Block copolymers distribution in coating formulations

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RSC Formulating Functional Films and Coatings IV

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

Coatings are functional materials

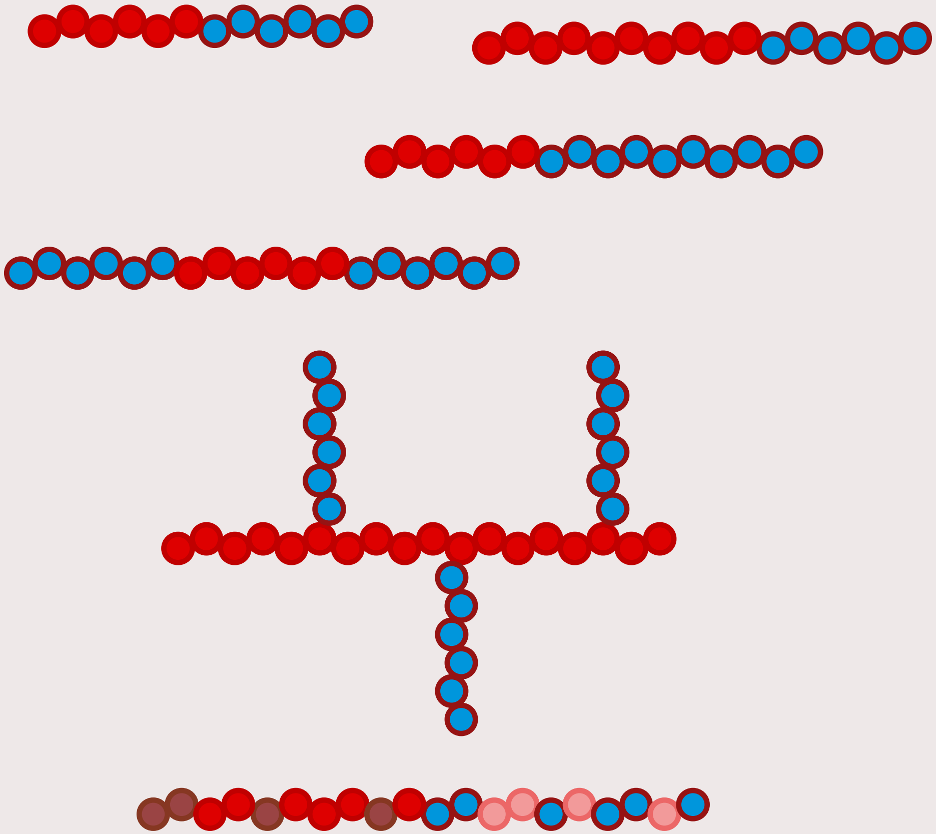
Decoration

Protection

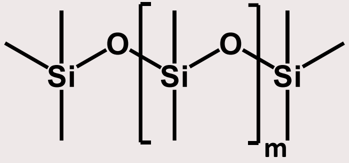
Surface functionality

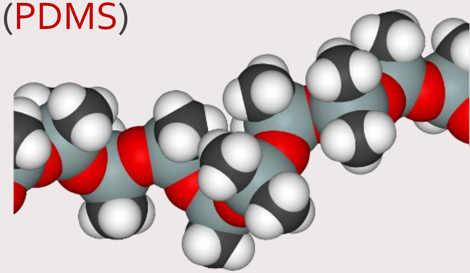

Sagging
Cracking & peeling
Orange peel
Crawling
Cratering
Solvent bubbles & blisters
Poor levelling

Surface tension differences prevent levelling of the applied film → surface additives

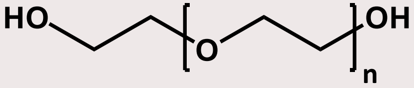


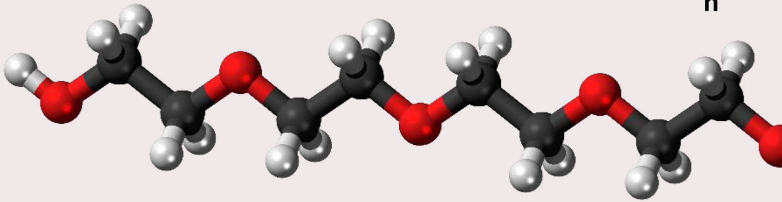
Polydimethylsiloxane (PDMS)





Poly(ethylene oxide) (PEO) or PPO





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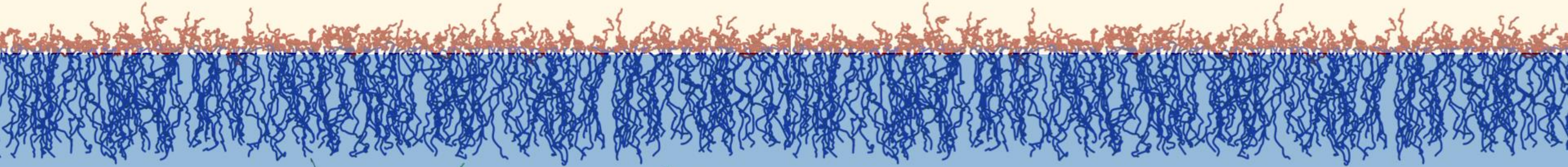
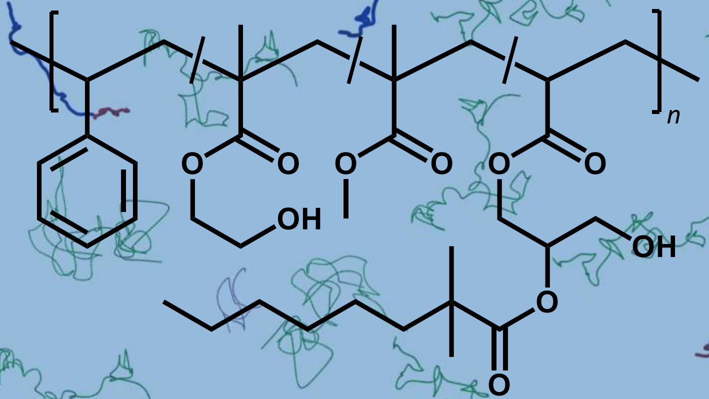
Solvent-borne coating formulation



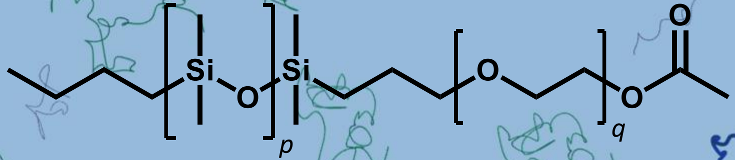
Acrylic resin

Macrynal® SM515/70BAC



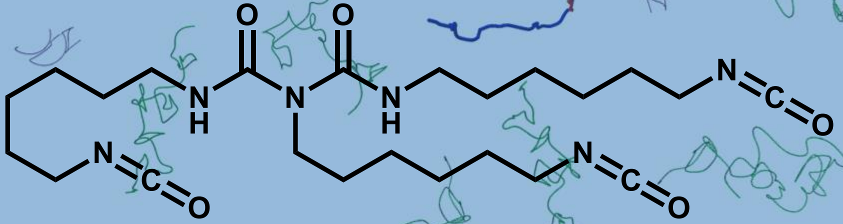
Block copolymer

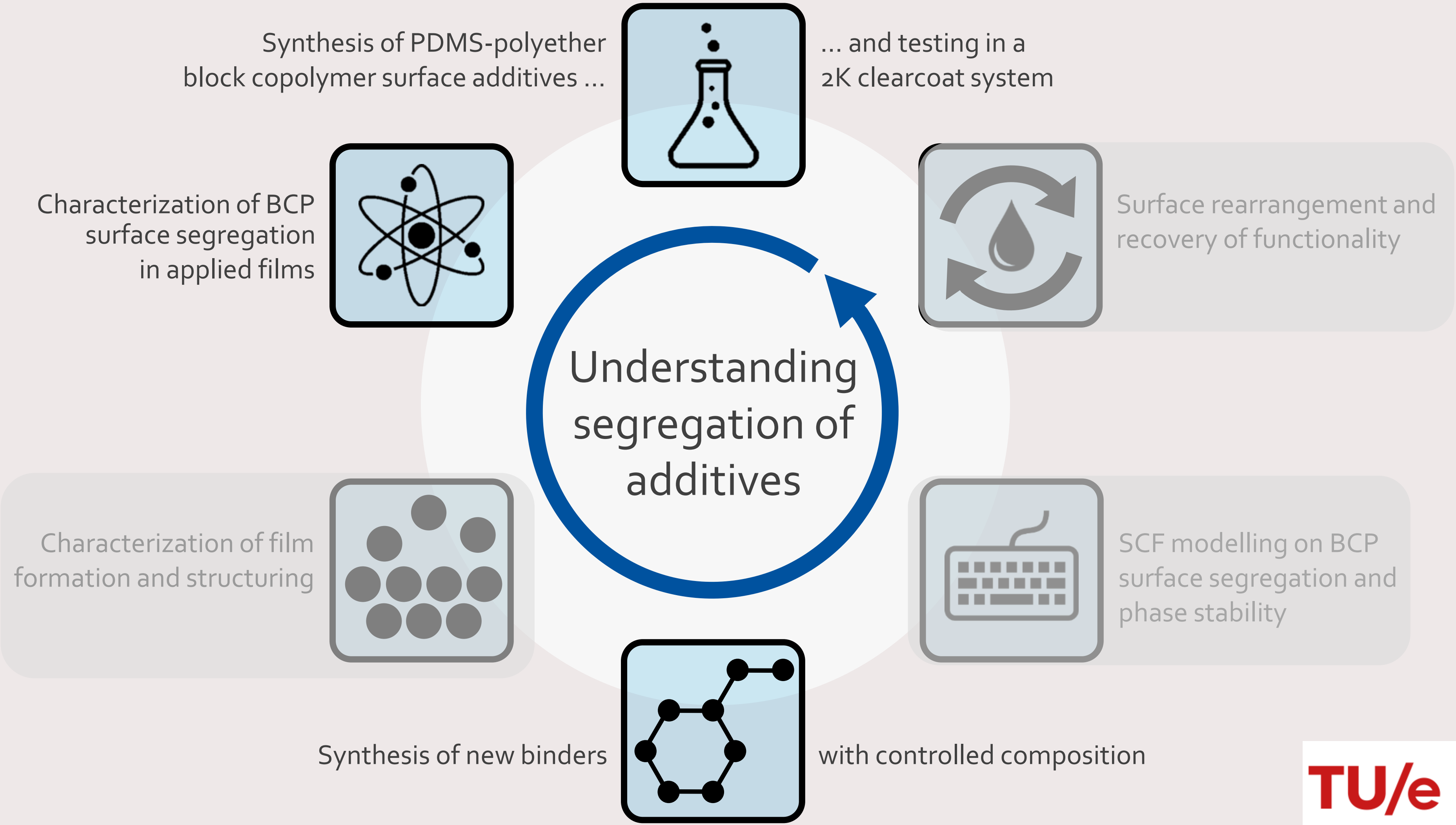
PDMS-PEO



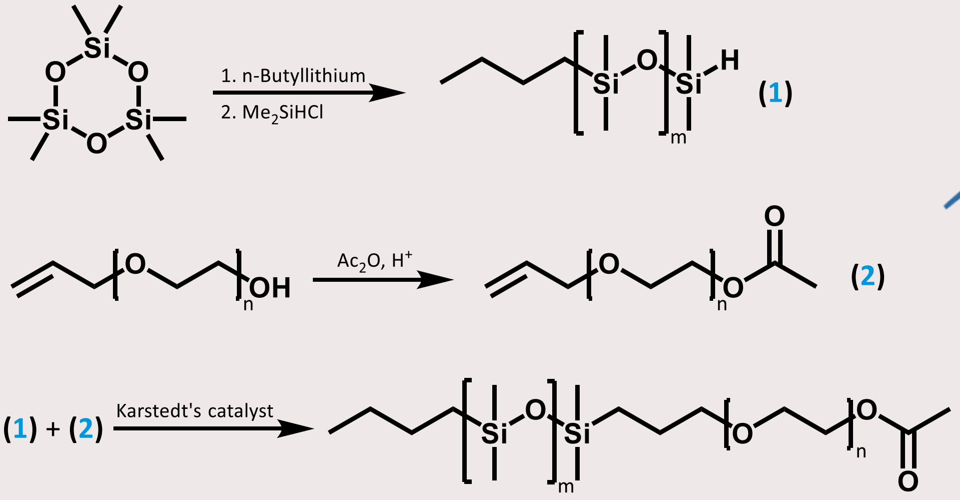
Isocyanate crosslinker

Desmodur® N 75 BA




Understanding segregation of additives
Synthesis of PDMS-polyether block copolymer surface additives …
… and testing in a 2K clearcoat system
Surface rearrangement and recovery of functionality
SCF modelling on BCP surface segregation and phase stability
Synthesis of new binders
with controlled composition
Characterization of film formation and structuring
Characterization of BCP surface segregation in applied films

Additive synthesis and coating formulation



Model clearcoat for automotive applications

Macrynal® SM 515/70BAC **acrylic resin**

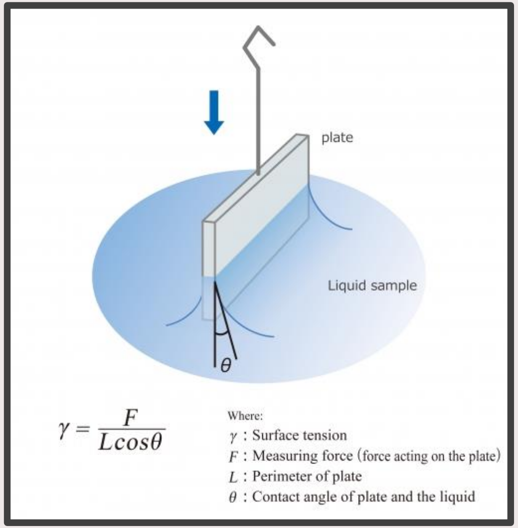
Desmodur® N 75 BA **isocyanate crosslinker**

Butyl acetate + BCP additive

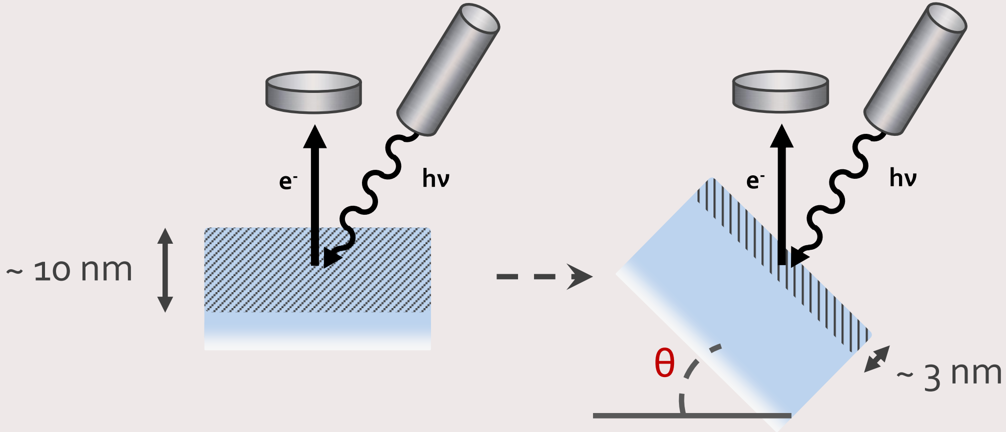
Govers *et al.*, Progress in Organic Coatings, 2021, 150, 105991

Characterization techniques

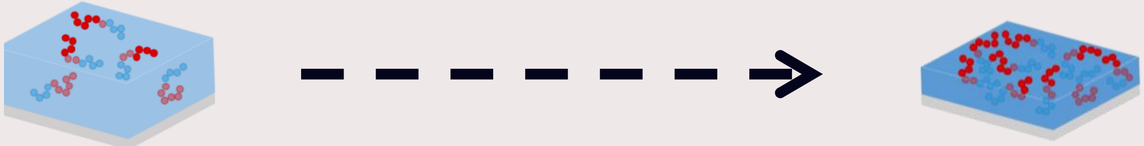
Surface tension measurements



Angle-resolved X-ray Photoelectron Spectroscopy (XPS)

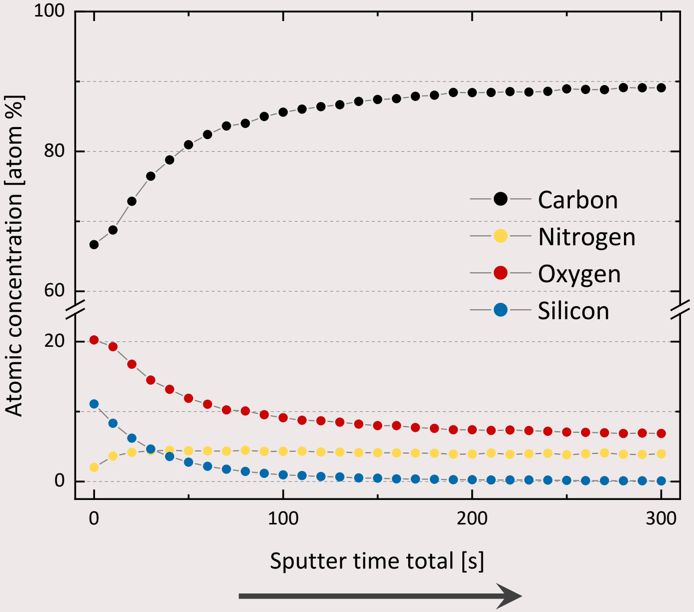


$$I = I_0 \exp\left(-d/\lambda\cos(\theta)\right)$$

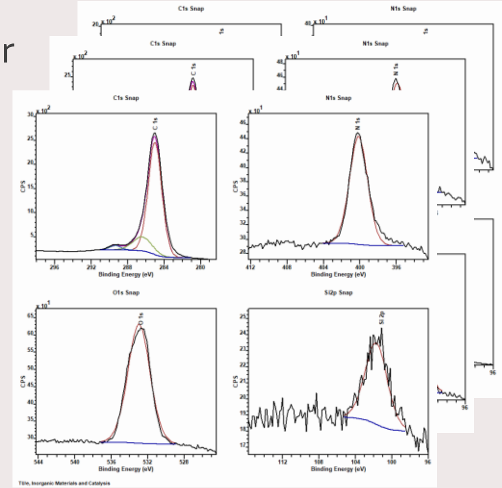


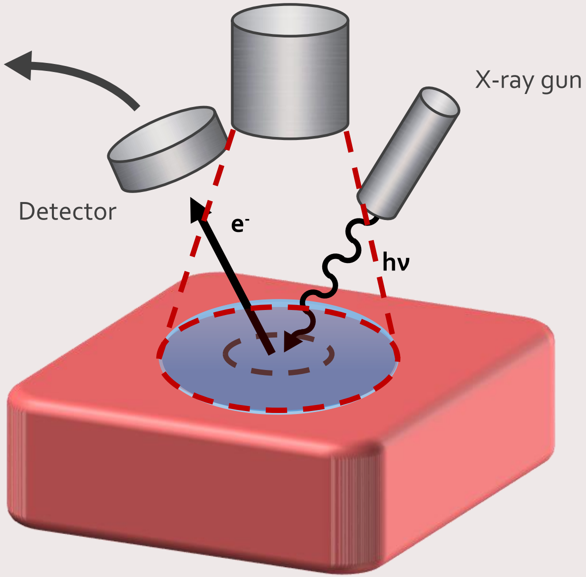
XPS – Concentration profile

Chemical composition layer by layer



Coating depth





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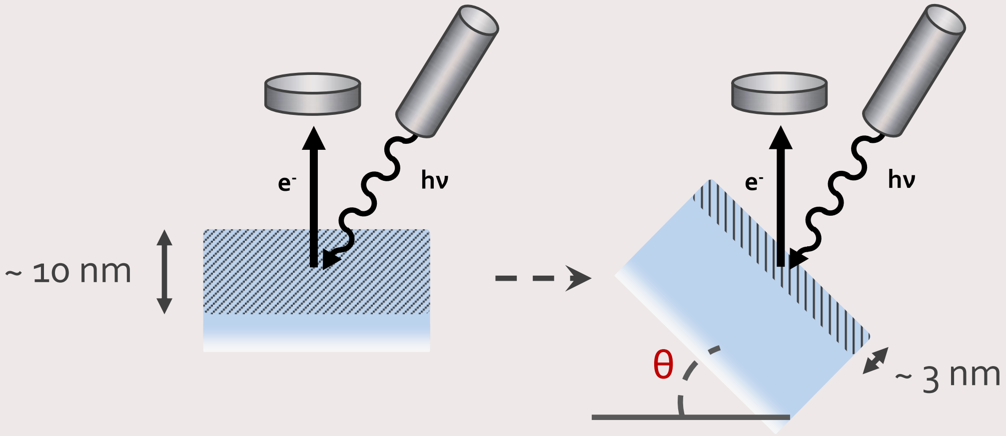
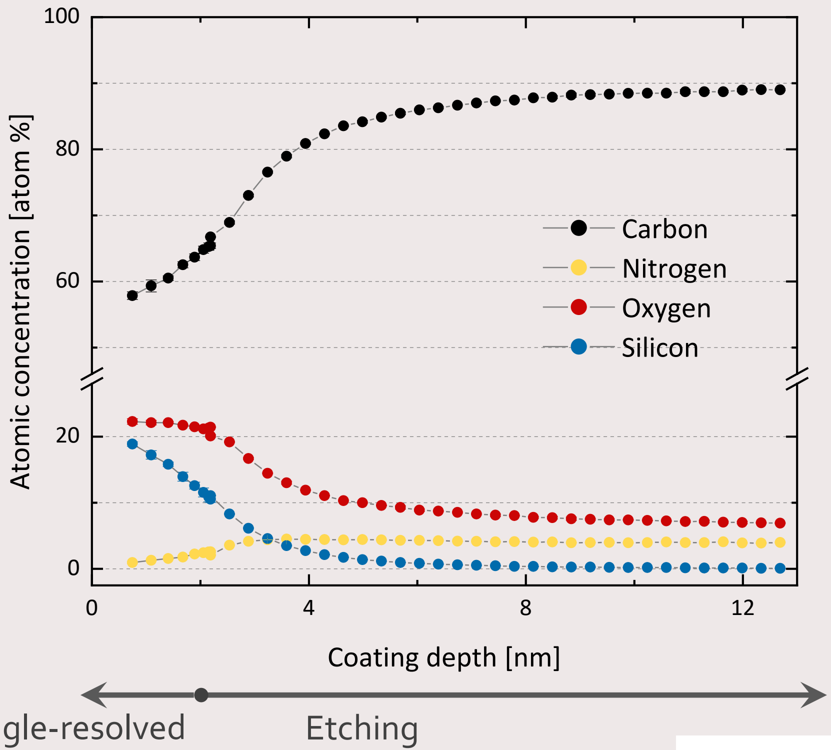
XPS – Concentration profile

Angle-resolved XPS: greater surface sensitivity!

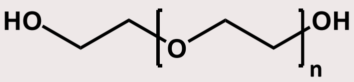


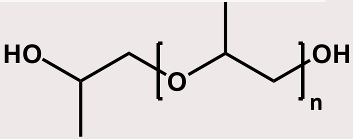
$$I = I_0 \exp\left(-d/\lambda \cos(\theta)\right)$$

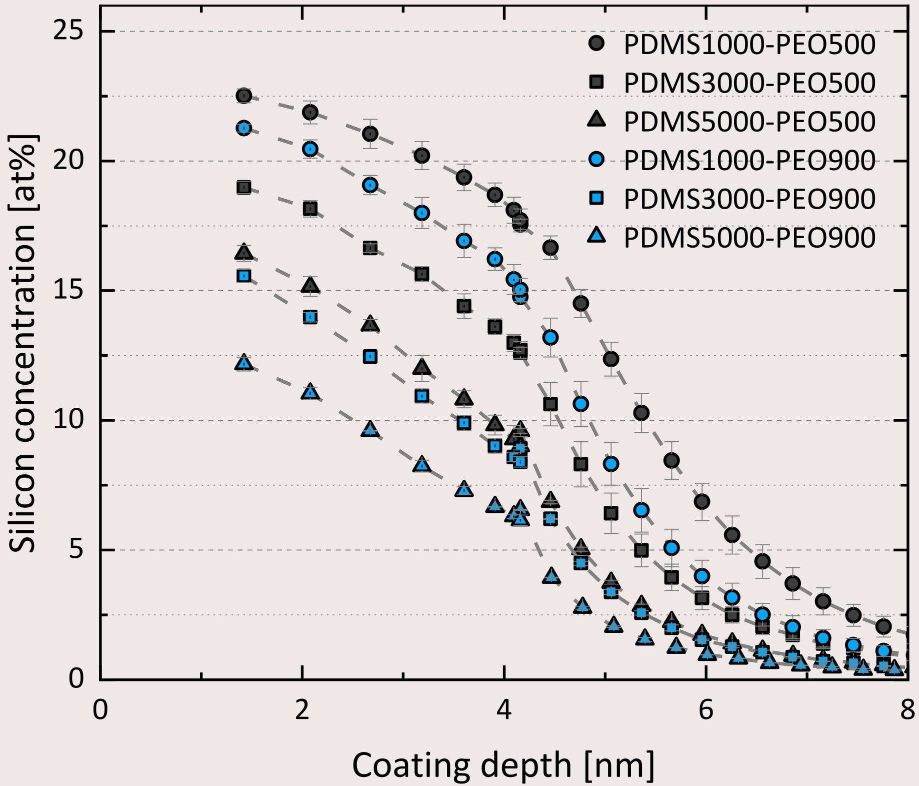


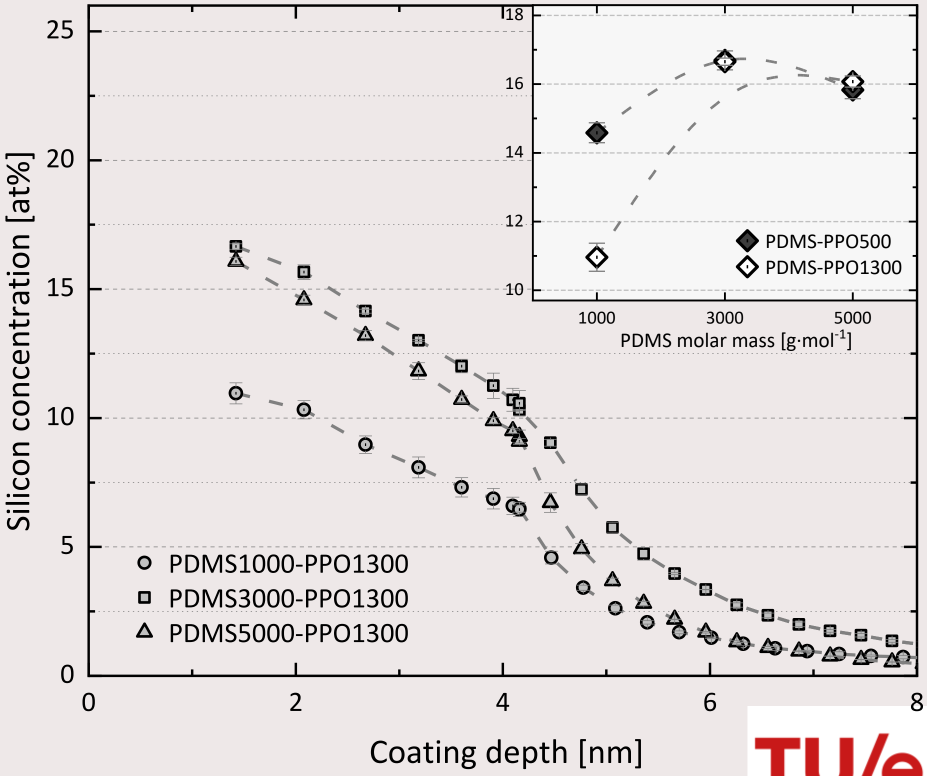
BCP segregation – PDMS-PEO

Nicky Alexander





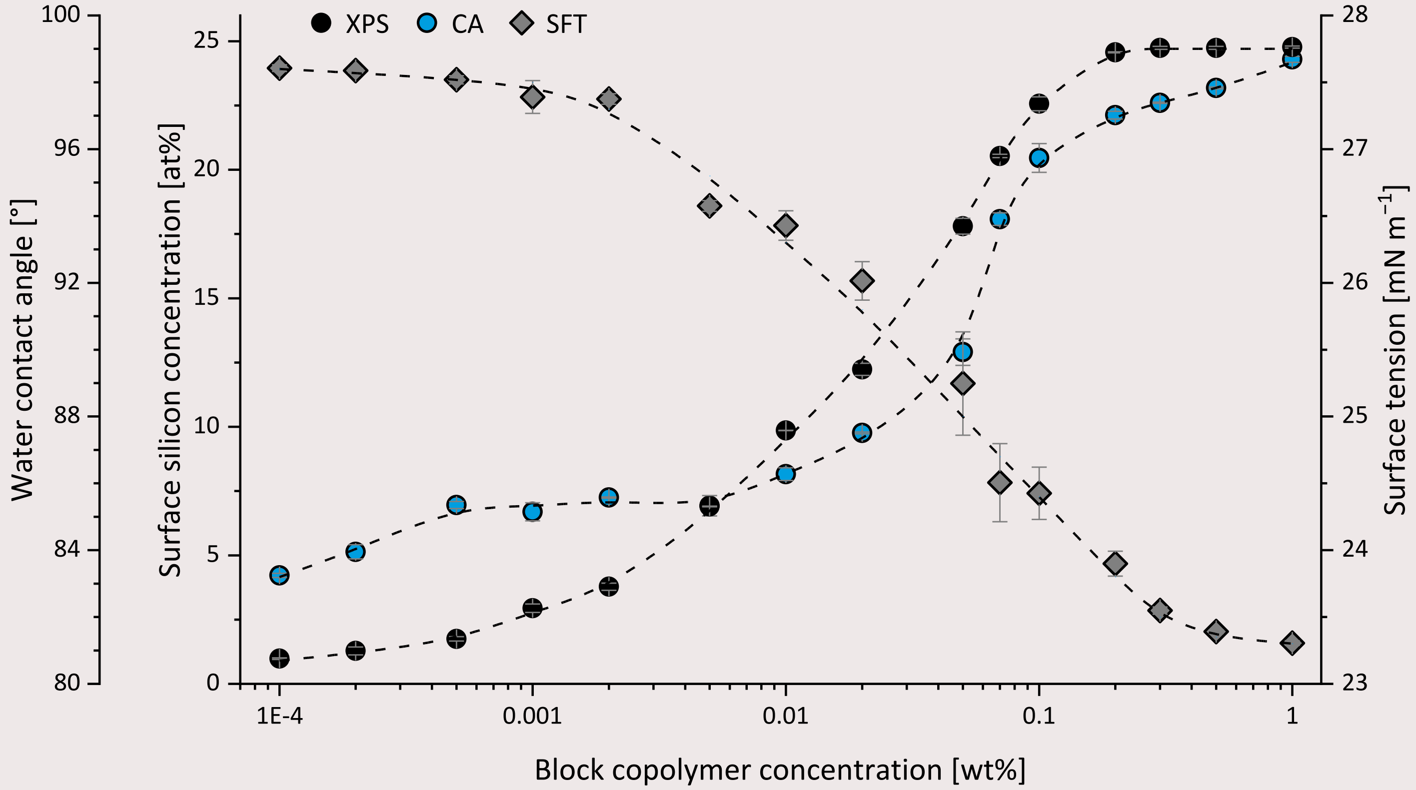




Govers *et al.*, Progress in Organic Coatings, 2021, 150, 105991

BCP segregation – PDMS-PEO

PDMS 1000-PEO 500



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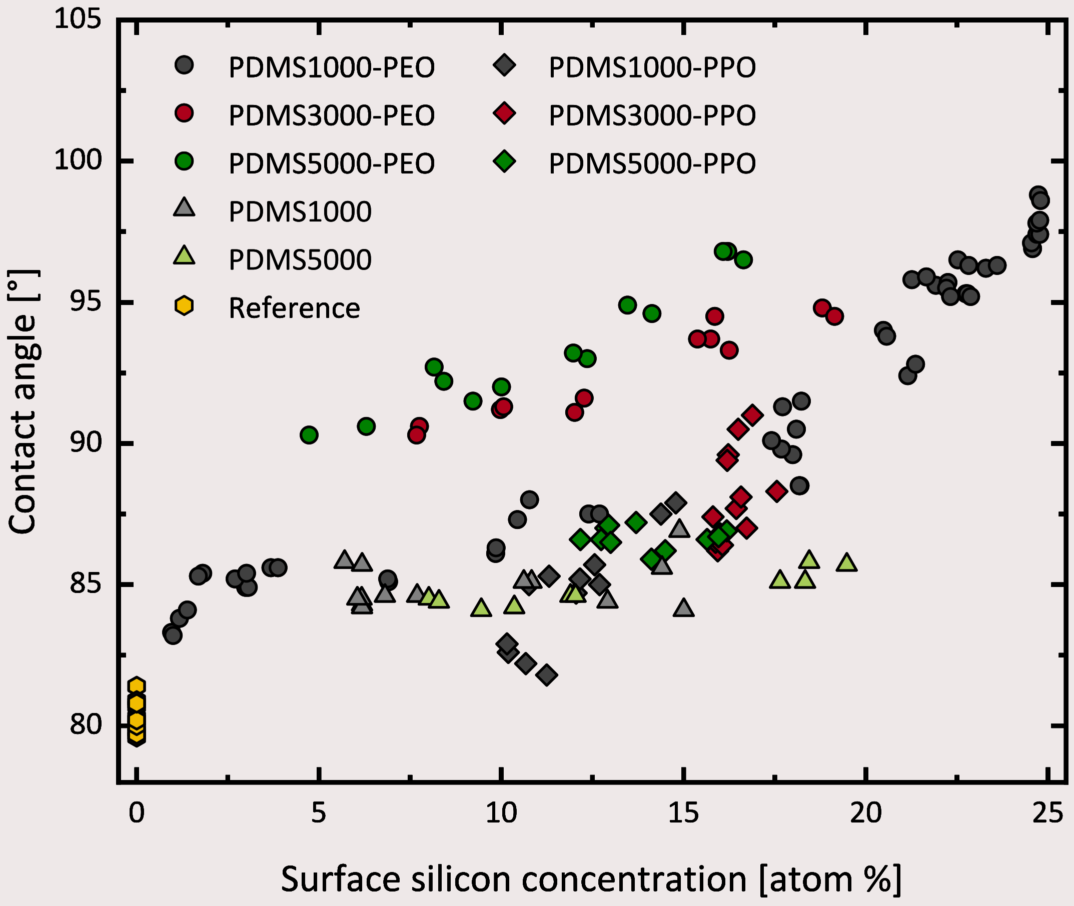
PDMS surface 'effectivity'



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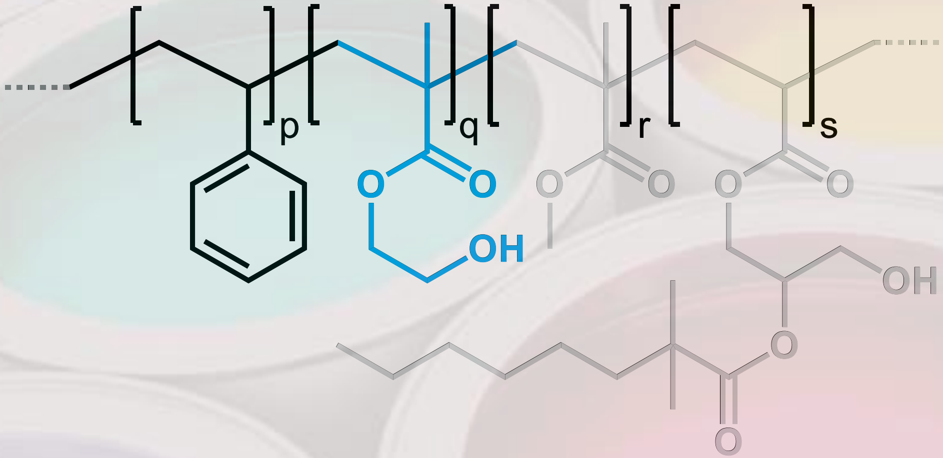
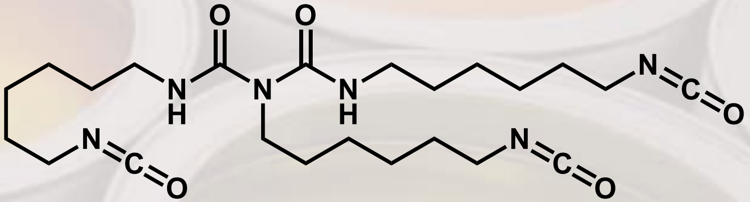
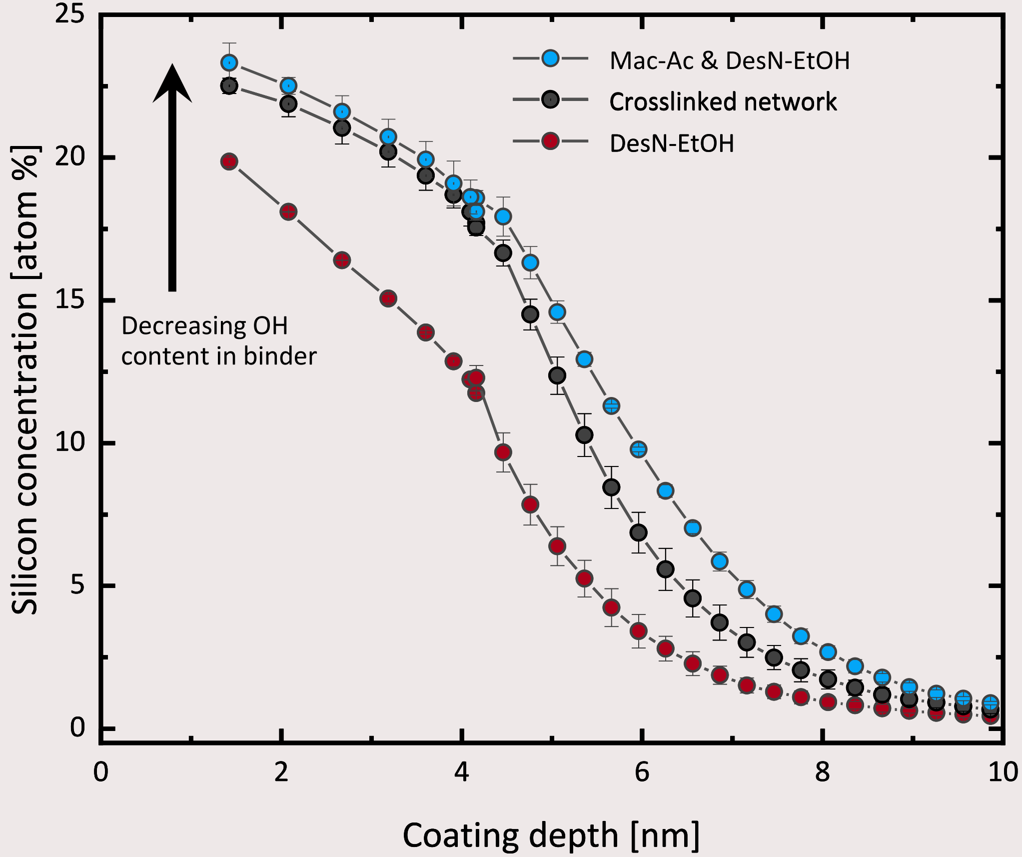
Binder composition – network crosslinking

Macrynal® SM 515-based resin

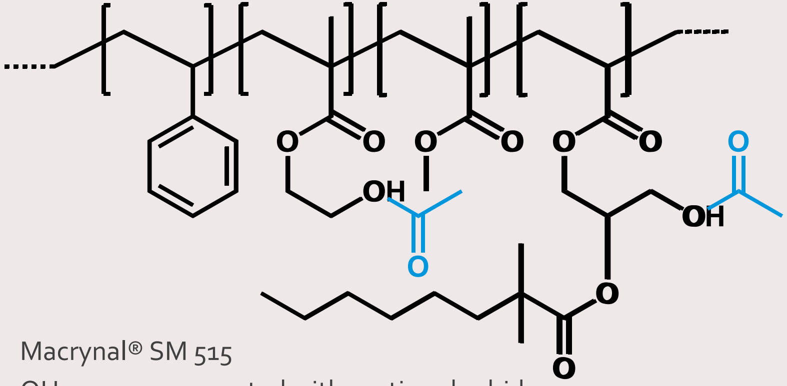




Binder composition – network crosslinking

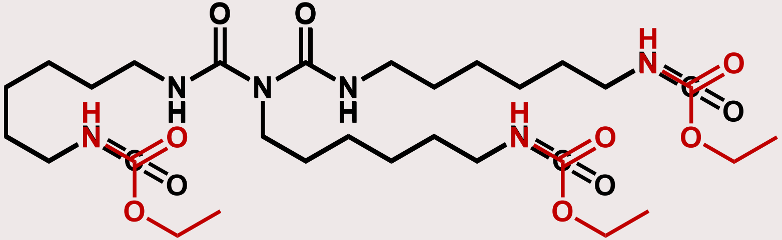


with 0.1 wt% PDMS 1000-PEO 500



Macrynal® SM 515
OH groups pre-reacted with acetic anhydride

"Mac-Ac"



Desmodur® N
NCO groups pre-reacted with ethanol

"DesN-EtOH"

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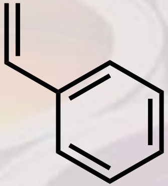
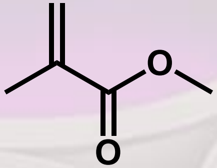
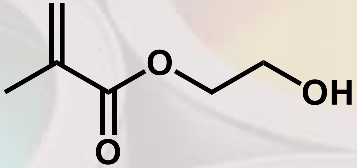
Styrene



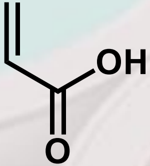
Methyl methacrylate (MMA)



Hydroxyethyl methacrylate (HEMA)

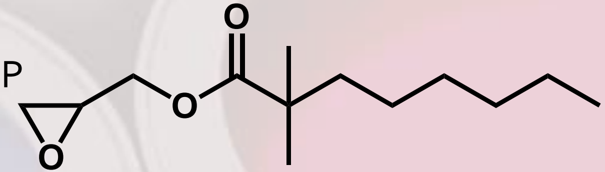


Acrylic acid (AA)

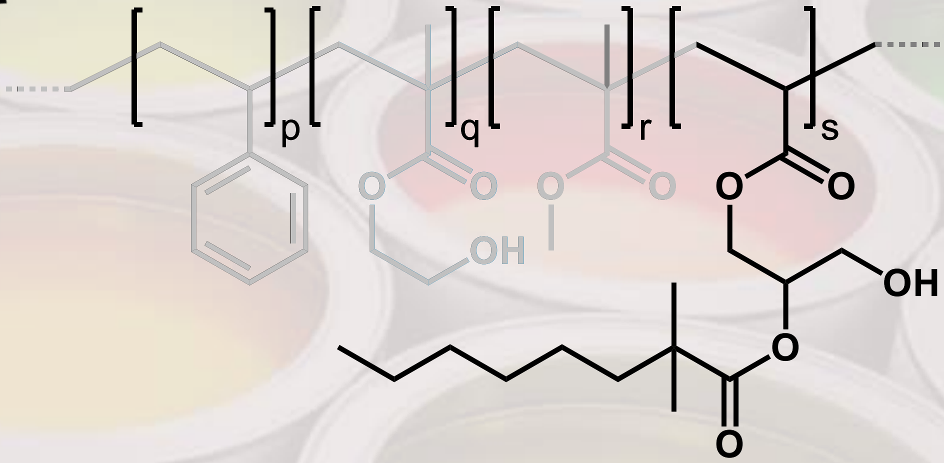


+

Cardura™ E10P



Macrynal® SM 515-based resin



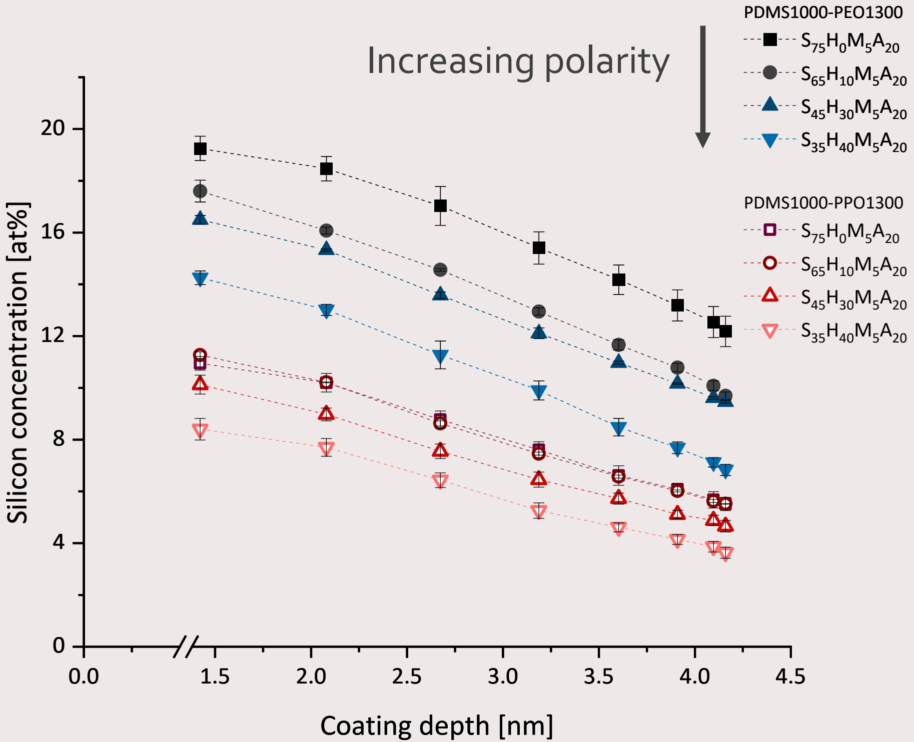
- Increasing polarity
  Styrene : HEMA ratio
- Architecture of the apolar parts
  AA-Cardura content

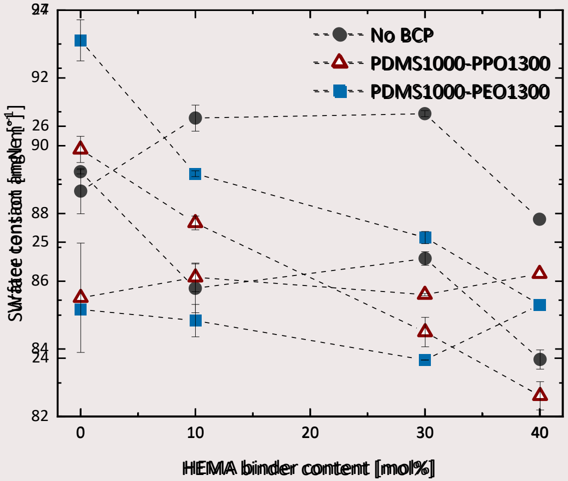
TU/e

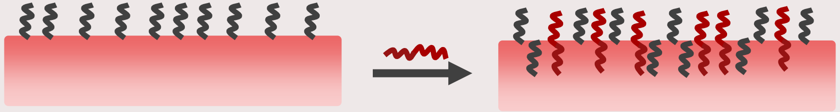
Binder influence on BCP segregation

Merel Nooijens
Patrick Schara

20% AA-Cardura, 5% MMA, varying Styrene: HEMA







Block copolymer may be an effective levelling agent, but an ineffective solid surface modifier!

Conclusions

PDMS-polyether block copolymers show high surface affinity in solvent-borne coatings

Strong influence of molecular characteristics on segregation and resulting surface functionality

Compatibility changes drive the segregation processes

Occurrence of phase separation is detrimental to the final surface enrichment

Binder characteristics play a key role in the compatibility of all components

Specific BCP may be effective levelling agents, but poor surface modifiers

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