Organic-inorganic Hybrid (OIH) Low-temperature Curable System For Industrial Coatings.

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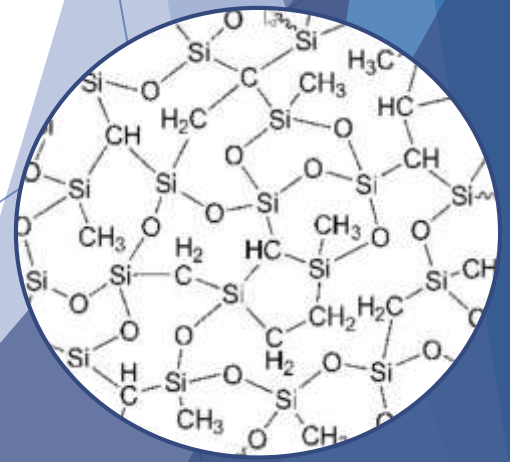
CTT Conference

September 2023

Coatings Trends & Technologies SUMMIT

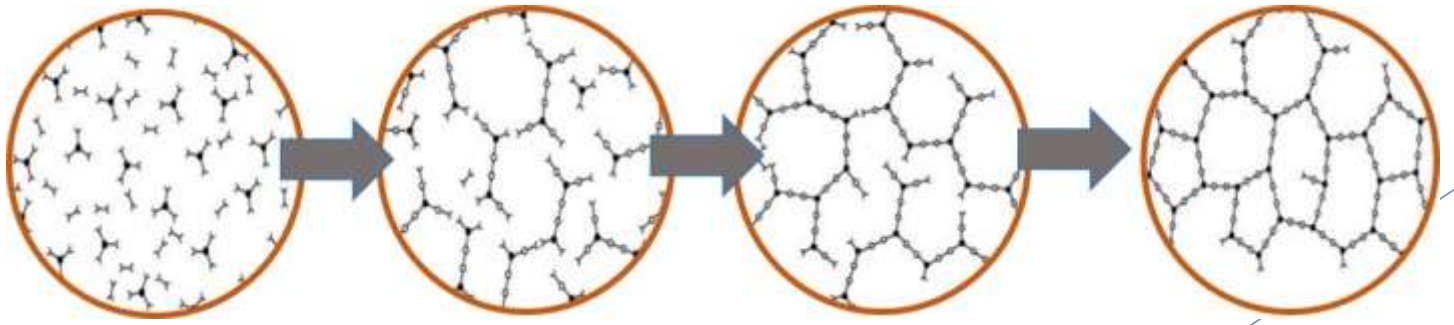
AGENDA

- Background
- Introduction of Sol-Gel
- Introduction of New Approach/New Precursor
- Development of Bio-Based Precursor
- Results and Discussion
- Reactive Diluent Study
- Conclusion



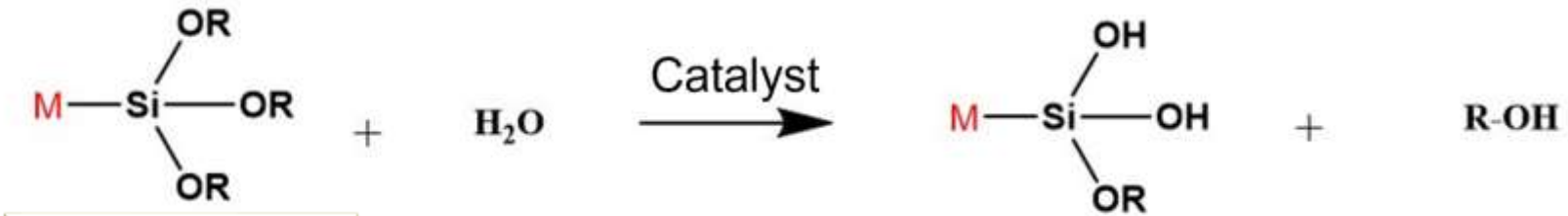
Conventional Thermally Curable Coatings

- Usually, High Temperature
- Substrate Limitation
  - Thermally Resistance Substrates: 120 to 160 ℃
  - Plastics: 80 to 90 ℃
- Needs Flash-off time around 10 min and baking time around 20 to 30 min
- High CO2 equivalent
- High Energy Consumption



Sol-Gel

INTRODUCTION

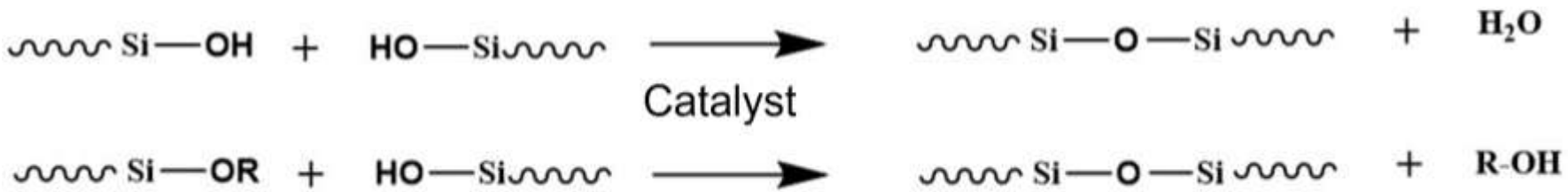


Organo-Silane

Organo-Silanol

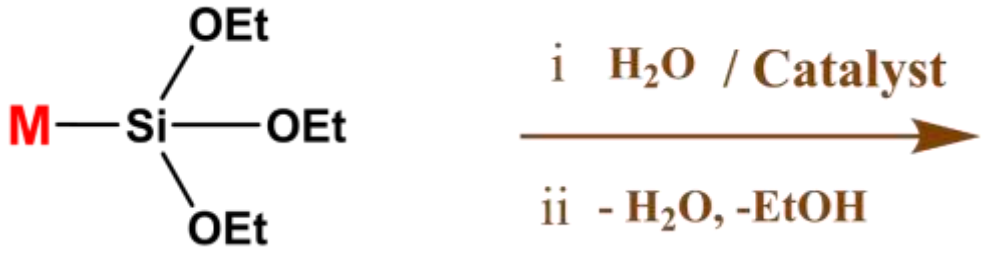
Sol

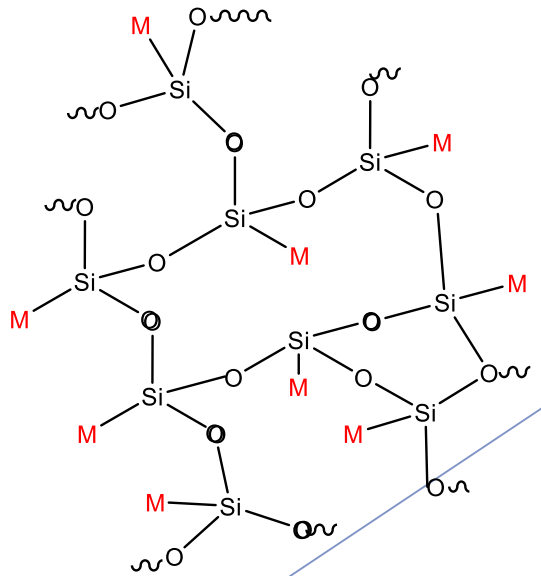
Sol-gel Reactions



Gel

Organo-Siloxane



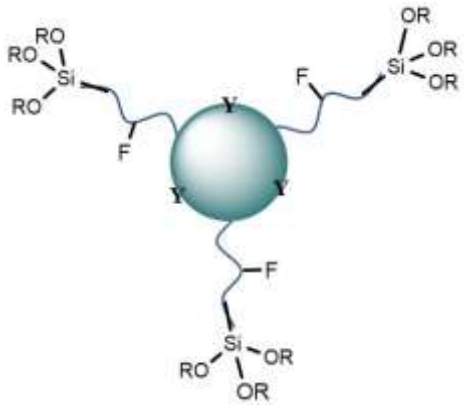


Organic-Inorganic Hybrid (OIH) Network

Organo-Silane Precursor

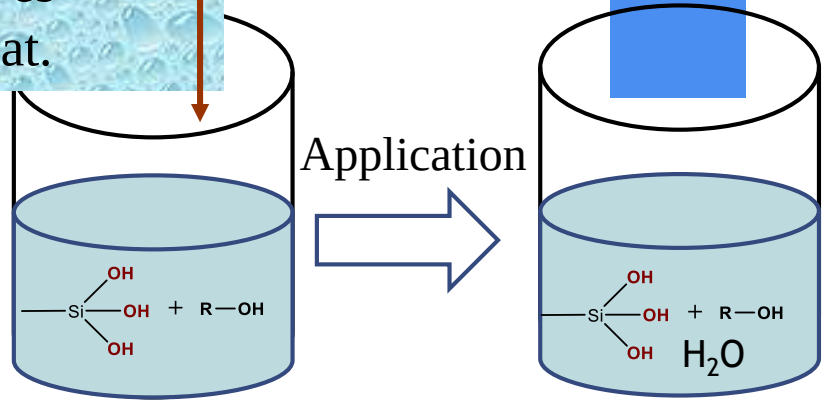
M: Alkyl, Aryl, or Organo-functional group

Conventional Sol-Gel Application Process



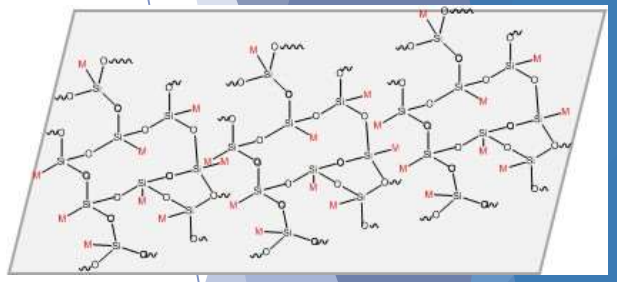
Organo-Silane Precursor

Silane precursor
Water
Alcohol
Additives
Acid Cat.



Application

(Thermal Curing)



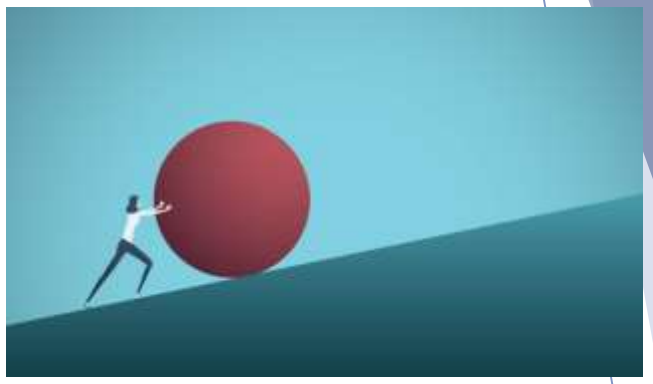
Application Bath-Sol

Coating Deposition - Gel

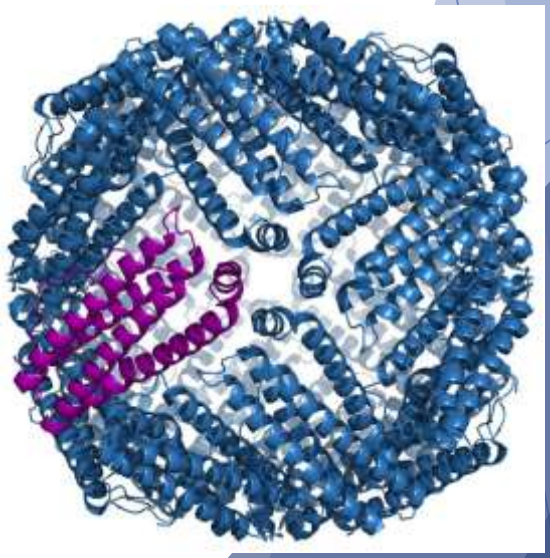
Optimize / Control

- pH
- Solid Content
- Water/alcohol ratio
- Solution age
- Withdrawal rate

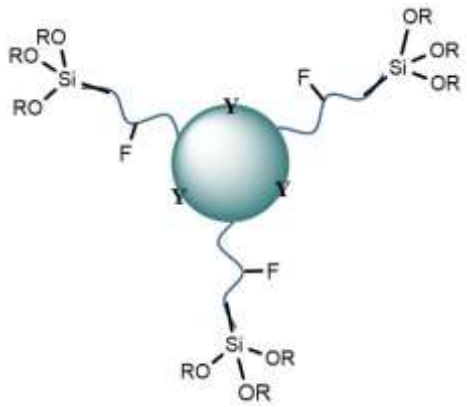
Challenges (Aqueous Process)



- Limited bath-solids
- Limited film thickness
- Limited self-life of application bath
  - Reduced operating freedom
- Needs careful monitoring of bath parameters
  - pH, solids, concentration…
- Often require post-curing
  - extra step, time/energy consuming step
- Produces hazardous waste



UV-SOL-GEL



Organo-Silane Precursor

+

Photo-Latent Base (PBG)

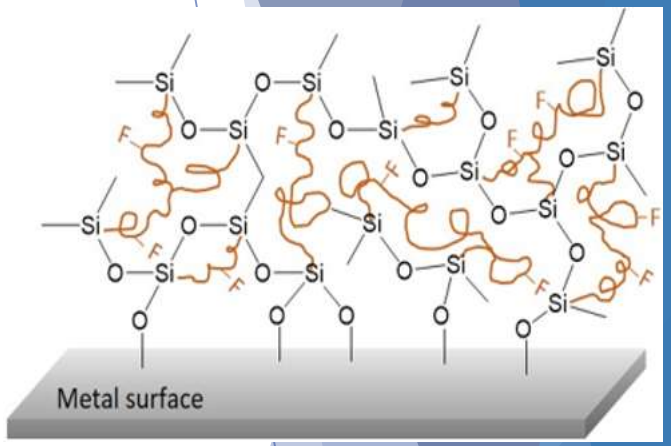
OR

Photo-Latent Acid (PAG)

UV radiation H-Bulb

UV Energy Density
2500 mj/cm^2

Ambient Moisture



Organic-Inorganic Hybrid (OIH) Coating

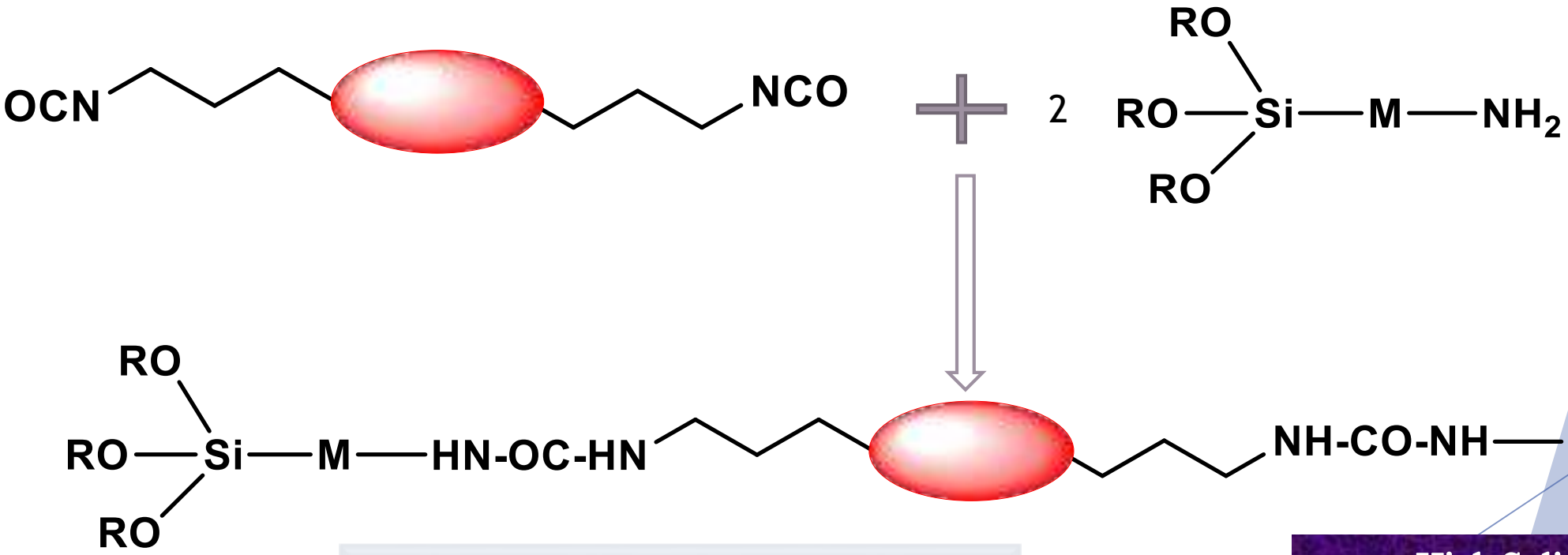
- *Mannari et al, US Patent – 11,414,524, Aug 16, 2022, Eastern Michigan University, USA*
- *Guillaume Bano, Céline Croutxé-Barghorn, Xavier Allonas / Laboratory of Macromolecular Photochemistry and Engineering / Mulhouse, France*

NEW PRECURSOR

Innovative Approach

Isocyanate Prepolymer

Amino Silane



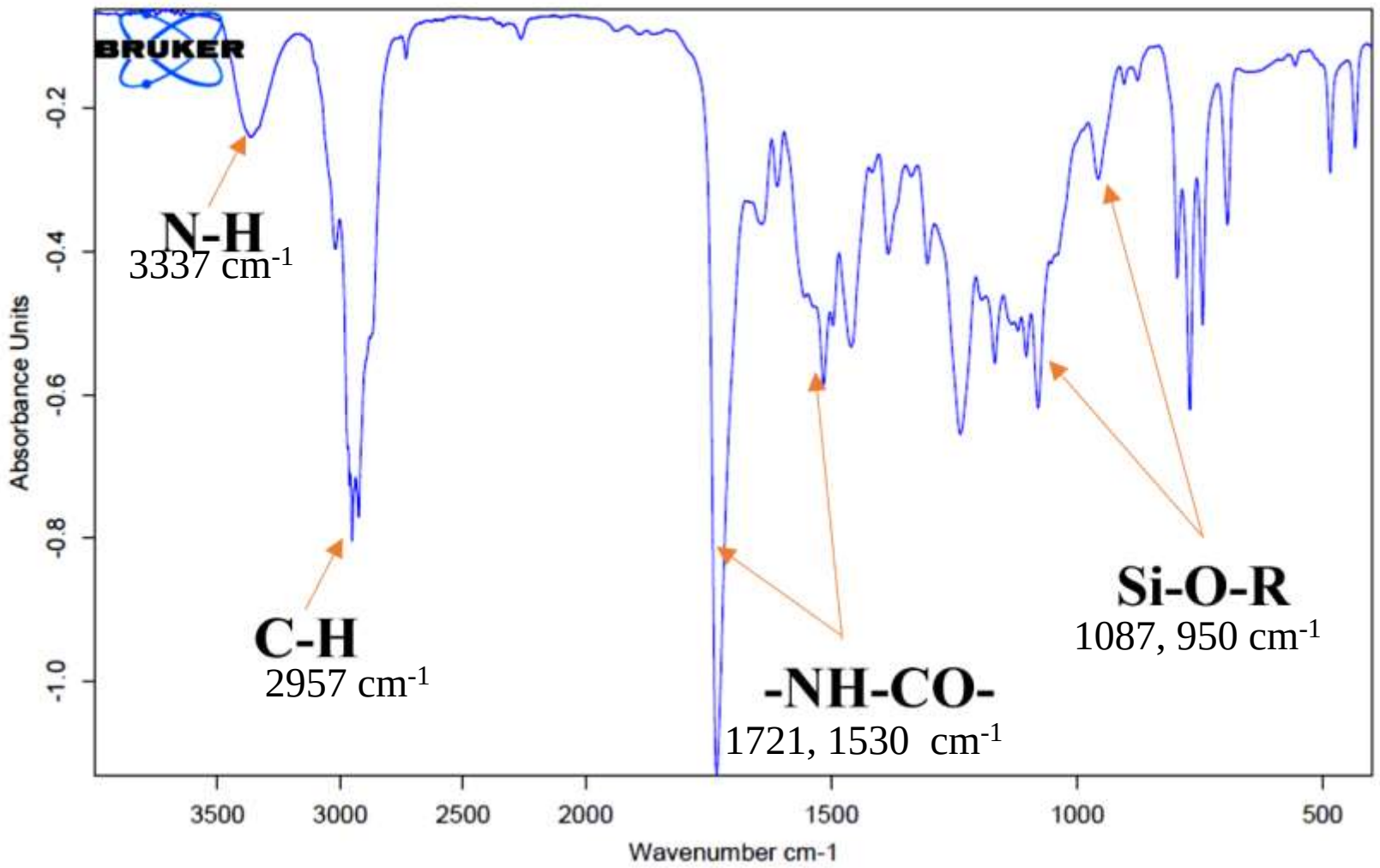
Multi-Functional Silane Precursor

High Solid Curable at Low Temperature

Characterization- FT-IR

TEST

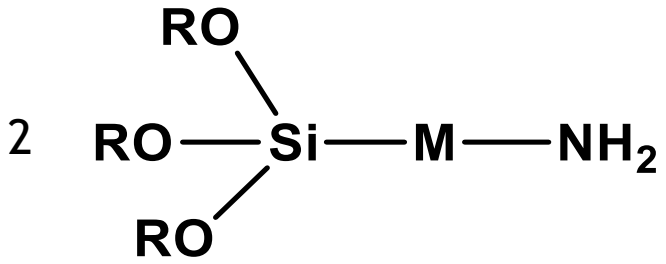
Multi-functional Silane Precursor

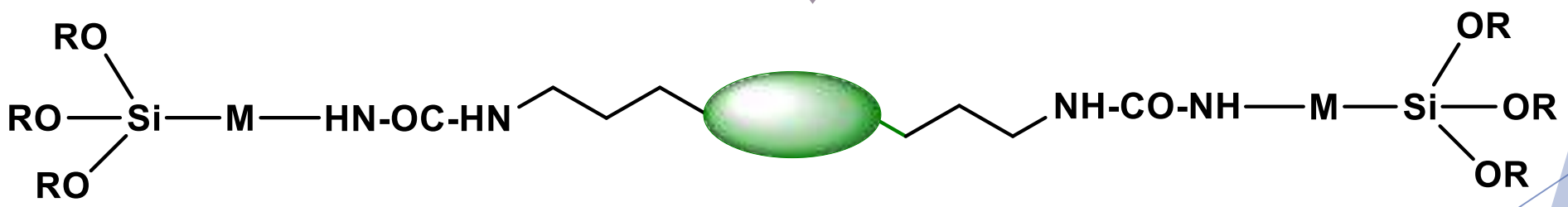


BIO-BASED PRECURSOR

Bio-Based Isocyanate Prepolymer

Amino Silane



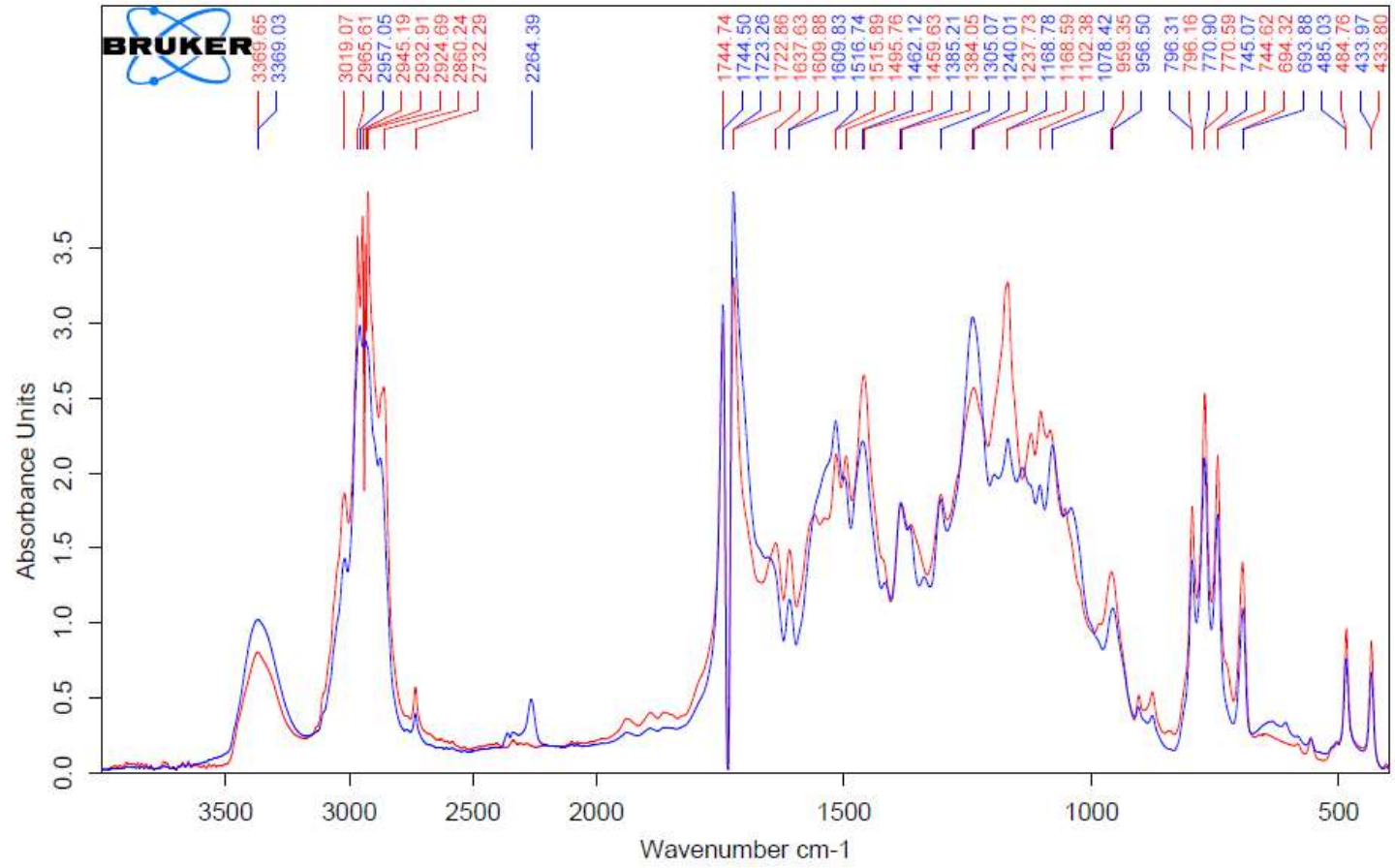


Bio-Based Multi-Functional Silane Precursor

100% Solid
VOC/HAPS Free

Characterization- FT-IR

TEST



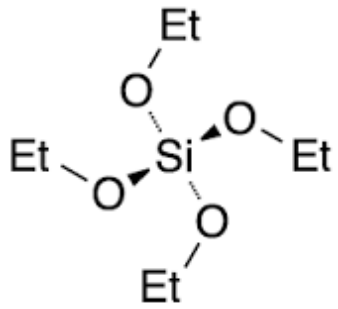
Petroleum-Based Oligomer

Bio-Based Oligomer

Coating Formulation

TEST

- **Multi-Functional Silane Precursor; Petroleum-Based and Bio-Based**
- **Curing Catalysts**
  - ✓ CXC-1612; King Industry (Thermally Blocked Super Acid)
- **Reactive Diluent (TEOS)**



TEOS

"Tetraethyl Orthosilicate"

TEST

Cure Study by FT-IR

Peak of Interest: 1050 cm^{-1} to 1140 cm^{-1}

Reference Peak: C=O, 1721 cm^{-1}

Bruker-Tensor 27 FT-IR spectrometer in the range of 4000 to 500 cm^{-1} wavelengths

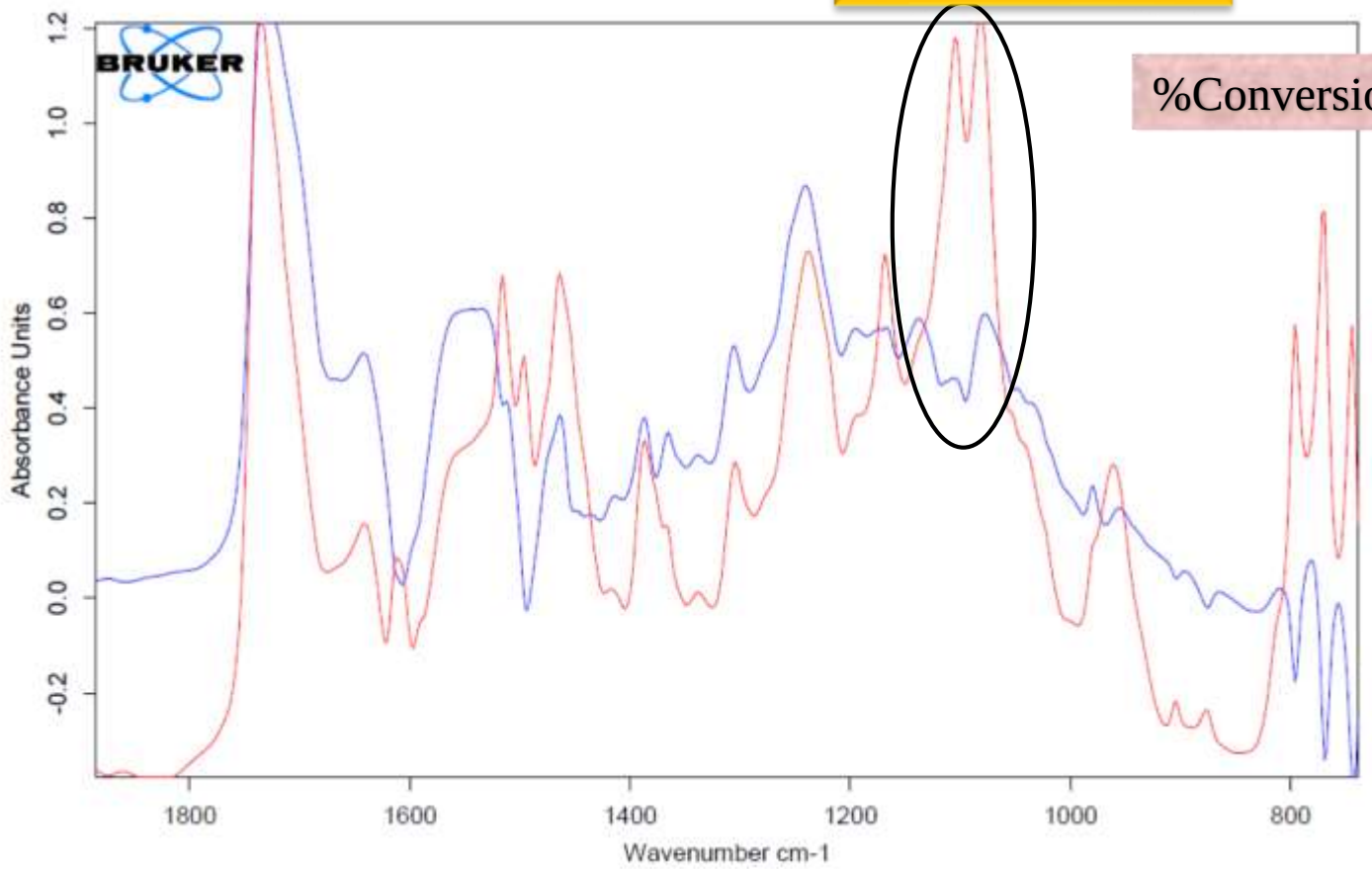
$$\boldsymbol{Conversion}\ (\%) = \mathbf{100}\ \times \mathbf{1}\ \frac{(\boldsymbol{A_{1087\ cm^{-1}}/A_{1720\ cm^{-1}}})_{\boldsymbol{Cured}}}{(\boldsymbol{A_{1087\ cm^{-1}}/A_{1720\ cm^{-1}}})_{\boldsymbol{UnCured}}}$$

5. Zareanshahraki, F. and Mannari, V. (2018), “Green” UV-LED gel nail polishes from bio-based materials. Int J Cosmet Sci, 40: 555-564. https://doi.org/10.1111/ics.12497

Cure Study by FT-IR

RESULT

1050-1110 cm^{-1}



%Conversion= 92.4%

Coating with Petroleum-Based OIH binder system

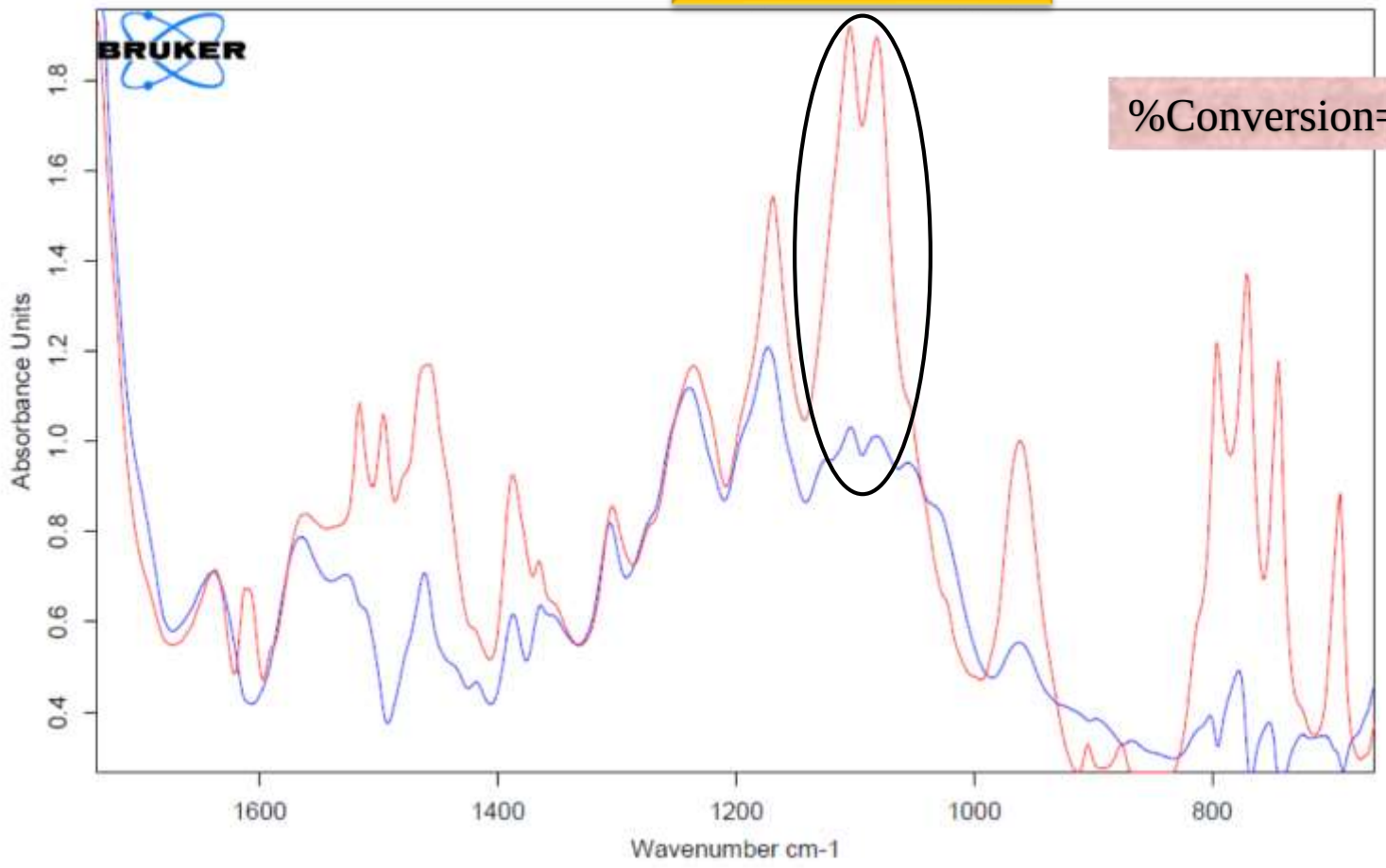
before (Red) and after (Blue)

Curing in the oven (20 min at 90 °C)

Cure Study by FT-IR

RESULT

1050-1110 cm^{-1}



%Conversion= 88.6%

Coating with Bio-Based OIH binder system

before (Red) and after (Blue)

Curing in the oven (20 min at 90 °C)

Cure-Extent Study (Gravimetric Method)

TEST

Si-OR + ½ H_2O= ½ Si-O-Si + ROH

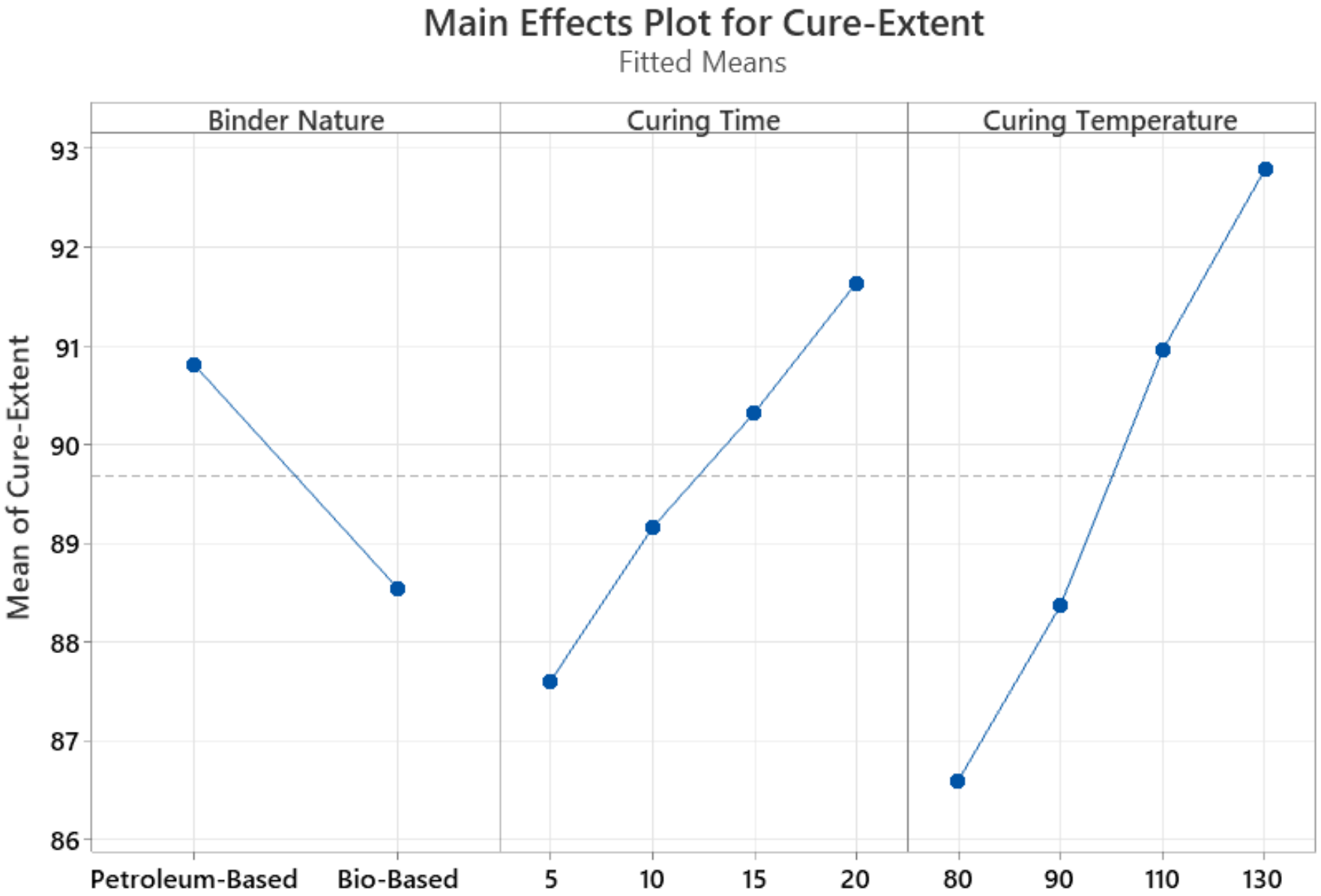
Volatile losses
Correspond to the Cure-Extent

- ✓ Variables
  - ❖ **Binder Nature**; Petroleum-Based and Bio-Based
  - ❖ **Curing Temperature**; 80 ℃, 90 ℃, 110 ℃, 130 ℃
  - ❖ **Curing Time;** 5 min, 10 min, 15 min, 20 min

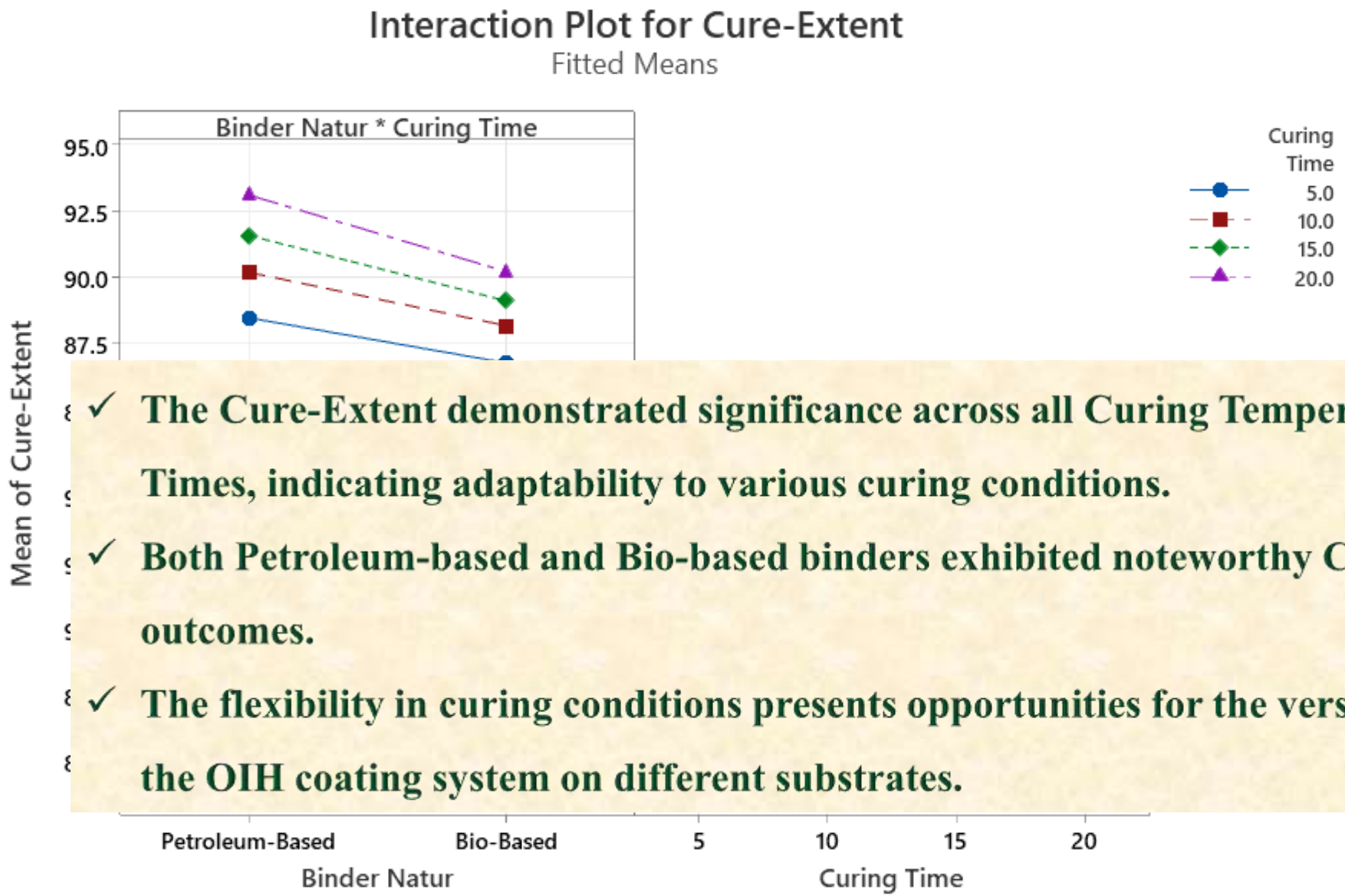
Analyze by MINITAB statistical software through Design of Experiment (DOE)

Analys

Source
Model
Linear
Binde
Curin
Curin
2-Way
Binde
Binde
Curin
3-Way
Binde
Error
Total



RESULT



- ✓ **The Cure-Extent demonstrated significance across all Curing Temperatures and Curing Times, indicating adaptability to various curing conditions.**
- ✓ **Both Petroleum-based and Bio-based binders exhibited noteworthy Cure-Extent outcomes.**
- ✓ **The flexibility in curing conditions presents opportunities for the versatile application of the OIH coating system on different substrates.**

Performance

TEST

- Primary properties have been tested.
- Significance in cure-extent across all curing conditions prompted evaluation of properties for each specific curing scenario.
  - MEK- Double Rub
  - König Pendulum Hardness
  - Static Contact Angle
  - Adhesion by Cross- Cut

Wet Film Thickness: 2 mill
Substrate: Aluminum

RESULT

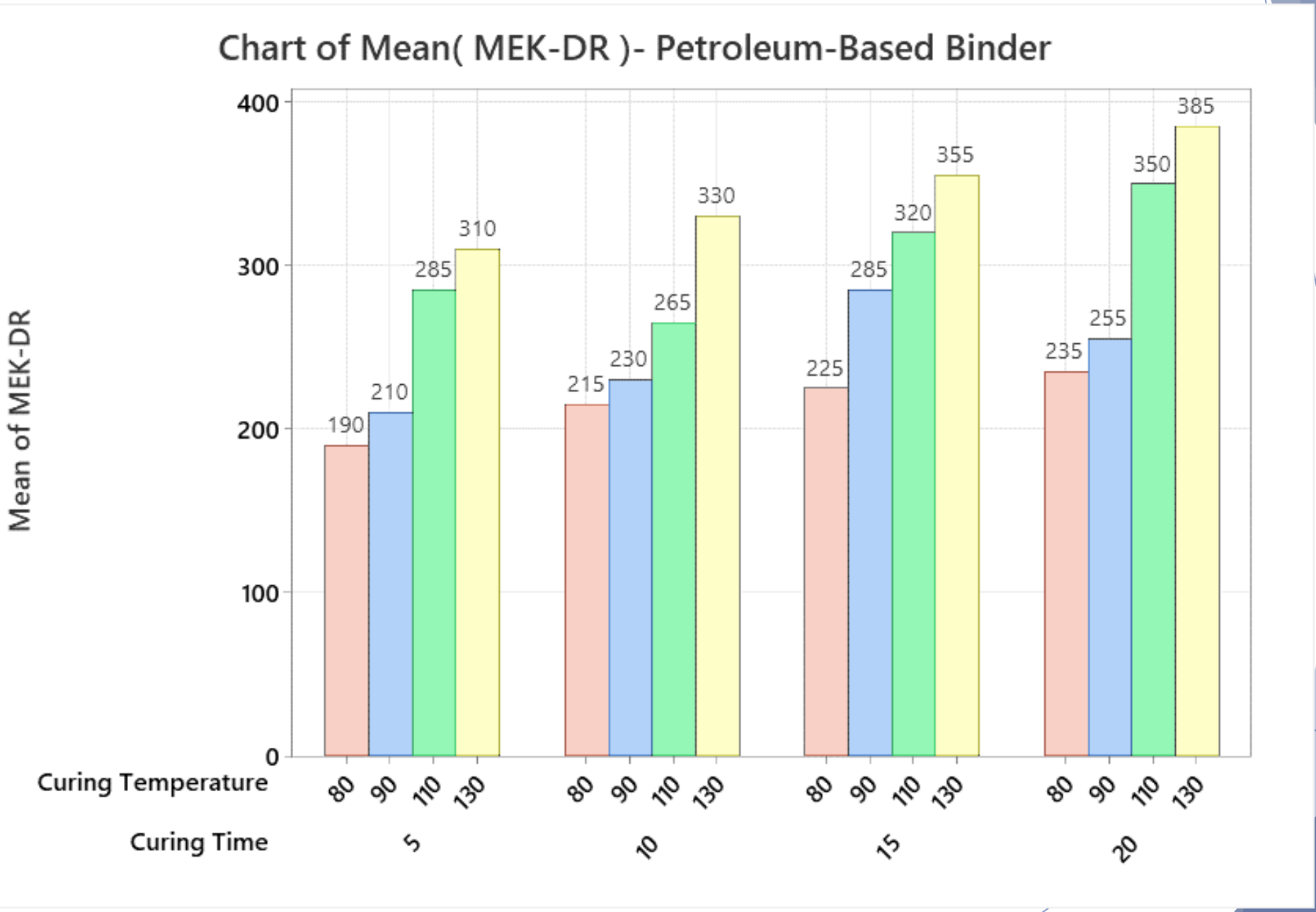


Chart of Mean(MEK-DR)- Petroleum-Based Binder
Mean of MEK-DR
400
300
200
100
0
190
210
285
310
215
230
265
330
225
285
320
355
235
255
350
385
Curing Temperature
80
90
110
130
Curing Time
5
10
15
20

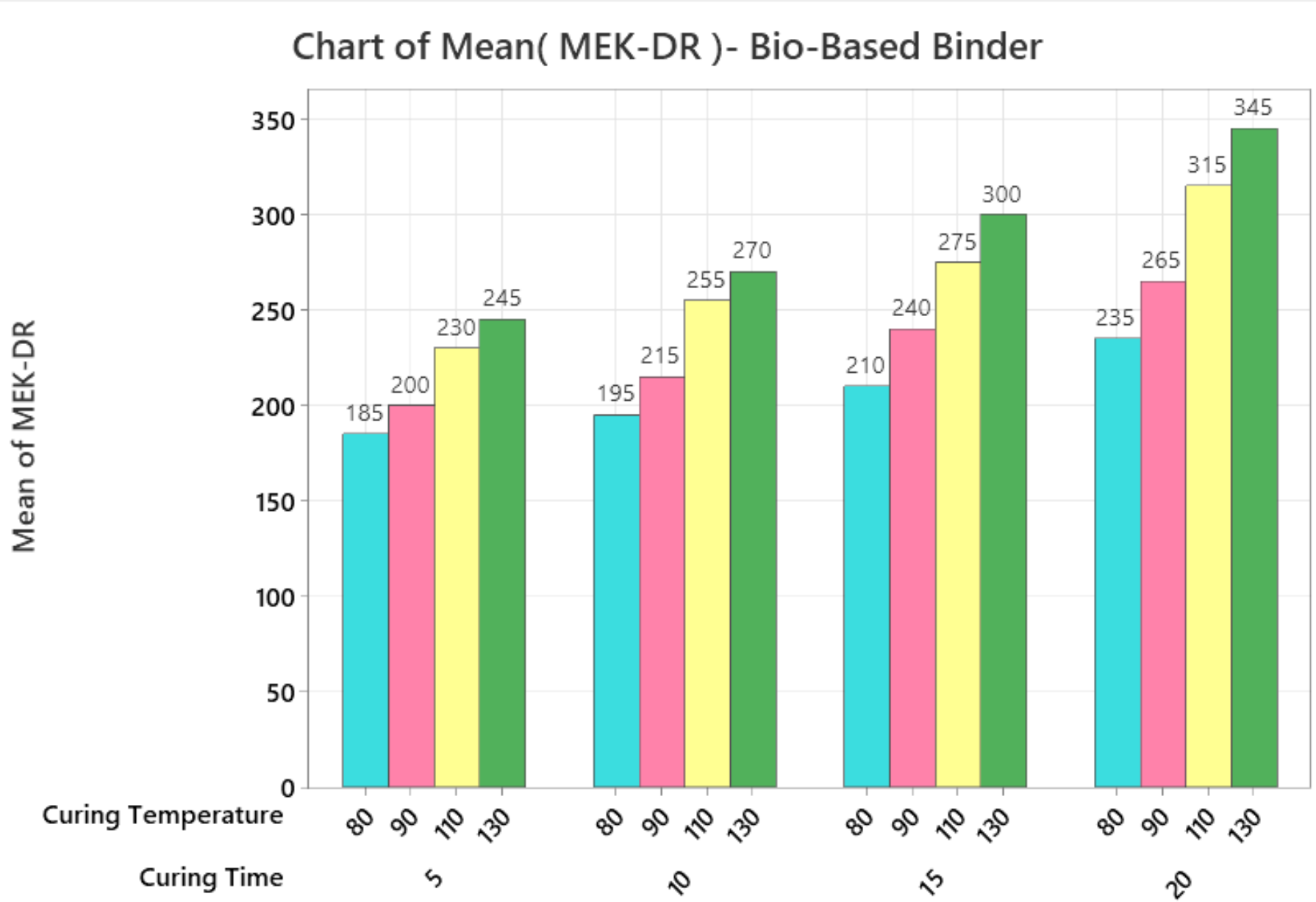


Chart of Mean(MEK-DR)- Bio-Based Binder
Mean of MEK-DR
350
300
250
200
150
100
50
0
185
200
230
245
195
215
255
270
210
240
275
300
235
265
315
345
Curing Temperature
80
90
110
130
Curing Time
5
10
15
20

RESULT

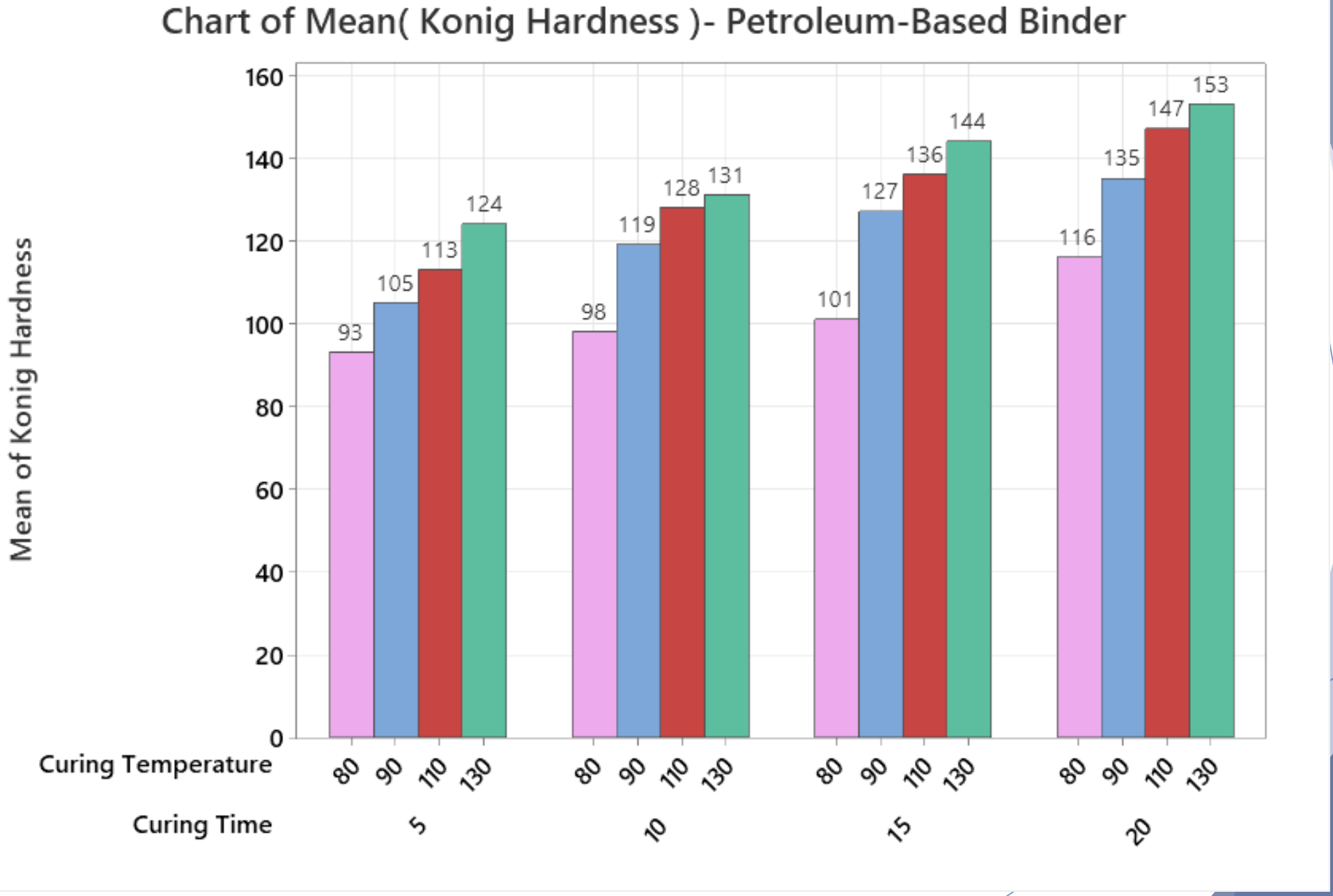


Chart of Mean(Konig Hardness)- Petroleum-Based Binder
Mean of Konig Hardness
160
140
120
100
80
60
40
20
0
93
105
113
124
98
119
128
131
101
127
136
144
116
135
147
153
Curing Temperature
80
90
110
130
Curing Time
5
10
15
20

RESULT

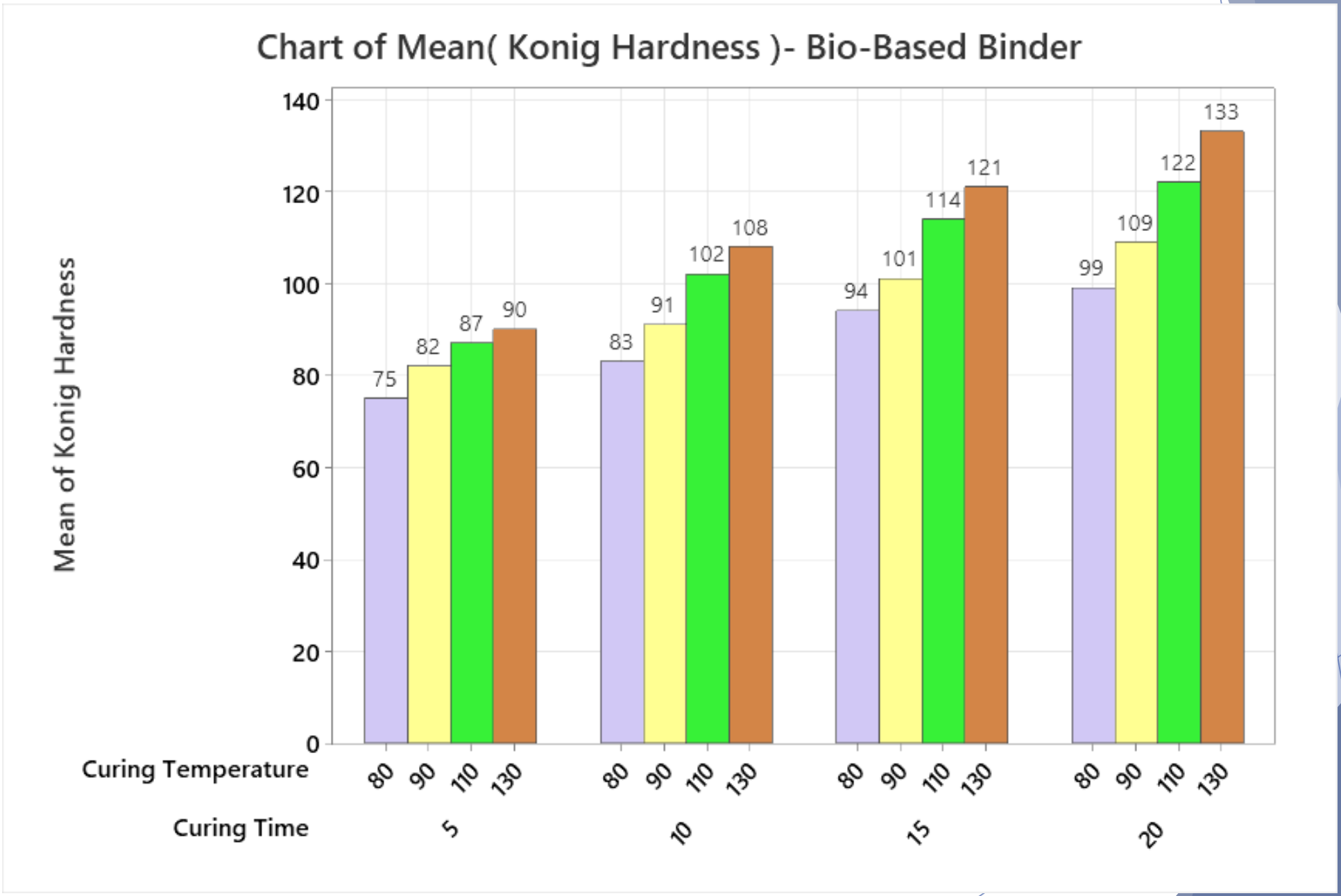


Chart of Mean(Konig Hardness)- Bio-Based Binder
Mean of Konig Hardness
140
120
100
80
60
40
20
0
75
82
87
90
83
91
102
108
94
101
114
121
99
109
122
133
Curing Temperature
80
90
110
130
Curing Time
5
10
15
20

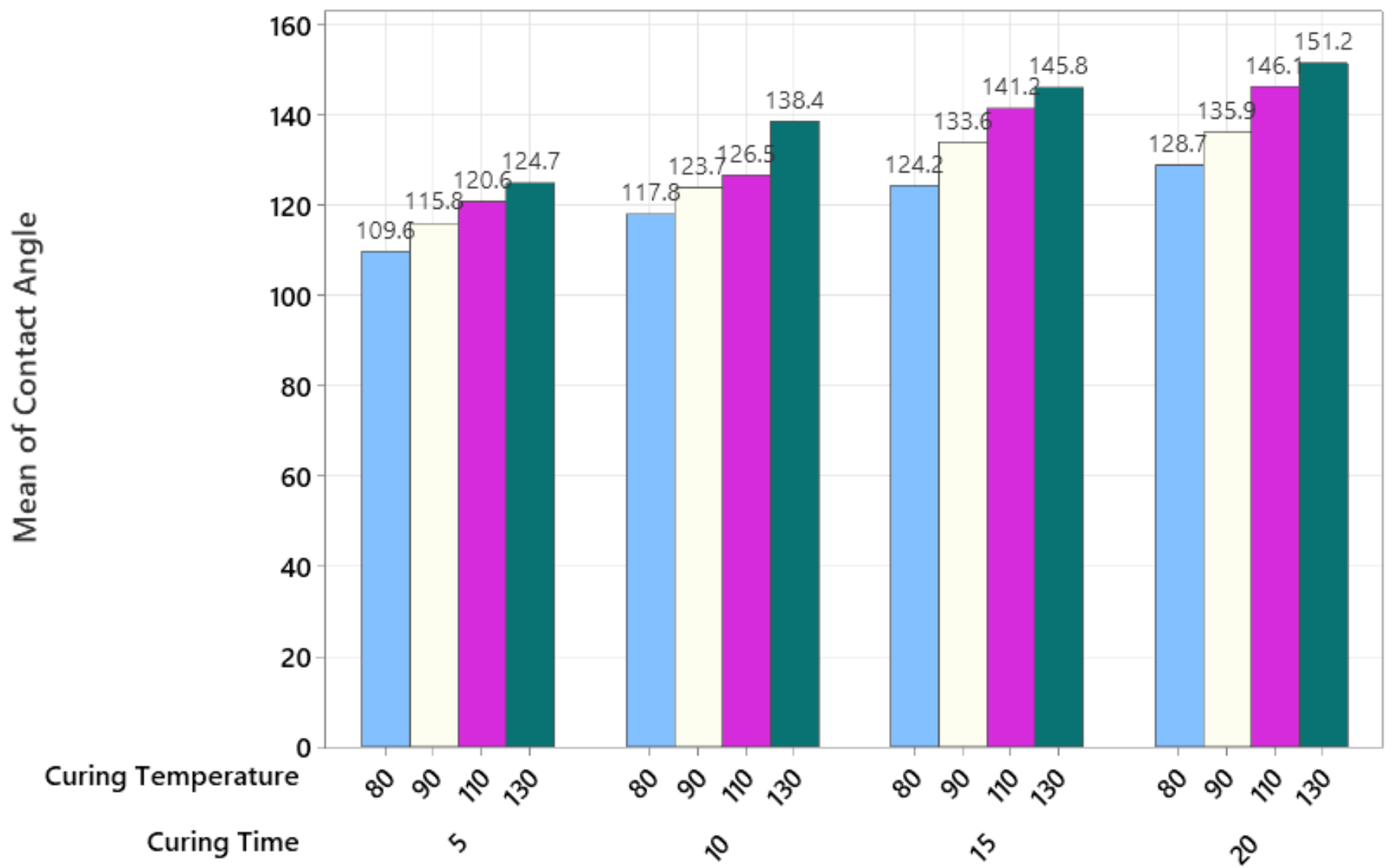


Chart of Mean(Contact Angle)- Petroleum-Based Binder
Mean of Contact Angle
160
140
120
100
80
60
40
20
0
109.6
115.8
120.6
124.7
117.8
123.7
126.5
138.4
124.2
133.6
141.2
145.8
128.7
135.9
146.1
151.2
Curing Temperature
80
90
110
130
Curing Time
5
10
15
20

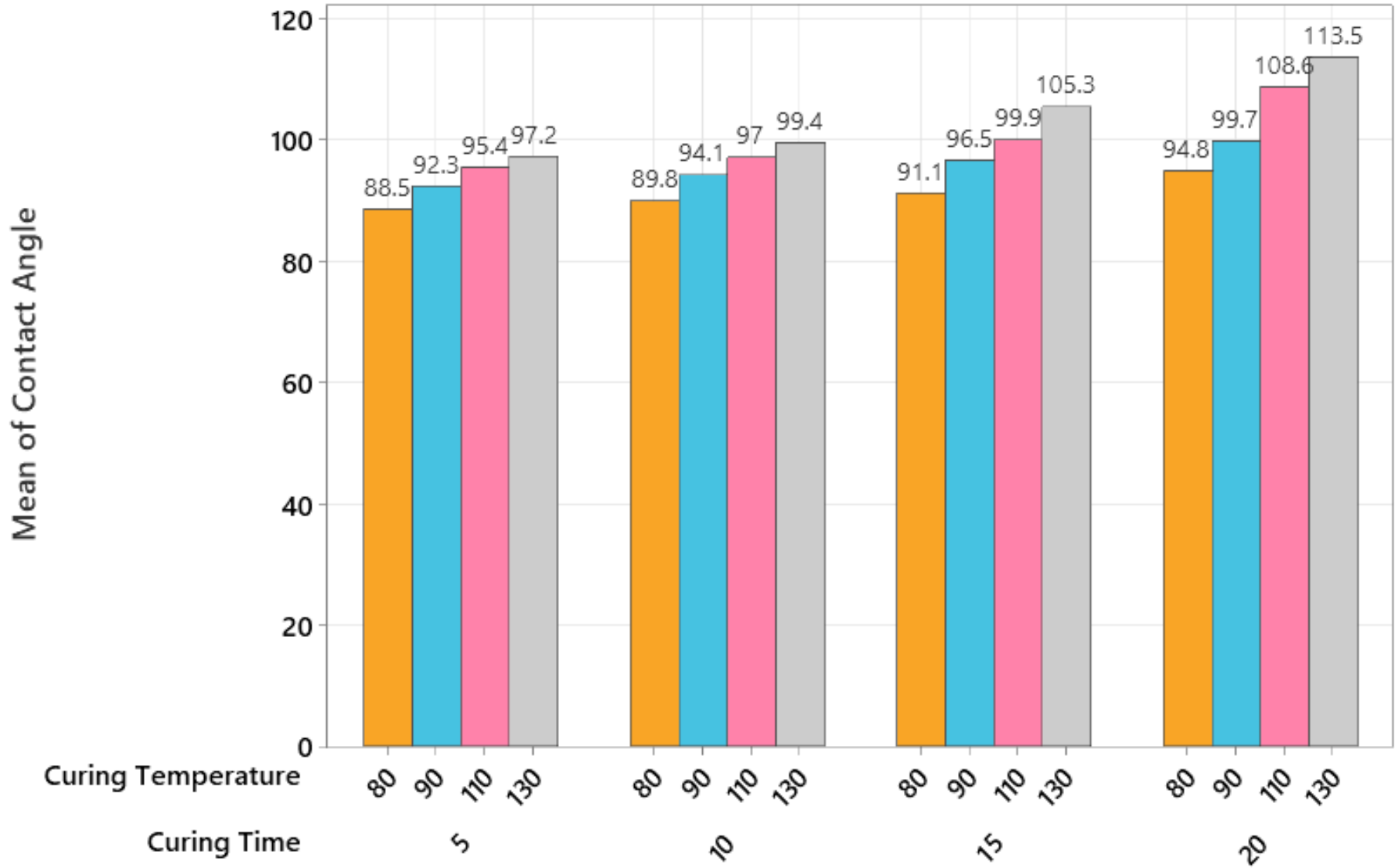
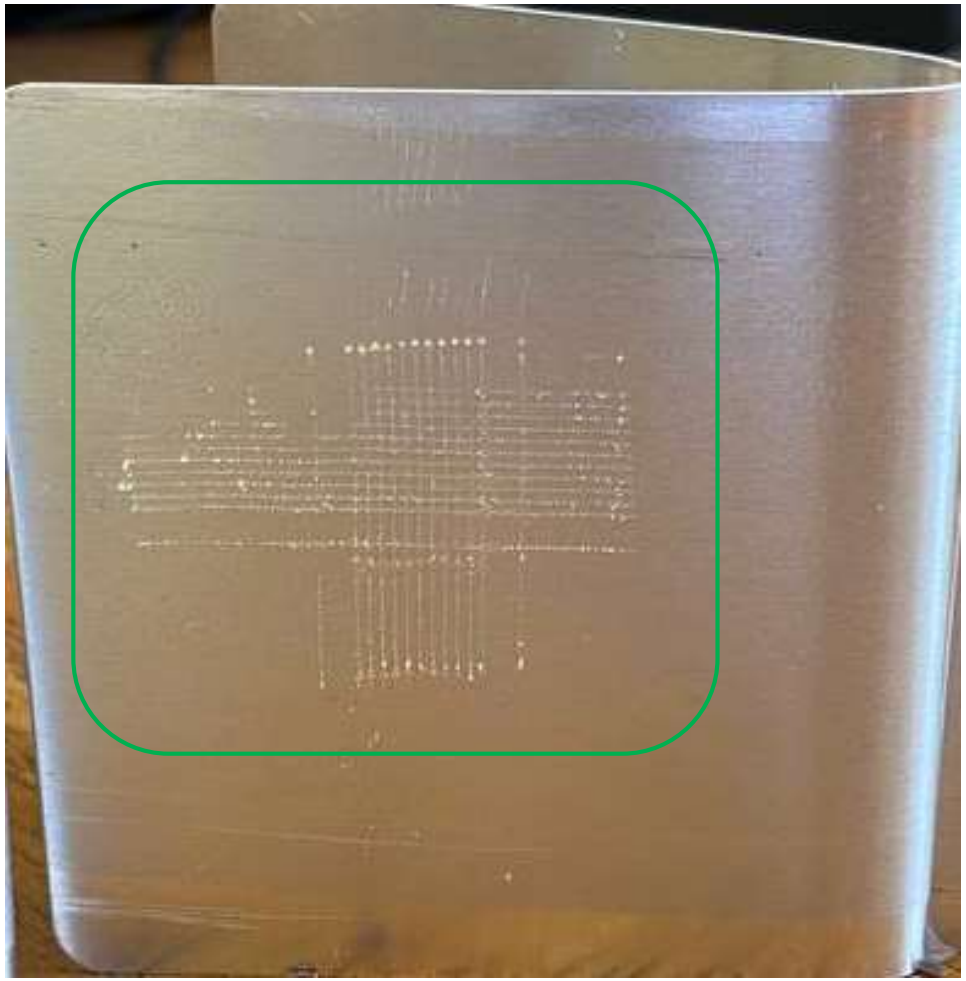


Chart of Mean(Contact Angle)- Bio-Based Binder
Mean of Contact Angle
120
100
80
60
40
20
0
88.5
92.3
95.4
97.2
89.8
94.1
97
99.4
91.1
96.5
99.9
105.3
94.8
99.7
108.6
113.5
Curing Temperature
80
90
110
130
Curing Time
5
10
15
20

RESULT

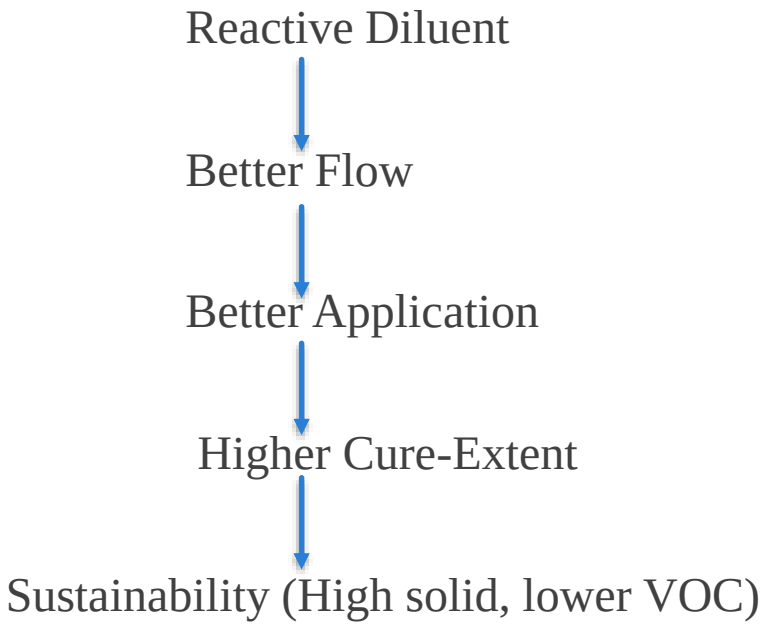
Adhesion by Cross-Cut



All coatings, under various curing conditions, demonstrated satisfactory cross-cut adhesion, achieving a grade 5B rating as per ASTM D3359.

Reactive Diluent Study

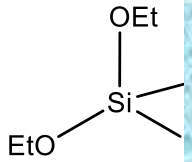
- High solid, High Molecular Weight, High Viscosity, VOC



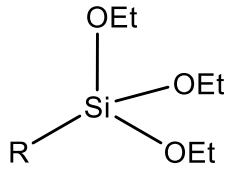
Silane/Organo-Silanes

Cure Mech.: Sol-gel

Catalyst: AG



TEOS



Organo-Silane,
R= Alky, cycloaliphatic

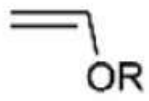
3 & 4 membered rings, Vinyl ethers

Cure Mech.: Cationic Polymerization

Catalyst: AG

- **The coating systems, utilizing both petroleum-based and bio-based binders, exhibited compatibility with all reactive diluents tested.**
- **By employing different reactive diluents, properties can be fine-tuned, resulting in enhanced performance across various application domains.**

Oxetanes



Vinyl ethers

CONCLUSION

- New oligomers offer versatility in curing conditions, allowing for application at various temperatures and with different curing times.
- Synthesis of new oligomers has led to the creation of 100% solid and environmentally friendly options, both in Bio-Based and Petroleum-Based variants.
- The current progression involves the incorporation of environmentally safe reactive diluents in the formulation.
- The synthesis of oligomers with diverse backbones is currently in progress.
- The application of new oligomers has been successfully demonstrated on diverse substrates, including Metal and ABS, with ongoing investigations into results for other substrates.
- Formulation possibilities are extensive, enabling new oligomers to cater to a wide array of applications, such as Automotive Interiors, Clear-coats, Wood Coatings, Anti-Corrosion coatings, and Pre-treatments.

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