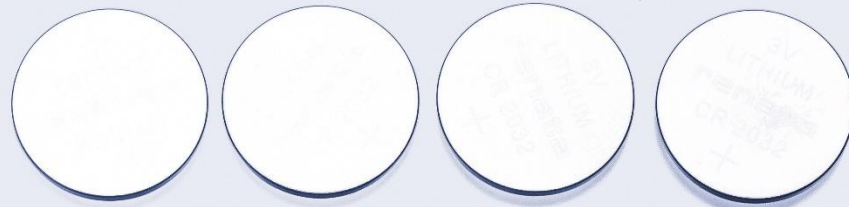


FIBRILLATION ABILITY OF PTFE BINDERS AND PREMIXES DETERMINED WITH SMALL-VOLUME SAMPLES IN A RHEOMETER

HELENA WEINGRILL, TAMARA EBNER,
AHMED ELABD, ABHI SHETTY

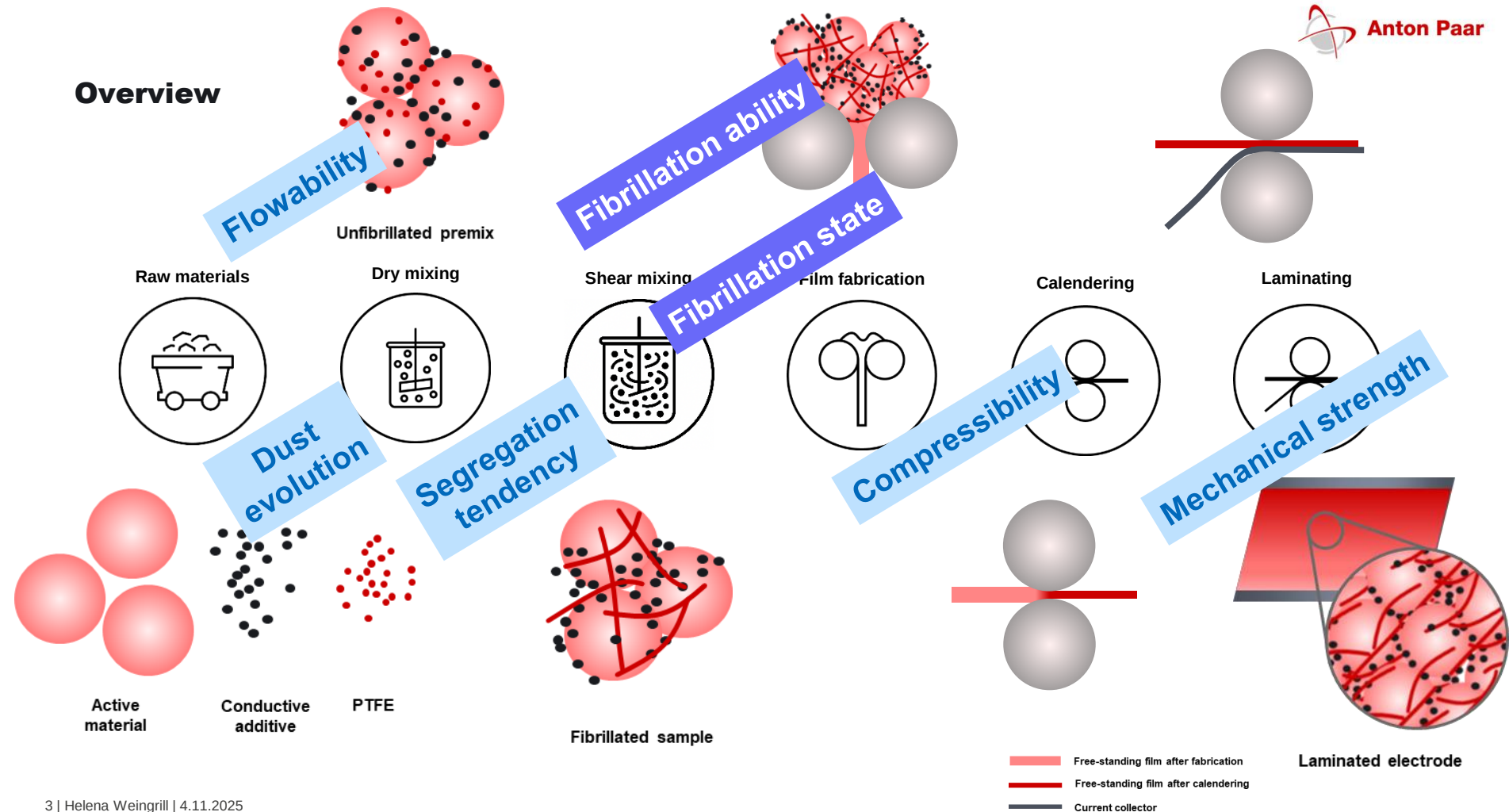


Why use a rheometer?

- › Highly sensitive device for characterizing materials in motion
- › Detects structural change of moved materials
- › Controlled atmosphere (temperature, humidity, ...)
- › Process imitation
- › **Small sample quantities**



Overview



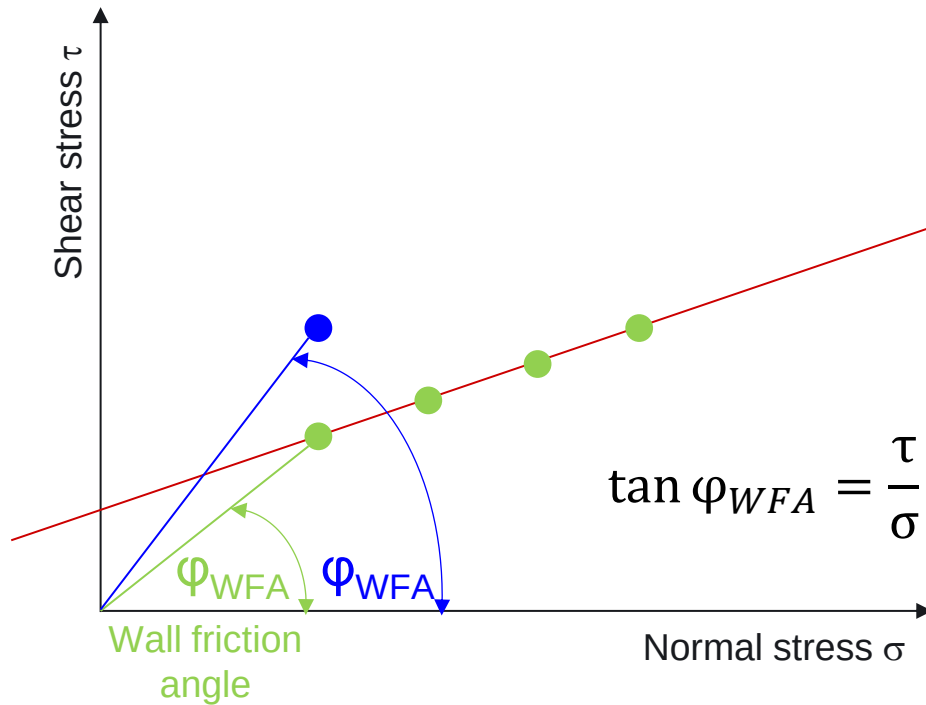
Fibrillation ability of PTFE

Wall friction

- > Friction between powder and any wall material
- > “When does something get sticky?”



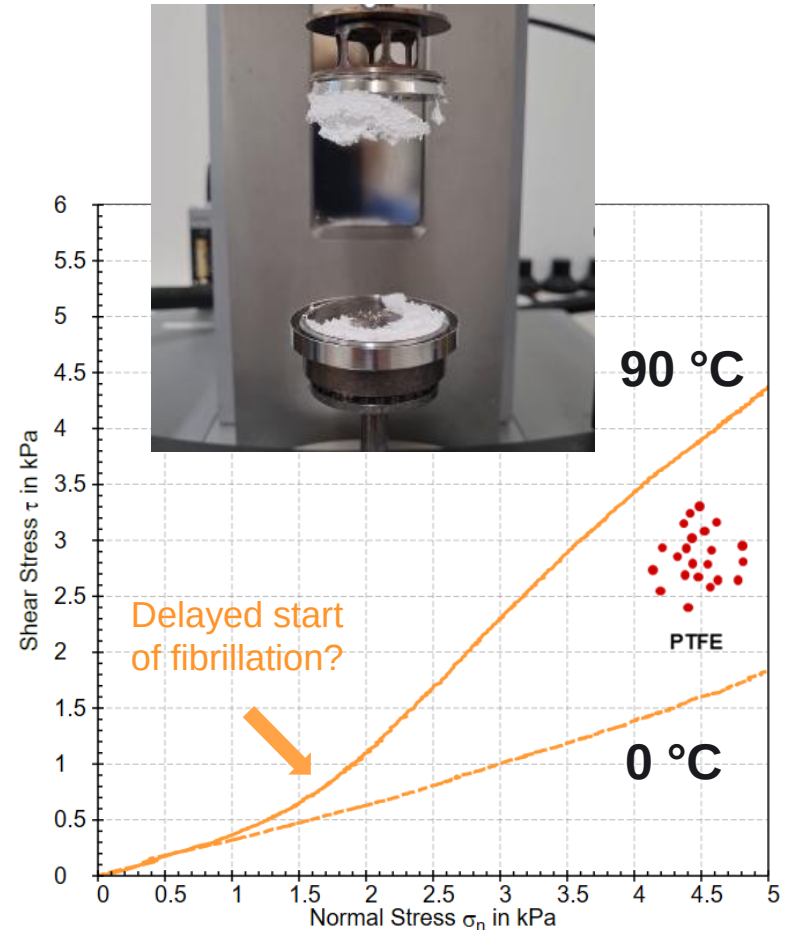
Wall friction



Wall friction stress ramp

- > Increase of normal stress from 0 kPa to 5 kPa at constant temperature
- > At 0 °C: Constant increase in shear stress with increasing normal stress
- > At 90 °C: At approx. 1.7 kPa normal stress, change in shear stress evolution

→ Stress minimum to induce fibrillation?



Wall friction stress ramp

Different binders

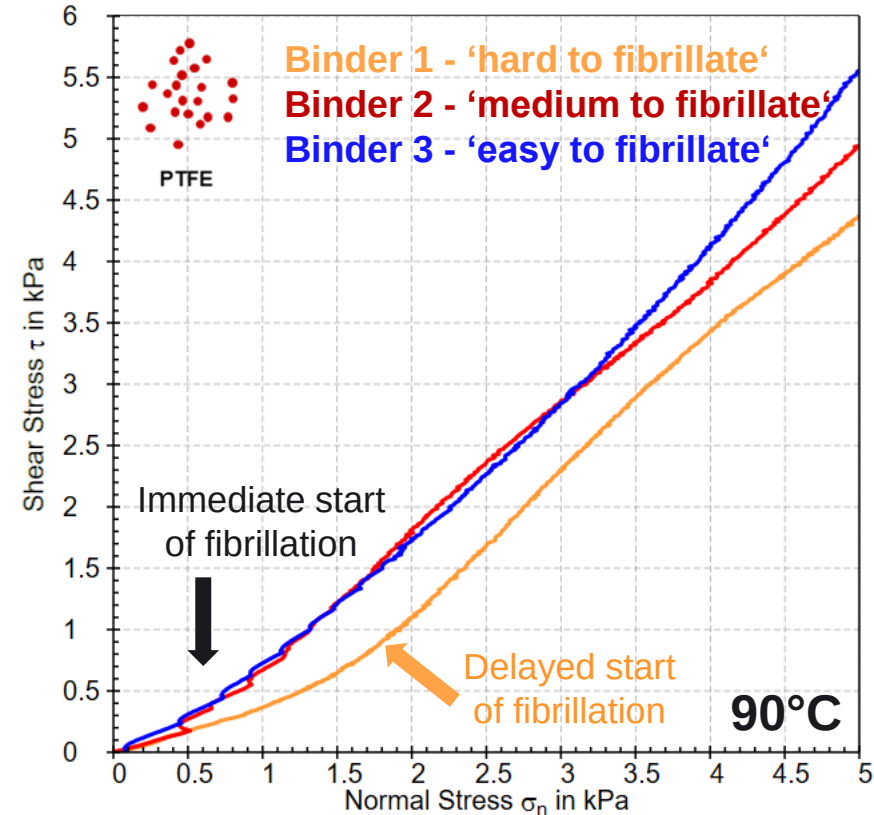
- > 3 differently synthesized PTFEs that differ in their ease to fibrillate according to the producer
- > Tested at 0°C and 90°C
- > 0.1 kPa up to 5 kPa normal stress
- > 0.05 rpm

Binder	Binder processability
1	Hard to fibrillate
2	Medium to fibrillate
3	Easy to fibrillate

Wall friction stress ramp

Different binders

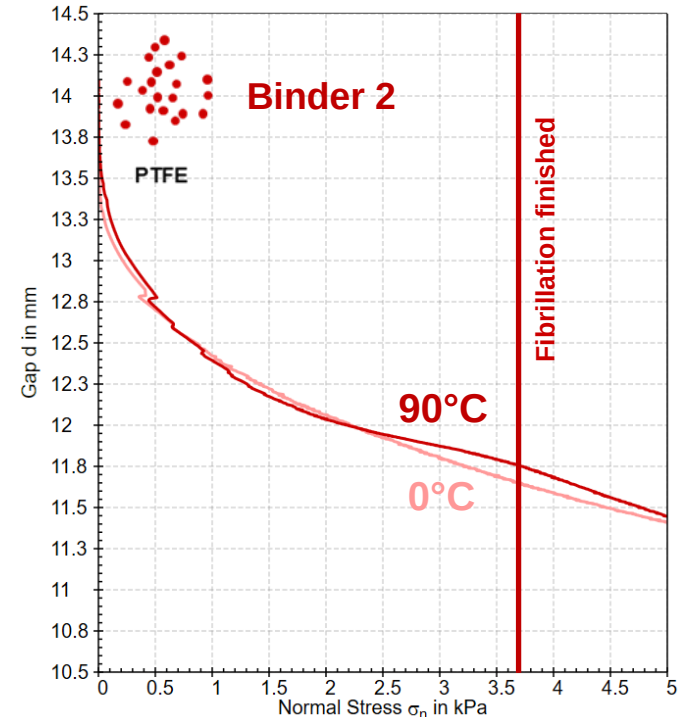
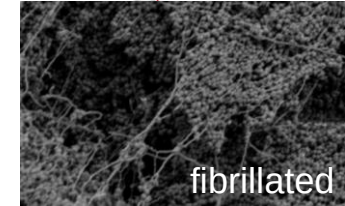
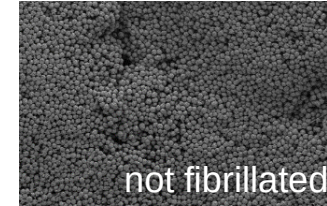
- > **Binder 1** shows „lag“ in fibrillation
 - certain stress condition needed to start fibrillation
 - aligns with manufacturer indication “**hard to fibrillate**”
- > **Binder 2** and **3** show similar wall friction/fibrillation behavior
 - immediate start of fibrillation
 - aligns with manufacturer indication “**medium** and **easy to fibrillate**”
- > However, shear stress signal only cannot differentiate “**medium** and **easy to fibrillate**”



Wall friction stress ramp

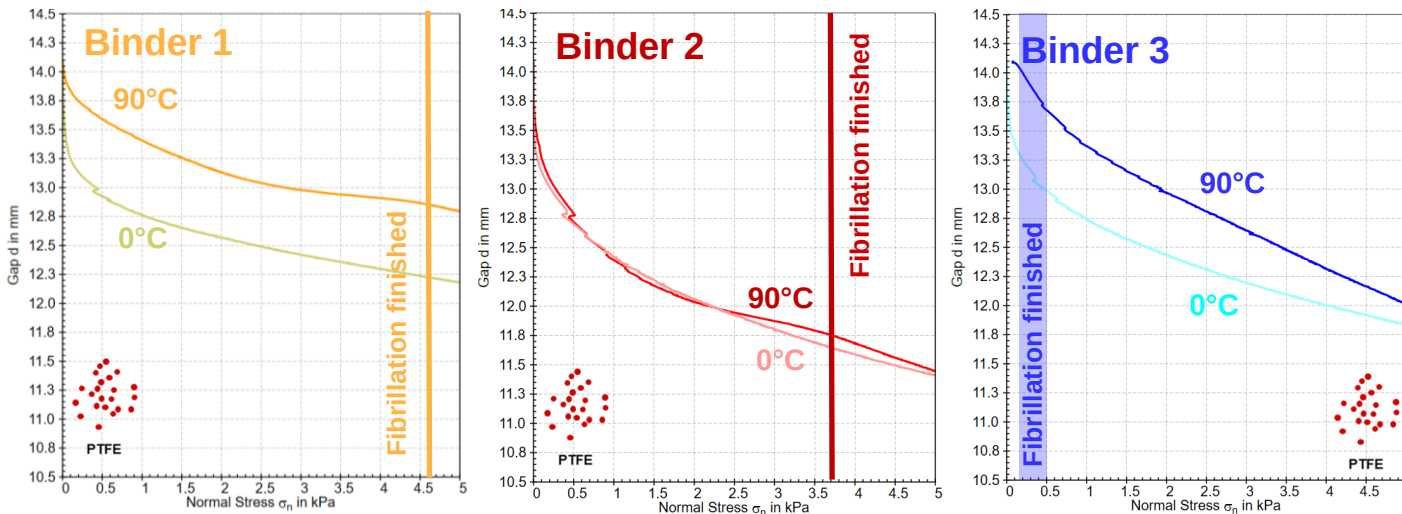
Change in volume

- › Fibrillation is also accompanied by increase in volume
 - represented by change of gap size during measurement
- › At 0 °C the volume decreases continuously due to continuous increase in normal stress
- › At 90 °C two mechanisms counteract
 - › Volume decrease due to increasing normal stress
 - › Volume increase due to fibrillation induced by shearing (PTFE fibrils increase occupied volume)
- › After reaching 3.7 kPa, the course of the curve at 90 °C resembles that of the curve at 0 °C again
 - fibrillation is finished



Wall friction stress ramp

Different binders – change in volume



Binder	Ease of fibrillation	Normal stress at which fibrillation is finished [kPa]
1	Hard	4.6
2	Medium	3.7
3	Easy	0.1–0.5

FIBRILLATION ABILITY OF PTFE IS MEASUREABLE VIA WALL FRICTION

Fibrillation ability of (anode) premixes

Measuring geometry - the graphite challenge

- › Graphite is slippery → wall friction geometry “polishes” premix but does not transfer shear stress to premix
- › Increased grip with shearing geometry → fibrillation takes place only at fin tops
- › Graphite is also fluffy → material is pushed out when applying more normal stress

→ How do we get the premix sheared to induce fibrillation (and characterize its mechanism)?



Measuring geometry

- › Increased shearing surface with large plate
- › Profiled plate for enhanced grip to overcome graphite's slippery character
- › Minimize gap between cup and measuring geometry to limit material build-up
- › **Measuring geometry is ready to go!**

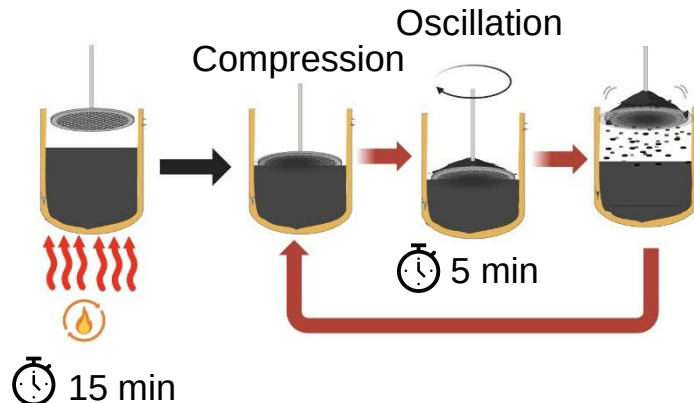
Experimental

- > 2 graphite types: artificial & natural
- > 2 PTFE types: 'easy-to-fibrillate' & 'hard-to-fibrillate'
- > 1 carbon black type

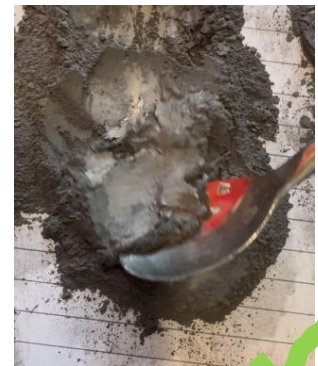
97.5 wt%
 1.5 wt%
 1 wt%

4 anode premixes

> Fibrillation procedure

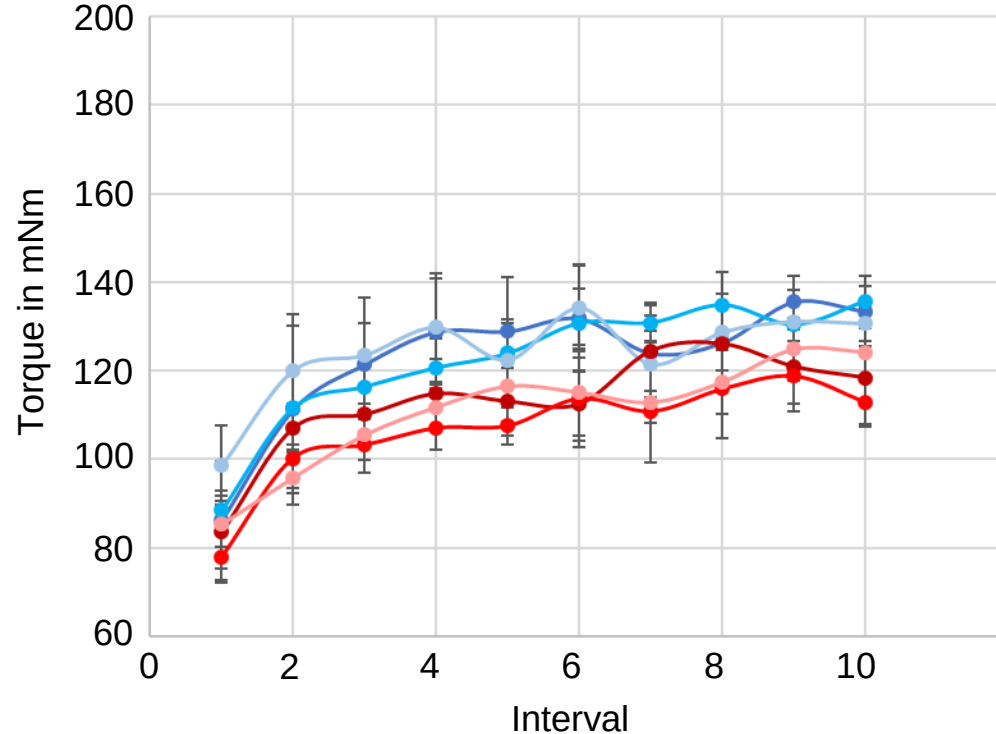


> Fibrillation verification



Spooning test

Short trials at 5 °C



Successful fibrillations:

'Easy' binder / natural graphite : 0/3

'Hard' binder / natural graphite: 0/3

No binder / natural graphite: 0/3

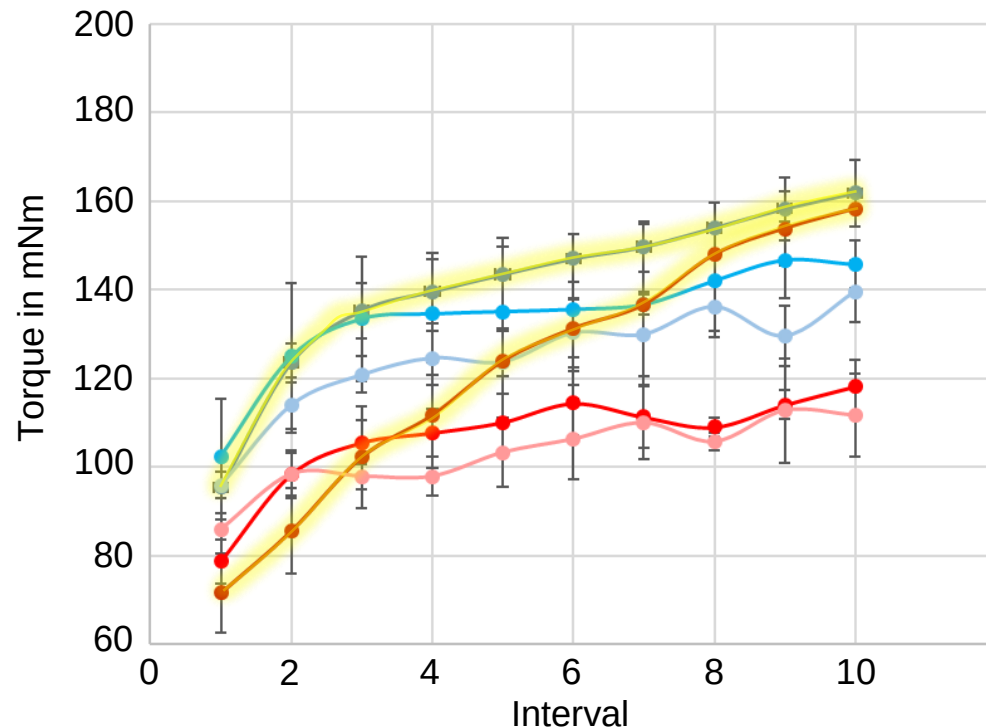
'Easy' binder / artificial graphite: 0/3

'Hard' binder / artificial graphite: 0/3

No binder / artificial graphite: 0/3

No fibrillation as expected at 5 °C

Short trials at 70 °C



Successful fibrillations:

'Easy' binder / natural graphite : 3/3

'Hard' binder / natural graphite: 0/3

No binder / natural graphite: 0/3

'Easy' binder / artificial graphite: 3/3

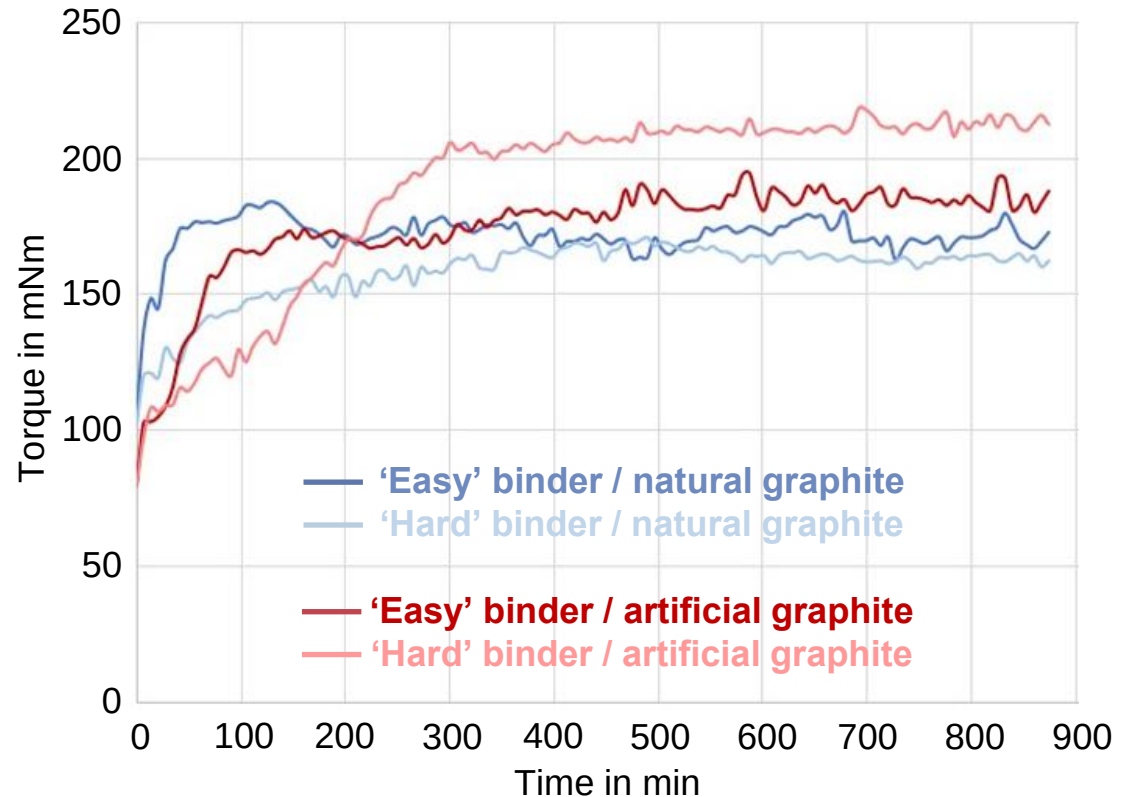
'Hard' binder / artificial graphite: 0/3

No binder / artificial graphite: 0/3

Fibrillated samples show highest torque signal after 10 intervals!

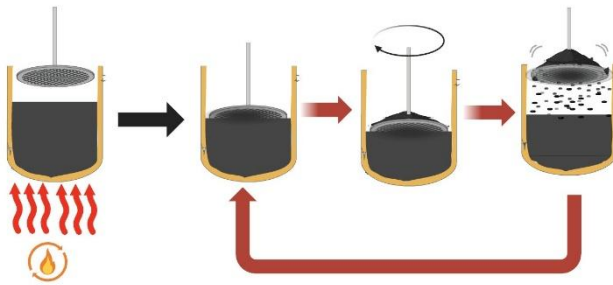
Long trials at 70 °C

- › 120 intervals – double determination
- › All samples fibrillated after 120 intervals
- › Initial slope comes from binder type
 - › Steep for 'easy' binder
 - › Flat for 'hard' binder
- › Starting torque signal comes from graphite type
 - › Higher for natural graphite
 - › Lower for artificial



To sum up

- > Fibrillation of premixes successfully performed in rheometer
- > Torque signal as most promising metric to characterize fibrillation
- > However, measuring system needs to be optimized
 - higher resolution of structural changes



Fibrillation procedure



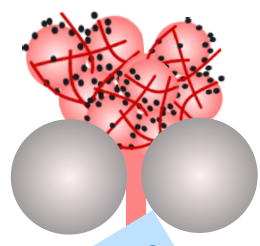
Material build-up during fibrillation procedure

Fibrillation state

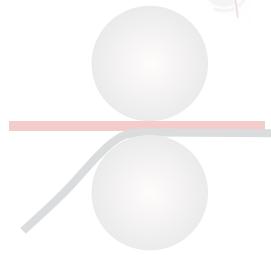
Materials used



Unfibrillated premix



Fibrillation state



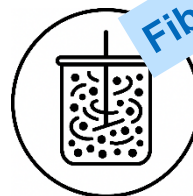
Raw materials



Dry mixing



Shear mixing



Film fabrication



Calendering



Laminating



Active material



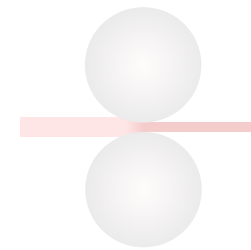
Conductive additive



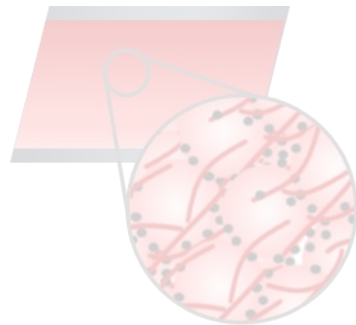
PTFE



Fibrillated sample



- Free-standing film after fabrication
- Free-standing film after calendaring
- Current collector



Laminated electrode

Why important?

- Multiple material grades and process equipment available → successful fibrillation difficult to predict
- Need for an (automated) verification test if fibrillation was successful (to replace “spooning test”)



1) place processed powder on paper towel



2) compress and shear powder



3) start scooping powder



4) scoop powder

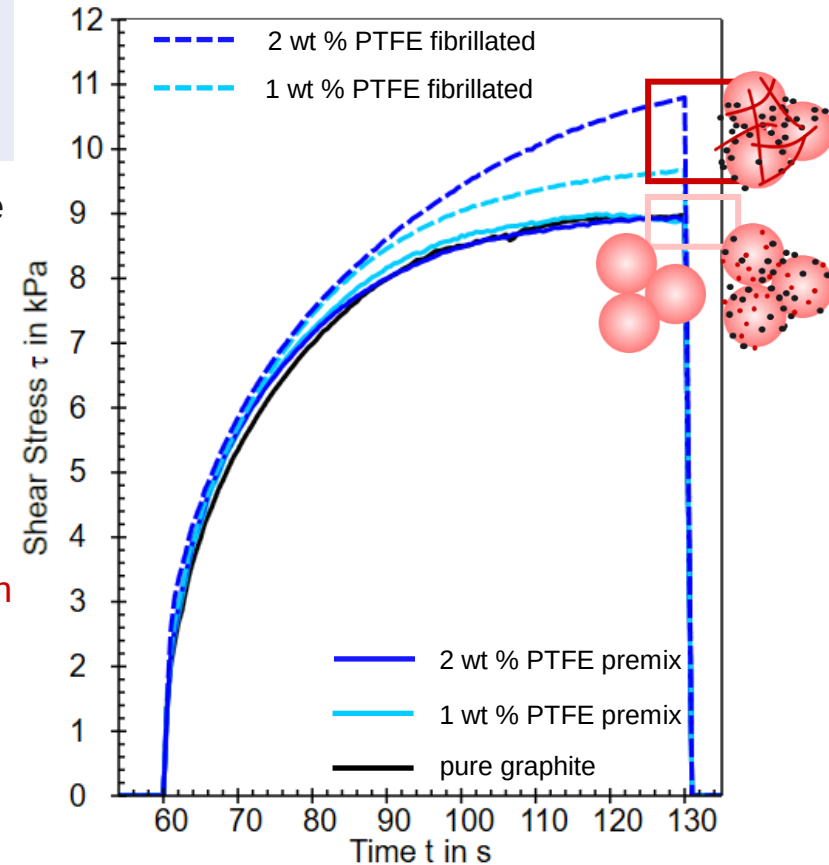


5) successfully fibrillated?

Internal friction



- > “Quick-and-dirty” shear test for determining fibrillation state
 - > Pure graphite vs. unfibrillated vs. fibrillated samples
 - > Shearing under at 15 kPa normal stress
 - > Shear stress at end of preshear interval
- > Graphite and unfibrillated premixes show same internal friction
- > Fibrillated samples show significantly higher internal friction
- > Extent of internal friction correlates with
 - > State of fibrillation
 - > Content of PTFE fibrils



FIBRILLATION STATE CAN QUICKLY (AND AUTOMATICALLY) BE DETERMINED

Conclusion & outlook

- **PTFE fibrillation ability** can be characterized via **temperature-controlled wall friction measurements**
- **Premix fibrillation ability** can be characterized via a **temperature-controlled material-circulating procedure**
 - Measuring geometry is being optimized!
- **Fibrillation state** of processed premix can be determined via **accelerated & shortened shear test**



**Thank you for listening
Your questions?**