Water-borne UV-curable Coatings Based on Renewable Materials

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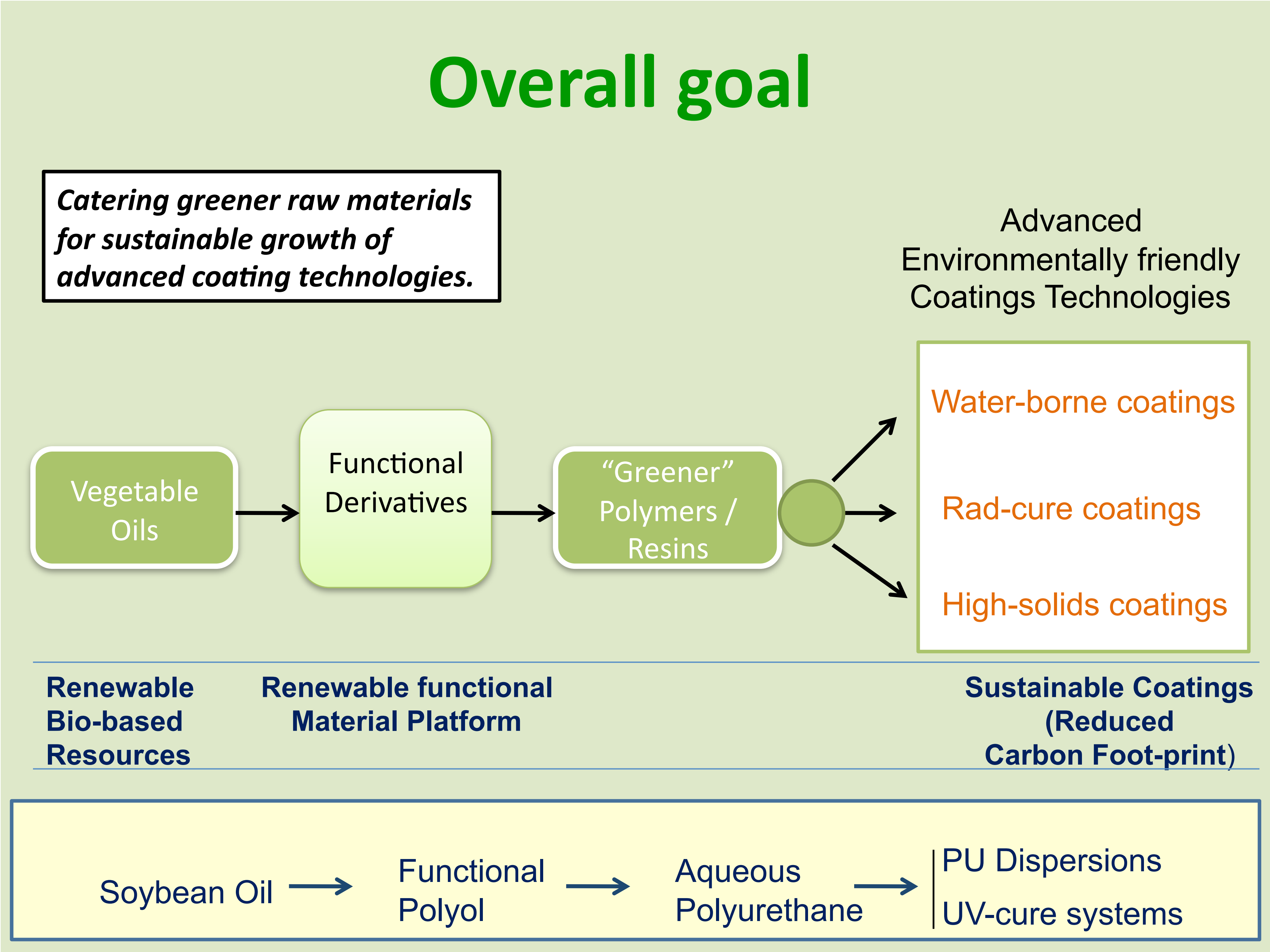
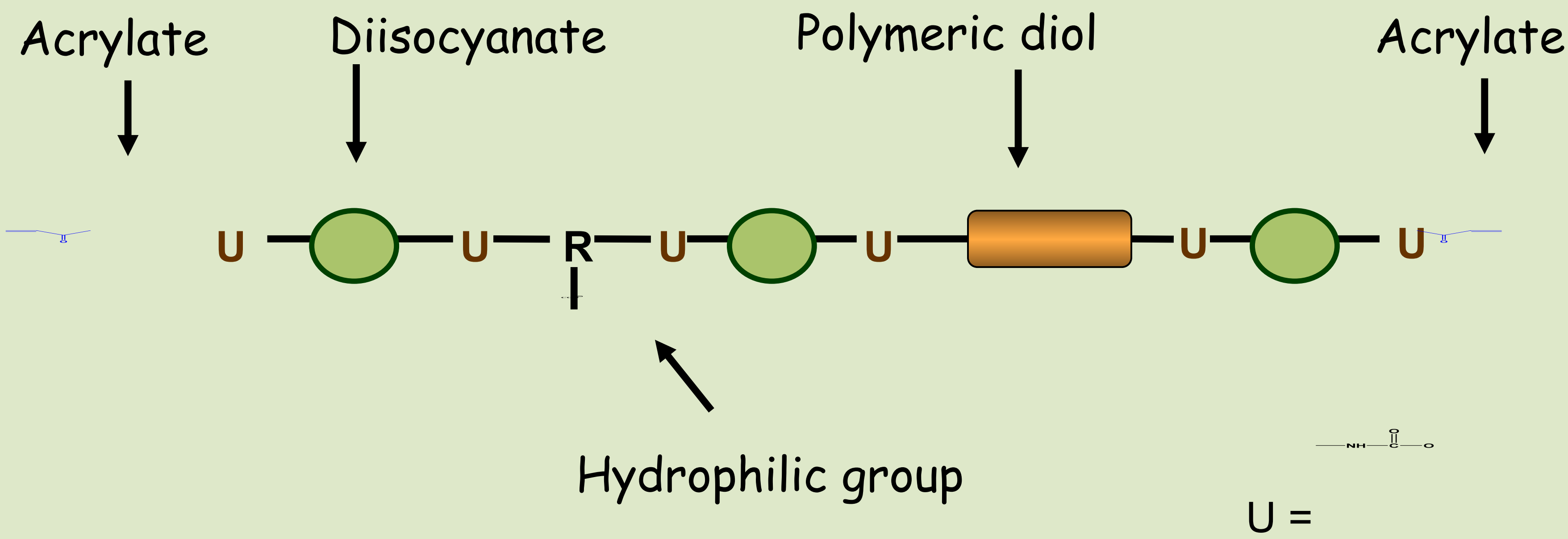

Overall goal
Catering greener raw materials for sustainable growth of advanced coating technologies.
Advanced Environmentally friendly Coatings Technologies
Vegetable Oils
Functional Derivatives
"Greener" Polymers / Resins
Water-borne coatings
Rad-cure coatings
High-solids coatings
Renewable Bio-based Resources
Renewable functional Material Platform
Sustainable Coatings (Reduced Carbon Foot-print)
Soybean Oil
Functional Polyol
Aqueous Polyurethane
PU Dispersions
UV-cure systems

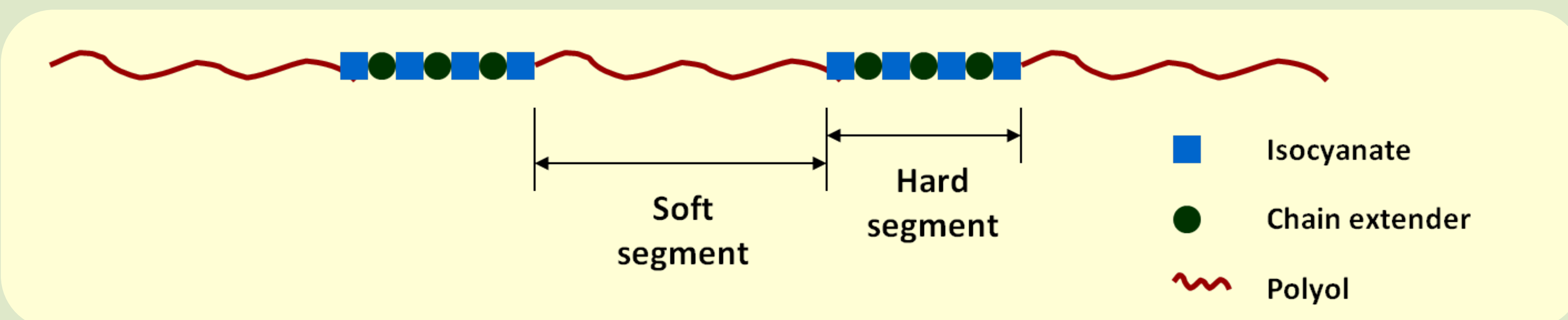
12 Principles of Green Chemistry

1. Prevention of waste
2. Atom Economy
3. Less Hazardous Chemical Syntheses
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstock
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice, Oxford* University Press: New York, 1998, p.30.

UV-curable Polyurethane Dispersions (UV-PUD)





Why UV-PUD?

- For high demanding industrial coatings, Cross-linkable (curable) PUDs are desirable
- Benefits of *Water-borne* & *UV-cure* systems.
- UV-curable PUDs combines benefits of UV-cure and water-borne technology
  - Low or zero VOC
  - No need for reactive diluents (odor, irritancy, cost..)
  - Reduced oxygen inhibition
  - “ready-to-handle” *before* UV cure

Soft-segment - significance

- **Soft Segments**
  - ~40-70% of PUD.
    - Significant contribution
  - Controls performance
    - Polyester, polyether, polycarbonate,…
  - Can be functionalized for special properties
    - Air-drying, hydrophobicity, compatibility
  - Substrate wetting, adhesion, cost…

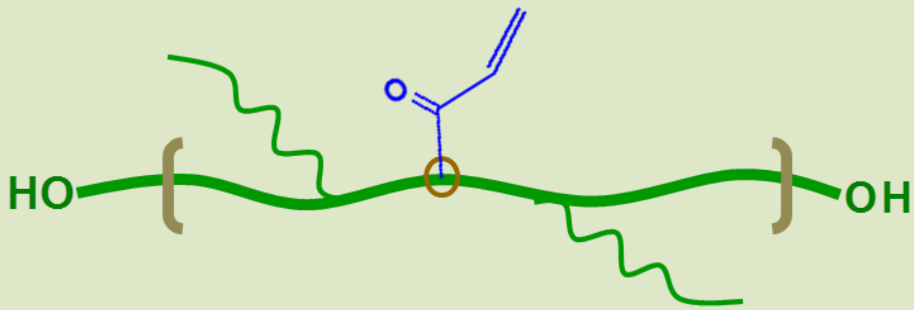
Invariably, all PUD components are petrochemical based

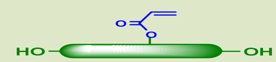
NOT SUSTAINABLE !!

UV-PUD :
Design for Sustainability & performance balance

- **Approach**
  - Combining two unique features
    - **Novel soft-segment development**
      UV-curable soy-polyol with acrylate functionality -
      - Bio-based content, Reducing carbon foot print Sustainability
    - **Use of silane functionality** to improve coating performance
      - Organic-inorganic hybrid nano-composite coatings.

Hyper-branched Acrylated Soy-polyol (HASP)



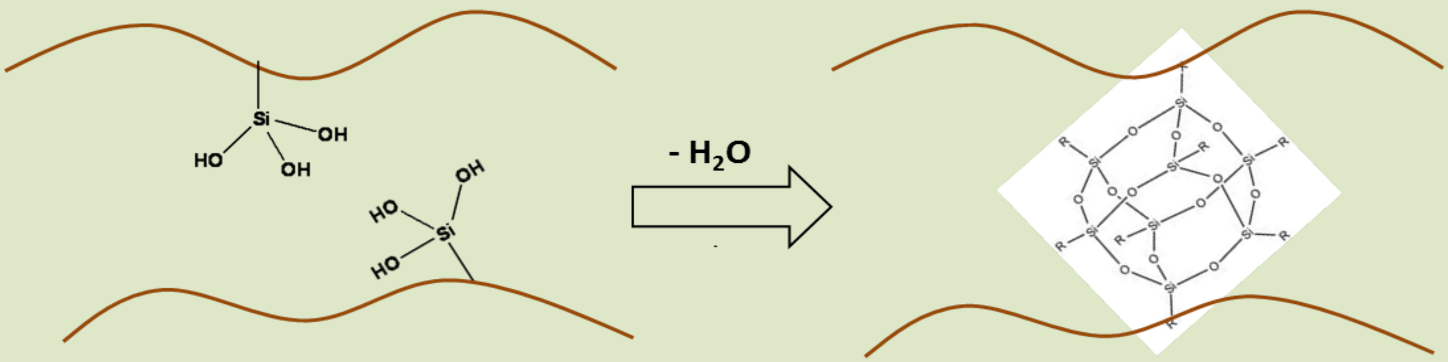


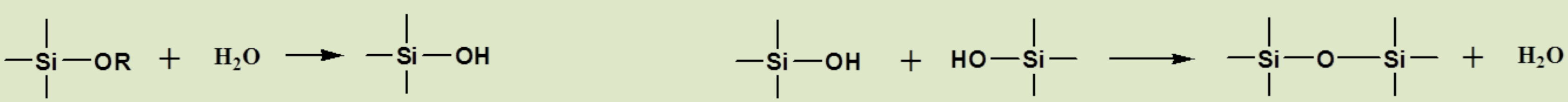
- Hyperbranched acrylated Soy-polyol prepared by ring-opening polymerization of epoxidized Soybean
  - Hyper-branched structure, polyether structure
  - Viscosity ~ 300 mPas
  - Hydroxy functionality = 2.0 – 2.5
  - Acrylate functionality = 1.0 -1.2 (pendent to the chain)

(Patent Pending)

Silane functionality

- In general, incorporation of high soy-polyol content reduces mechanical performance of cured film
- Silane functionalization and crosslinking can be used to enhance mechanical properties.





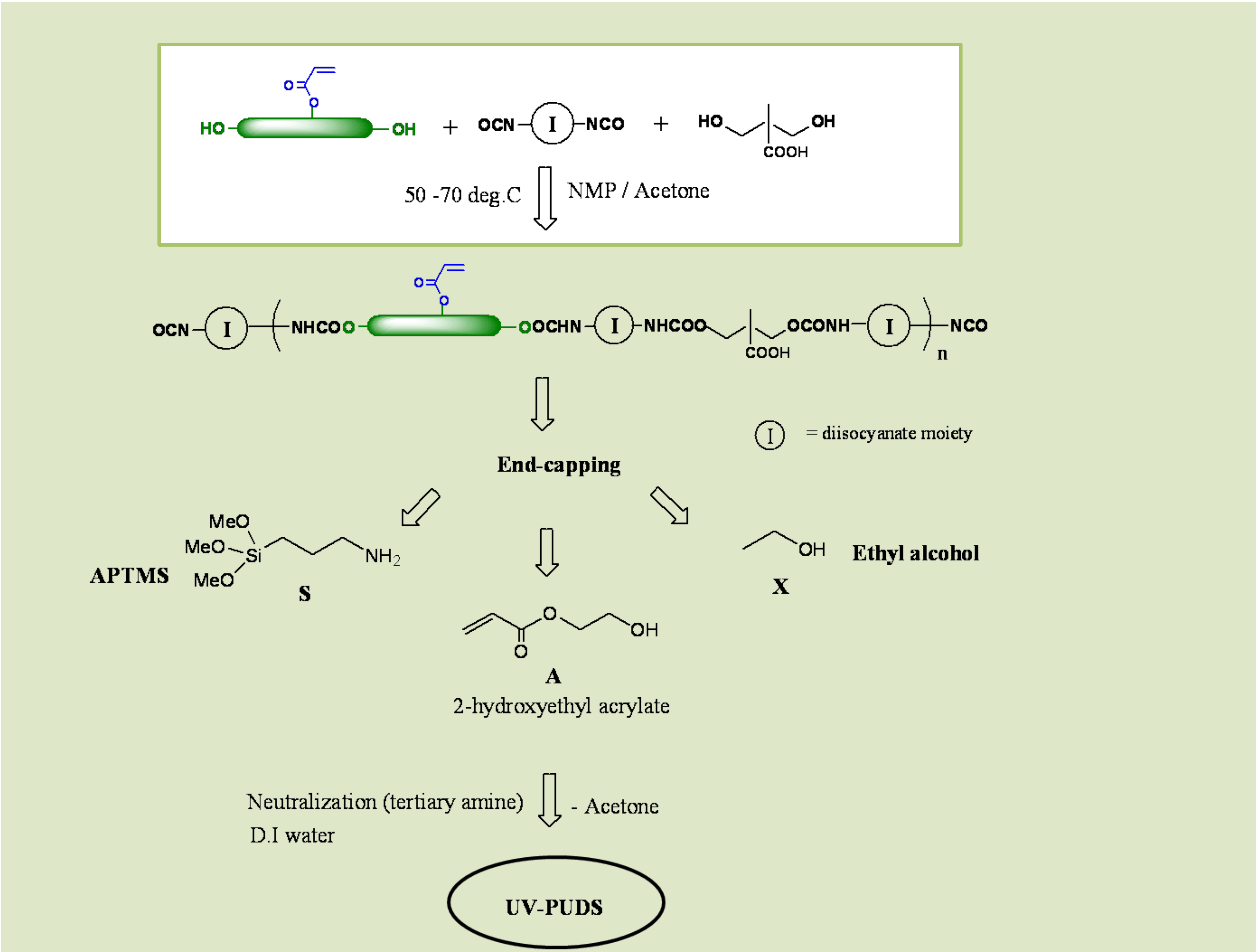
Silane hydrolyzed to silanol
In the dispersion,
Stable during storage

During drying, as water evaporates
silanol condense to form siloxane network.
Significantly reinforces mechanical properties

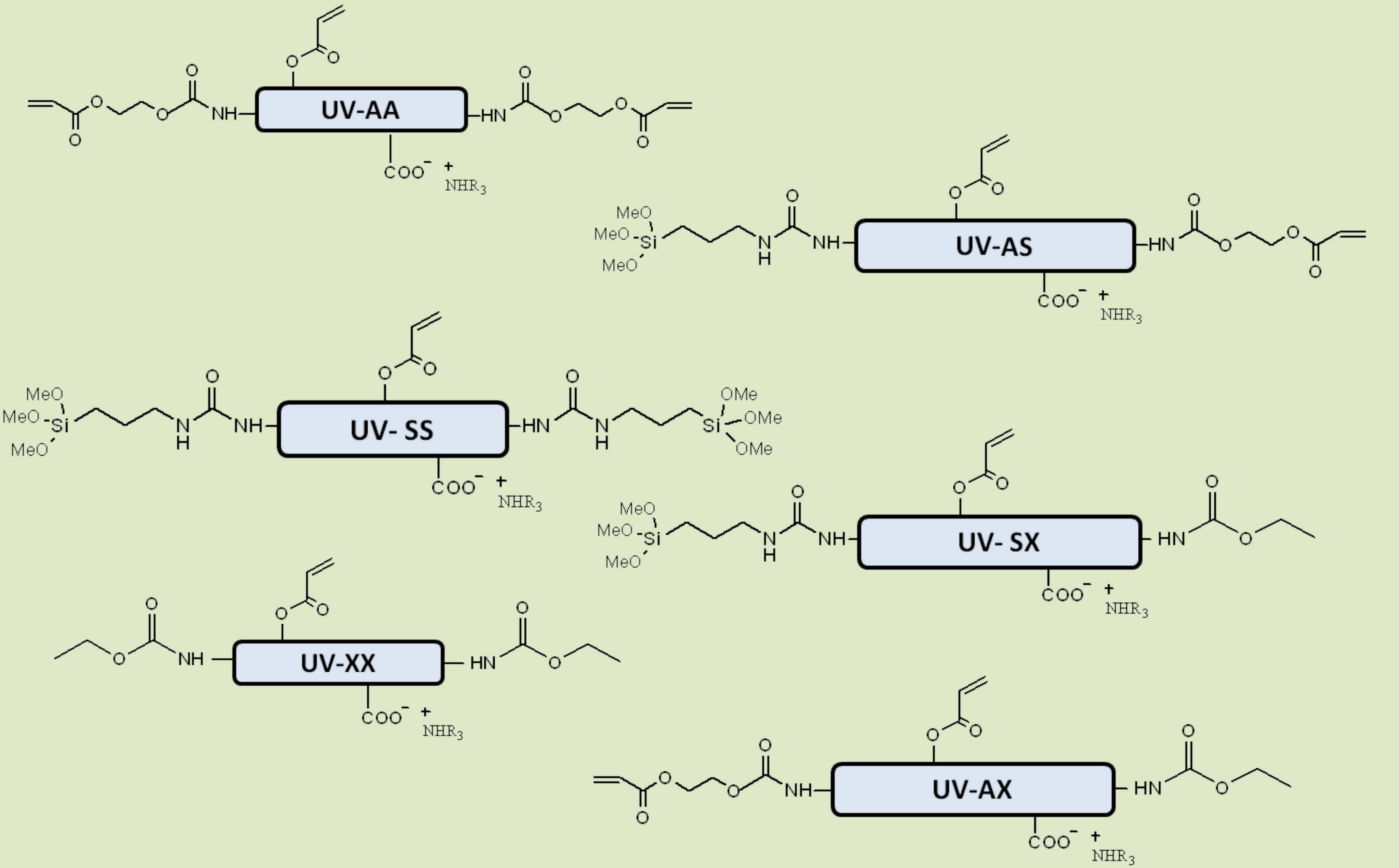
UV-PUD composition

– HASP used as "Soft Segment"
  - Bio-based content
  - Pendent acrylate grp.: UV-cure, uniform distribution of crosslinks in cured film
  - Low shrinkage : Flexible structure
  - Good substrate and pigment wetting
– PUD chains with:
  - End-capped acrylate functions
  - End-capped Silane functions
  - End-capped acrylate + Silane functions

– DMPA for hydrophilic centers


HO
OH
OCN
I
NCO
HO
OH
COOH
50 -70 deg.C
NMP / Acetone
OCN
I
NHCOO
OOCHN
I
NHCOO
COOH
OCONH
I
NCO
n
I
= diisocyanate moiety
End-capping
MeO
MeO
Si
MeO
NH2
APTMS
S
OH
Ethyl alcohol
X
O
OH
O
A
2-hydroxyethyl acrylate
Neutralization (tertiary amine)
D.I water
- Acetone
UV-PUDS

UV-PUDs varying functionality



UV-PUDs - Compositions

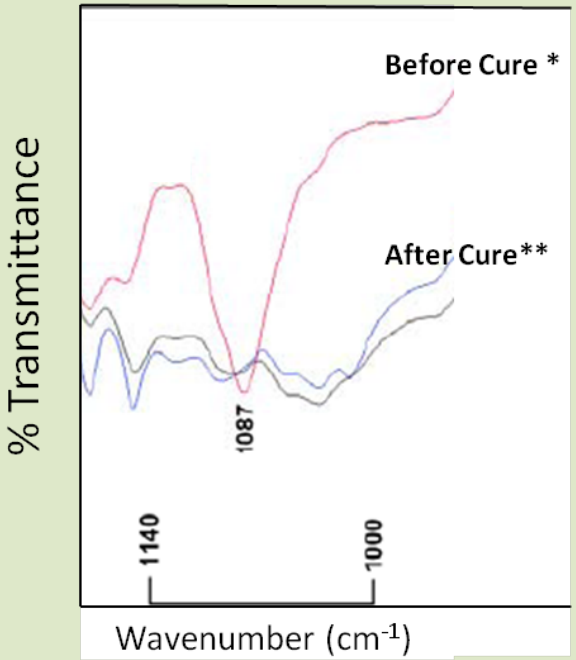
UV-PUD Sample code	End-cappind functionality	Weight per Acrylate, g	Bio-based content, %
UVAA	Acrylate/Acrylate	528.4	25.86
UVAS	Acrylate/Silane	825.7	25.57
UVSS	Silane/Silane	1719.7	25.19
UVAX	Acrylate /No function	756.3	27.00
UVSX	Silane/No function	1588.2	26.57
UVXX	No function /No function	1428.6	28.12
UVxT	Chain extended PUD, No end function	1134.0	26.70

$$\% \text{ Bio-based content} = \frac{\text{Amount of bio-based carbon}}{\text{Amount of total carbon}} \times 100$$

Cure Characterization

FT-IR Study

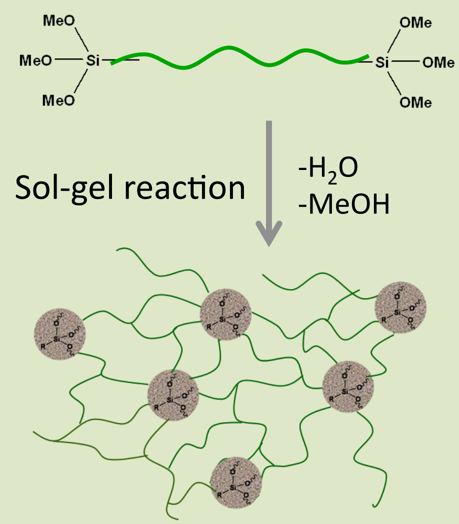
Disappearance of C=C peaks at 1408cm^{-1}, and 1635 cm^{-1}
Indicates acrylate conversion.



Formation of silica network is confirmed by Displacement of Si-O-C peak with Si-O-Si.

Si-O-C asymmetric stretching 1087 cm^{-1}

Si-O-Si stretching , wide band 1000-1140 cm^{-1}



Organic-inorganic hybrid coating

* characterized in the prepolymer before dispersion in water

** in the UV-cured film

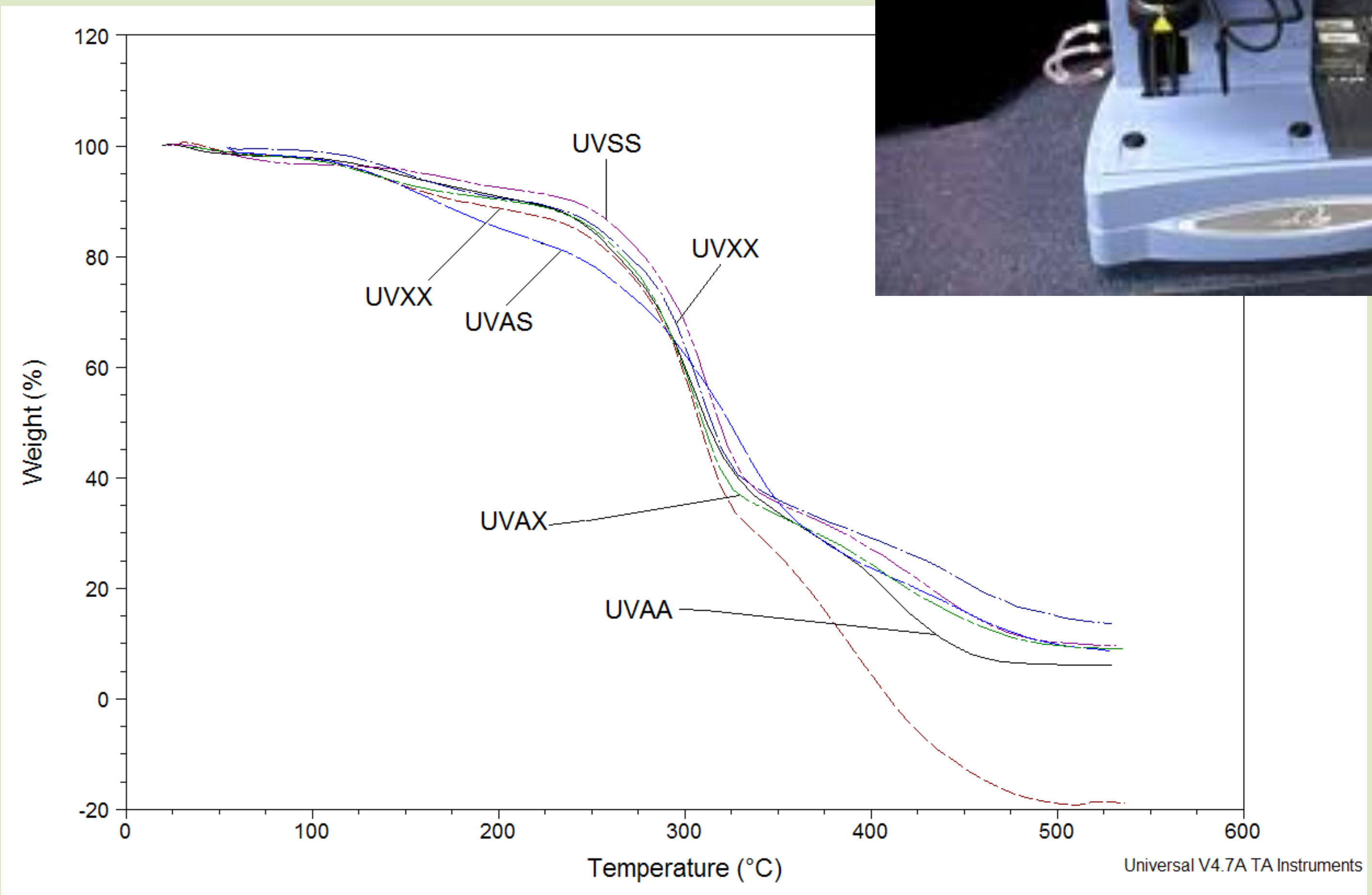
1. Pantoja, et al., *Applied Surface Science* 255, 6386–6390 (2009)
2. Zhao, at al., *olloids and Surfaces A.* 346, 75–82 (2009)

Film Properties

Before UV-cure

Properties	UVAA	UVAS	UVAX	UVSX	UVSS	UVXX	UVxT
Koenig Hardness (sec)	120	112	101	102.4	137.2	84	170
Pencil Hardness	H	3H	H	2H	4H	H	3 H
Adhesion (Cross-Hatch)	5B	3B	5B	4B	5B	3B	4B
MEK Double-rubs	0	25	0	25	25	0	0
Impact strength (Direct/Reverse)	120/100	55/60	70/60	60/60	50/40	60/50	50/50

Thermogravimetry



TGA thermogram UV-cured films

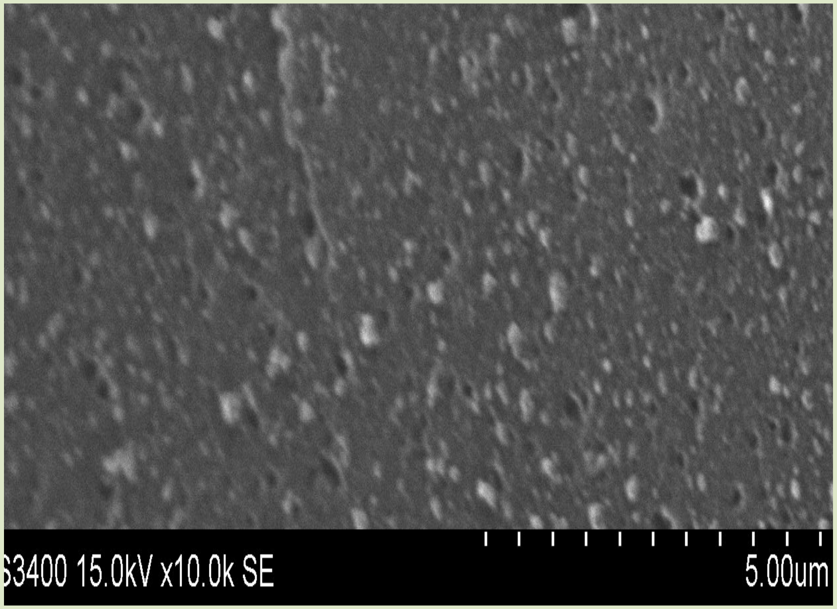
Thermal Properties

Properties	UVAA	UVAS	UVAX	UVSX	UVSS	UVXX	UVxT
Temp. for 5% weight Loss ºC	145	137	131	138	151	129	-
Temp. for 50% weight Loss ºC	315	324	309	307	315	311	287
Tg ^{0}C (DSC)	109	48	5	3	17	2	50

- Acrylate functions have significant contribution to Tg than Silane
- XLD is important factor in controlling Tgs (samples with X have low Tg)

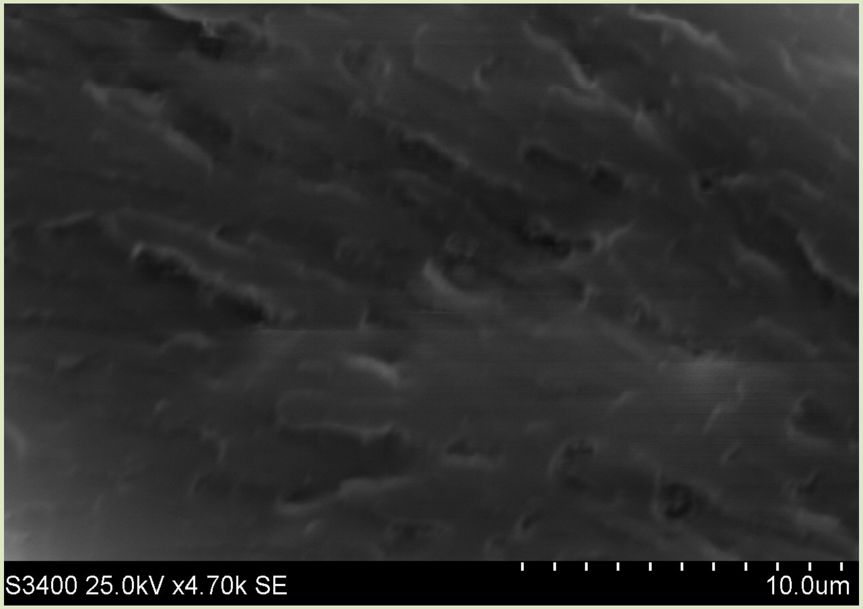
Scanning Electron Microscopy

UV-PUDs



Silane containing (UVSS

Formation of silicate particle domains



Only acrylate containing UVAA.

No particle domains

Conclusion

- **Soy-based UV-PUD building blocks prepared**
  - Polyol, -Acrylated oligomer
- **Novel stable UV-PUDs prepared**
  - high Bio-based content (up to 28%)
  - Acrylate AND Silane functionality
- **UV-Cured films with good performance properties and bio-based content**
- **Acrylate content is primary factor controlling Tg and other mechanical properties.**
- **Silane functionality is shown contribute to hardness and adhesion, while maintaining low Tg**
- **Possible to optimize properties through Acrylate / Silane functions**
- **PU technology based on sustainable material**

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