

Influence of Glass Fibre Sizing and Storage Conditions on Composites Properties

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Wind Turbine Rotor Blades , June 23-24, 2015,
Haus der Technik, Essen, Germany

- ❑ 3B-the fibreglass company
- ❑ How glass fibre is produced
- ❑ How sizings work
- ❑ Sizing ageing study
 - Rovings
 - Fabrics drying
- ❑ Conclusions



a reference in fibreglass...

innovative, entrepreneur and eco-enthusiast

- ❑ 3B is part of The Braj Binani Group which is a conglomerate with diversified interests in cement, zinc, glass fibre and composites

Major and dynamic actor in **composite reinforcement solutions**

- ❑ A special focus on **thermoplastics, wind energy, performance composites**
- ❑ 1000 experts building upon a long heritage of 45 years of expertise
- ❑ 160 000 tons of glass produced per year
- ❑ **Innovating and setting new standards** within the fibreglass industry based on our **two unique high performance and eco-responsible glass technologies: Advantex[®] glass and HiPer-tex[™]**

unique glassfibre solutions

high performance and eco-responsible

Chopped Strands



Applications

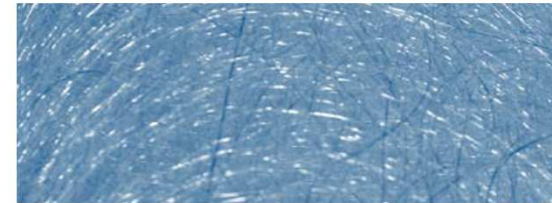
Automotive, Electrical & Electronics, Consumer, Transportation, Construction

Direct Rovings



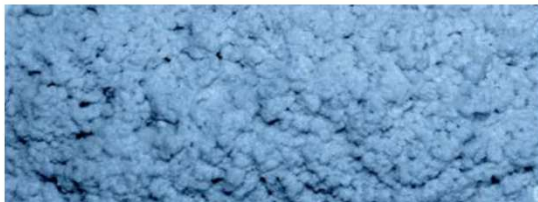
Wind, Infrastructure, Transportation, Electrical & Electronics, Pipes & Tanks

Continuous Flament Mat



Automotive, Infrastructure, Construction, Electrical & Electronics

Textured Yarns Milled Fibres



Applications

Construction, Electronics, Automotive

Chopped Strand Mat



Electrical & Electronics, Transportation, Pipes & Tanks

Assembled Roving



Automotive, Transportation

...with global presence

to most effectively serve our partners

□ Sales Offices

- Europe
 - **B**ruxelles
- India
- China

□ Productions

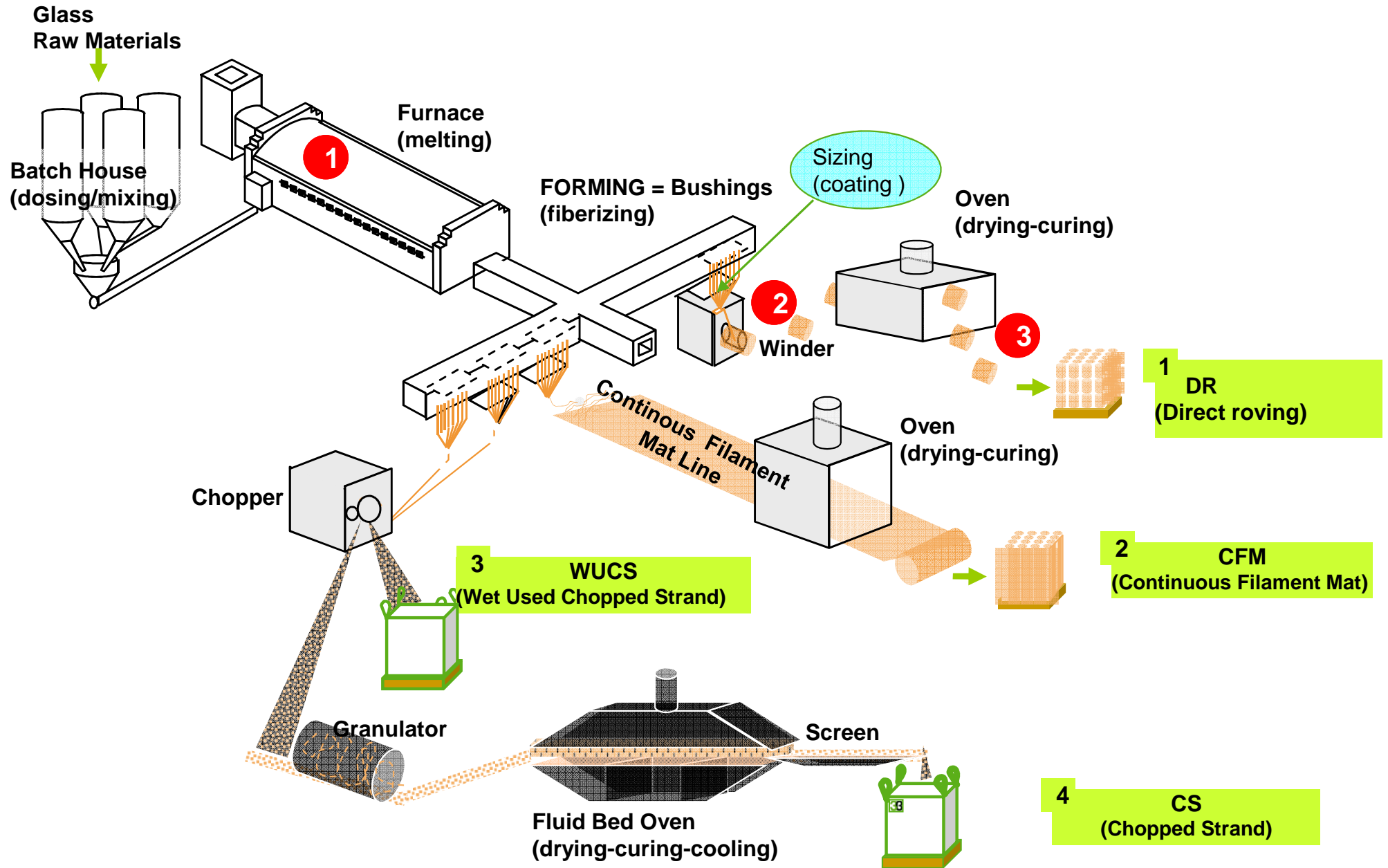
- **B**irkeland, Norway
- **B**attice, Belgium
- Goa, India

□ Research & Application Development

- Battice, Belgium (Lüttich, 25 km from Aachen)
- Activities in Glass – Fibre coating – Composite



3B glass fibre processes



Note : Multi end roving and Chopped Strand Mat from Goa plant not represented here

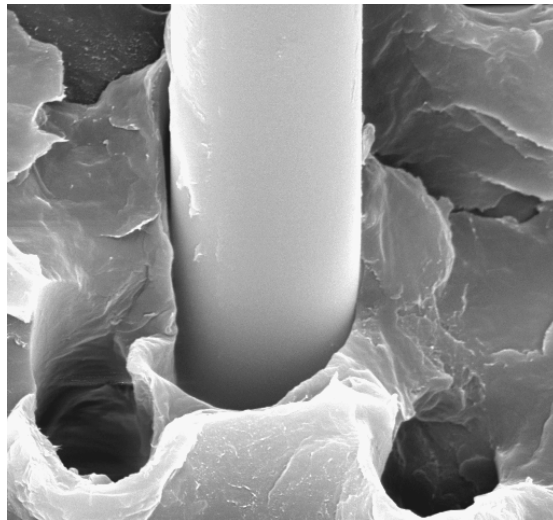
Size is applied as a water based formulation,

it contains:

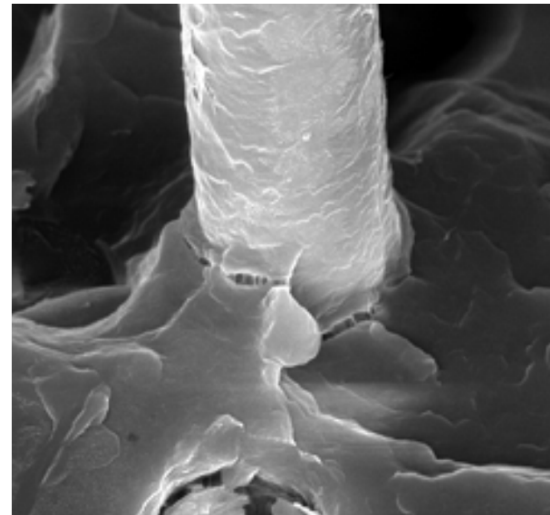
- ❑ **Coupling agent(s)** : Provides adhesion between glass surface and the resin => Silanes,
- ❑ **Film Former(s)** : Provides protection and strand integrity to the roving as well as compatibility with the resin => EP, PU, VE, ...
- ❑ **Lubricant(s)** : Provides lubrication and protects the filaments during processing
- ❑ **Other Additives** : antistat, emulsifier, anti foaming, bactericide, ...

Role of GF sizing = ensure good transfer of load applied on the composite from the polymer matrix to the glass.

GF sizing are **specific** to polymer matrix and final application



Poor sizing

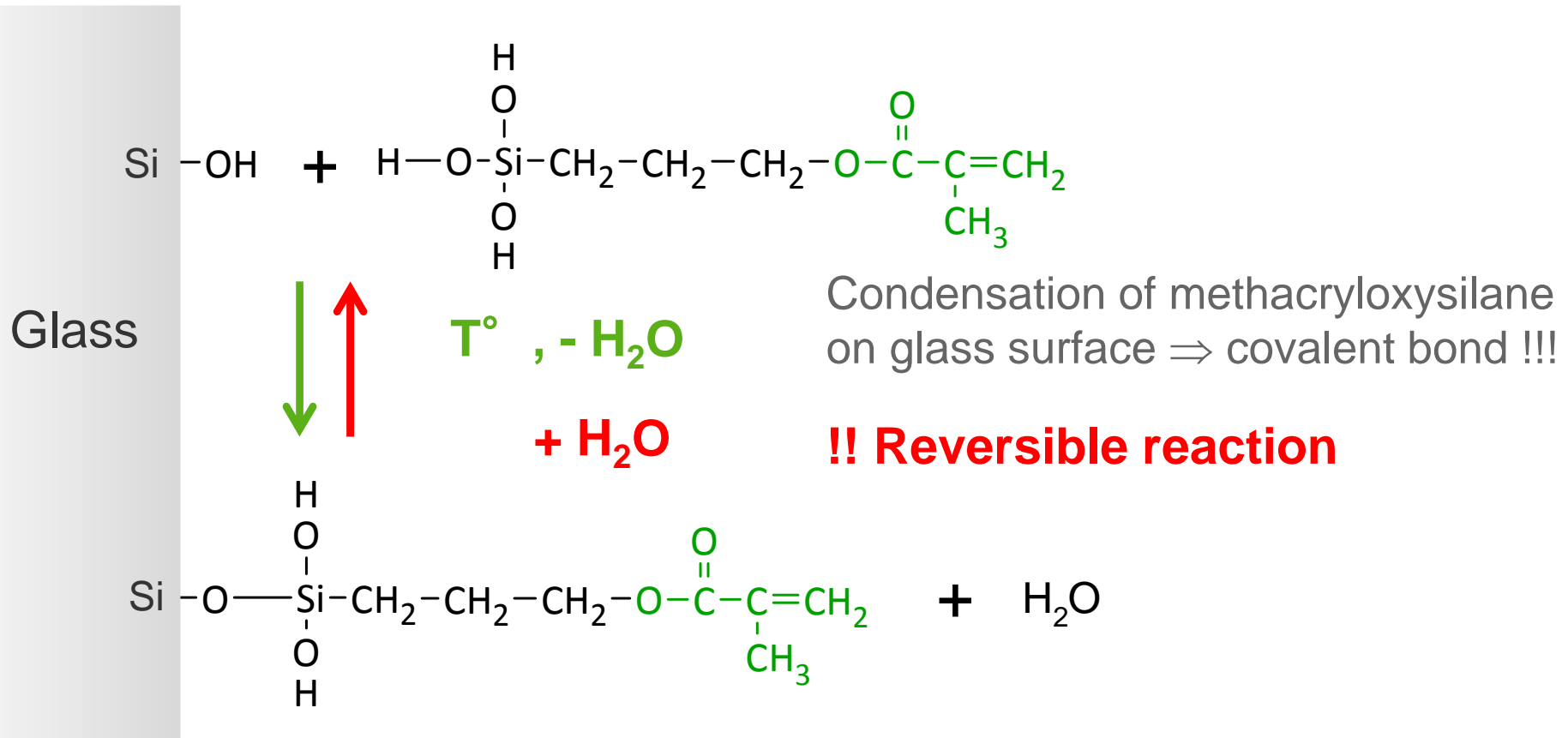


Good sizing

PA66 - 50%wt GF	Poor coating	Good coating
Tensile strength (MPa)	50	180
Notched Impact Strength (kJ/m ²)	< 5	18

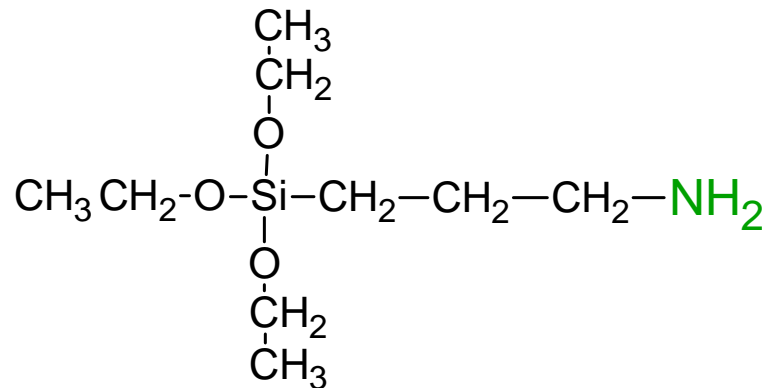
Silane condensation on the glass surface

- Function = coupling glass (inorganic) to other sizing ingredients and polymer matrix (organic)
- Chemical nature = functionalized silane

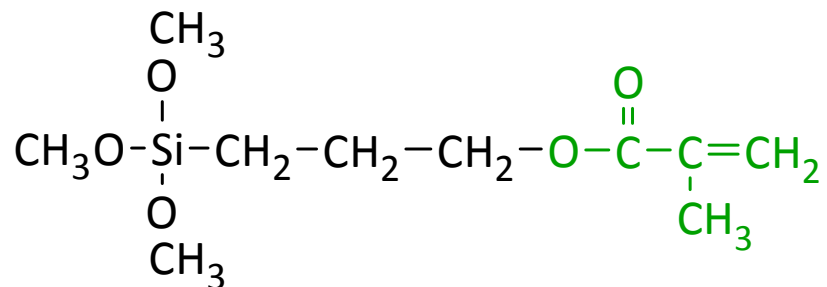


Types of Silanes used in thermoset sizings

- γ -aminopropyltriethoxysilane → Epoxy resin

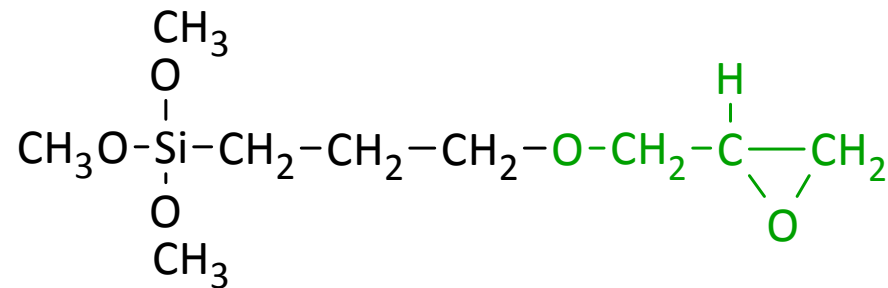


- γ -methacryloxypropyltrimethoxysilane → VE and UPE



Types of Silanes used in thermoset sizings

- γ -glycidoxypropyltrimethoxysilane → Epoxy resin

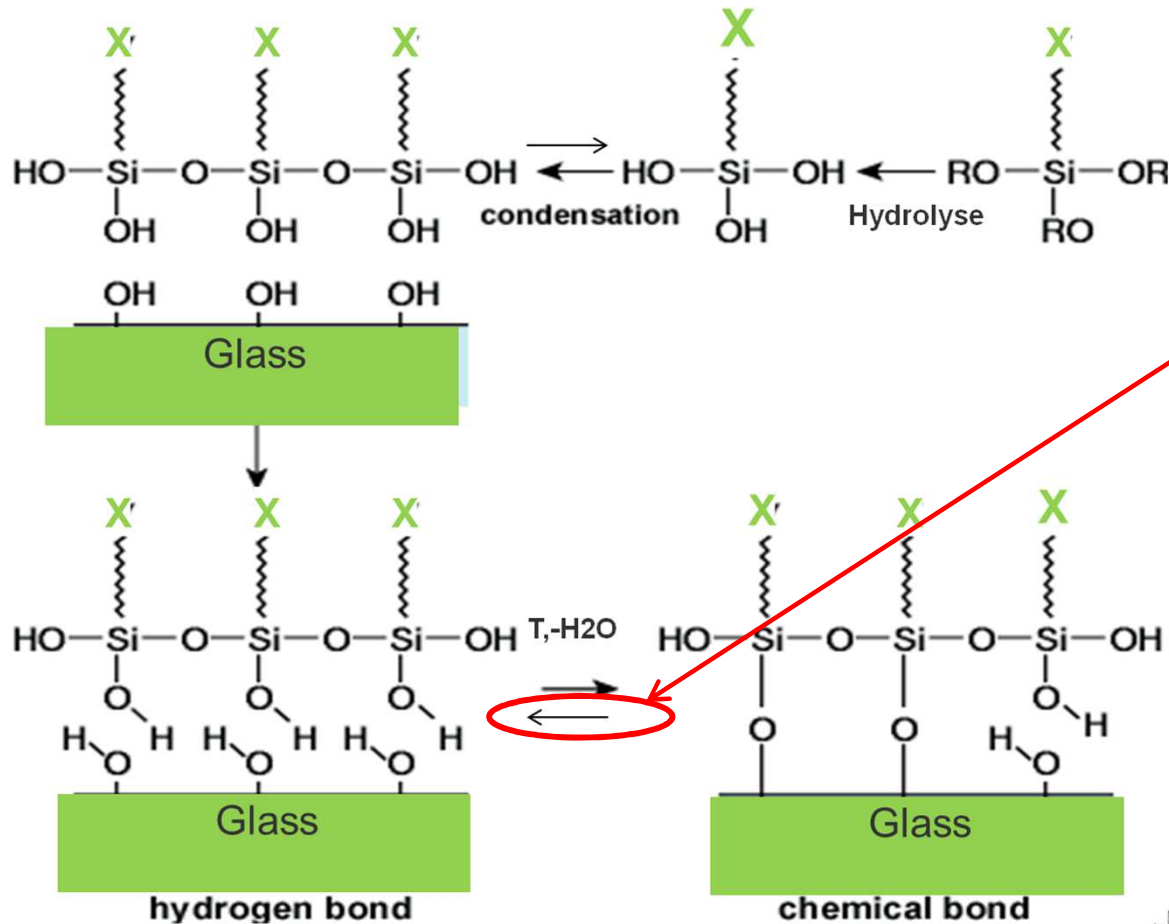


Glycidoxy = Epoxy

Stability of silane in water related to hydrolysis – condensation equilibrium

- Silane is hydrolysed in water during sizing preparation \Rightarrow formation of silanol bonds
- Hydrolysed silane tends to condensate with time and to form silane oligomers
 - Solubility \searrow and gel formation \Rightarrow reduction of sizing stability
 - Silane oligomers will not properly cover/react at glass surface \Rightarrow reduction of composite mechanical properties

Silane Hydrolysis



Ageing of composites and sizing in presence of water => lower adhesion
 Reversible reaction !
 Main factors: temperature, H₂O,

❑ Coupling agents:

❑ Amino:

- ❑ continue to crosslink and to react with film former → reduced solubility, less wetting by the matrix.

❑ Methacryl:

- ❑ when inhibitor is consumed, then can homopolymerise or crosslink if unsaturated polyester film former → reduce speed of dissolution or solubility in the matrix,.

❑ Epoxy:

- ❑ Could progressively react with amine or acid if present → reduced solubility
- ❑ Epoxy functionality can be progressively hydrolysed → reduced reactivity

Sizing ageing and rovings storage conditions impact on mechanical properties

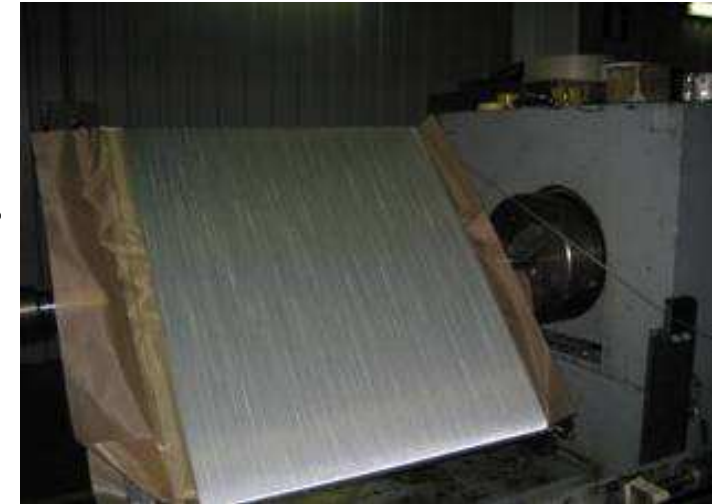


Laminate construction (with one roving)

-Dry winding of flat panel:

- 4x 845gr/m² = 3380 gr/m² (4 layers UD roving) at 0°
=> laminate of 2 mm

-Infusion in Epoxy resin Hexion RIMR 135/137 at 35° c,
full vacuum, 4 products/infusion in most cases
4 hours at 90° post-cure



Testing

- Tensile at 90°
- Short beam test according ISO 14130.
- Glass contents by weight range 72 to 75.5 %



Typical set up of infusion of 4 products in one shot

- ❑ Pallets from Birkeland plant (rovings have different starting « age »)
 - Reference sizing (SE1500) 17-2400 production date : 4/3/2013
 - New sizing (SE2020) 17-2400 production date : 11/4/2012
 - New Multi Compatible sizing (W3030)17-2400 production date : 5/9/2013
- ❑ Static test before conditioning
- ❑ Trip to/from Dubai for SE1500 & SE2020 from August to December
- ❑ 1 week at -18° C (check Epoxy crystallisation)
- ❑ 2.5 months in oven at 50°C in Lab (RH=2-3%)
- ❑ 2.5 + 2.5 months at 30° /80%RH (21,5 gr H2O / Kg air)
- ❑ 2.5 +2.5 months at 30° /80%RH in 2 PE bags sealed

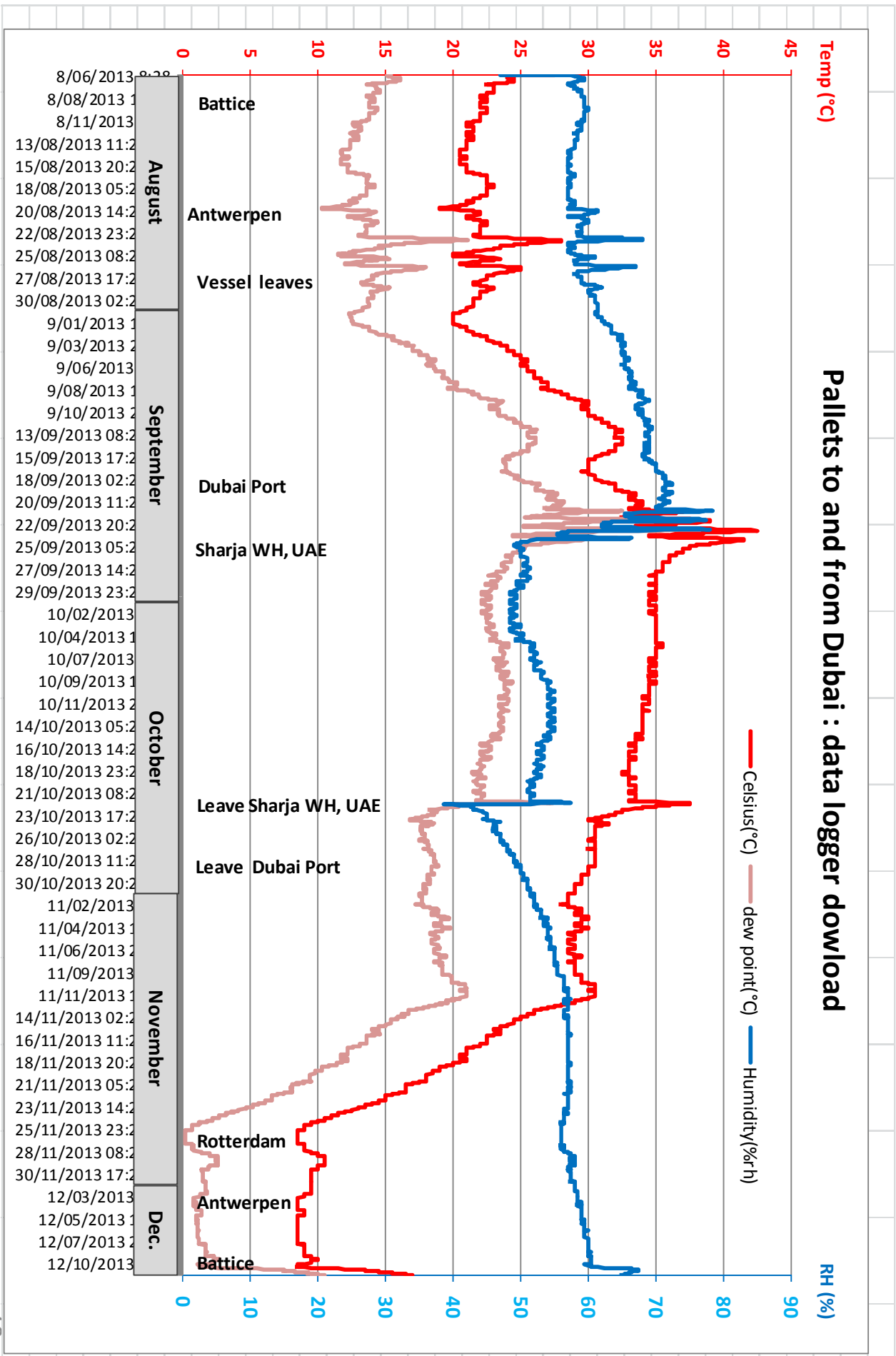
Note: 2020 sizing is epoxy specific and 3030 sizing is multi resins (UP, VE, EP) compatible
SE means the sizing is applied on Advantex glass, W means it is applied on HiPer-tex glass

Conditioning room & bobbins

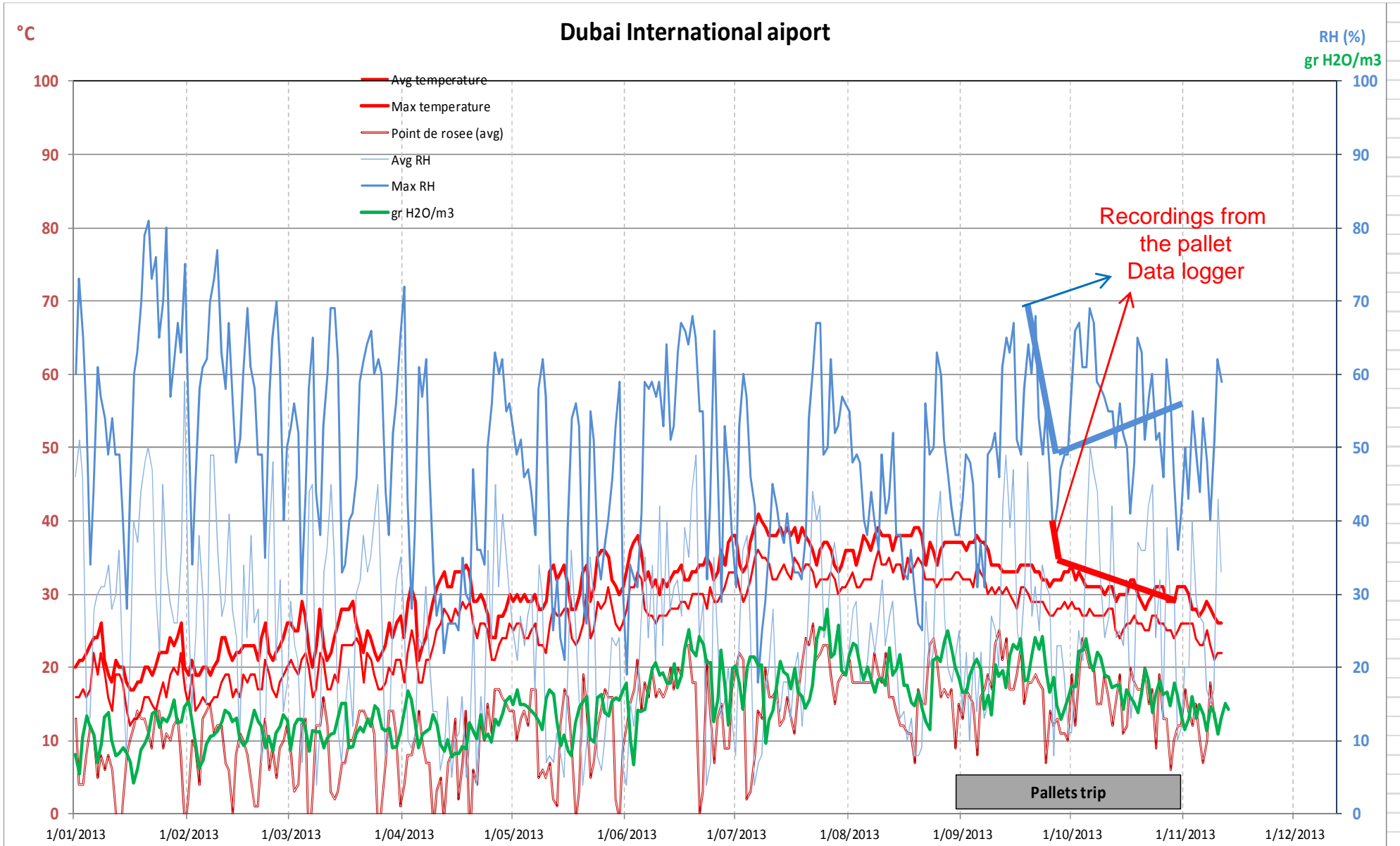


Bobbins in sealed PE bags

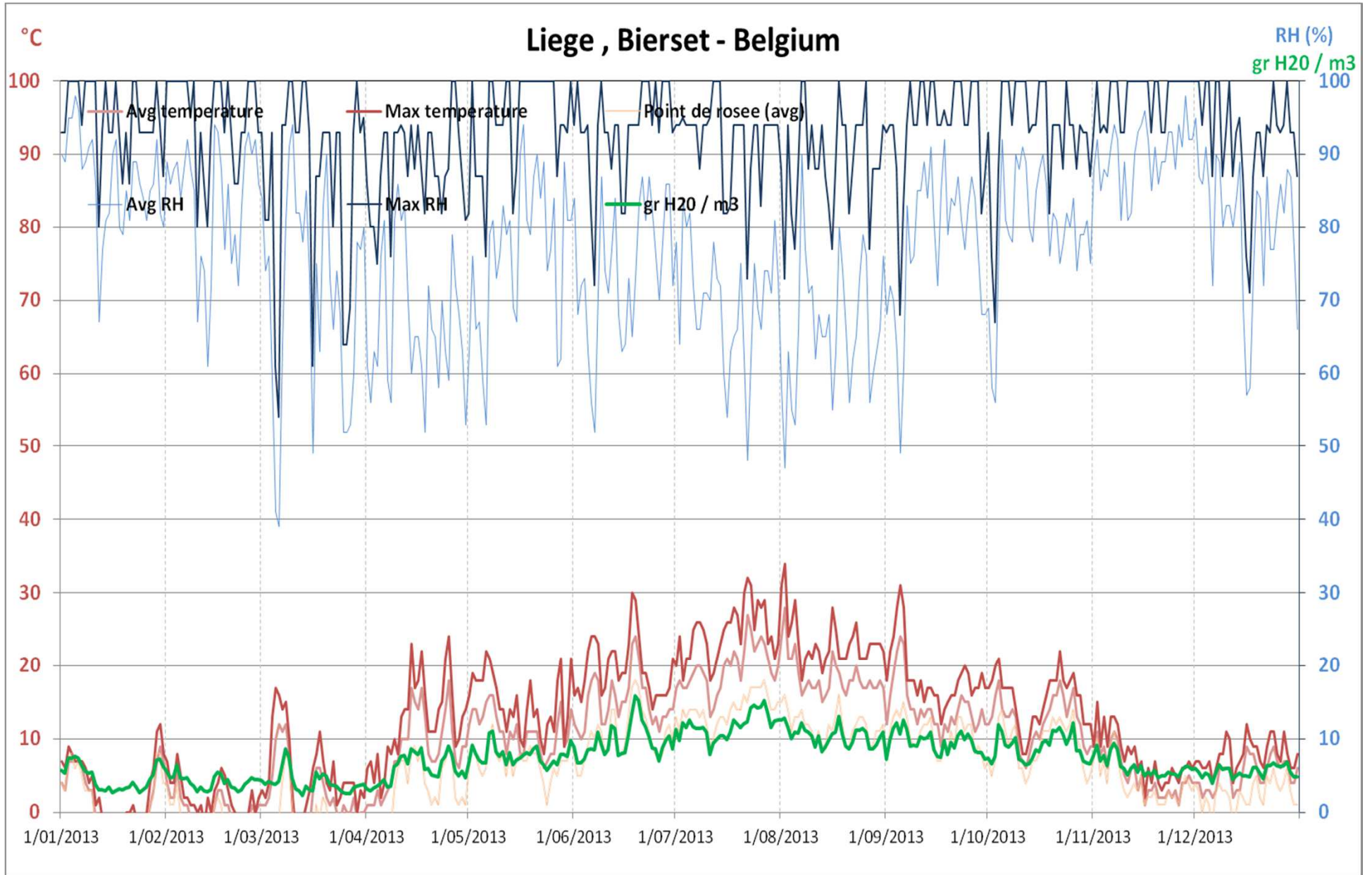
Bobbins



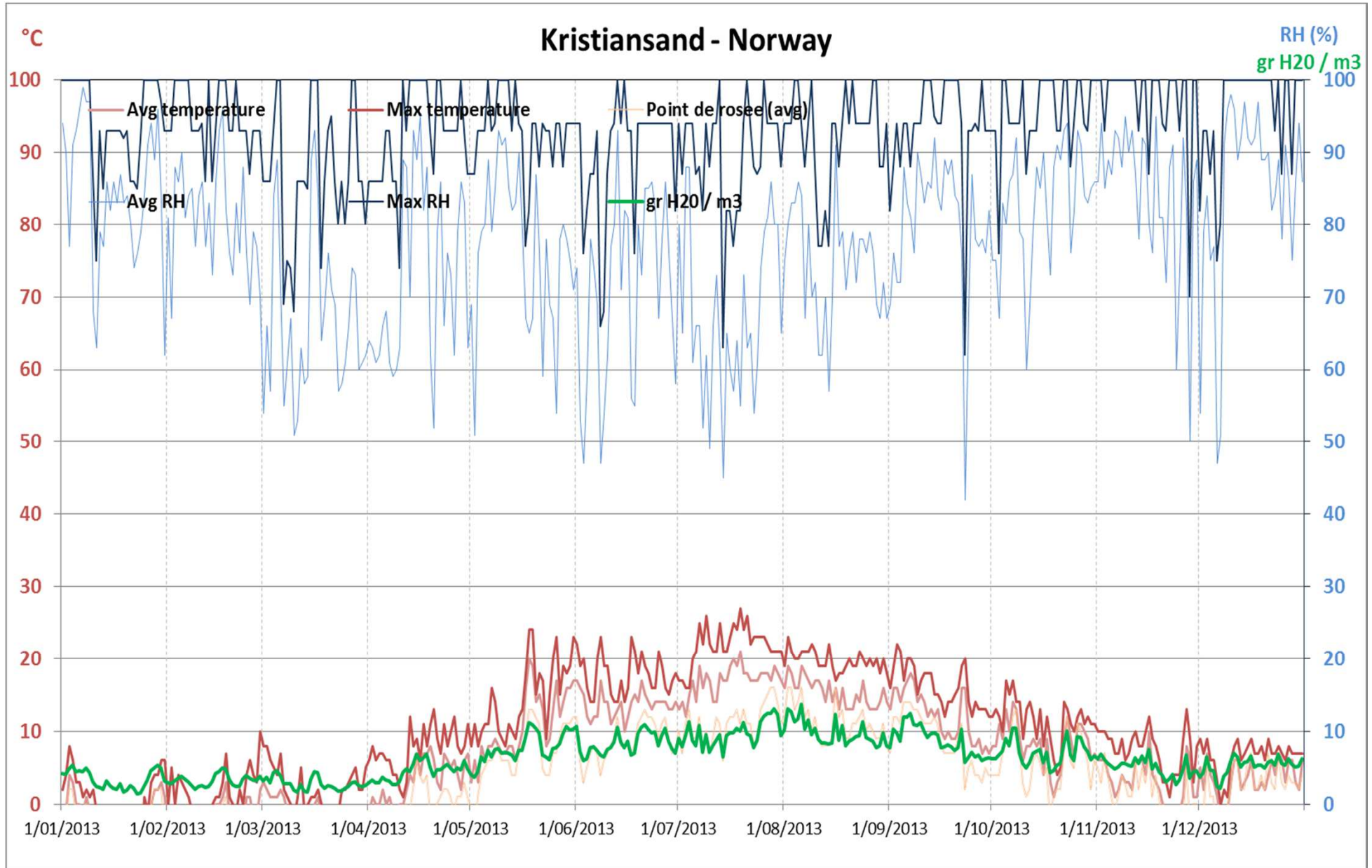
2013 Temperature /RH history in Dubai

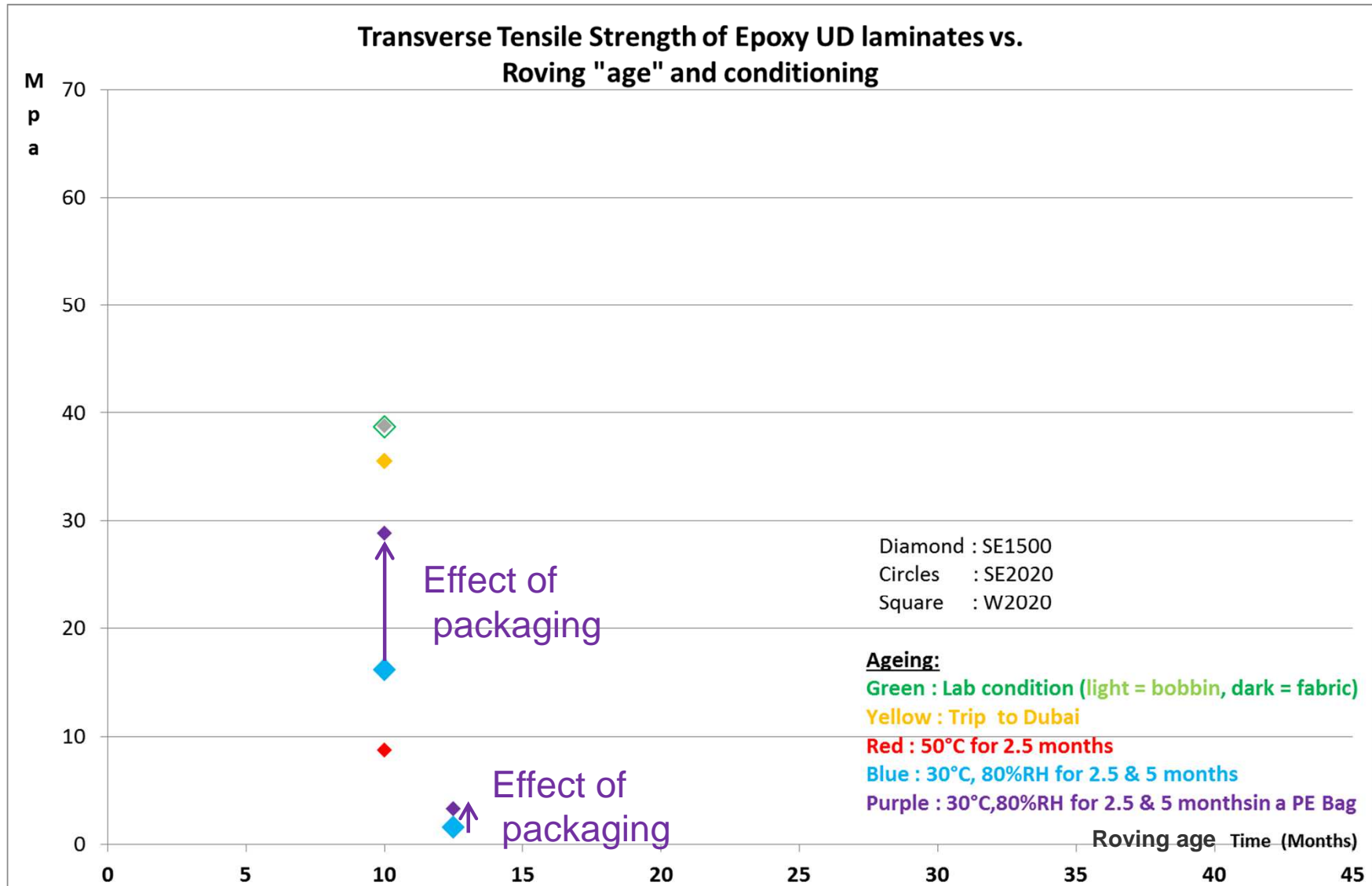


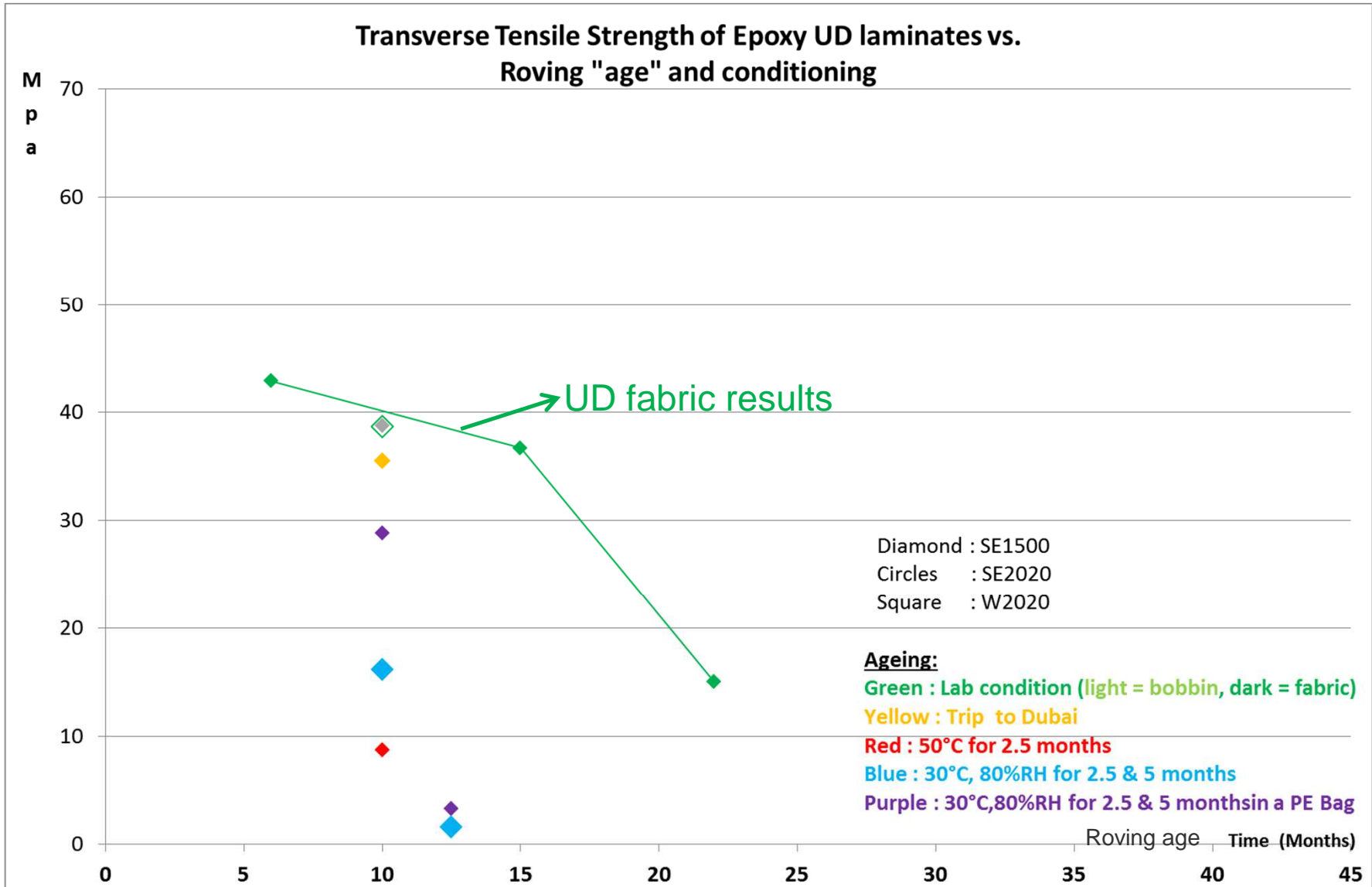
2013 Temperature /RH history in Liege / Bierset (close to where bobbins & fabrics were stored)



2013 Temperature /RH history in Kristiansand - Norway





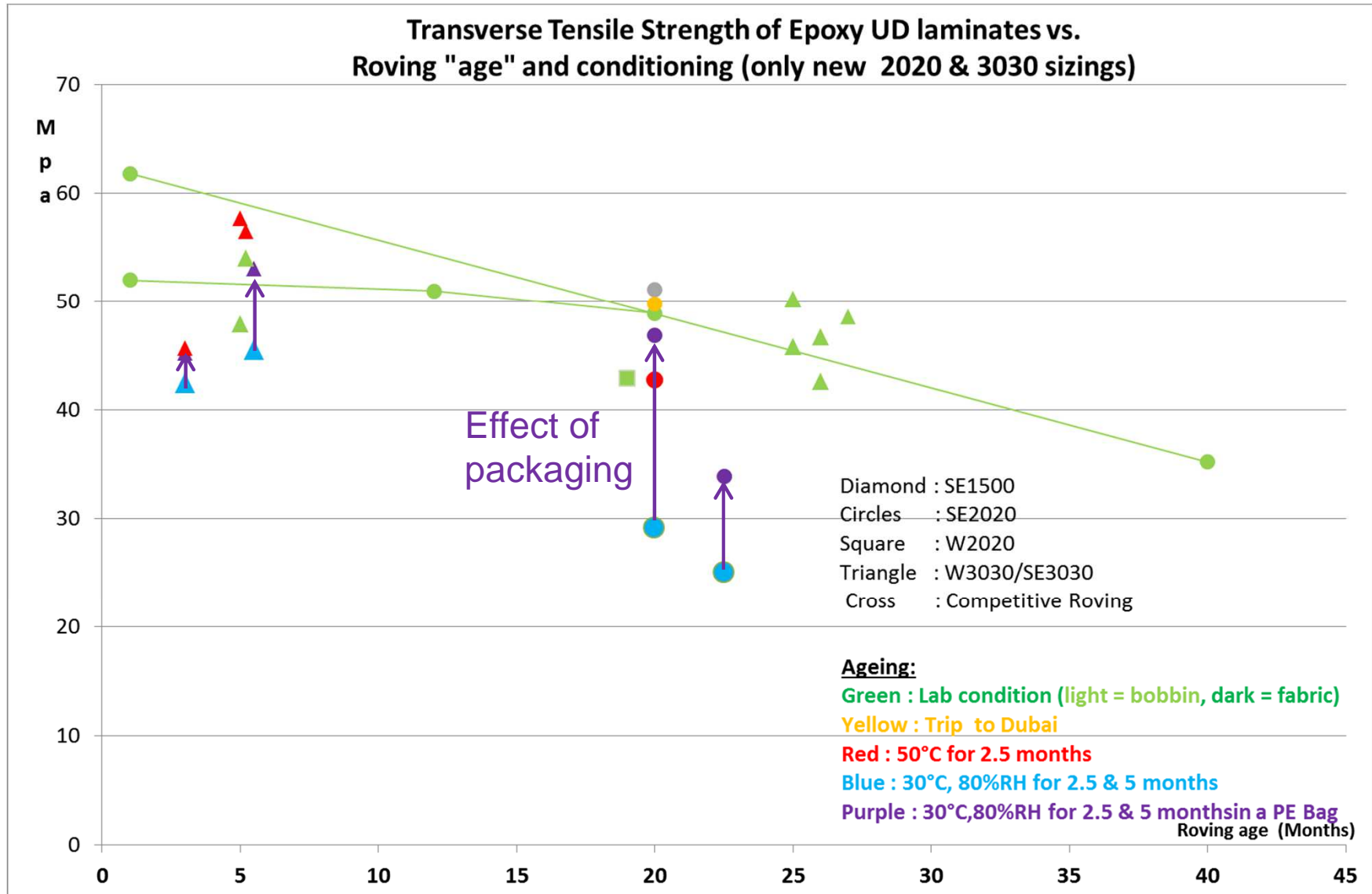


Laminate quality



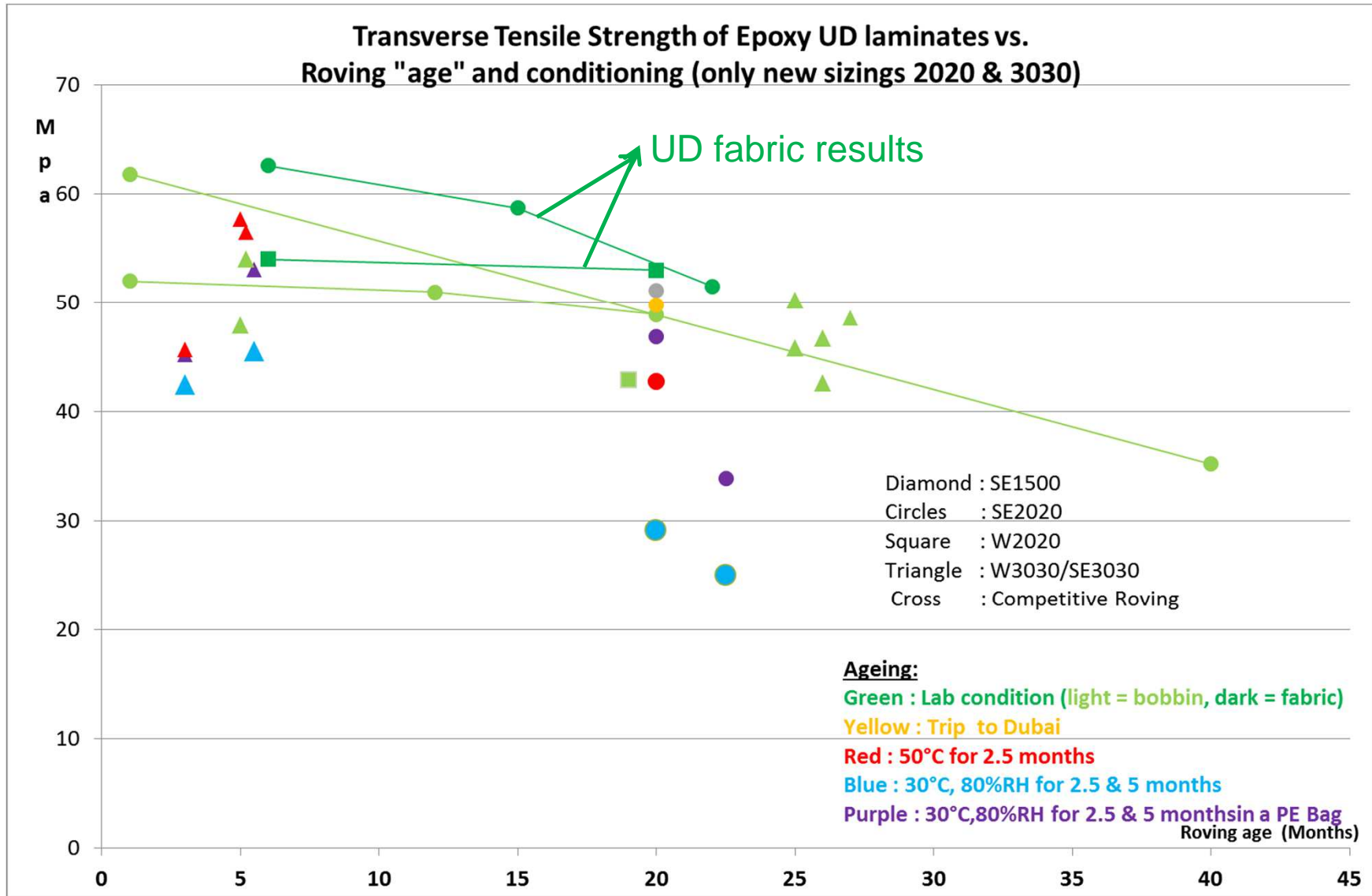
When Transverse tensile strength of UD laminates made by dry winding is low ($<10\text{MPa}$), laminates are already full of cracks prior demolding

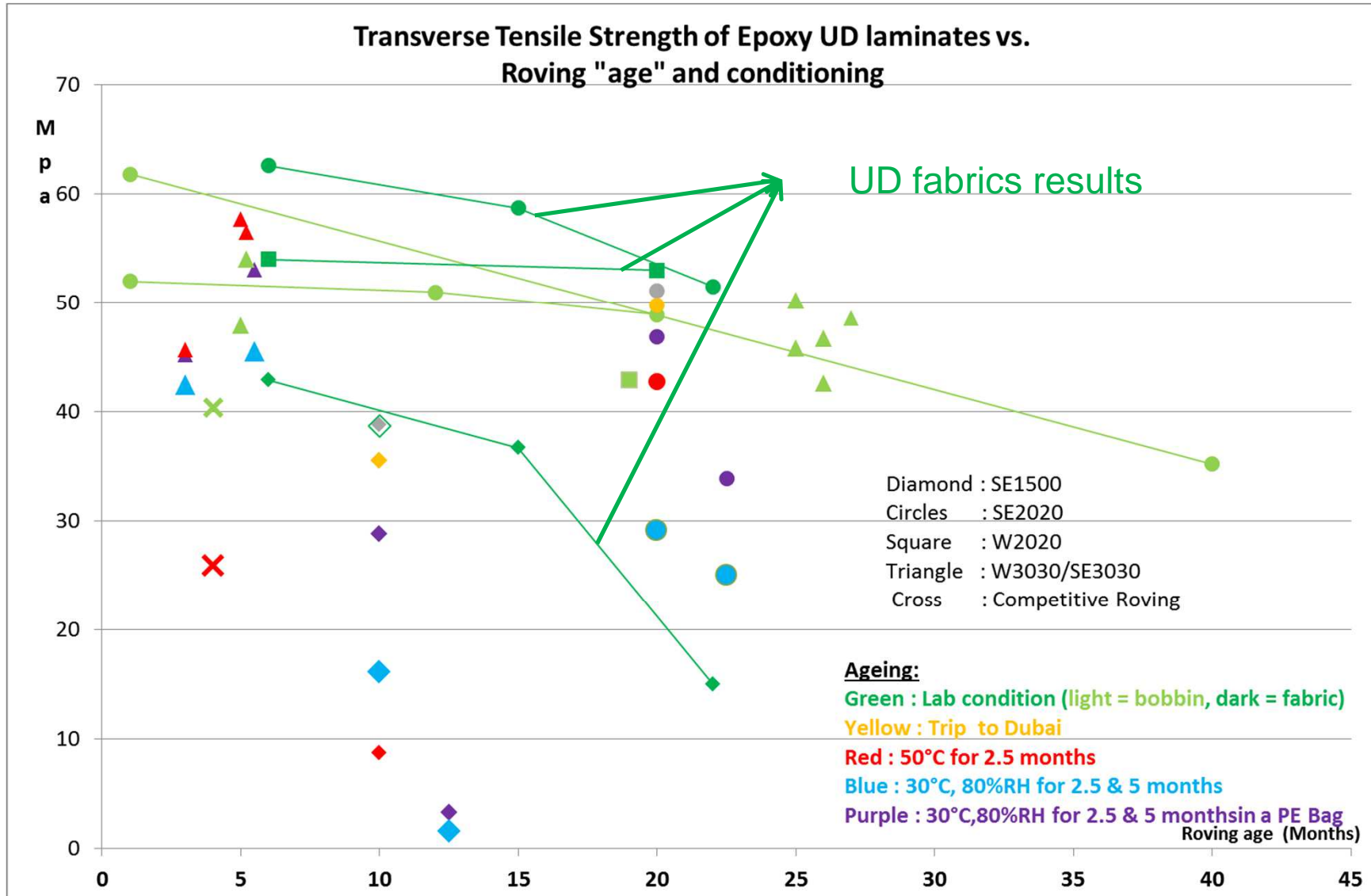
TTS for SE2020 and SE/W3030



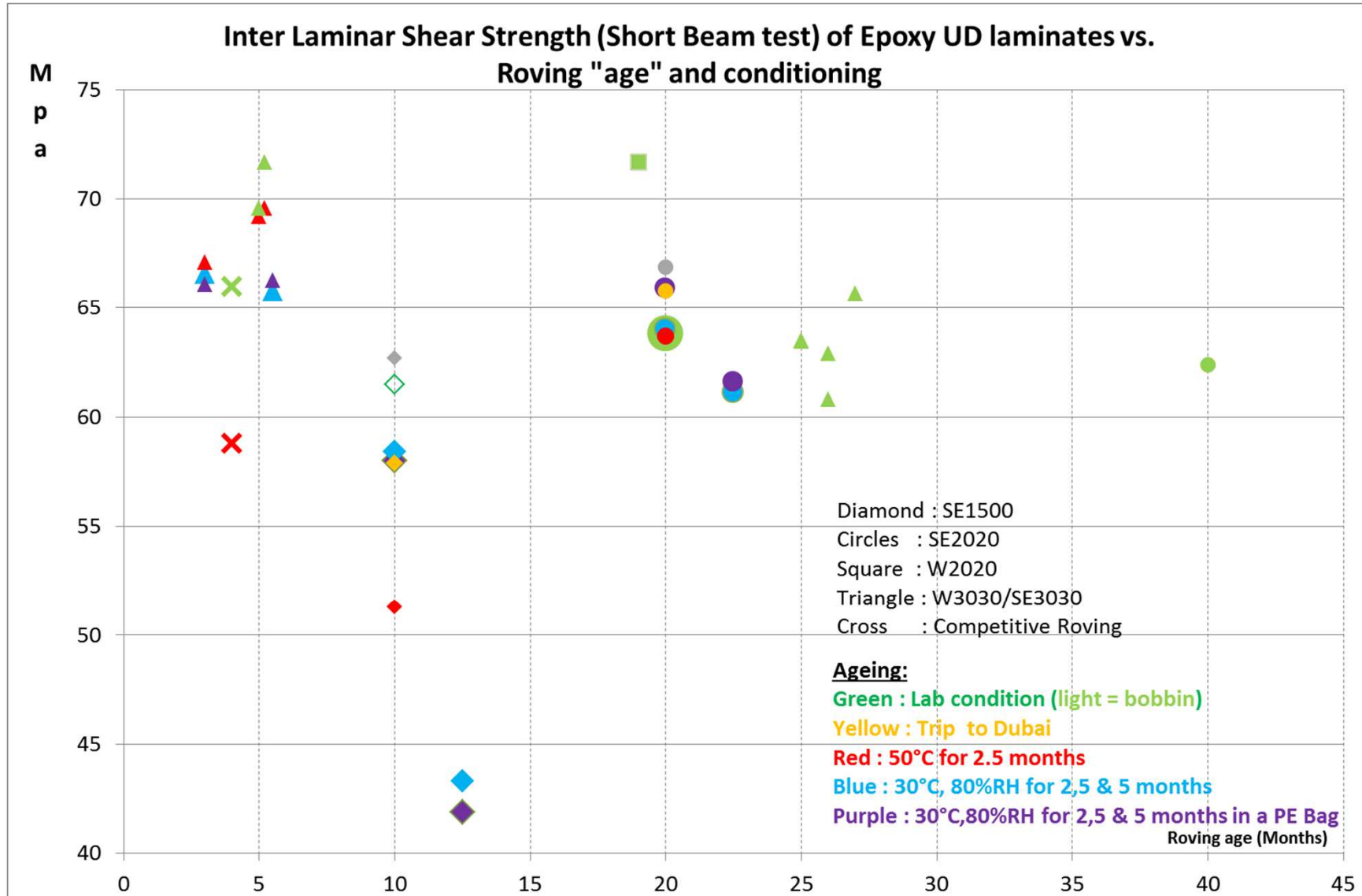
TTS for SE2020 and SE/W3030

+ fabric





Short Beam Test results

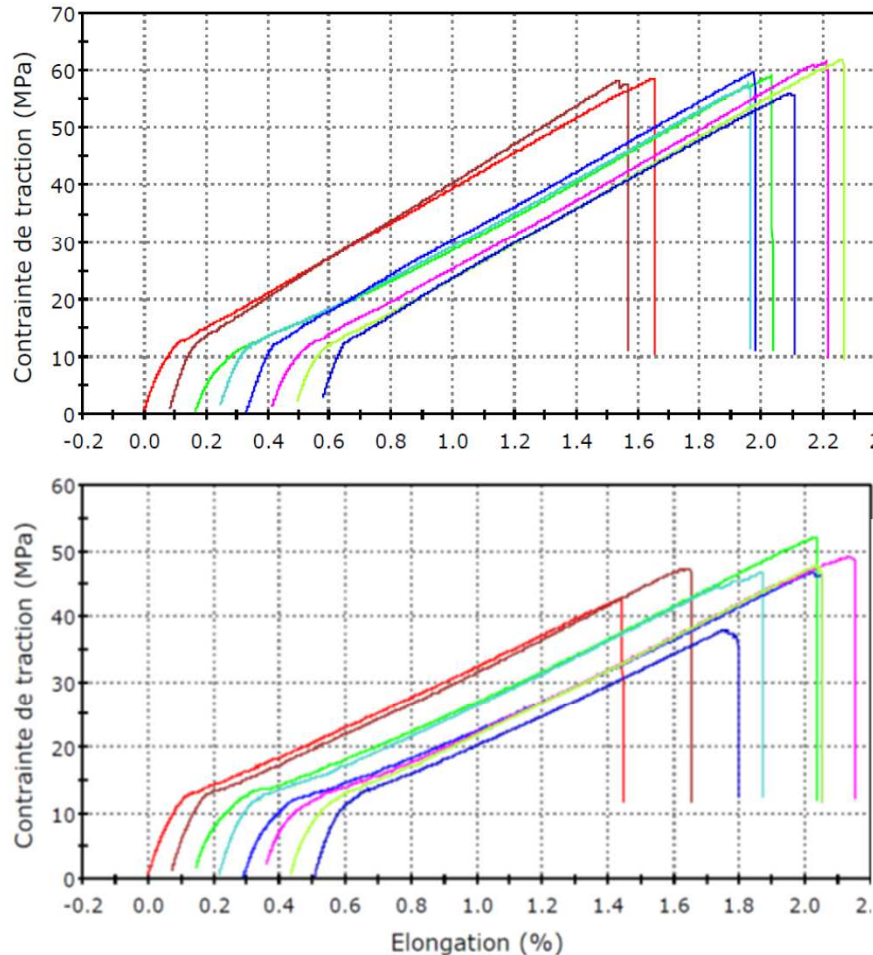


UD Fabric drying

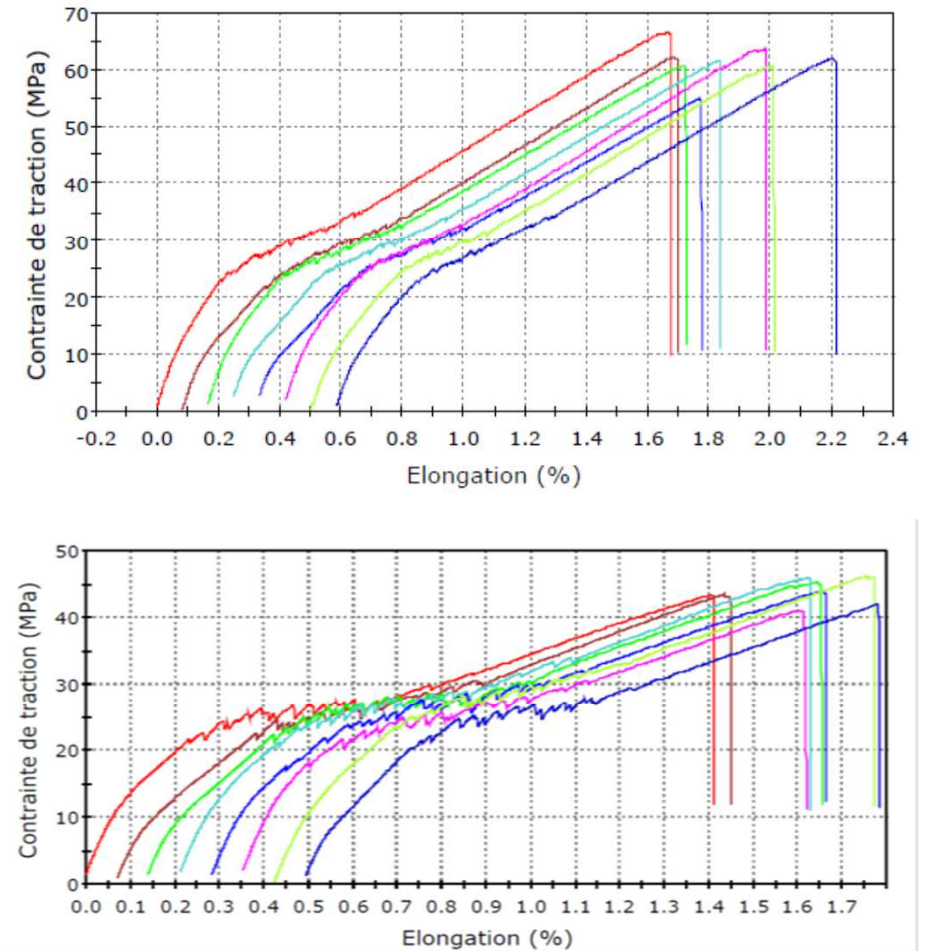


Epoxy laminate based on 2 «severely aged » SE1500 UD fabrics Transverse tensile test before and after fabric drying 2 h at 105° C

As received



Dried 2h at 105° C



Both laminates quality looked good, initial H2O in the fabrics was 0,03% (not high)

Drying could only increase the TTS from 12 to 20-22 Mpa (+70-75%)
ILSS was improved from 30 to 43-46 Mpa (+43-45%)

- As reported from the field, some « old » reference sizings confirmed to be very sensitive to storage conditions (especially temperature) and demonstrated significant reduction of Inter Fiber properties over time.
- The newly developed sizings demonstrate much reduced degradation over time in rovings and fabrics forms on Advantex and HiPer-tex glasses. They are much less sensitive to temperature, and provide significantly higher initial Inter Fiber Strength.
- After 2 years of storage at normal « western storage conditions », these new sizings still demonstrate excellent Inter Fiber properties.
- Degradation in hot and humid environment (high amount of water in the air) is still happening most likely at the interface at the glass (hydrolysis of silane)
 - ✓ Tight packaging can help => ! water might still diffuse through
 - ✓ Controlled moisture level can help (i.e. < 25gr H₂O / Kg = 35C / 70%RH)
- Newly developed sizings ensure better laminate properties consistency

Thank you for your attention

