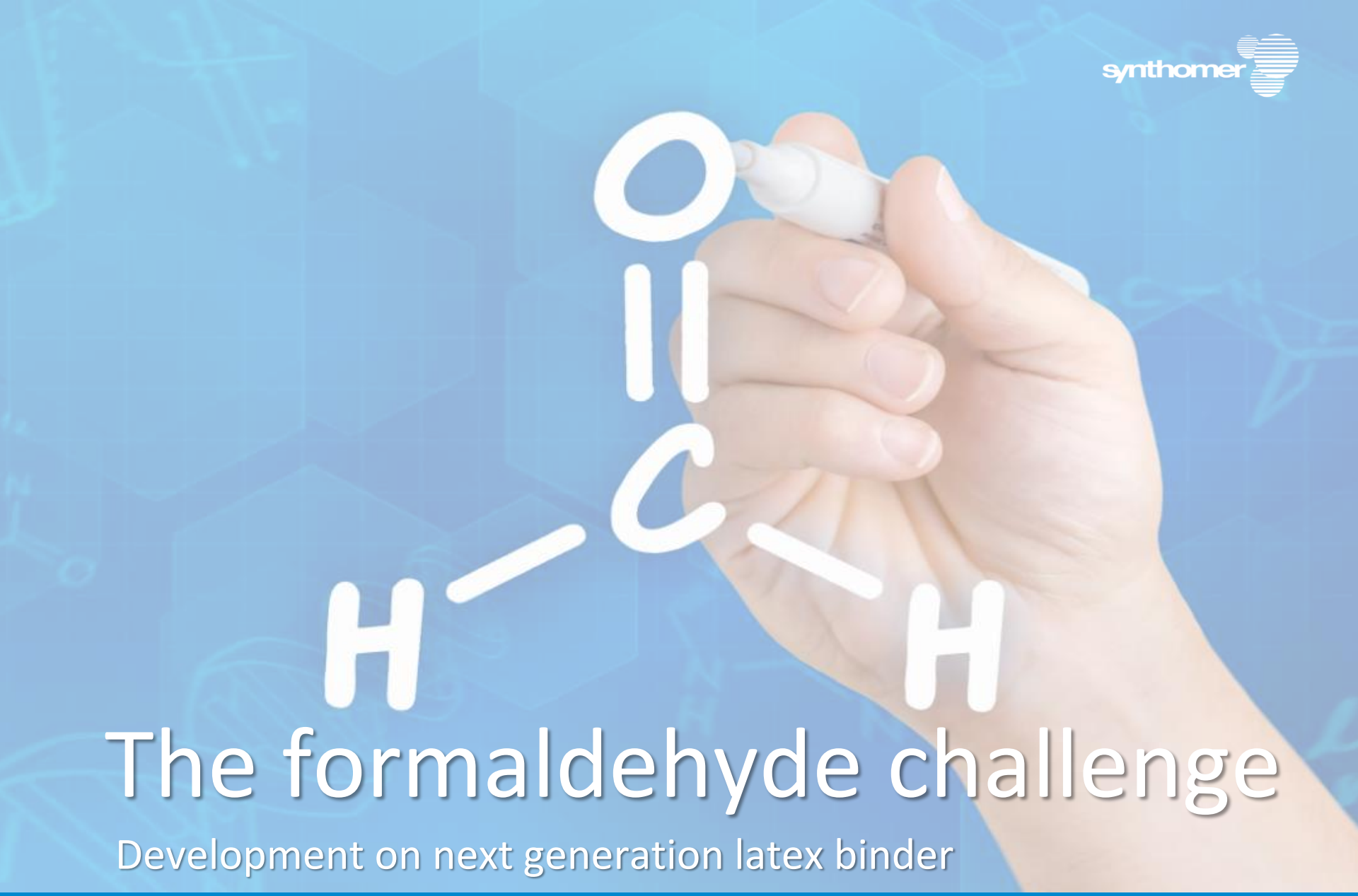

The formaldehyde challenge

Development on next generation latex binder

Matthias Renka

November 07-08, 2018

33. Hofer Vliesstofftage

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The formaldehyde challenge - Development on next generation latex binder



1. Synthomer at glance
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SYNTHOMER AT GLANCE

Leading in Speciality Polymers

Top 5

Global supplier of emulsion and speciality polymers

FTSE250

Listed company

€ 1.67 bn

Group revenue

25

Production sites

2800

Employees

>100

Countries

SYNTHOMER AT GLANCE

Our Locations

Synthomer Headquarters

London (UK)
(Synthomer Headquarters)

Europe

Marl (Germany) (Regional Centre),
Accrington (UK), Asua (Spain), Evergem (Belgium), Filago (Italy), Hasselt (Belgium), Harlow (UK), Langelsheim (Germany), Pischelsdorf (Austria), Oss (Netherlands), Oulu (Finland), Ribecourt (France), Sant' Albano (Italy), Sokolov (Czech Republic), Stallingborough (UK), Worms (Germany)

Middle East

Dubai (UAE) (Regional Centre),
Dammam (Saudi Arabia), 10th of Ramadan City (Egypt)

Americas

Atlanta (GA) (Regional Centre),
Roebuck (SC)

Asia

Kuala Lumpur (Malaysia)
(Regional Centre),
Chonburi (Thailand), Ho Chi Minh City (Vietnam), Kluang (Malaysia), Pasir Gudang (Malaysia), Shanghai (China)

REVIEW 2017

Regulations / Crosslinking

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 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

What can be done by the Latex supplier…

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

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)

MAC values	• No new limits set yet • 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)

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

*: Germany, individual regulation per country

Cross-linking – high performance by polymer networks

Key for may high performance Latices – chemical bonding & finishes

Concept of cross-linking

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

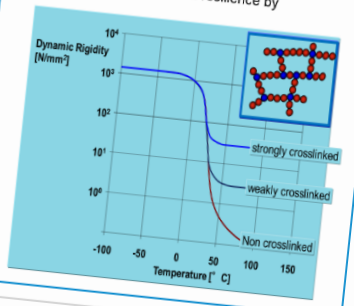
A) Cross-linking during the polymer synthesis
-> monomers with 2 or more double bonds
-> process conditions
B) Cross-linking during the polymer film drying
-> by functional group within the polymer backbone
-> more sophisticated than A
Allows ideal wetting and bonding to the fiber substrate

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

Cross-linking

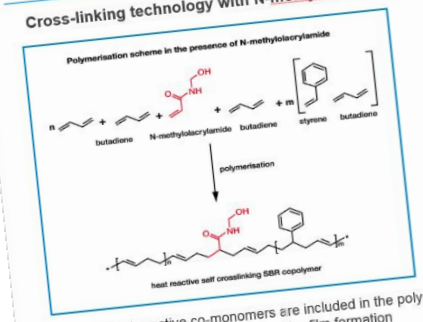
Impact on elasticity and resilience by

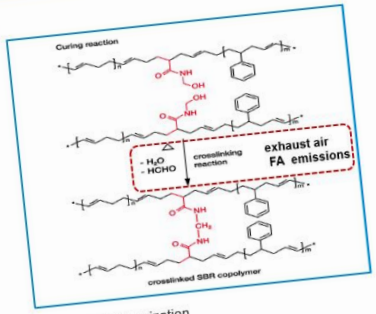


Cross-linking during film formation as preferred approach

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

REVIEW 2017

Analytics

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)

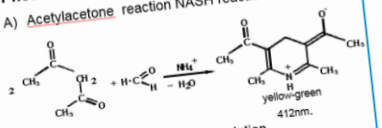
Some textile test standards

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

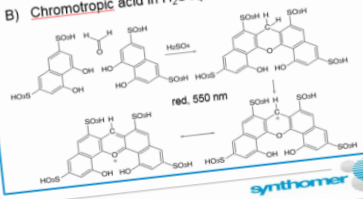
(1) Method of de Jong and de Jonge

Photometric FA identification

A) Acetylacetone reaction NASH reaction



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 at processing of aqueous based systems

- 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

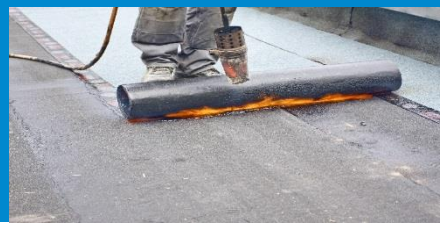
VDI 3862 (part 6)
Determination of FA in exhaust gases

- 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 SO_2

TEGEWA test set up

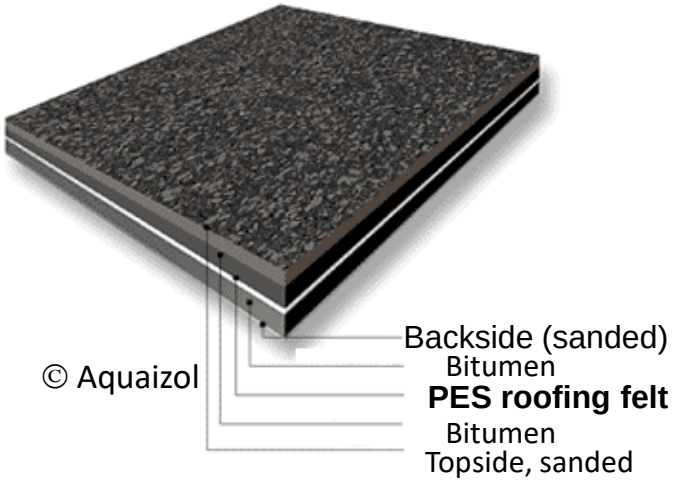
SBR for PES roofing felts

General information / Product requirements / Manufacturing process



Current state of art manufacturing process

- staple fibres or spun bond non woven
- Foulard impregnation – foam or liquid
- addition of up to 20% thermoset resin (FA) => 2-K System



Product requirements

- high water resistance
- high tensile strength (TS)
- stiff handle w/o kink or crack at flex test
- high aging stability
- outstanding thermo-dimension stability (TDS) at 200°C
- broad compatibility with thermo-set resins

Current state of art product offering

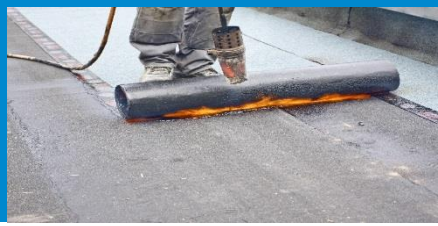
- self cross-linking SA or XSBR Latex (FA emitting); TG: ≥ 30°C ; PS: ≈130 nm ; TSC: ≈50%

Target of new development

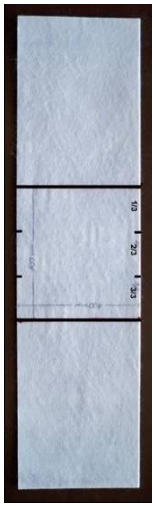
- self crosslinking Latex without FA emission & no addition of thermoset resin => 1-K System

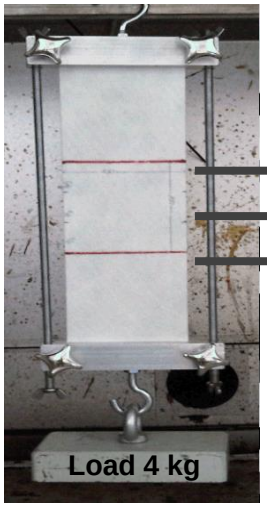
SBR for PES roofing felts

TDS & TS as most demanding product features



Thermo dimension stability





Elongation
Shrinkage
Elongation

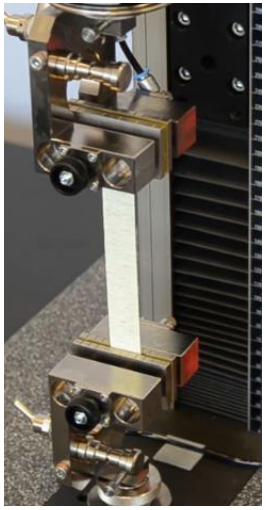
- 10min at 200°C, 5min conditioning at RT

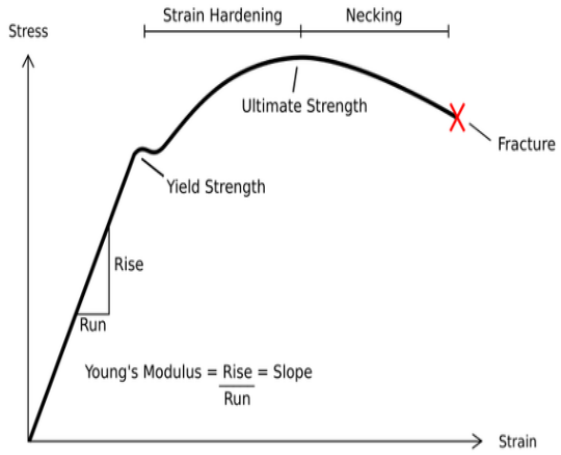
Targets (DIN 18192)

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

=> additional non DIN tests performed

Tensile strength



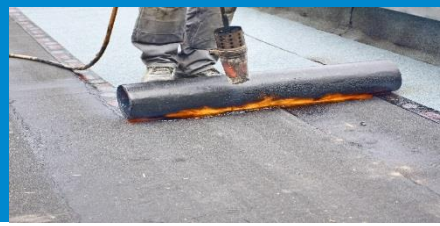


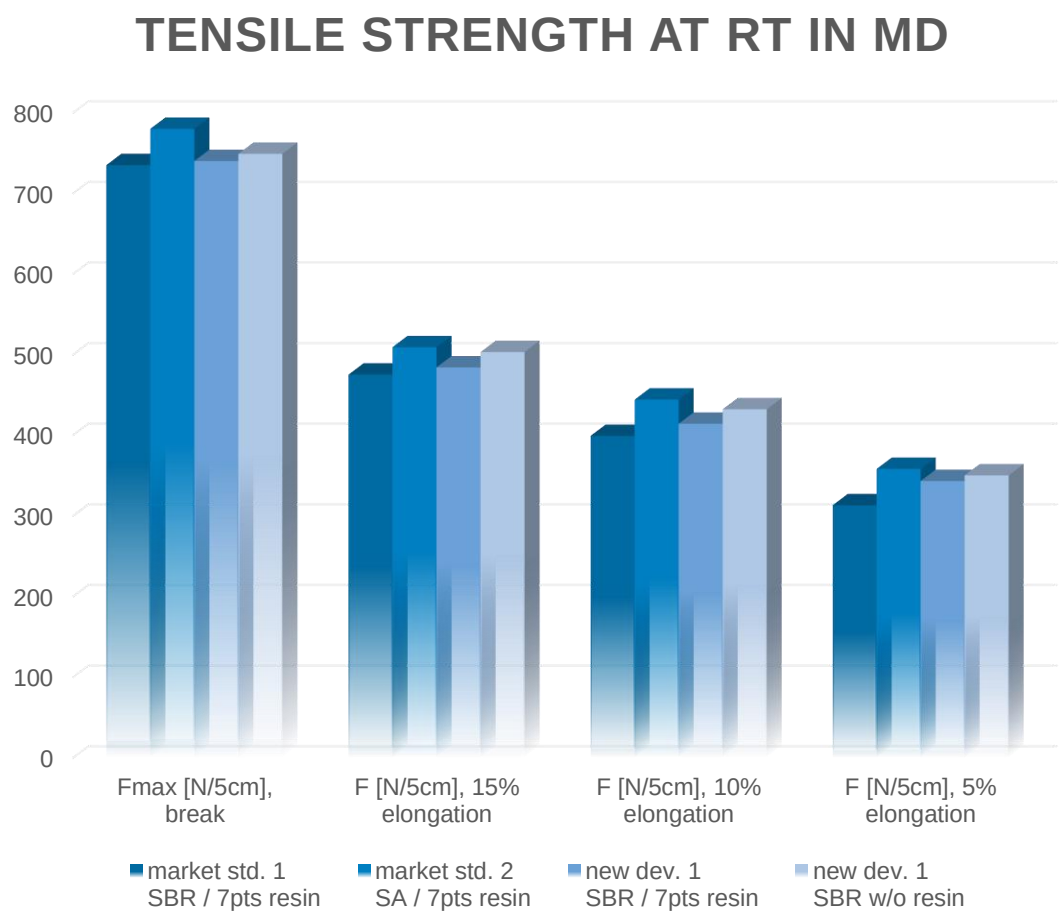
- ultimate tensile strength
- tensile strength at 5%, 10%, 15% elongation
- hot tensile strength (180°C)
- wet tensile strength

=> Additional tests performed

SBR for PES roofing felts

Very good performance on tensile strength





- PES non woven, 160gsm
- 20% coating weight d/d
- two market standards with resin
- new development w and w/o resin

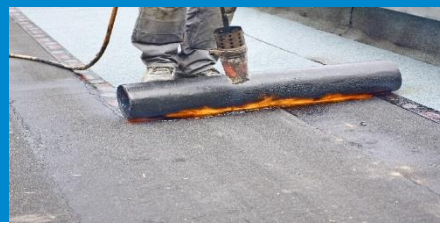
⇒ High performance on tensile strength fulfilled by all products

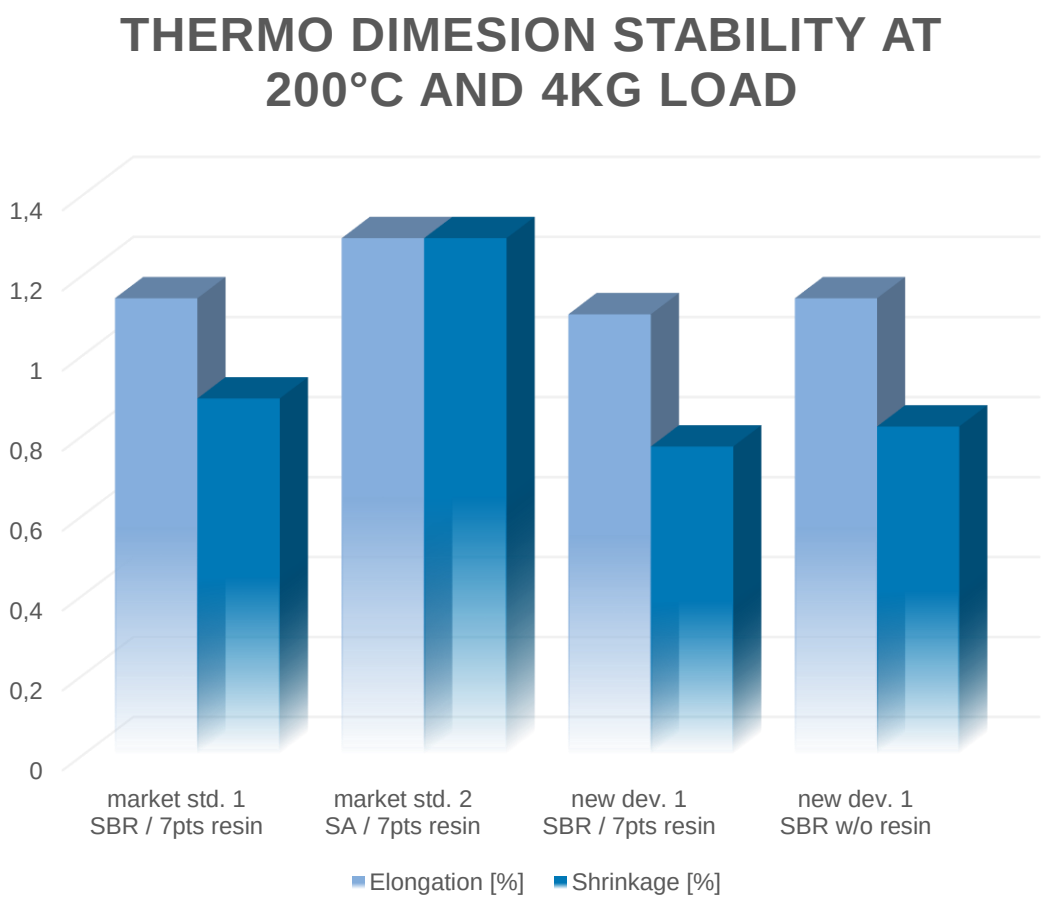
⇒ Only new developed product in 1K system feasible

⇒ Only new developed product FA free

SBR for PES roofing felts

surpassing DIN standard for TDS even as 1K-System





- PES non woven, 160gsm
- 20% coating weight d/d
- two market standards with resin
- new development w and w/o resin

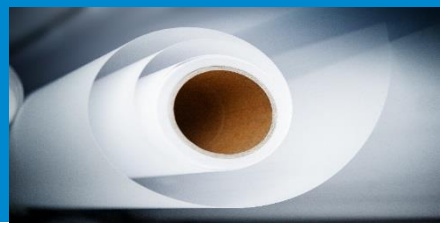
⇒ High performance on thermo dimension stability at 200°C fulfilled by all products

⇒ Only new developed product in 1K system feasible

⇒ Only new developed product FA free

SA for fleece wallcovers

General information / Product requirements / Manufacturing process



Manufacturing process

- similar to conventional paper production but with glass or other synthetic fibers
- additionally Foulard impregnation afterwards or
- addition of binder to pulp
- 15-20% binder uptake

Product requirements

- low water uptake / good wet tear strength
- absolute block free behaviour
- lightfast / low yellowing
- good filler tolerance (TiO_2)
- good fiber bonding / self crosslinked

Current state of art product offering

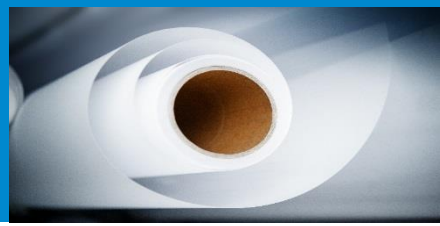
- self cross-linking SA (FA emitting)

Target of new development

- self crosslinking Dispersion without FA emission => interior application

SA for fleece wallcovers

Whole product range from soft to hard / all FA-free self crosslinkable



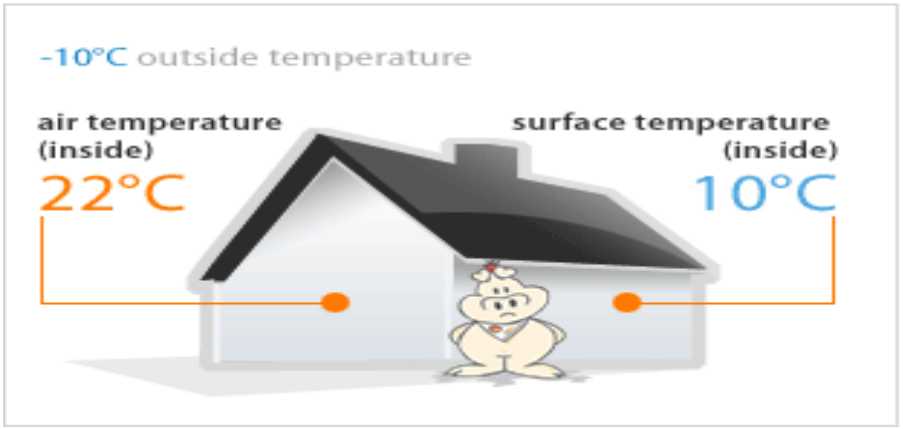
	New development	Revacryl X 9020H	Revacryl AE 4522
TSC [%]	50	50	50
pH value	8,5	8,5	7,5
Viscosity [mPas]	300	250	350
T_G [°C]	-16	4	22
MFFT [°C]	0	0	18
Water absorption (24h) [%]	12	11	10
tensile strength [N/mm²]	5	6	9

Litex QuickShield 1545 for glass mesh

General information / Product requirements / Manufacturing process

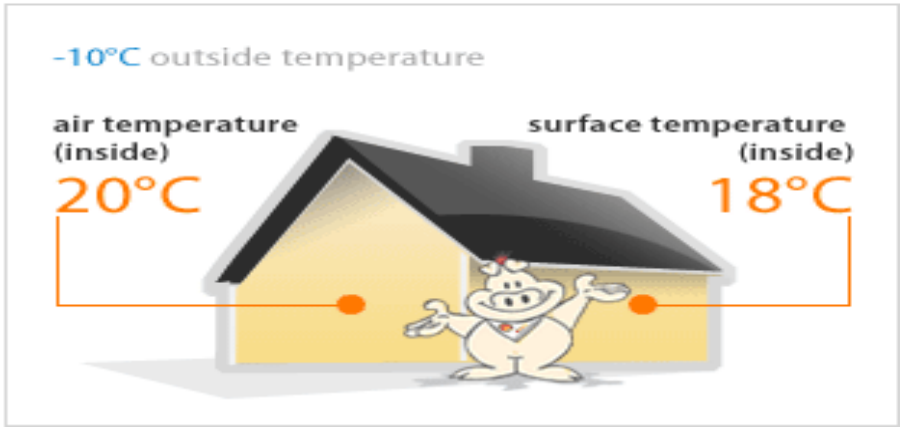
Outside wall without ETICS:

Poor heat insulation: Temperature differences lead to draughts – no living comfort

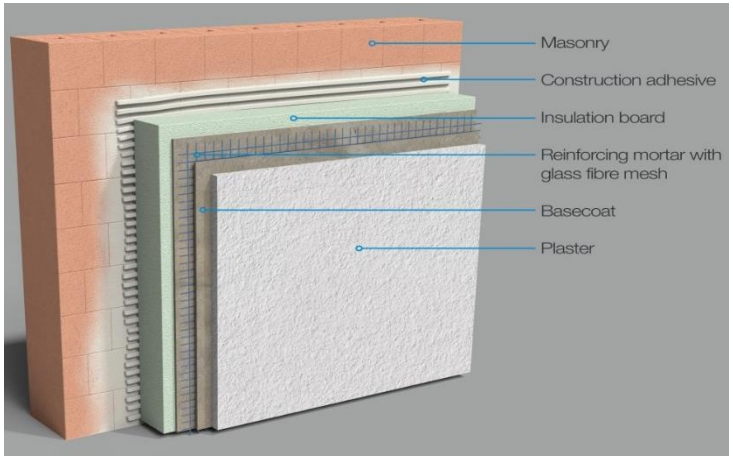


Outside wall with ETICS:

Low temperature differences – pleasant indoor climate, significant savings in heating energy



- outstanding alkali resistance for all relevant standards: ETAG 004, DIN EN 13496, DIBt, EIMA 105.01
- wide range of handle from very soft to hard tailor-made solutions
- very good workability / runability
- non displaceable / good node fixation
- non blocking finishes
- good compatibility with thermoset resins



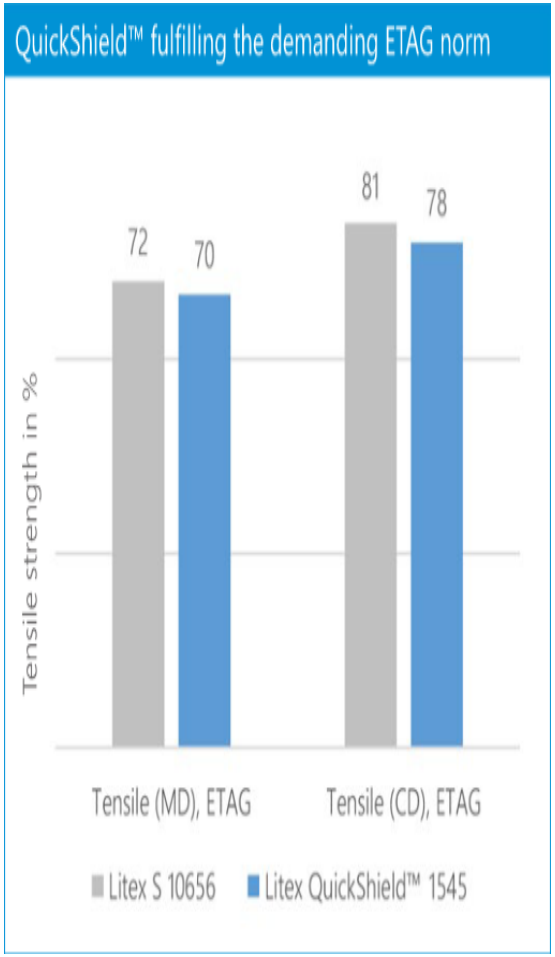
Litex QuickShield 1545 for glass mesh

results on demanding ETAG norm / efficiency potentials

- comparable tensile strength on ETAG vs. market standard
- formaldehyde-free self crosslinking
- significant cost saving potentials in production process
  - lower surface temperature (crosslinking at RT)
  - reduced exhaust air temperature
  - up to 30% faster impregnation speed
- significate increased productivity
  - low foaming behaviour
  - low deposit formation

⇒ currently in tests for glass non woven material for insulation

⇒ first results on tensile strength after ETAG promising



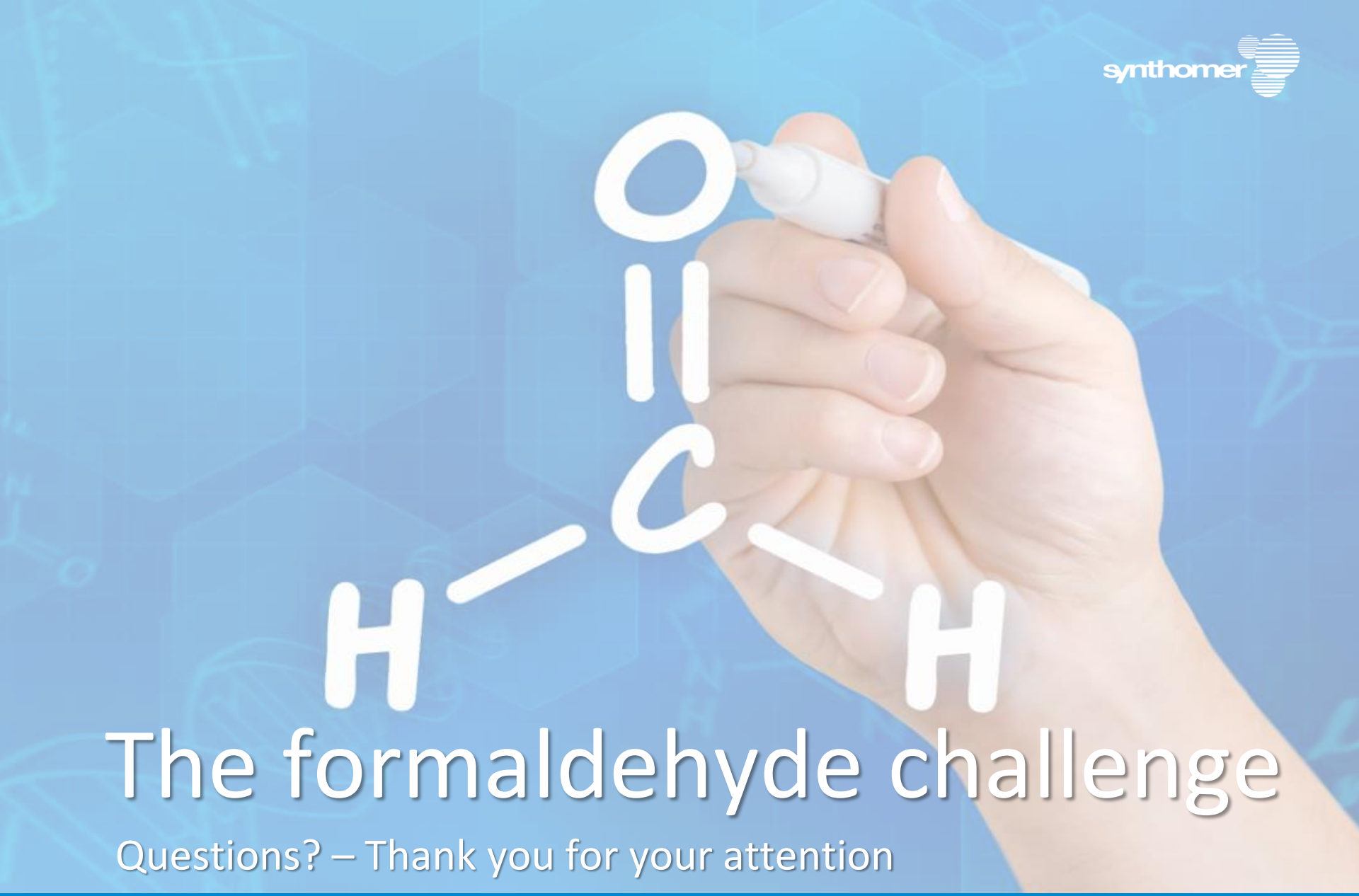
Conclusion / Summary

The formaldehyde challenge - Development on next generation latex binder



- same performance achieved in various application with FA-free self crosslinked Latex
- Synthomer green technology is transferable through different chemistries (SBR / SA / PA)
- beside ecological benefit of FA-free self crosslinking often new added values
  - reduced crosslinking temperature = reduced energy needed
  - complexity reduction in production processes = 1K solution
  - increased line speed = high productivity

=> Economically benefits



The formaldehyde challenge

Questions? – Thank you for your attention

Matthias Renka

November 07-08, 2018

33. Hofer Vliesstofftage