


Relever le défi du formaldehyde

New latex binder innovation for technical textiles





Enjeux de substitution dans les Textiles 23/11/2021

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Tackling the formaldehyde challenge - New binder Innovation for Technical Textiles

Transfering an environmental challenge into new technological advantages for the Textile industry

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2. About the Formaldehyde challenge & regulation landscape
3. Conventional self crosslinking technology & Formaldehyde analytics
4. New Formaldehyde free cross-linking technology
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Synthomer – A Growing supplier of Speciality Polymers

- A Top 5 Global Supplier of water based emulsion and speciality polymers with ~£2.1bn of sales
- 38 production sites in 24 geographies, 9 technical centres globally, sales across all geographies to over 6000 customers
- A strong track record of organic growth and M&A
- ca. 4750 employees around the world
- Listed on London Stock Exchange with a market capitalisation of £ ~ 1.1bn

FTSE 250

Let us face the Formaldehyde (FA) Challenge – the general view

Key raw material with significant Health and Safety implications

Some FA key facts

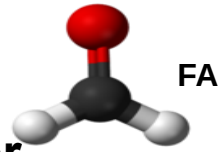
- naturally occurring compound
- colorless gas with pungent odor
- density: 0,815 g/ cm^3
- vapor pressure: 0,43 – 044 MPa
- high water solubility

- estimated production 8,7 Mio t per year [1]
- precursor for industrial resins (urea, melamine, phenol etc.)
- exemplary resin applications: plywood, coatings, textiles (as finishing component)

- classification: Toxic (T), corrosive (C) Carcinogen , Mutagen , Reprotoxic cat 1B, H 350

Health and Safety Implications for the Textile industry

- multiple regulations on end articles and product labels
- workplace: standards on MAC levels, emission levels, air quality control requirements…
- limitation of FA emissions to lowest possible level by process - & technical measures
- regular check on substitution potential



FA

What can be done by the chemical supplier…

- no use of FA in raw material formulations ✓
- ban of FA emitting biocides ✓
- *development and implementation of new options for product crosslinking (-> resin substitution)*

[1] Wiley-VCH, Ullmann´s Encyclopedia of Industrial Chemistry

Let us face the FA Challenge – the regulations view

Reclassification to carcinogen category 1 B as strong driver of regulation change

Reclassification in January 2016

Old
carcinogen category 2 B
H 351

New
carcinogen category 1 B
H 350

Effects on current limits

MAC values *
0,3 ml / m³ (0,3 ppm)
0,6 ml / m³ (0,6 ppm)

TRGS 900*
0,3 ml / m³ (0,3 ppm)

carcinogen category 1
mutagen category 2

regulated by carcinogen EU Directive in EU workplaces

exposure should be as low as technically possible using hierarchy of preventions

MAC values

- France: TWA: 0.5ppm, STEL: 1ppm
- WHO recommendation 0,08 ml/m³

Emmission values

- No new limits set yet – current TA Luft: 20 mg /m³
- LAI recommendation 5 mg / m³ or 12,5 g/h (Feb 2020)

*: Germany, individual regulation per country

Crosslinking – high performance by polymer networks

Key for may high performance Binders – chemical bonding & finishes

Concept of crosslinking

Creation of **chemical bonds** leading to an increase of the molecular weight and the formation of **polymer networks**

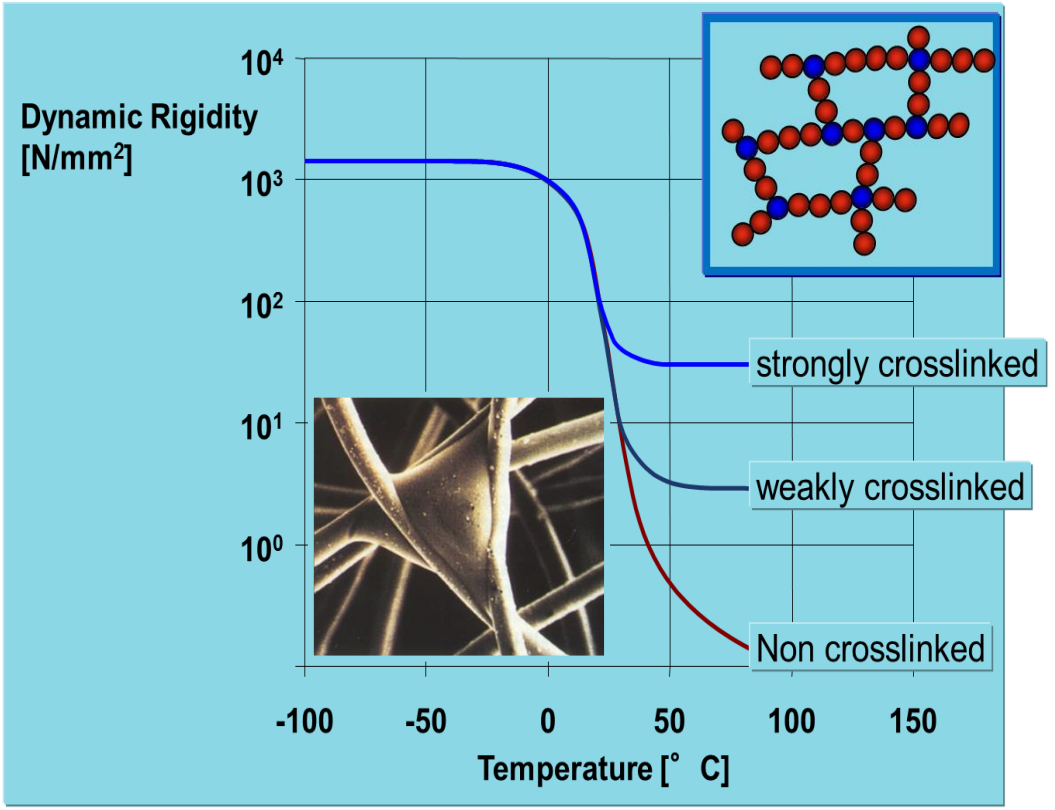
A) Cross-linking during the polymer synthesis
-> monomers with 2 or more double bonds
-> process conditions
B) Cross-linking during the polymer film drying
-> by functional group within the polymer backbone
-> more sophisticated than A
Allows ideal wetting and bonding to the fiber substrate

Cross-linking leads to high performance on:

- elasticity and resilience
- heat resistance
- tensile - / bonding strength
- resistance against solvents, acids, chemicals
- combination of soft handle & none blocking features
- better abrasion resistance
- improved wrinkle behavior

Crosslinking

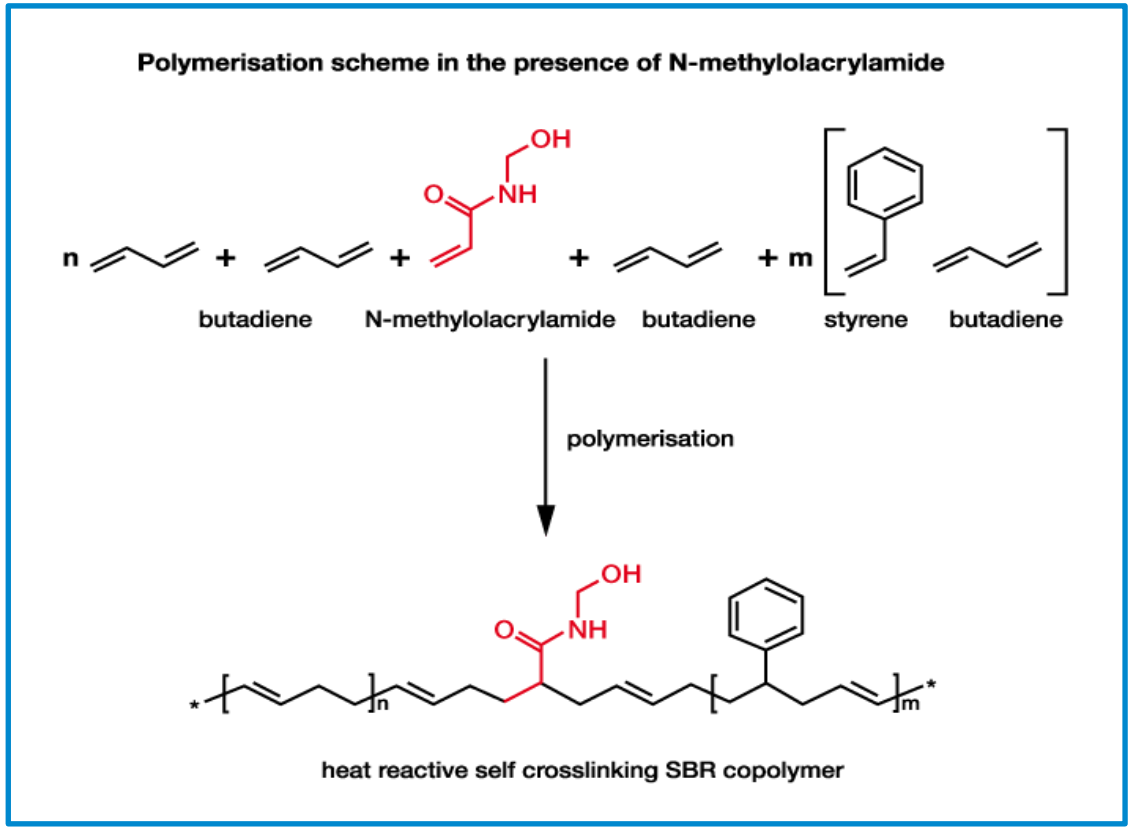
Impact on elasticity and resilience by DMA

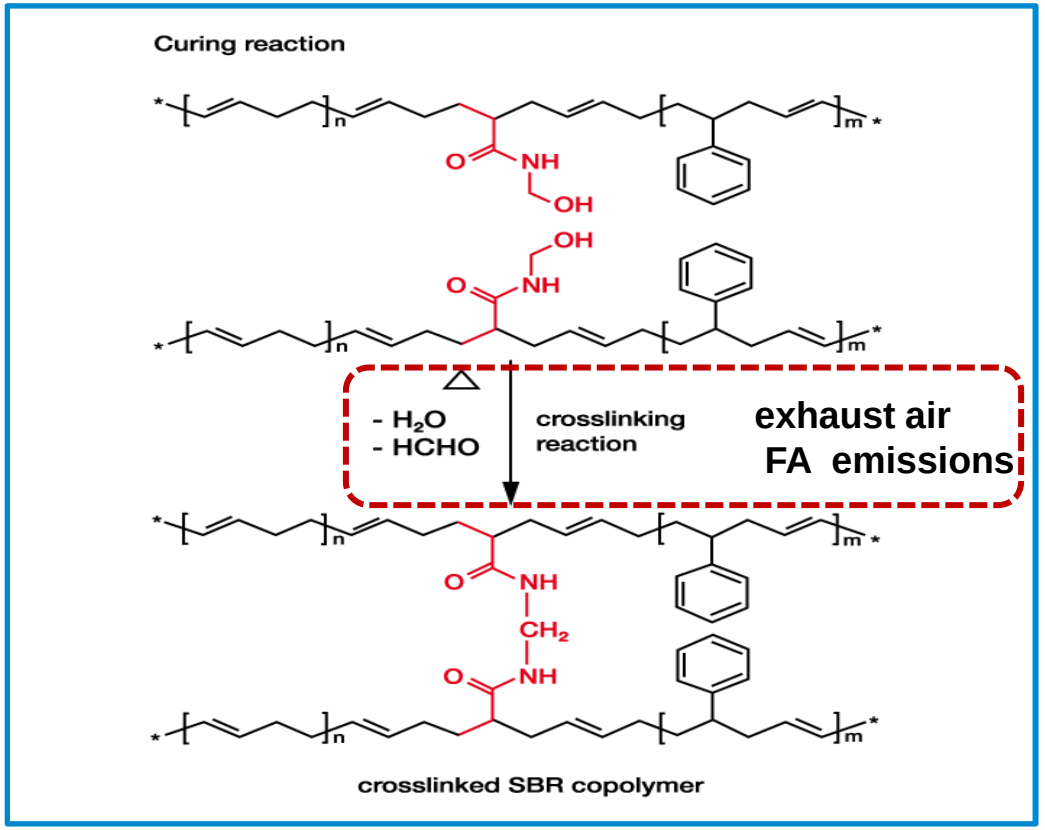


Cross-linking during polymer film formation as preferred approach

State of the art technology… but FA emissions in ppm range

Cross-linking technology with N-methylolacrylamide





- special heat reactive co-monomers are included in the polymer chain during polymerization
- reaction at 130° C in the dry state after film formation

FA Analytics (1) - A method overview for finished Textiles

The method matters – focus on free and hydrolysable FA

Analysis of Textile samples

- analysis of water extract
- photometric identification via colored reaction products
- detection of free and hydrolyzable FA
- significant differences on
- -> sample size
- -> extraction conditions (temp., time, mixing)
- -> hydrolysis level
- hydrolysis level depending on temp. and pH
- single detection of free FA requires high pH and low temperature (1)

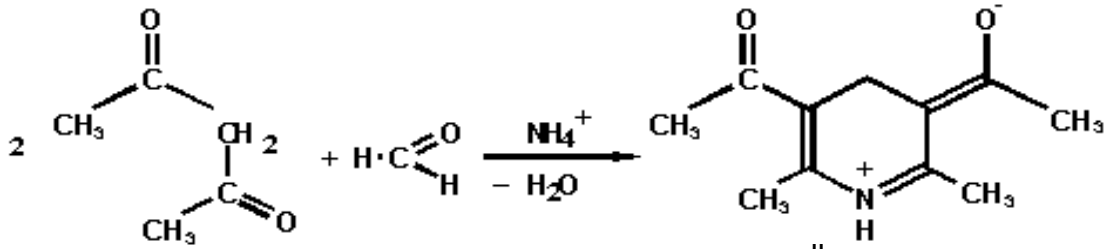
Some textile test standards

USA:	AATCC Test
Japan:	MITI – JIS Law 1041, Law 112
UK:	Shirley I (“free”) , Shirley II (“released”)
D:	DIN ISO 14184-1

(1) Method of de Jong and de Jonge

Photometric FA identification

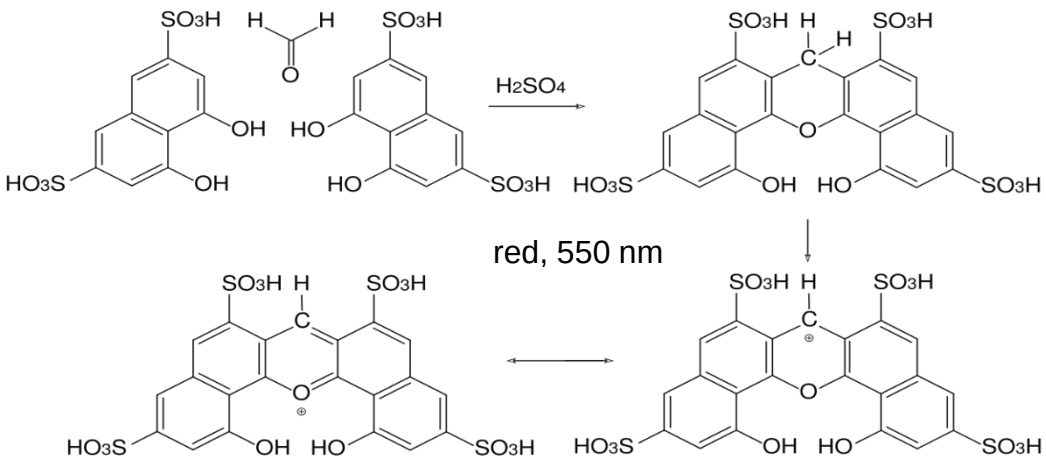
A) Acetylacetone reaction NASH reaction



yellow-green

412nm.

B) Chromotropic acid in H_2SO_4 solution



FA Analytics (2) - A method overview for finished Textiles

A detailed look into the most common tests used for Textiles

Method	MITI Law 1041	Japan Law 112	AATCC 112-82	Shirley I "free"	Shirley II "released"	DIN ISO 14184-1
Extraction conditions	1g 100 ml water 1h, 25 ° C wetting agent	1g 100 ml water 1h, 40° C	1g 50 ml water 20 h, 49° C sample cage	2g 20 ml water 20min, 25° C	2g 20 ml water 20 h, 49° C	1 g (2,5g) 100 ml water 1 h, 40° C
FA detection	Phloroglucin photometric	Acetylaceton photometric	Phloroglucin photometric	Chromotropic acid photometric	Chromotropic acid photometric	Acetylaceton photometric

hydrolysis level will increase with extraction time and temperature

Shirley I < MITI < Law 112
LAW 112 ~ DIN ISO < AATCC
AATCC ~ Shirley II

Other standards

- **Chinese Standard** T -18585-2008 most demanding due to steam distillation -> 2,5 g sample (textile *or Latex*), steam distillation to 250 ml volume, Acetylaceton
- **Total FA content** VDL RL03 (paint industry) steam distillation at low pH -> 10 g sample (sample *or Latex*) , 50 ml water, 20 ml 20%ige H_2SO_4, Acetylaceton

FA Analytics (3) - FA release at processing

TEGEWA method as reference point for FA emissions / FA exhaust emissions by VDI 3862

TEGEWA Method

FA emissions during binder application (drying/curing)

- 1g liquid sample evenly dispersed over 3 g of sand
- heating for 5 min at 160 ° C
- emissions are carried over to 2 water filters with 50 and 25 ml water using a nitrogen flow of 200ml/min
- IR heating to prevent condensation in the tube connections
- FA analytics via Acetylaceton method in the collected water made up to 250 ml volume

VDI 3862 (part 6)

Determination of FA in exhaust gases

- 2 water filters (collectors) with 30 ml each
- exhaust gas flow rate 1 L / min (pump system) for 30 min
- typically 30 min measurement time
- heated sampling probe and dust filter (prevent condensation)
- FA analytic via Acetylaceton method
- recording of sample volume, time, temperature,
- cross sensitivities at higher levels of NH_3 and with $S0_2$

TEGEWA test set up

Case Study: XSBR polymer binder for PES roofing Felts

Manufacturing process / Product requirements / Development target

Application

- PES Felts for bituminous roofing systems

Manufacturing process

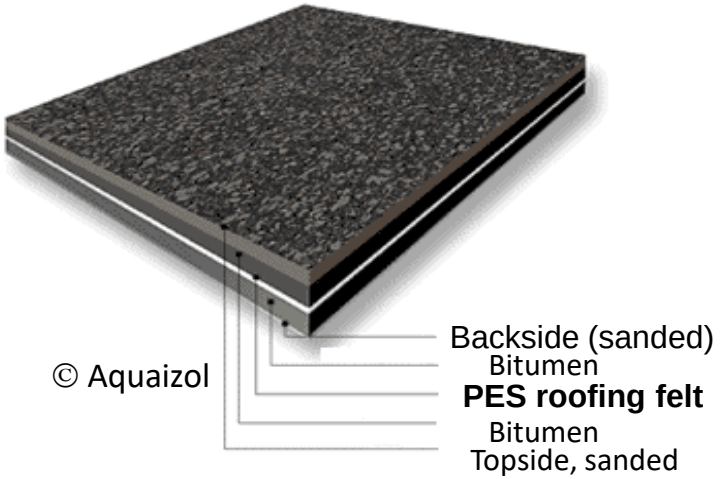
- staple fiber or spun bond non woven
- foulard impregnation, foam or liquor
- addition of up to 20 % thermoset resin (FA) => 2 K System

Product requirements

- water resistance - > max reduction of tensile strength of 5%
- high tensile strength -> min. 700 N all 3 key dimensions
- high stiff handle but no kink or crack at flex test
- broad compatibility with thermo-set resins
- high aging stability and filler compatibility
- thermo- dimension stability at 200° C

Current state of the art product offering

- self cross-linking XSBR Latex (FA emissions in ppm range)
- Tg: 35° C, PS: 130 nm, TS: 50%, Viscosity: < 500 mPAs
- Curing > 130° C



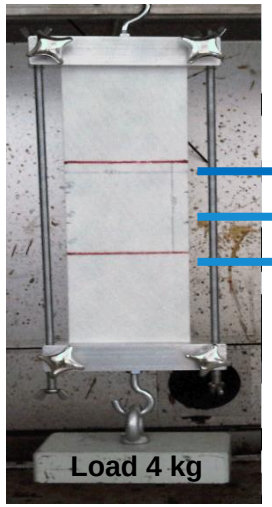
Development target

- self crosslinking Latex without FA emission
- withdraw of thermoset resin (FA emissions!) => 1 K System with no pot life limitations
- low temperate curing

Case study: PES roofing felts

TDS & TS as most demanding product features

Thermo Dimension Stability (TDS)



Elongation
Shrinkage
Elongation

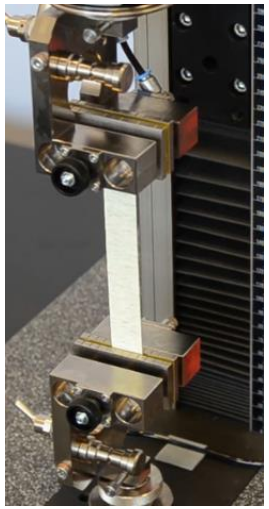
- 10min at 200° C, 5min conditioning at RT

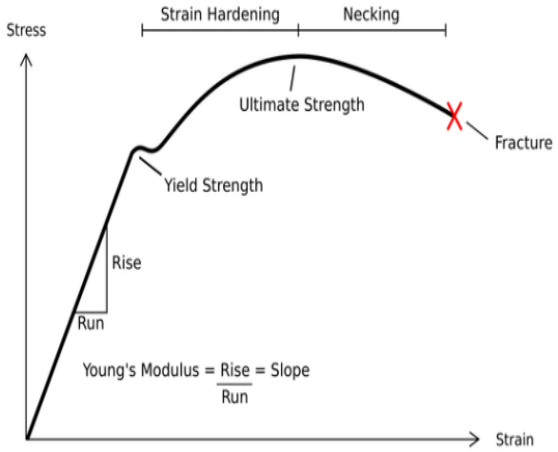
Targets (DIN 18192)

- dimensional elongation MD max. 1,5%
- dimensional shrink CD max. 1,5%
- test series with 4kg load (8 kg load)

=> additional non DIN tests performed

Tensile strength



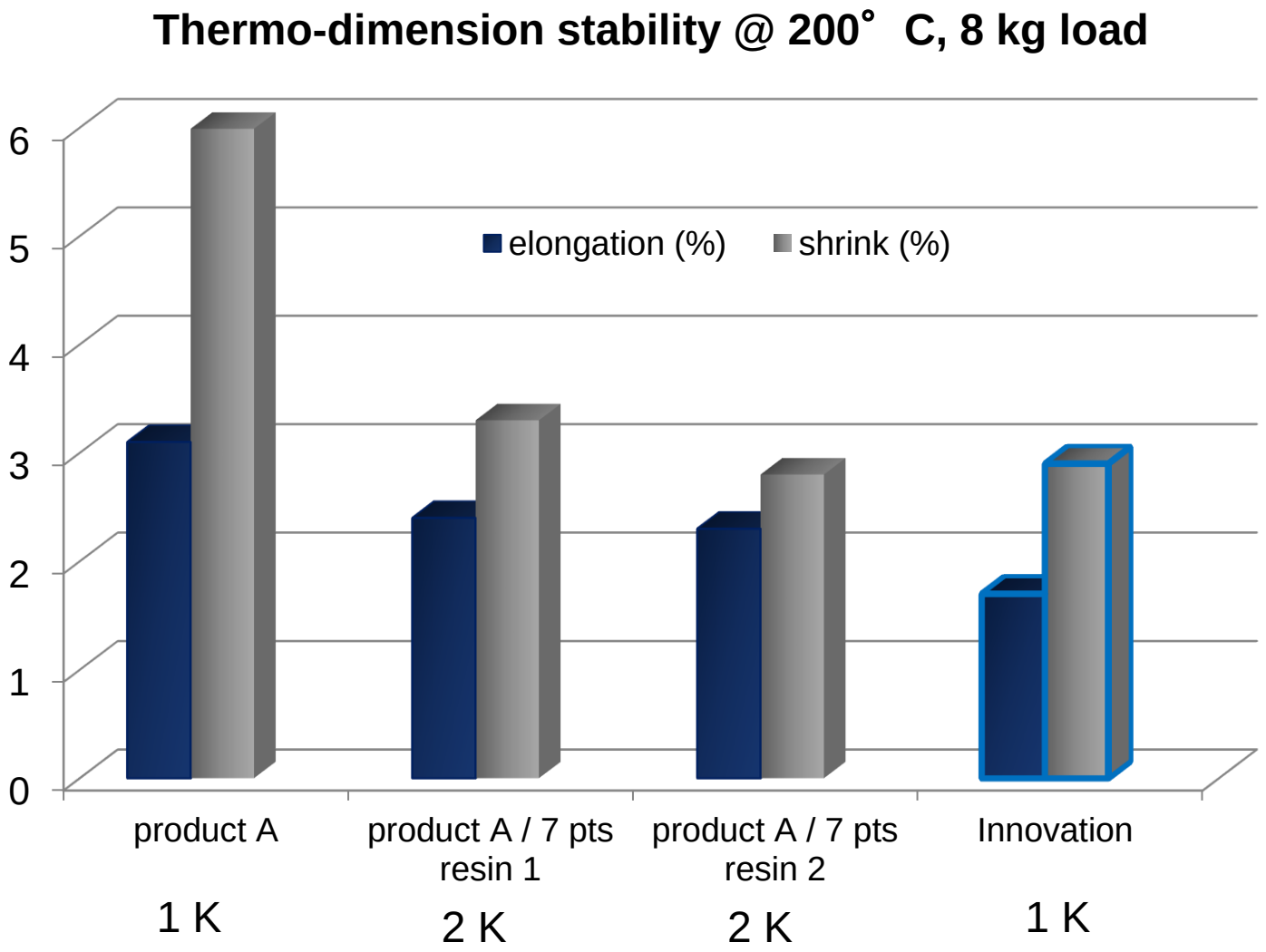


- ultimate tensile strength
- tensile strength at 5%, 10%, 15% elongation
- hot tensile strength (180° C)
- wet tensile strength

=> Additional tests performed

Case study: PES roofing felts – FA free crosslinking technology

Strong performance on Thermo Dimension Stability (TDS) even as 1 K-System



- PES non woven, 160 g/sqm,
- 20% coating weight d/d
- product A: market reference, **FA releasing**
- resins: MF resins, **FA releasing**
- Innovation: NEW **FA free** cross-linking XSBR

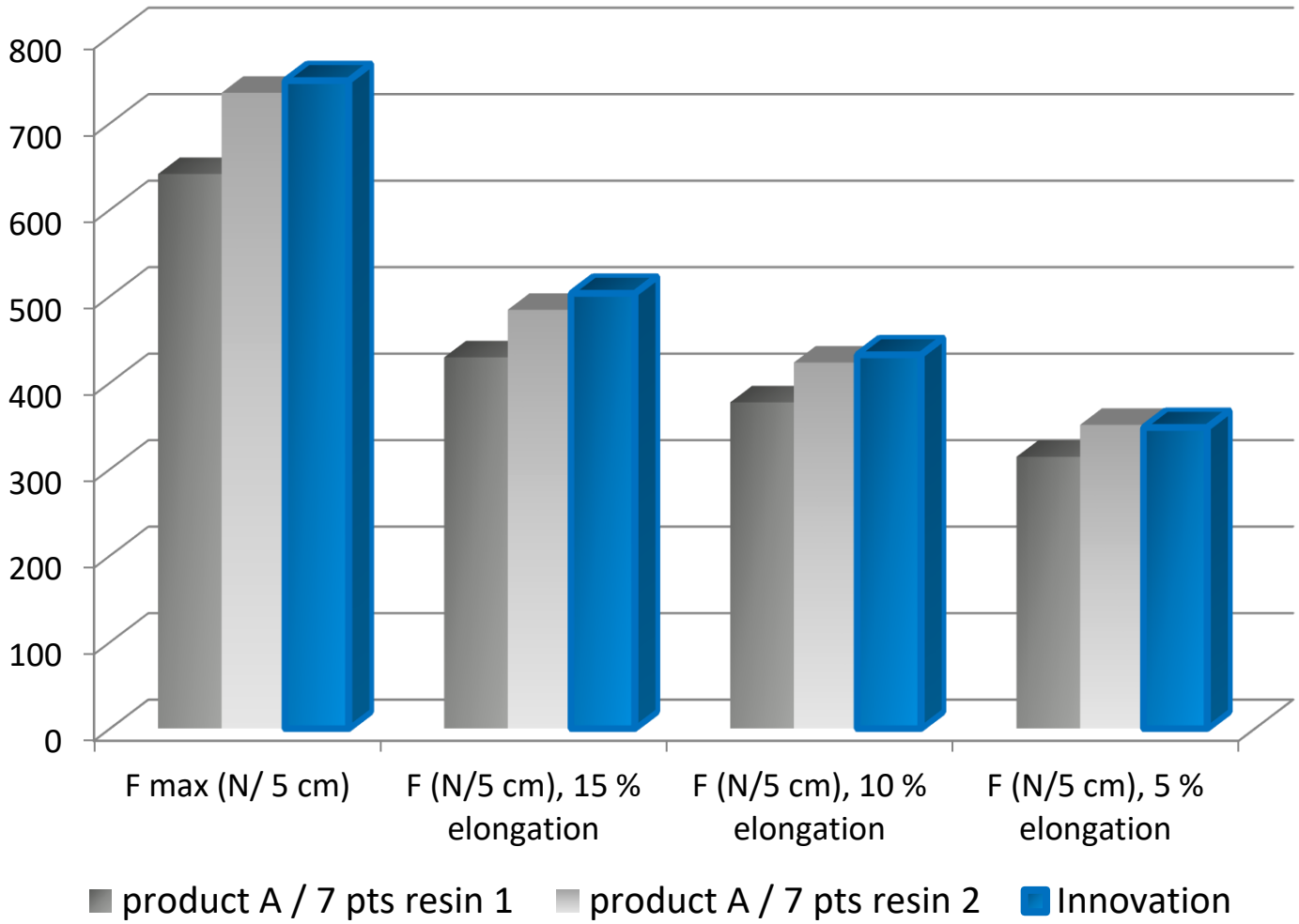
Results

- Innovation product outperforms TDS of market reference
- Innovation product with excellent TDS
- Innovation feasible as 1 K System
- Only Innovation product FA free solution

Case study: PES roofing felts – FA free crosslinking technology

Strong performance on Tensile Strength even as 1K-System

Tensile strength, RT, MD, DIN 18192



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Results

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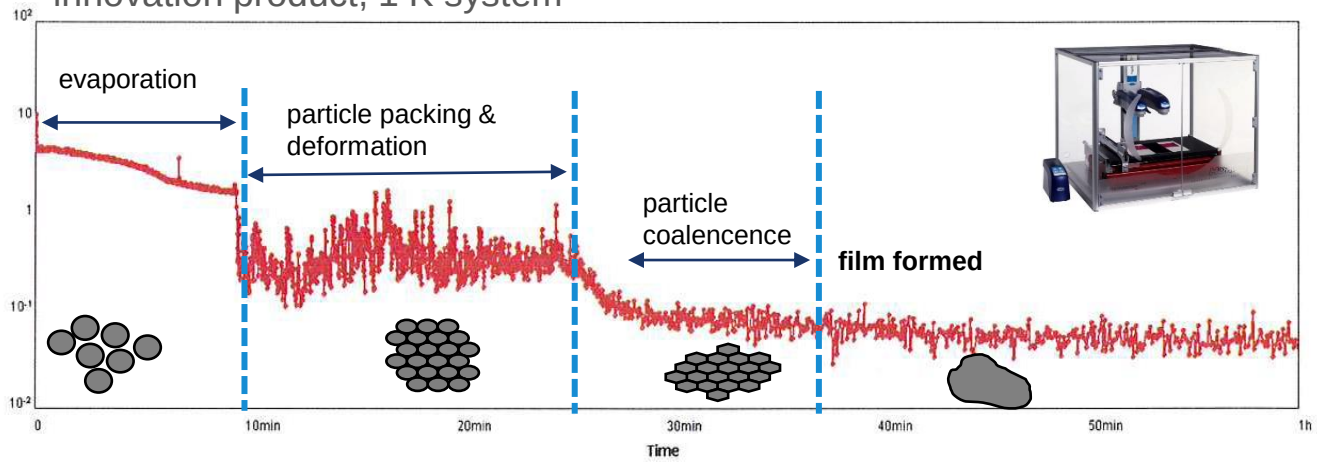
- Innovation feasible as 1 K System
- Only Innovation product FA free solution

Case study: PES roofing felts – Analysis of film formation

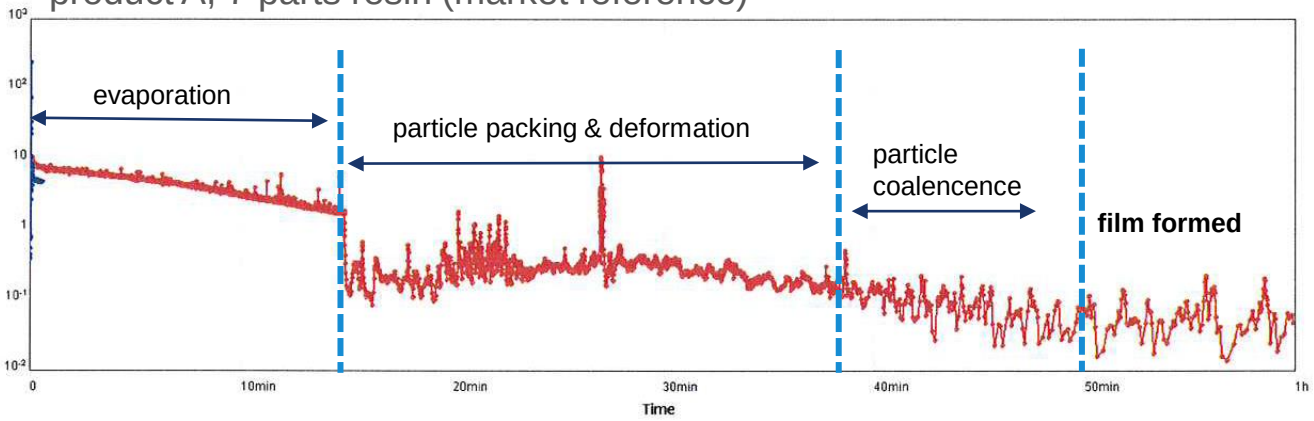
FA Free 1 K System with excellent film formation – outperforming market reference

Film formation Analysis with Rheolaser technology

innovation product, 1 K system



product A, 7 parts resin (market reference)



- Monitoring of microstructure changes during film formation by scattered laser beam
- TSC: 50% / air humidity: 50% / temp: 22° C
  film thickness: 100 µ / time: 1 h
- product A: market reference, **FA releasing**
- resins: MF resins, **FA releasing**
- Innovation: NEW **FA free** cross-linking XSBR

Results

- Innovation product outperforms drying speed of 2 K market reference
- Analysis proposes energy saving potential for Innovation product
- Processes with drying & curing as speed limitation -> analysis proposes output increase potential for innovation product

Summary & Outlook – Synthomer´s green Technology

Ultra low FA measurements results – Below detection limits of Law 112 and VDI 3862

FA Analytics

Market reference - self crosslinking

- Latex sample, Free FA (similar to Shirley I) : 100 – 200 ppm
- Latex sample, TEGEWA: several hundred ppm

Innovation products – FA free self crosslinking

- Latex samples
  free FA similar to Shirley I: < 10 ppm, at detection limit
  total FA according to VDL R03: < 10 ppm, at detection limit
- FA exhaust emissions
  VDI 3862 (part 6) < 0,16 ppm - below detection limit
- Textile samples
  according to Japanese Law 112 – below detection limit (5 ppm)

- high performance features based on FA free crosslinking
- no extra requirements on process conditions regarding coating / impregnation

Summary & Outlook – Synthomer´s green technology

How the FA challenge can turned into advantages for the industry …

New Opportunities by FA free crosslinking

Case Study: PES roofing felts

- 1 K product solution looks now feasible
  -> reduction of complexity
  -> no handling of extra thermo-set resins
  -> no process limitation by pot life

- Faster film formation (drying)
  -> energy saving possible
  -> higher line output possible

Several other projects for FA free cross-linking

- PA -> sun blinds, block out curtains
- SA -> Deco Laminates, wall covers
- XSBR -> alkali resistant glass mesh (EIFS)
- …

Our commitment to environmentally preferred solutions translates into :
FA free cross- linking, APEO free, low VOC, high material efficiency




Tackling the formaldehyde challenge

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Thank you for your attention !

Questions ?





Daniele ZIMMERMANN, Synthomer GmbH