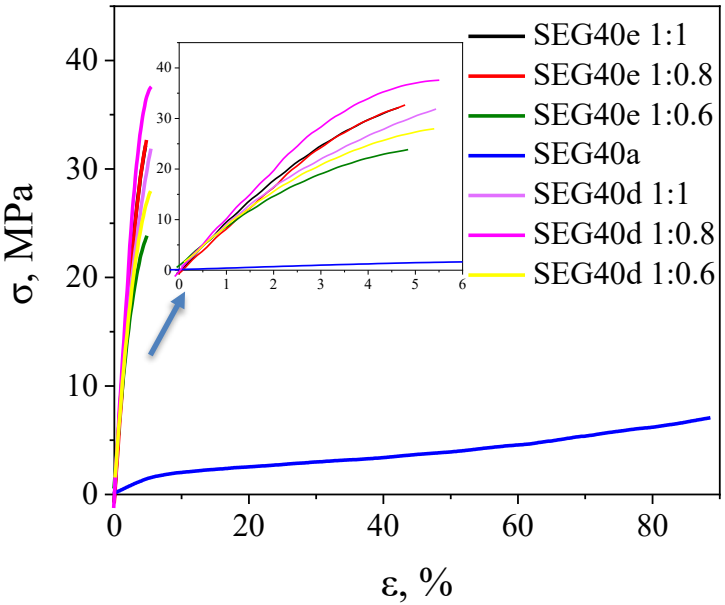
DGEBA+MDA (1:1) E'_g = 1635 MPa

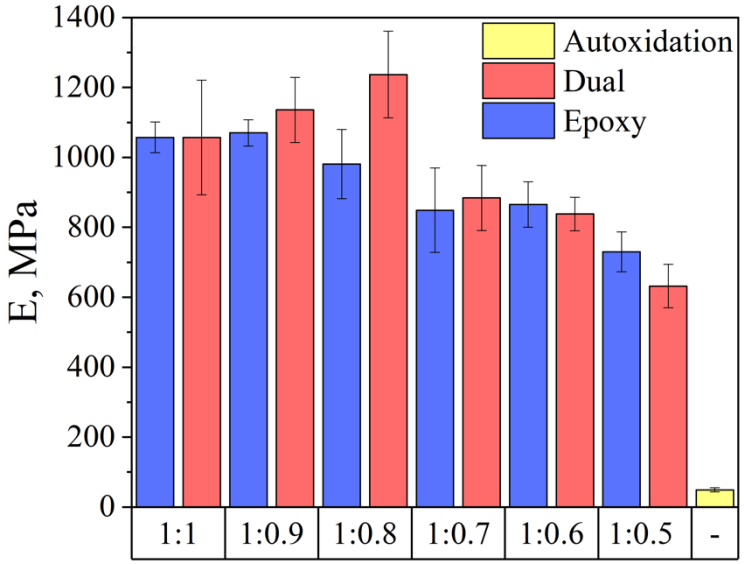
e – epoxy-cured, a – autoxidation-cured, d – dual-cured thermosets (1:n) (epoxy-to-amine ratio)

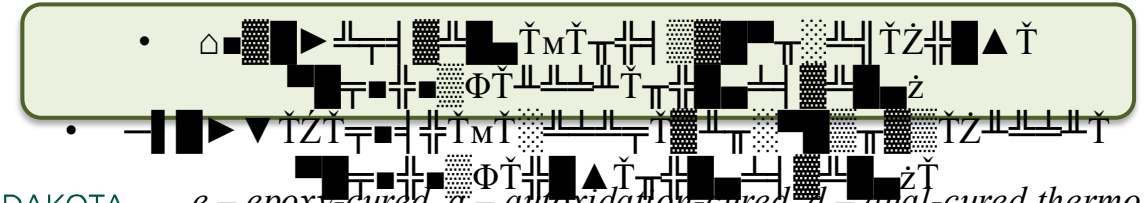
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Fache, M. New Vanillin-Derived Diepoxy Monomers for the Synthesis of Biobased Thermosets. European Polymer Journal 2015, 67, 527–538.
Vanlandingham, M. Relationships between Stoichiometry, Microstructure, and Properties for Amine-Cured Epoxies. Journal of Applied Polymer Science 1999, 71 (5), 699–712.

Characterization of cured thermoset films







e – epoxy-cured, a – autoxidation-cured, d – dual-cured thermosets (1:n) (epoxy-to-amine ratio)

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Characterization of cured thermoset coatings



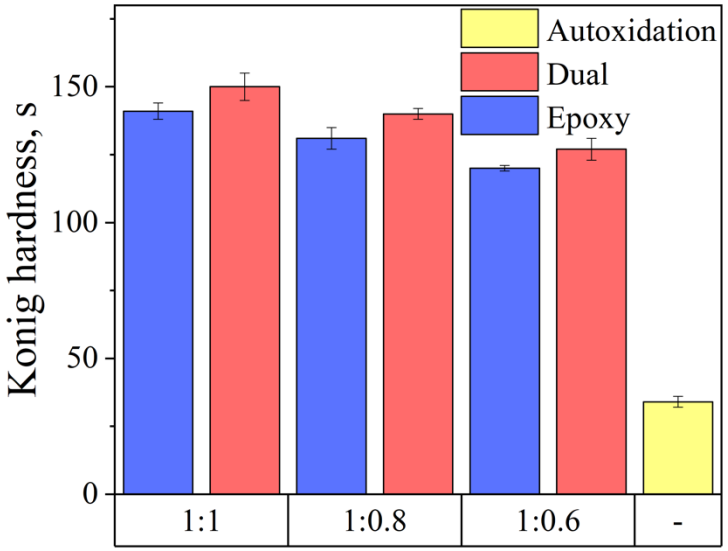
Sample	DFT, mkm	MEK double rubs	Pencil hardness
SEG40e 1:1	84±7	>400	2H
SEG40e 1:0.8	74±5	□Ť!!σσ	H
SEG40e 1:0.6	78±6	145	F
SEG40a	76±8	60	8B
SEG40d 1:1	77±3	>400	2H
SEG40d 1:0.8	75±4	>400	F
SEG40d 1:0.6	71±5	340	B

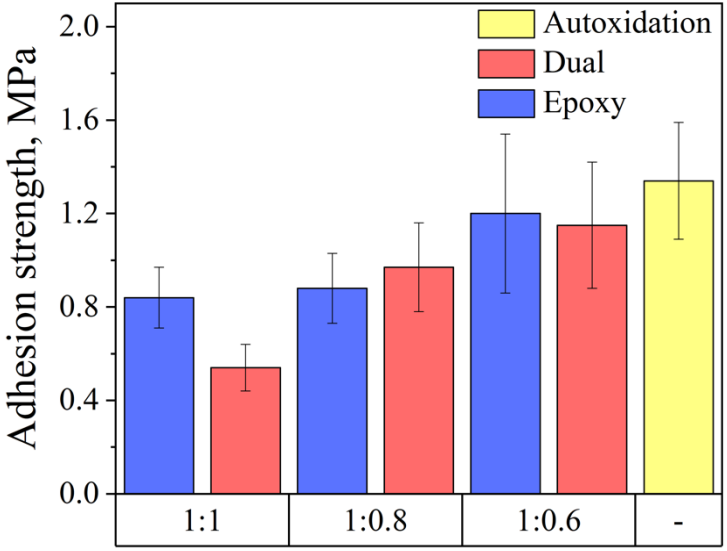
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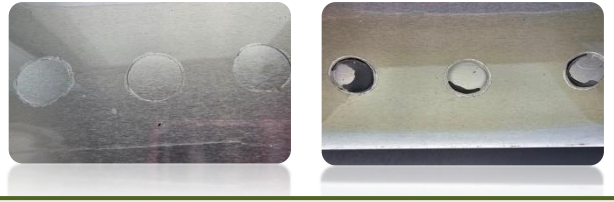
e – epoxy-cured, a – autoxidation-cured, d – dual-cured thermosets (1:n) (epoxy-to-amine ratio)

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Characterization of cured thermoset coatings







- Autoxidation → elastomeric (low damping time)
- Epoxy & dual → rigid (high damping time)

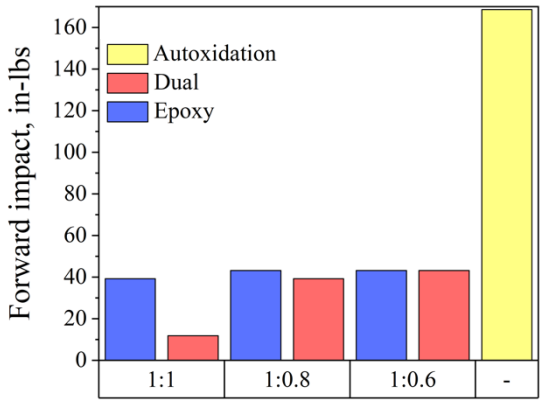
Residual uncured epoxy groups contribute to enhanced adhesion strength.

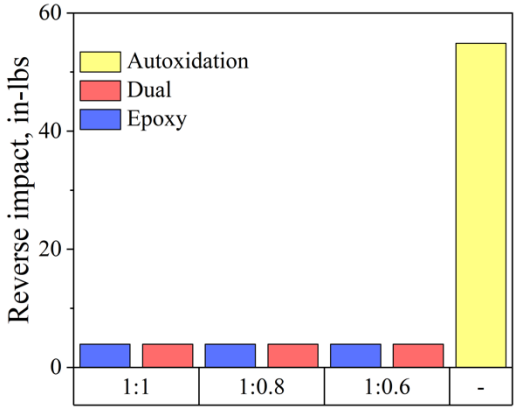
(1:n) (epoxy-to-amine ratio)

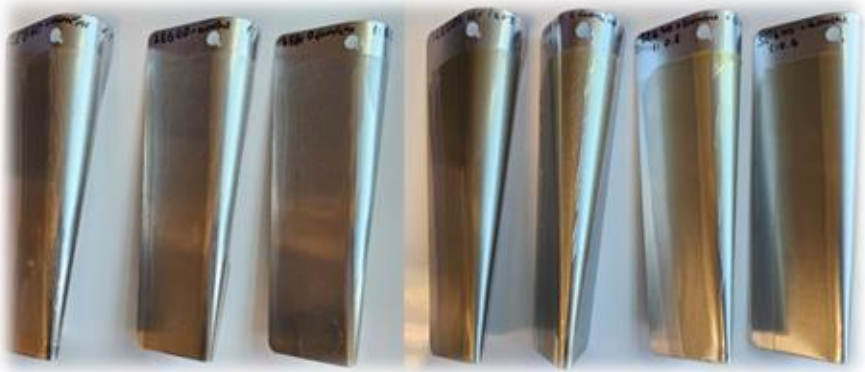
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Characterization of cured thermoset coatings







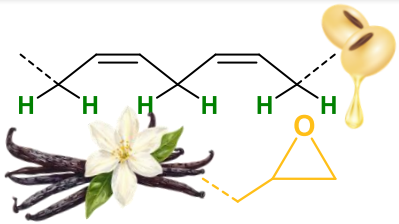
Sample	Conical mandrel
SEG40e 1:1	Cracked
SEG40e 1:0.8	Cracked
SEG40e 1:0.6	Cracked
SEG40a	Did not crack
SEG40d 1:1	Cracked
SEG40d 1:0.8	Cracked
SEG40d 1:0.6	Cracked

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e – epoxy-cured, a – autoxidation-cured, d – dual-cured thermosets (1:n) (epoxy-to-amine ratio)

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Conclusions



High allylic functionality, combined with controlled variation of epoxy-amine stoichiometry, enables effective tuning of network structure and thermomechanical properties of dual-cured thermosets.

Storage modulus, E' at 0 °C	
Autoxidation	~1300 MPa
Epoxy–amine	1310 – 2340 MPa
Dual curing	2030 – 3030 MPa
Optimized epoxy:amine ratio (1:0.8)	3030 MPa

MEK double rubs	
Autoxidation	60
Epoxy–amine	145 – 400
Dual curing	340 – 400

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Acknowledgment

Dr. Andriy Voronov

Dr. Bohdan Domnich

Dr. Mukund Sibi, Sagar Thorat, Gangadurai Chinnakuzhanthai

Dr. Voronov group

Chunju Gu, Greg Strommen

CPM Department

[redacted]

My family and friends



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