From melt to fibers

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Aalborg University, Denmark

ICG Spring School, Glass for a sustainable future, Lloret del Mar, Spain, April 29 – May 03, 2024

Outline of my talk

1. Background
2. Fiber spinnability of a melt
   - I. Glass-forming ability
   - II. Melt dynamics (liquid fragility and viscosity)
   - III. Glass fiber spinnability
3. Fracture of fibers and fiber mat
4. Challenging questions….

*We focus on **glass fibers for reinforcement and insulation**.*
We also consider general aspects of glass fibers.

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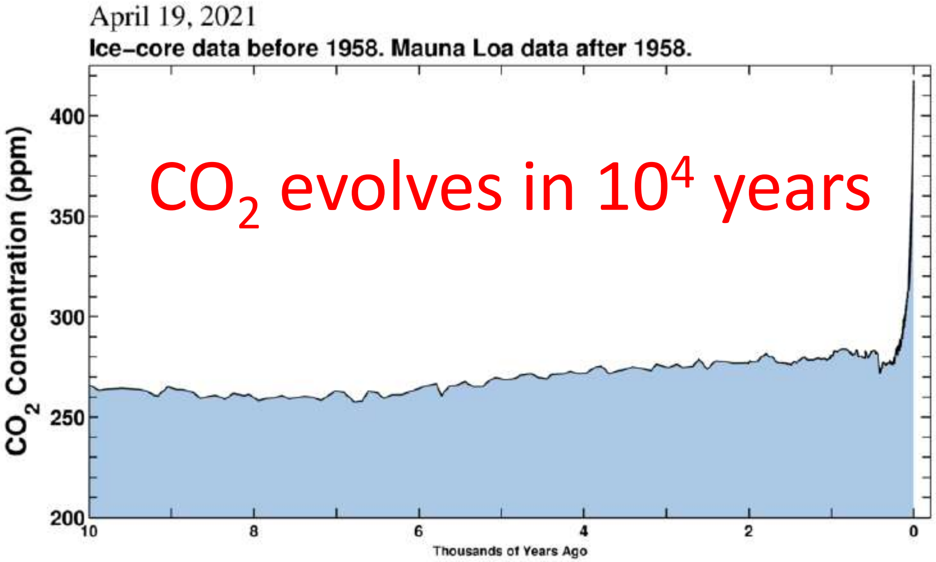
Climate change is real and man-made!
To mitigate this, we need glass fibers……

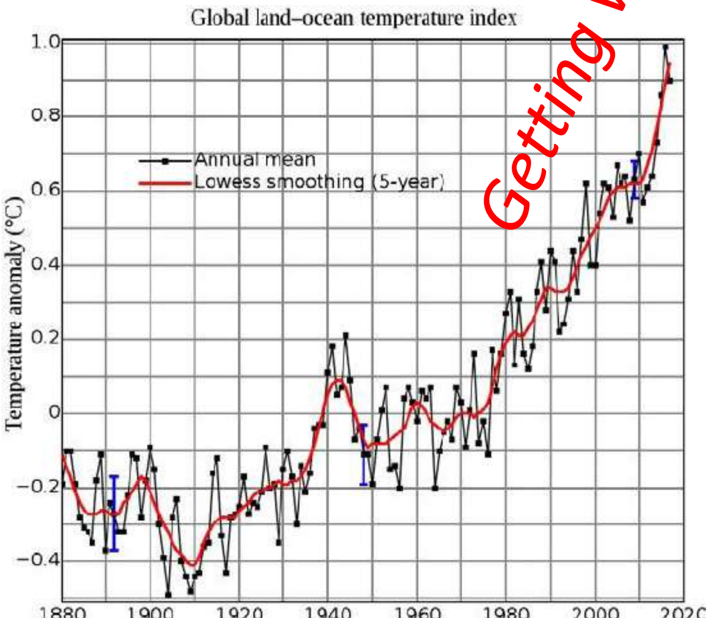
Winter

Summer

Getting warmer drastically!!



CO_2 evolves in 10^4 years



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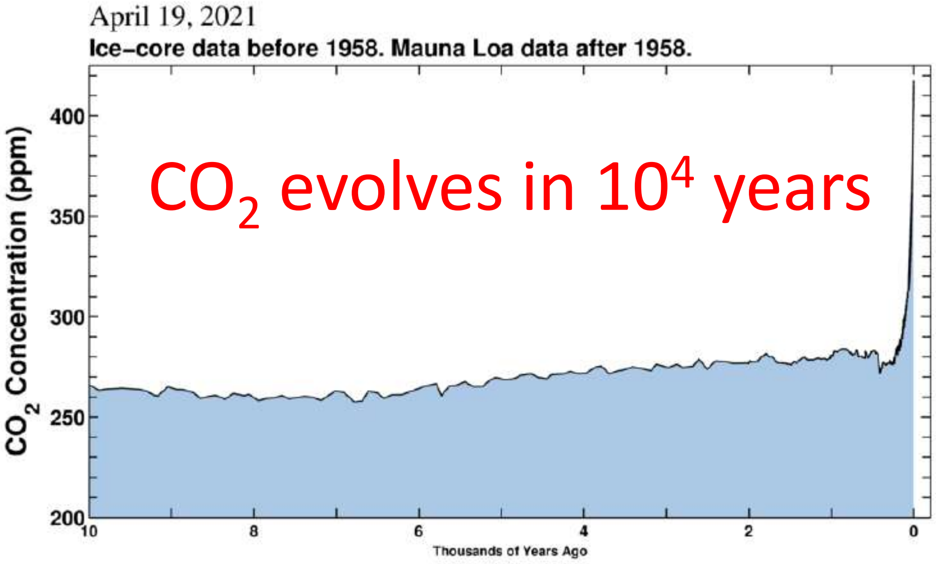
To mitigate this, we need glass fibers……

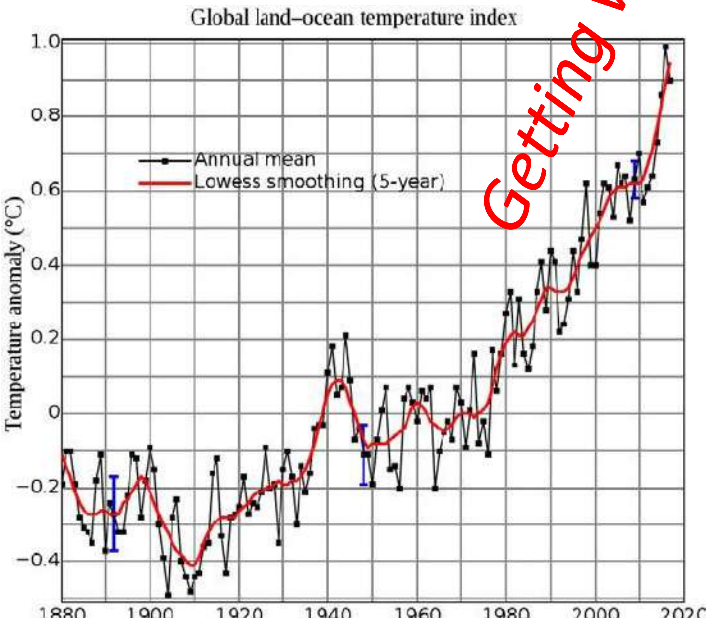
Summer☹

Winter☹

Getting warmer drastically



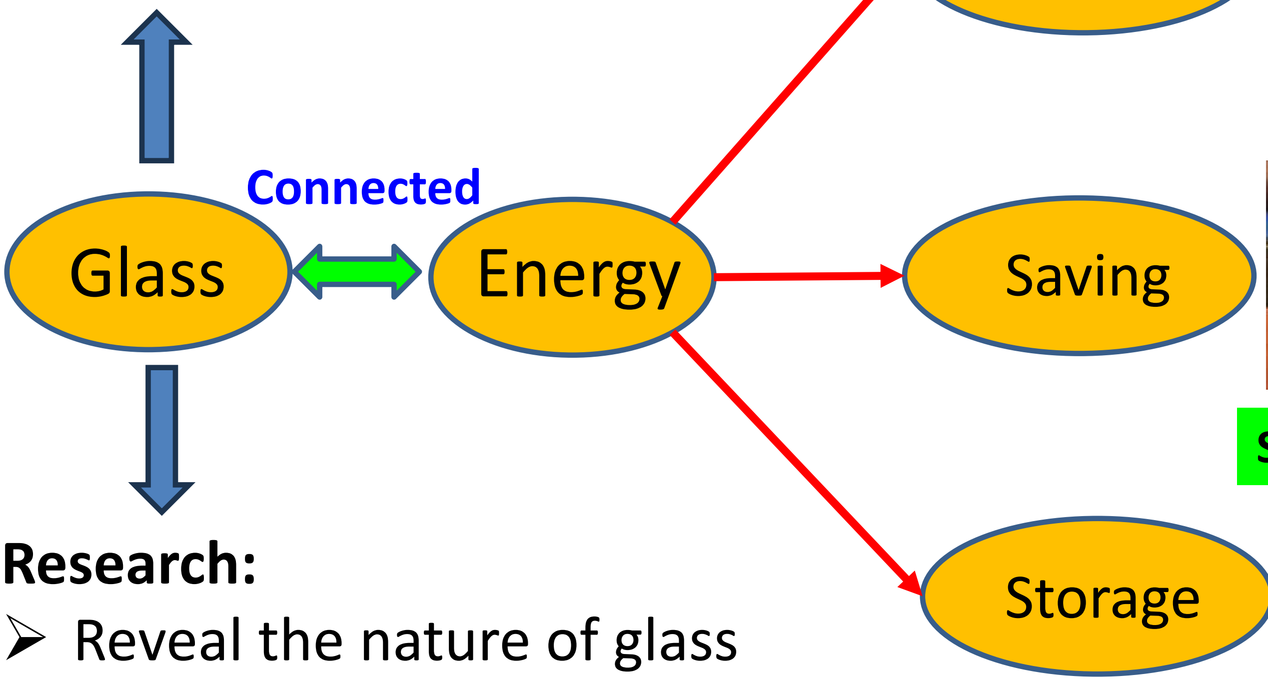
CO$_2$ evolves in 10^4 years



Apart from basic research, my team is dedicated to advancing green energy solution **using glass**!

Impact:

- Mitigate climate change
- Make all sustainable



Glass

Connected

Energy

Generation

Saving

Storage

Green energy

Stone wool

Glass foam

Research:

- Reveal the nature of glass
- Make better glasses

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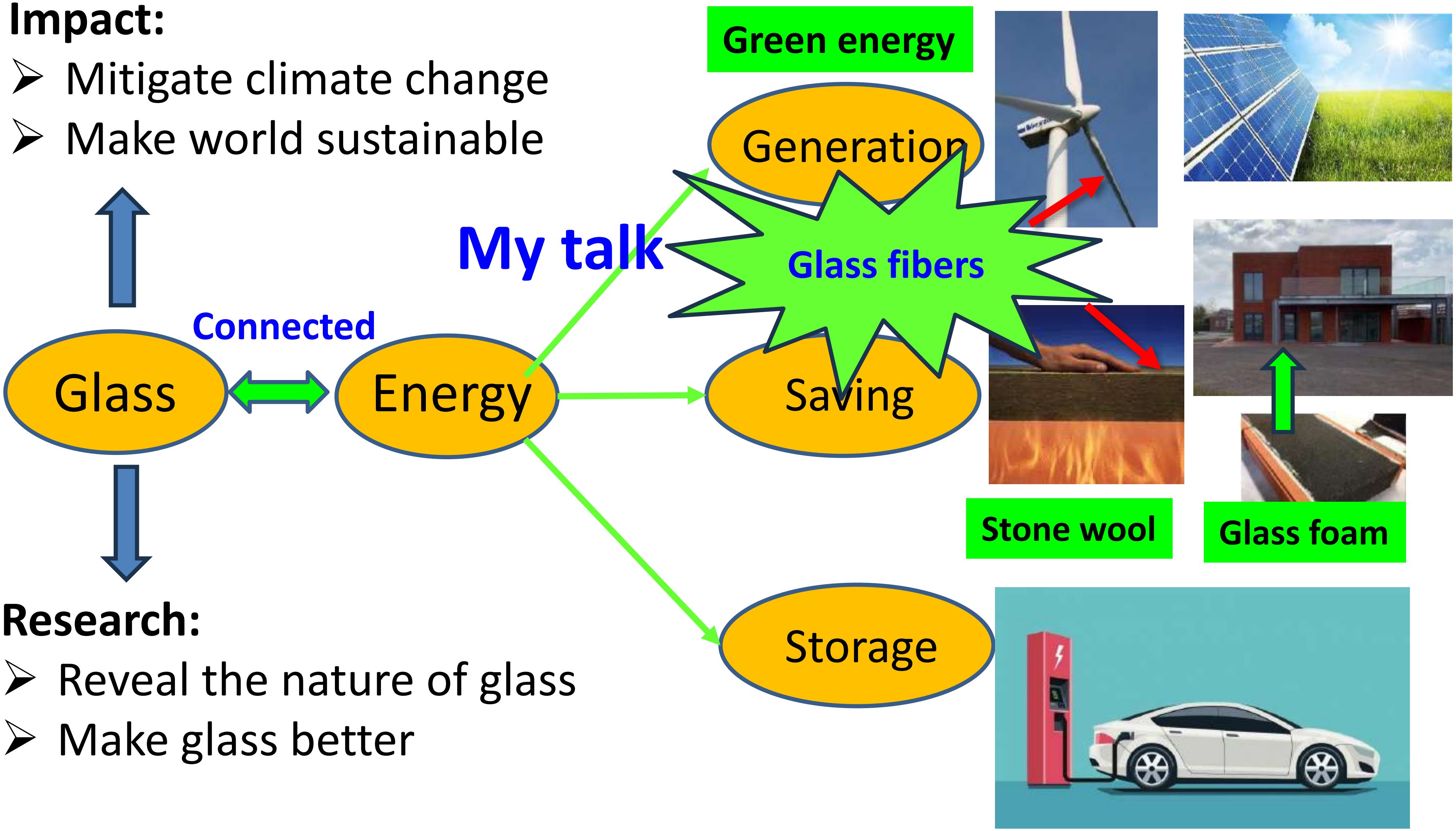

Impact:

- Mitigate climate change
- Make world sustainable

My talk

Connected

Glass

Energy

Green energy

Generation

Glass fibers

Saving

Storage

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Glass foam

Research:

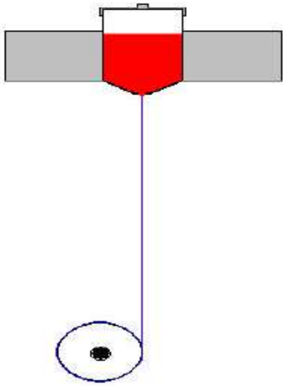
- Reveal the nature of glass
- Make glass better

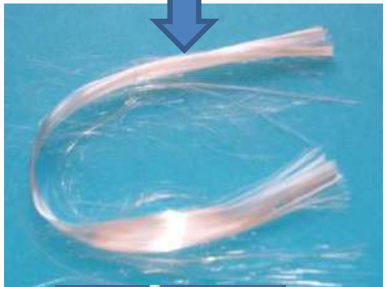
Fiberizing processes and fiber applications

Cascade

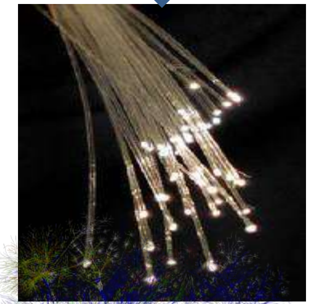
Rotary

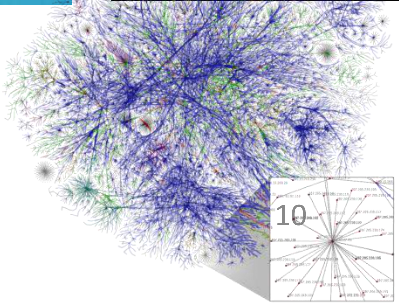
Cucible





Preform





To produce 'good and green' glass fibers, the following conditions should be fulfilled:

Melt should be vitrifiable

Melt should be spinnable

Spinnability is measurable

Spinnability are predictable

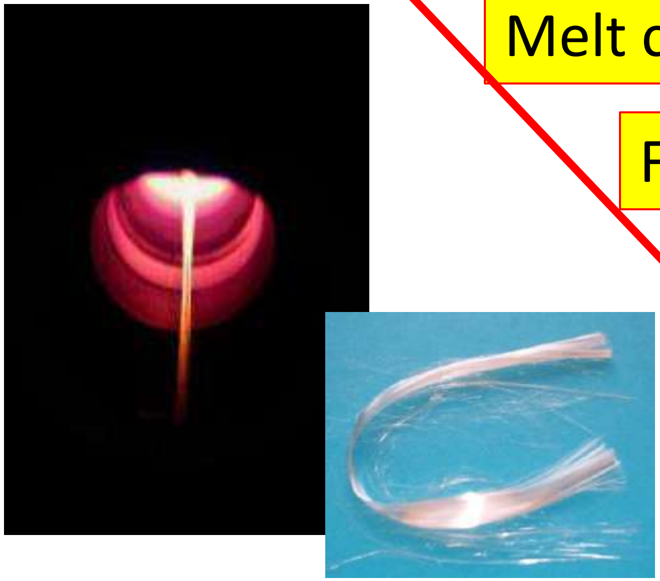
Melt converts into strong fibers

Fiber should be thermally stable

Melting should be energy-effective

Process should be stable & smart

Then one will be happy☺



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High glass-forming ability

$\eta\,(T_m)$ might be the best criterium, as it can be measured for all liquids.

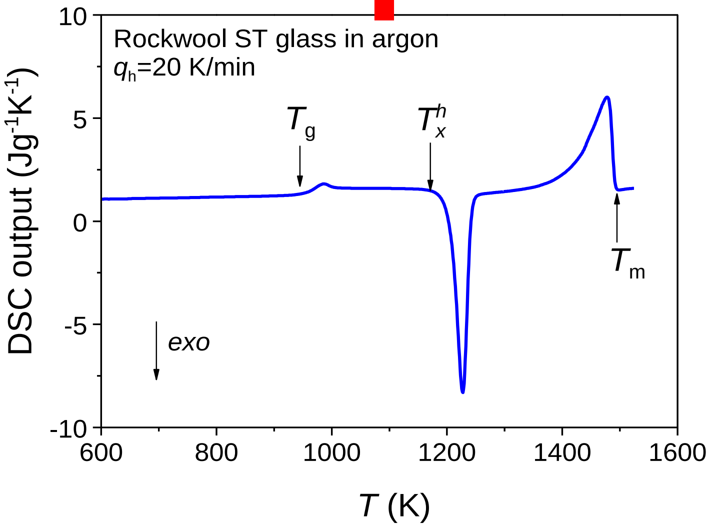
High critical cooling rate (q_c) in TTT diagram

High glass stability

high T_g/T_m and $\eta\,(T_m)$

Hruby parameter $K_H = \dfrac{T_x^h - T_g}{T_m - T_x^h}$

K_H cannot be obtained for **extremely poor glass formers**, e.g., water, due to the overlap of crystallization with glass transition.



K_H cannot be obtained for **good glass formers**, e.g., silica, due to absence of crystallization peak.

Zheng, Zhang, Montazerian, Gulbiten, Mauro, Zanotto, Yue*, *Chemical Reviews* 2019

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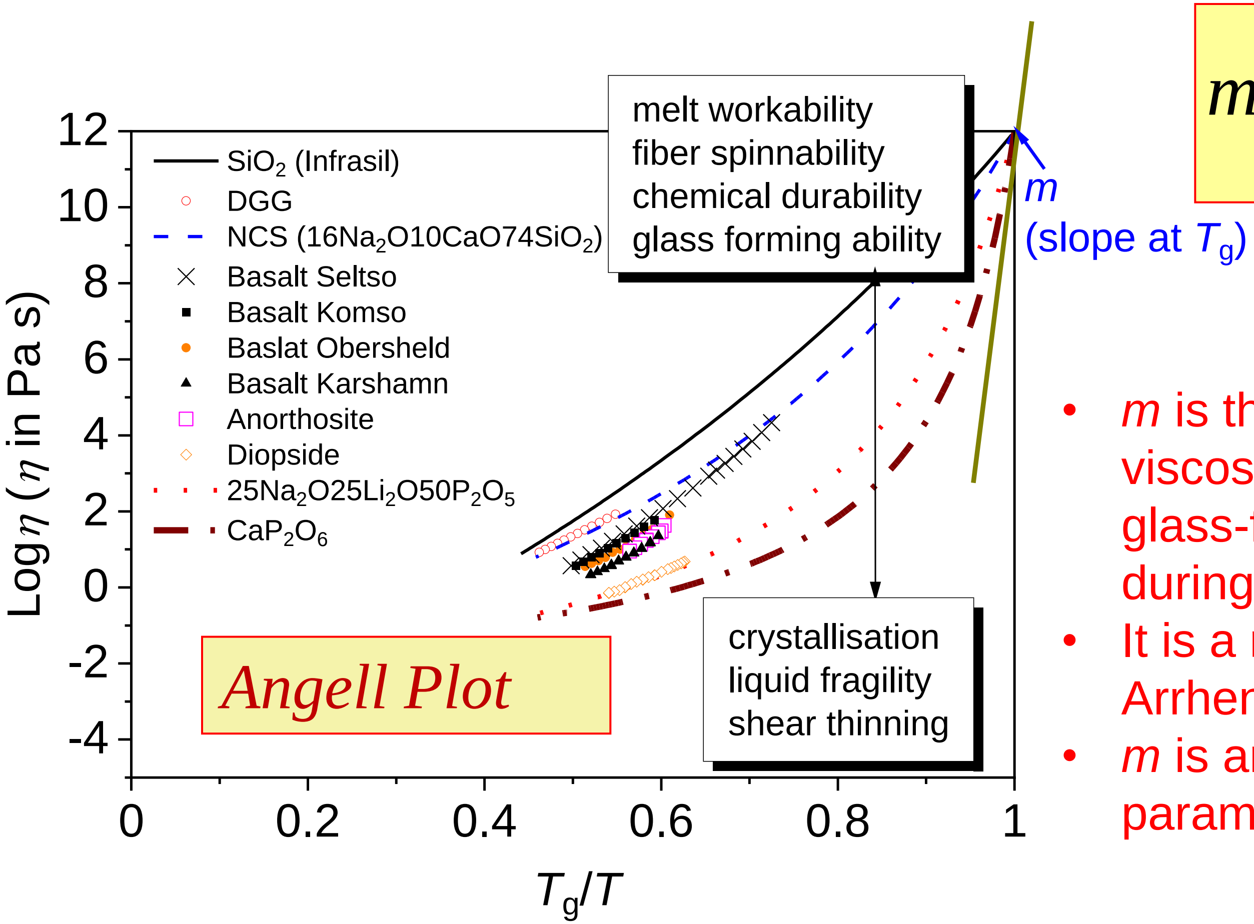
Liquid fragility (a measure of the non-Arrhenian behavior)
A crucial dynamic parameter for fiber drawing

It is quantified by the kinetic liquid fragility index *m*.

$$m = \left.\frac{d\log\eta}{d(T_g/T)}\right|_{T=T_g}$$



- *m* is the rate of the change of viscosity or relaxation time of a glass-forming liquid at T_g during cooling or heating.
- It is a measure of the non-Arrhenian behavior
- *m* is an important dynamic parameter

The Mauro-Yue-Ellison-Gupta-Allan (MYEGA) Model can be used to describe melt dynamics

$$log_{10}\eta(T) = log_{10}\eta_\infty + \frac{K}{T}exp\left(\frac{C}{T}\right)$$

where η_∞ is the high temperature limit of viscosity, K and C are constants.

$$log_{10}\eta(T) = log_{10}\eta_\infty + (12 - log_{10}\eta_\infty)\frac{T_g}{T}exp\left[\left(\frac{m}{12 - log_{10}\eta_\infty} - 1\right)\left(\frac{T_g}{T} - 1\right)\right]$$

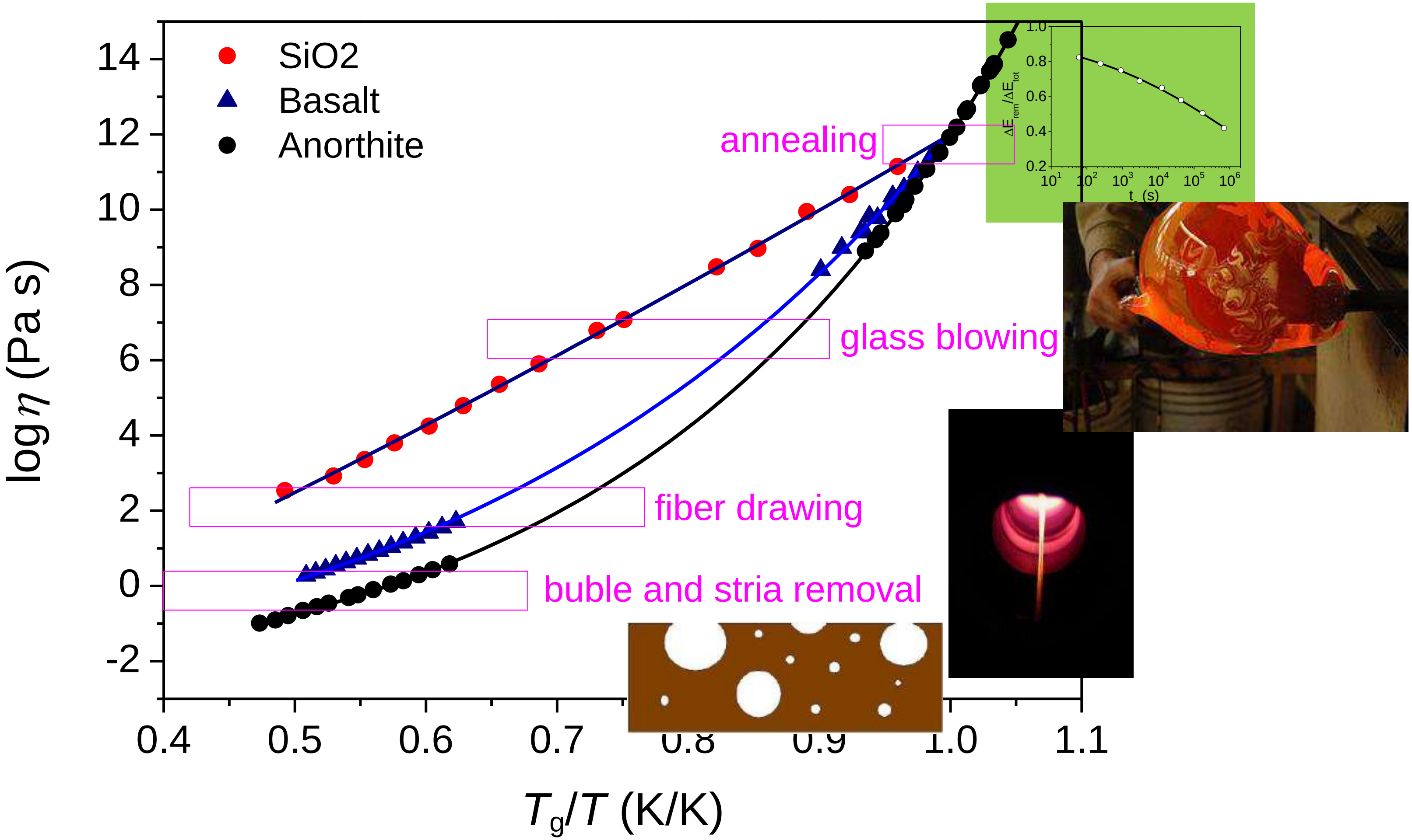
Mauro, Yue, Ellison, Gupta, Allan, *Proc. Nat. Acad. Sci. U.S.A.* **106** (2009) 19780

As $\log_{10}\eta_\infty$=-3 and $\log\eta$ (at T_g)=12, the MYEGA is simplified to:

$$log_{10}\eta(T) = -3 + 15\frac{T_g}{T}exp\left[\left(\frac{m}{15} - 1\right)\left(\frac{T_g}{T} - 1\right)\right]$$

Zheng, Mauro, Ellison, Potuzak, Yue, *Phys. Rev. B* **83** (2011) 212202

Importance of melt viscosity and liquid fragility to glass technology

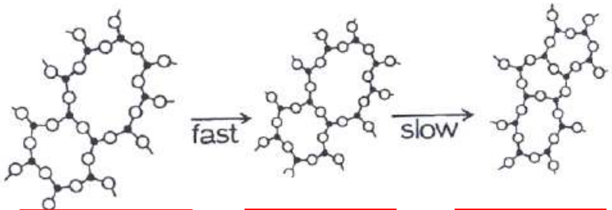


Continuous fiber drawing

Fast cooling (hyperquenching) (> 10^5 K/s)

Lower density
Larger $C_{p,exc}$
Larger ΔS_{excess}
Higher T_f

than bulk glass



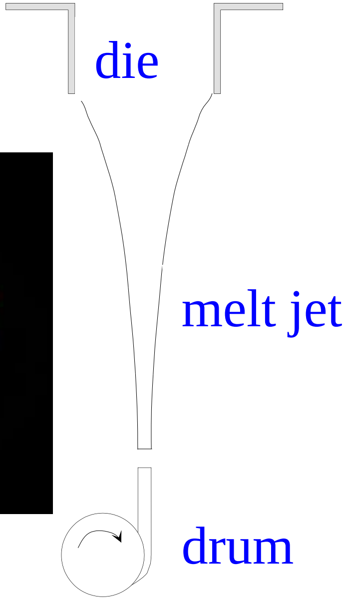
liquid

fiber

Bulk

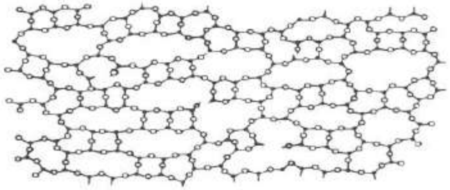
Heterogeneity

1200-1300°C melt



Large axial stress hyper-stretching (> 60~70 MPa)

Non-Newtonian flow
Oriented structure
Large ΔS_{excess}
Oriented defects

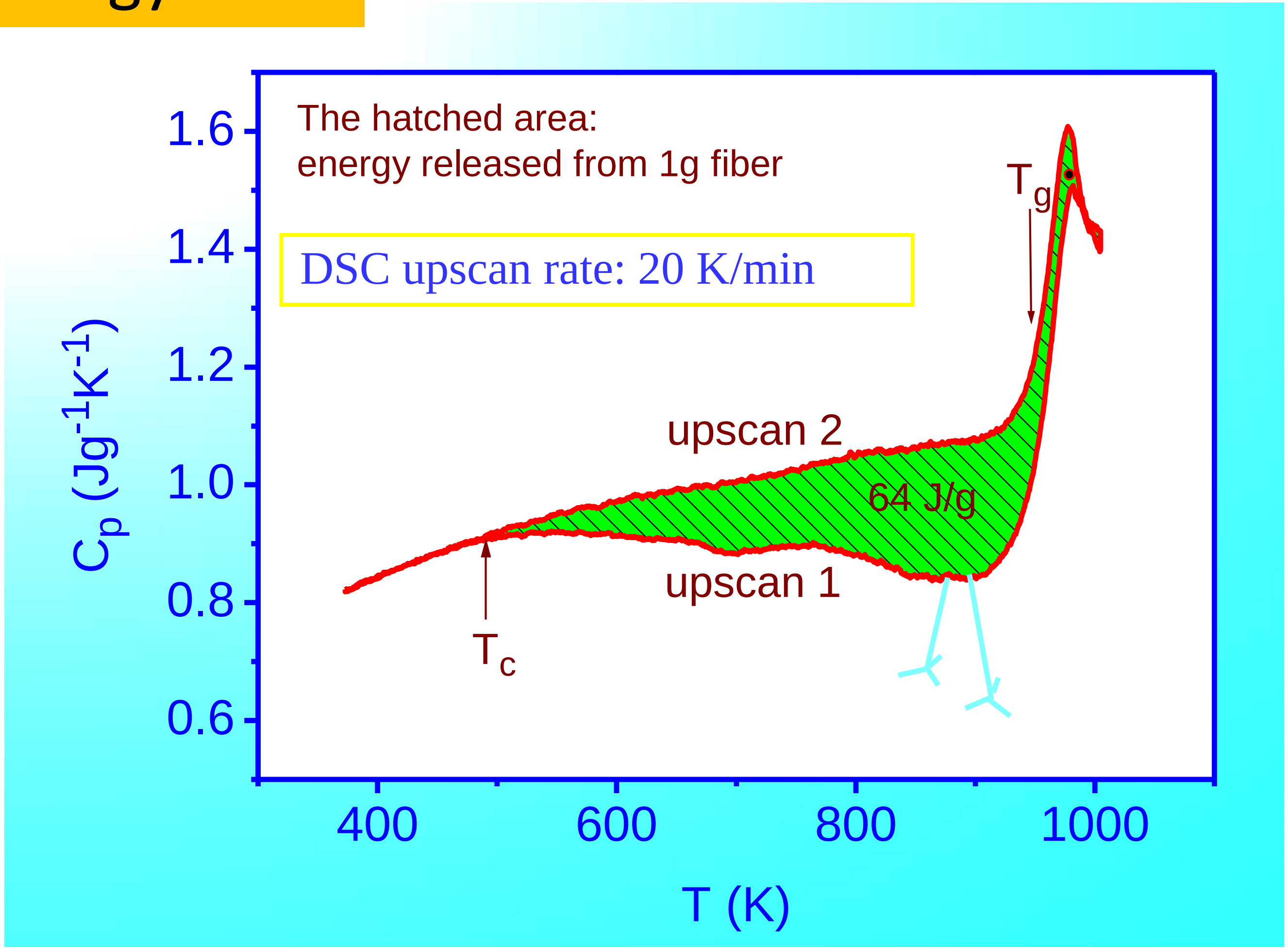


Extraordinary properties compared to bulk glass!

Surface

Heat capacities of stone wool (cooled at 10^6 K/s)

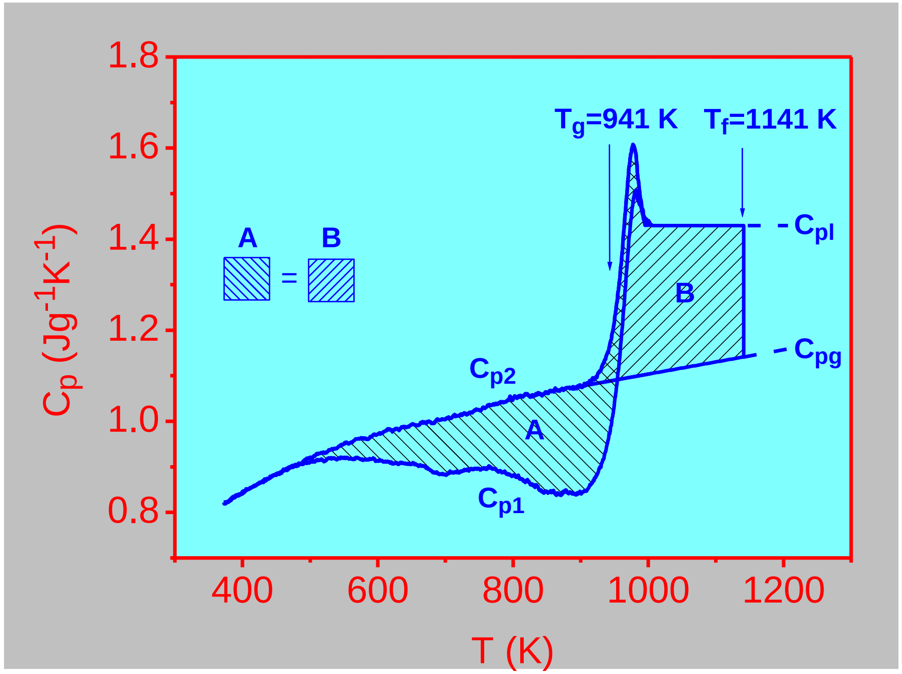
Energy ‘bird’

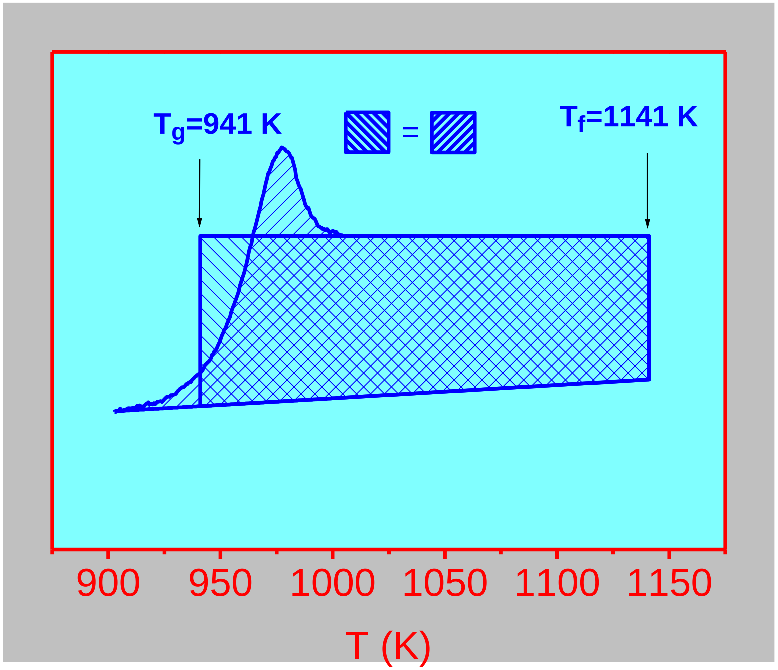


Yue, et al., *APL* 2002; *JCP* 2024

Yue and Angell, *Nature*, 2004

Determination of the glass transition (T_g) and the fictive temperatures (T_f)



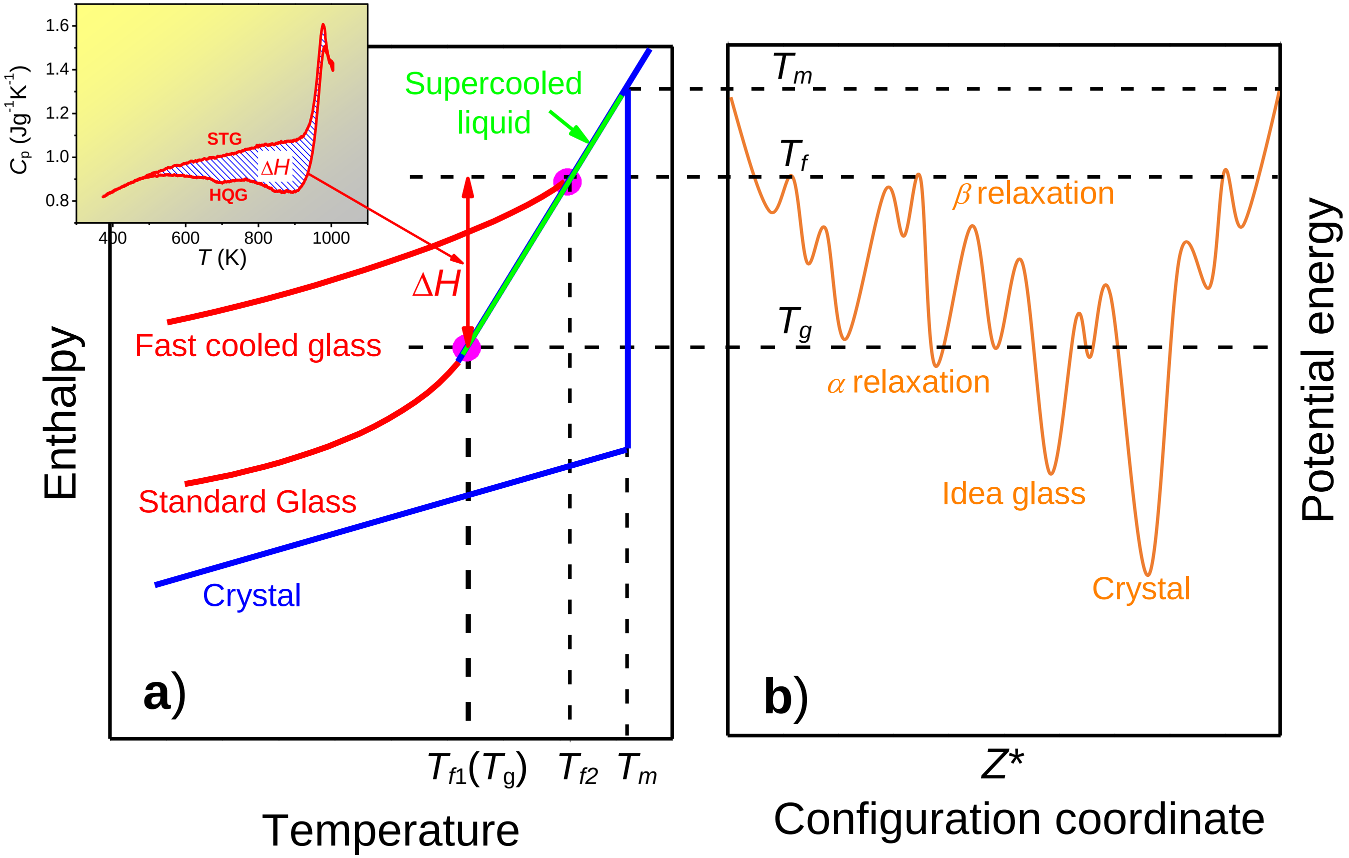


Basic equation: $$\int_{T_c}^{T_{eq}} (C_{p2} - C_{p1})dT = \int_{T_g}^{T_f} (C_{pl} - C_{pg})dT$$

$$C_{pg} = a + bT + c/T^2 + d/T^{0.5}$$

Y. Z. Yue, et al., *Chem. Phys. Lett*. 2002; *J. Chem. Phys*. 2004

Quenching, relaxation and phase transition in melt/glass



Zheng, Zhang, Montazerian, Gulbiten, Mauro, Zanotto, Yue*, *Chemical Review* 2019

Yue, *J. Non-Cryst. Solids* 2022

Change of viscosity during fiber spinning for a basaltic melt

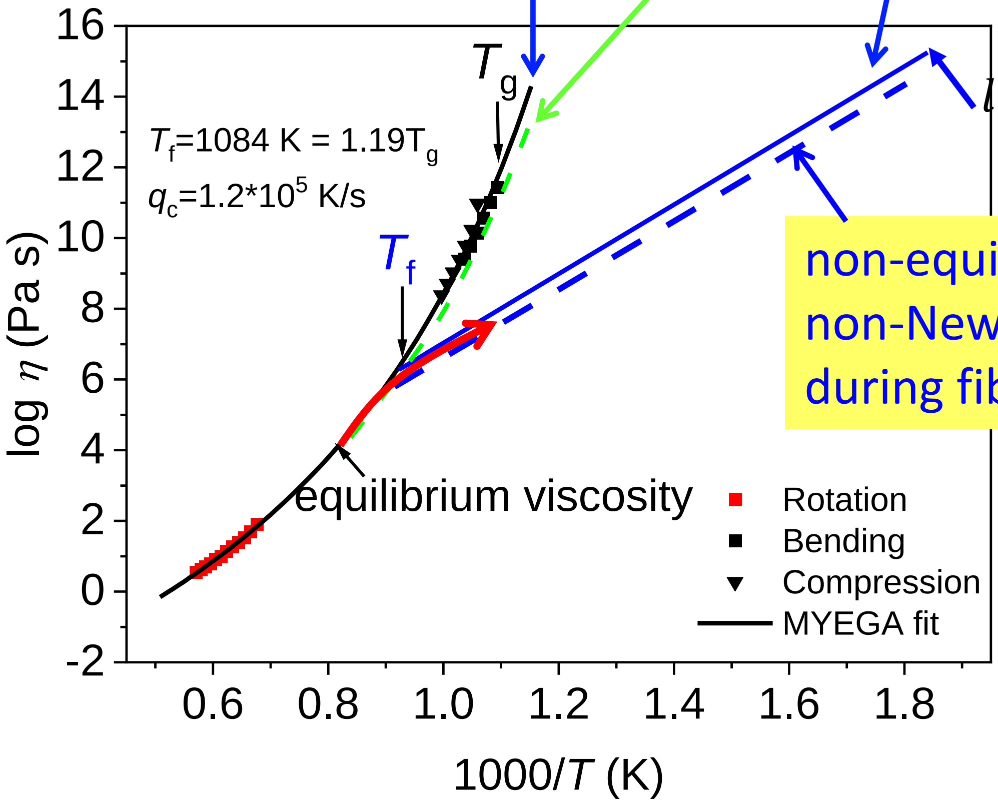
MYEGA equation:

$$log\eta = log\eta_\infty + \frac{K}{T}\exp\left(\frac{C}{T}\right)$$

Equilibrium, Newtonian flow

Equilibrium, Non-Newtonian flow

Non-equilibrium flow



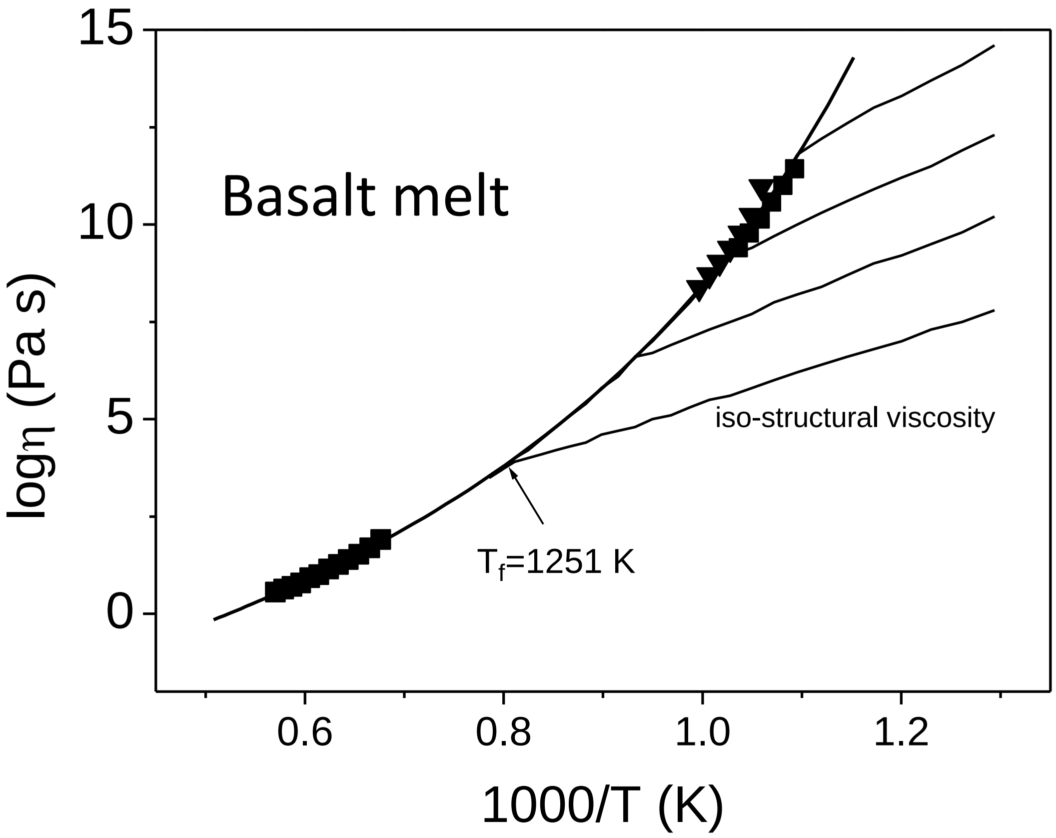
$$log\eta = log\eta_\infty + \frac{K}{T}\exp\left(\frac{C}{T_f}\right)$$

non-equilibrium, non-Newtonian flow during fiber drawing

Non-Netonian flow:
Yue, Brückner, JNCS 1994

Fiber drawing involves hyperquenching, large tension, heat dissipation, possibly non-Newtonian flow!

The iso-structure viscosity as a function of cooling rate or fictive temperature (T_f)



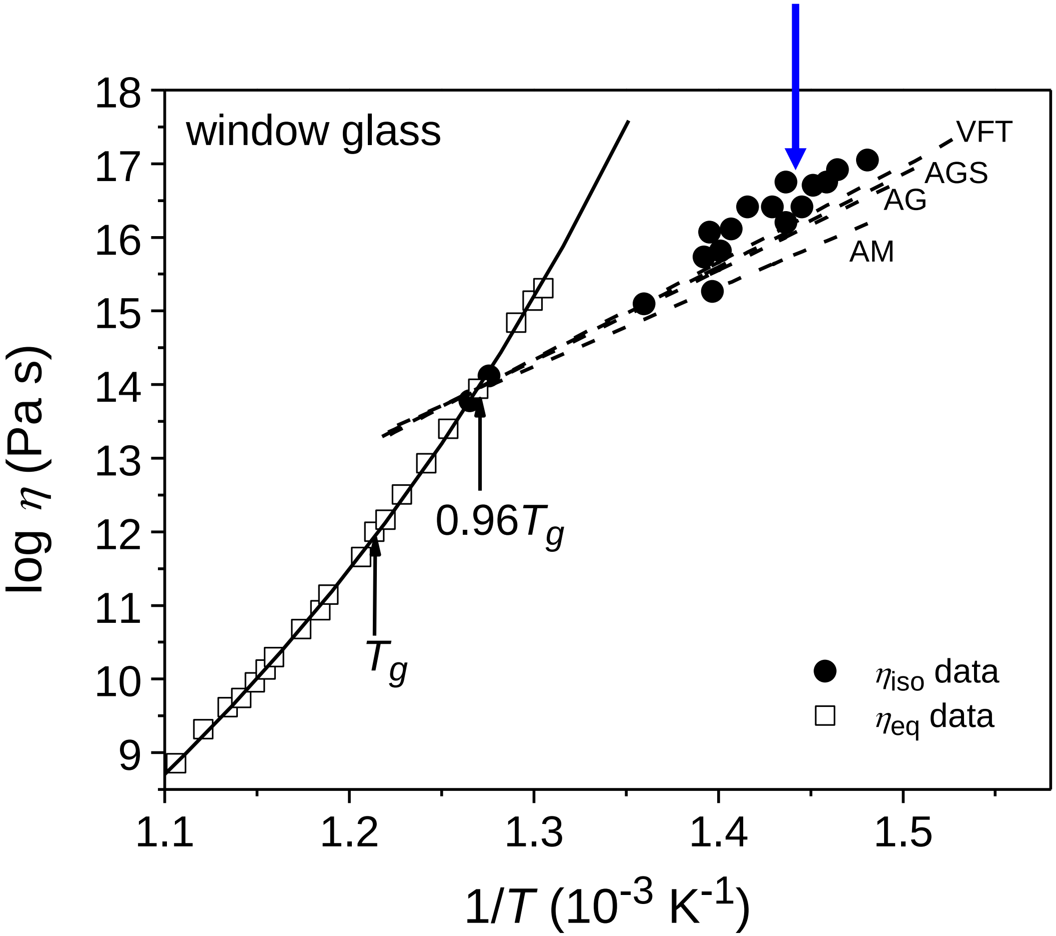
MYEGA equation:

$$log\eta = log\eta_\infty + \frac{K}{T}\exp\left(\frac{C}{T}\right)$$

When T=T_f,

$$log\eta = log\eta_\infty + \frac{K}{T}\exp\left(\frac{C}{T_f}\right)$$

Measured iso-structure viscosity data



Mazurin et al. *J. Non-Cryst. Solids* 1982

Yue, *J. Non-Cryst. Solids* 2009

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Two important terms for fiberizing

- **Fiberizing window:**

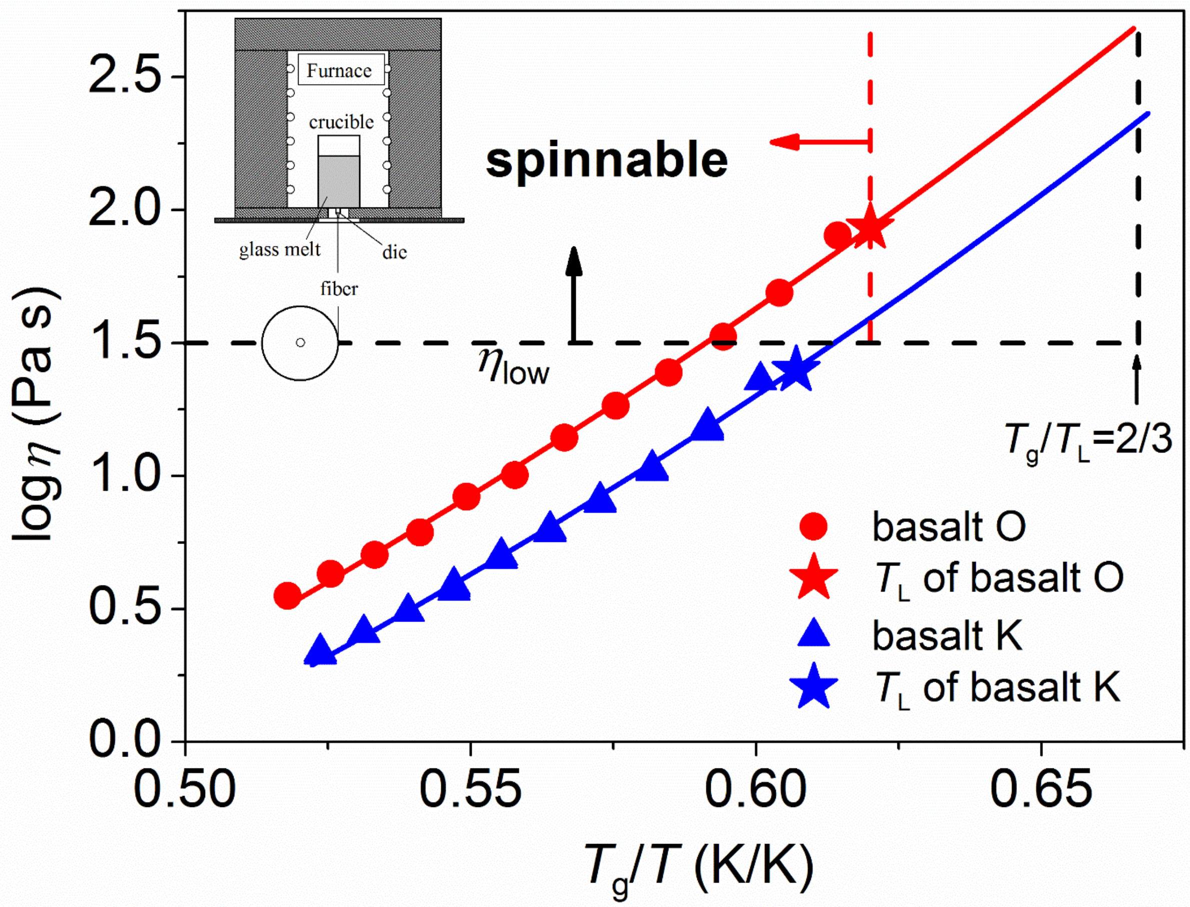
Temperature-viscosity region, where a melt is stable and spinnable.

  - If $T < T_L$, crystallization occurs, hindering fiber formation.
  - If η is too low, the melt stream breaks due to low cohesive force.

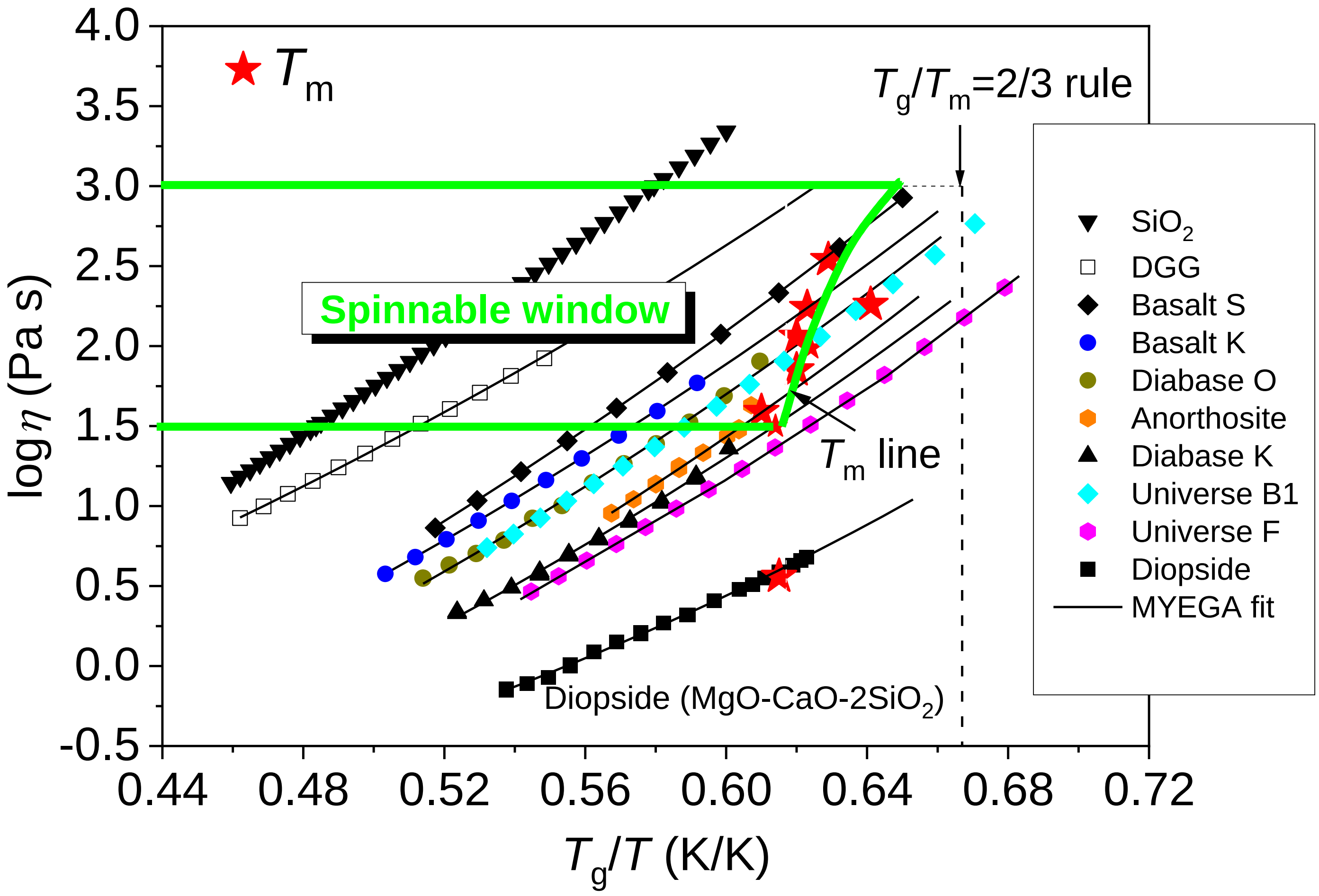
- **Fiber Spinnability:**

It is the ability of a glass-forming melt to be stretched and spun into defect-free fiber filaments either continuously or discontinuously.

The Angell plot as a guide to define the fiberizing window (useful for designing spinnable glass compositions)



Fiber drawing window defined by viscosity (η) and liquidus (T_m or T_L) within the Angell plot



My proposal about how to define and determine fiber spinnability

Fiber spinnability (F_s) increases with viscosity at T_L (η_L) but decreases with surface tension (λ_L). Based on this, I propose the following equation to quantify F_s:

$$F_s = \frac{1}{\gamma_L} \log\left(\frac{\eta_L}{\eta_c}\right)$$

where γ_L is the surface tension at liquidus temperature (T_L), η_L is the viscosity at T_L, and η_C is the lower limit of viscosity for fiber drawing.

Considering that γ differs only slightly among oxide melts, the fiber spinnability can be simplified to

$$F_s{}' = \log\left(\frac{\eta_L}{\eta_c}\right)$$

According to experiments, η_C can be 50-200 Pa s. Here we set 50 Pa s as the lower limit of viscosity for continuous fiber drawing.

If $F'_S \geq 0$, a melt is spinnable, otherwise it is not.

Yue, Zheng, *Int. J. Appl. Glass. Sci.* (2017)

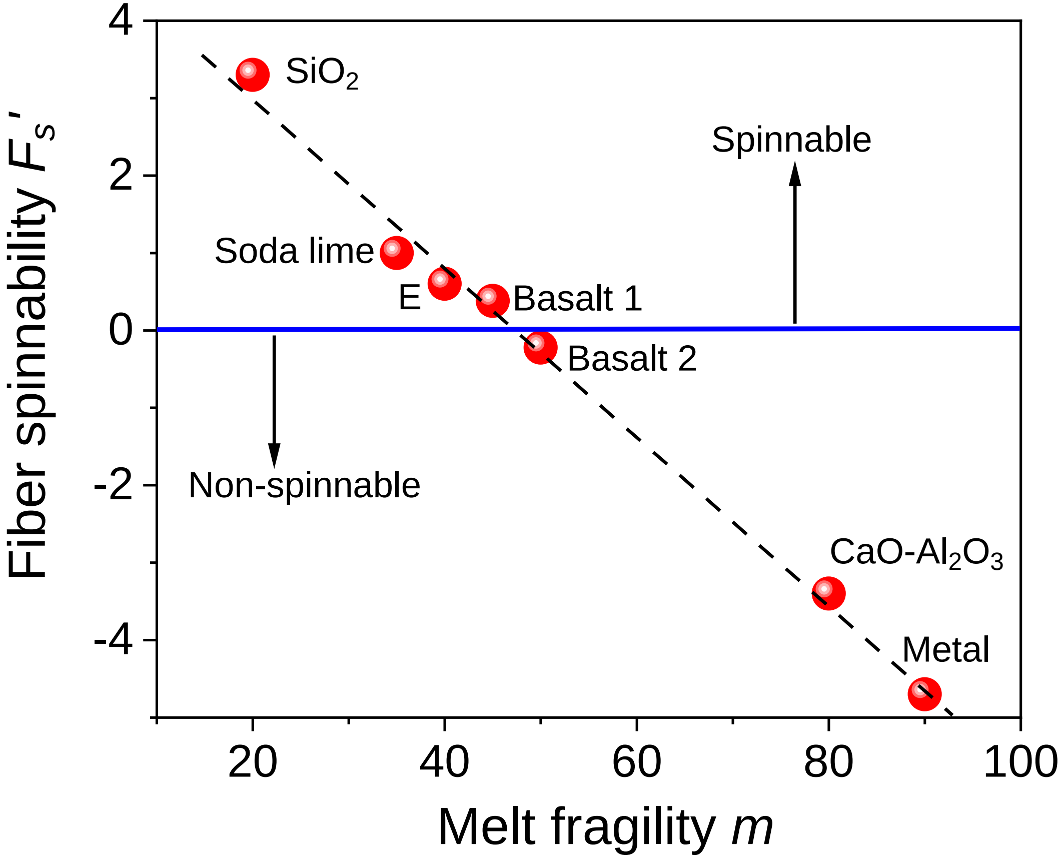
Determination of liquidus viscosity (η_L)

- Determine T_L using DSC.
- Measure the η-T relation.
- Fit the $\eta \sim T$ relation to the MYEGA model.
- Introducing T_L into MYEGA, we get

$$log_{10}\,\eta_L = -3 + 15\frac{T_g}{T_L}exp\left[\left(\frac{m}{15} - 1\right)\left(\frac{T_g}{T_L}\right) - 1\right]$$

Meaning:
If T_g, *m* and T_L are known, we will know the liquidus viscosity.

A relation between fiber spinnability and liquidus fragility



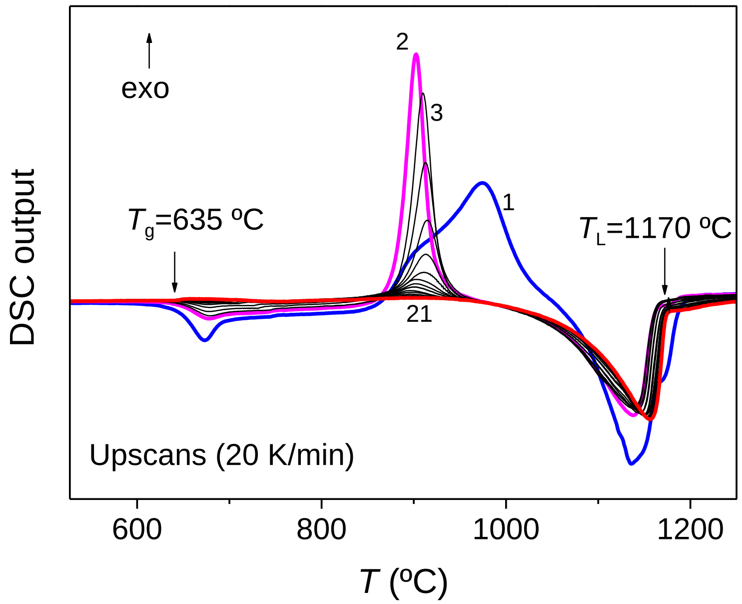
A simple calculation:

When using a typical draw stress (60 MPa) to draw fibers, the strain rate should be ~**4x10^5 s^{-1}** and fiber diameter should be **~5 μm**.

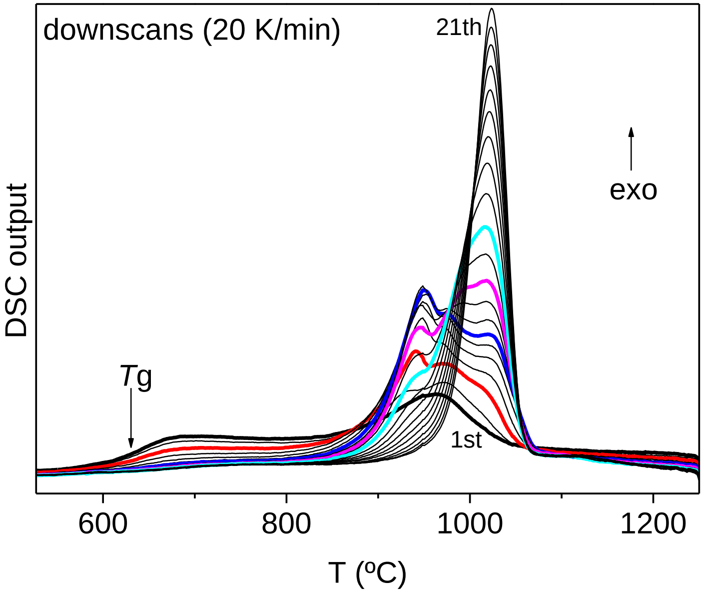
Applying this strain rate to stretch SiO$_2$ fibers, the draw stress would be **120 GPa** to get fibers with similar diameter!

When applying the drawing stress for E glass fibers to draw SiO$_2$ fibers, the drawing temperature must be raised to **~3200 K (2927 °C)**.

Crystallization and melting of a basalt by repeating DSC scans (Maximum scanning *T*: T_L+70 ºC)



Heating curves



Cooling curves

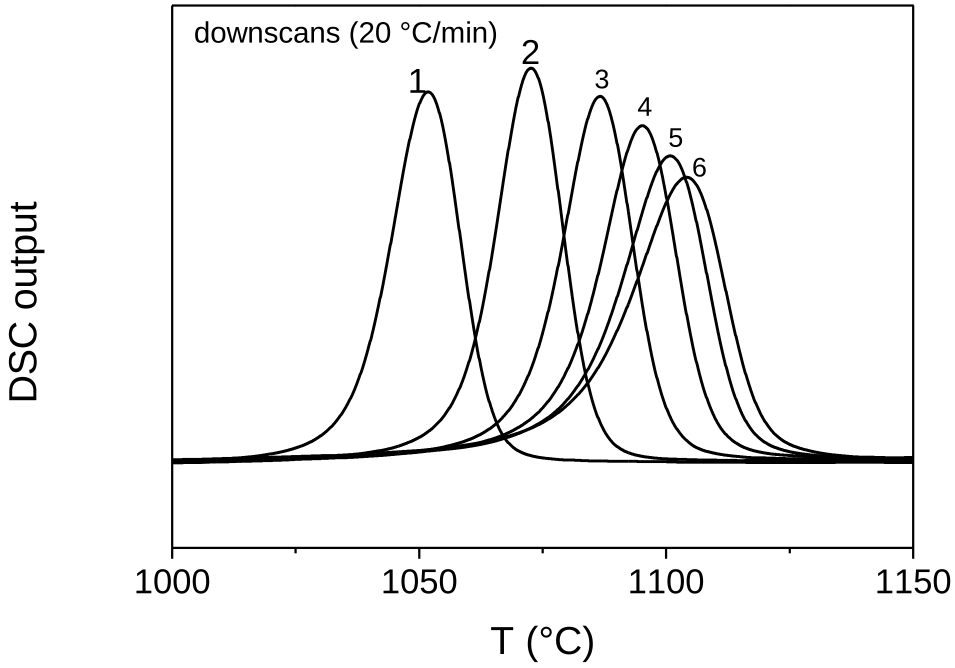
Implications:

- There is crystal memory effect.
- Structural order still exists at 70 °C above T_L.

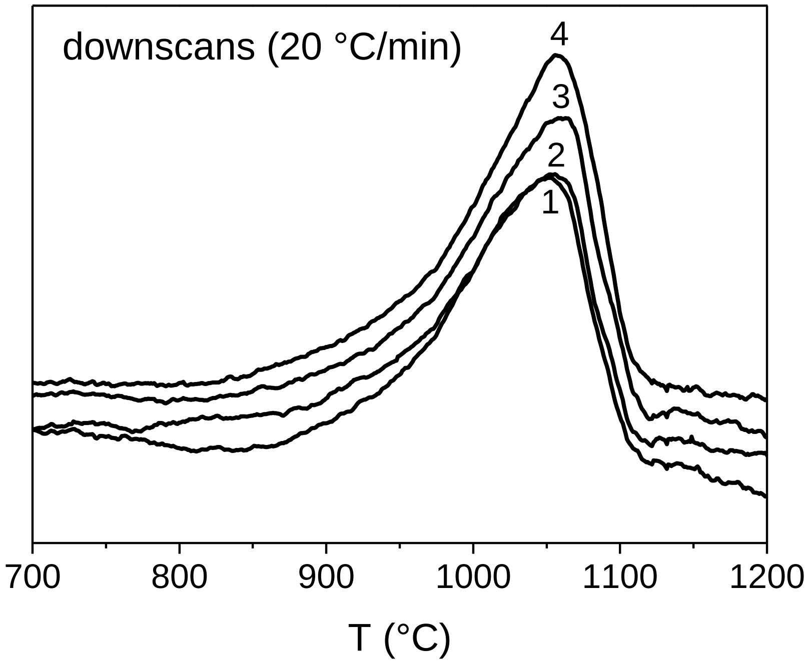
Yue, *J. Non-Cryst. Solids* 2004

Cooling of a basalt melt

from 1300 °C (T_L+120°C)



from 1400 °C (T_L+220 °C)



Implication:

Structural order disappears only at sufficiently high *T*.

Open questions

- What is the physical meaning of η_C? Can η_C be predicted or calculated?
- Why and how does a melt filament break?
- How can η_L be predicted?
- Does the non-Newtonian flow occur during fiber drawing?
- How does fibe structure evolve during drawing?
- How do forming conditions affect properties?

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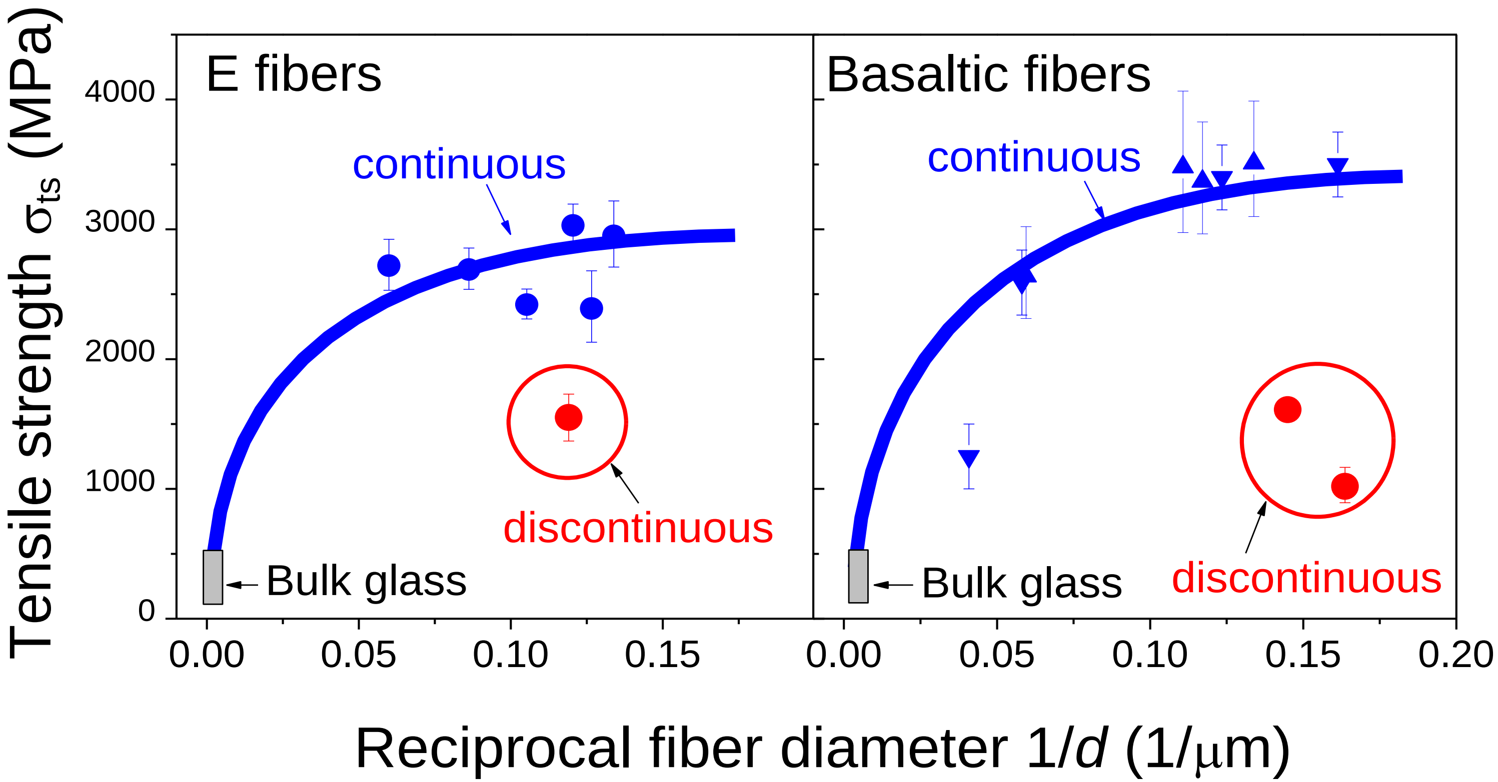
Tensile strength of fibers increases with decreasing their diameter! Why?

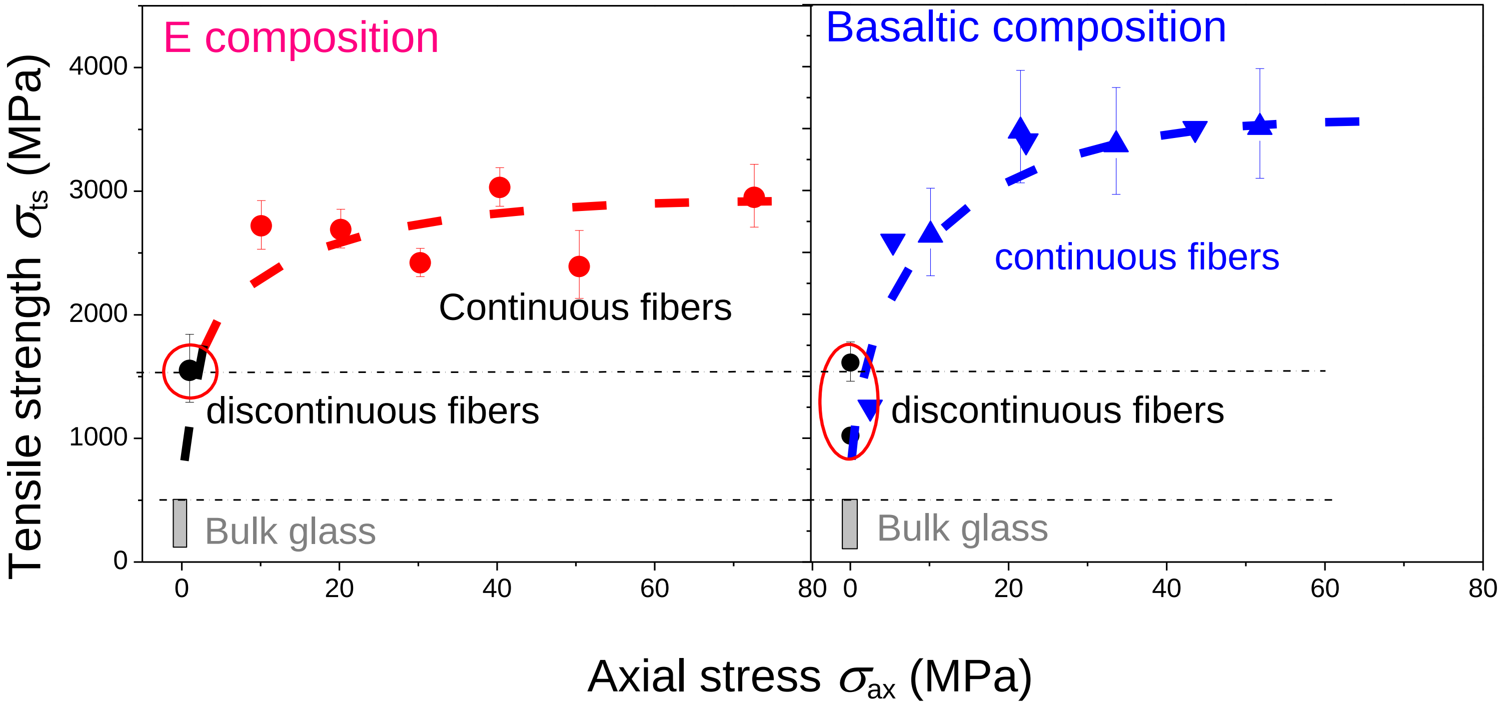


An increase in axial stress, and hence, in anisotropy will enhance the strength of glass fibers!

Striking difference btw wool and continuous fibers!

The drawing force is a key factor determining the fiber tensile strength.

(Note: other factors: composition, surface …..)



Indication: once fiber diameter is known, we can derive the fiber strength. Fiber diameter is related to optical birefringence.

Lund and Yue, *J. Am. Ceram. Soc.* 2010

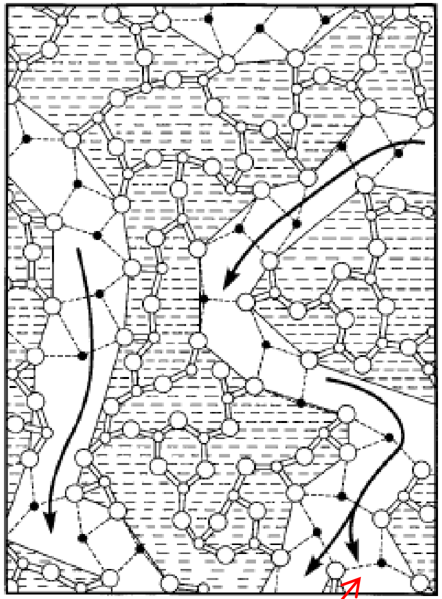
Ya, Deubener, Yue, *J. Am. Ceram. Soc.* 2009

Stretching of modified random network

Tensile strength is enhanced by orientation of

- Structural units
- Microchannels
- Internal flaws
- Surface flaws
- Heterogeneous domains

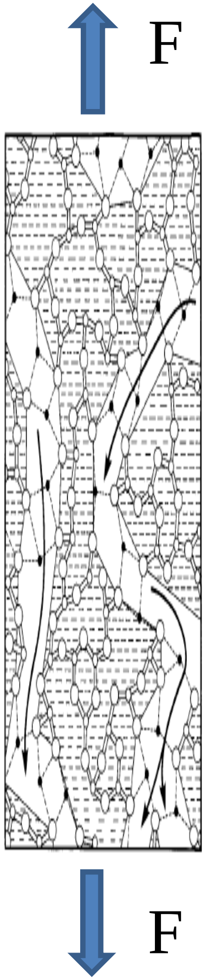
- The alignment of micro-channels requires smaller drawing force than that of the random structural voids
- But require larger force than that of macroscopic defects.



Modifier channels

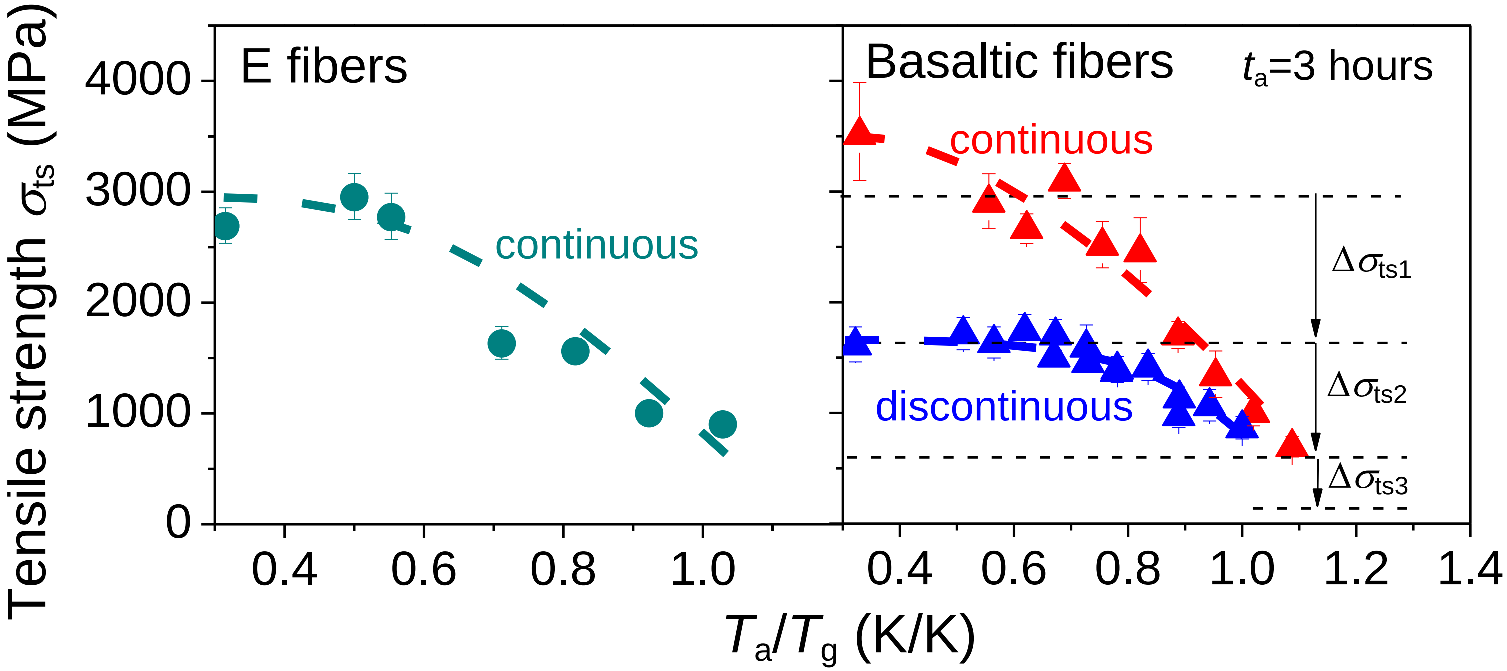
Greaves, JNCS (1985)

draw →



Hypothesis

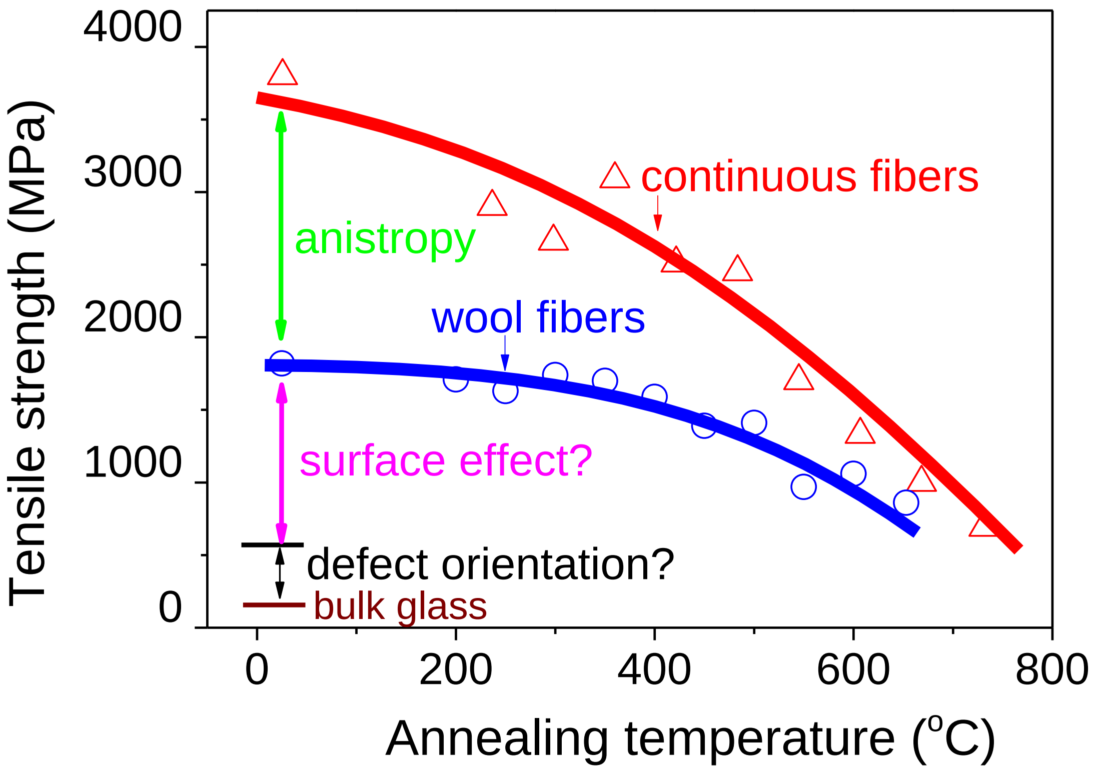
Scaling the tensile strength with the annealing temperature (T_a)



Implications:

- Three factors governing the tensile strength of fibers, i.e., anisotropy, surface defects, orientation of defects.
- From the annealing temperature, we can predict the strength decay of fibers.

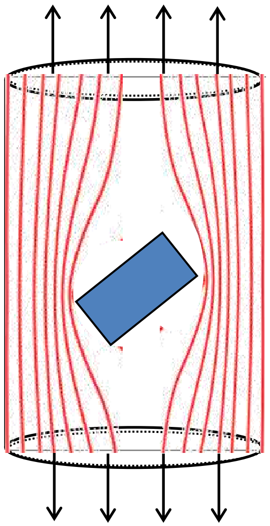
Contributions of anisotropy and other factors (Insight from annealing experiments)



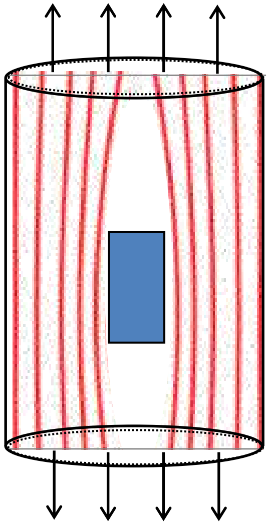
Mechanical history plays a much larger role in enhancing the tensile strength than thermal history!

Effect of orientation of macroscopic defects on fiber strength

Wool fibers



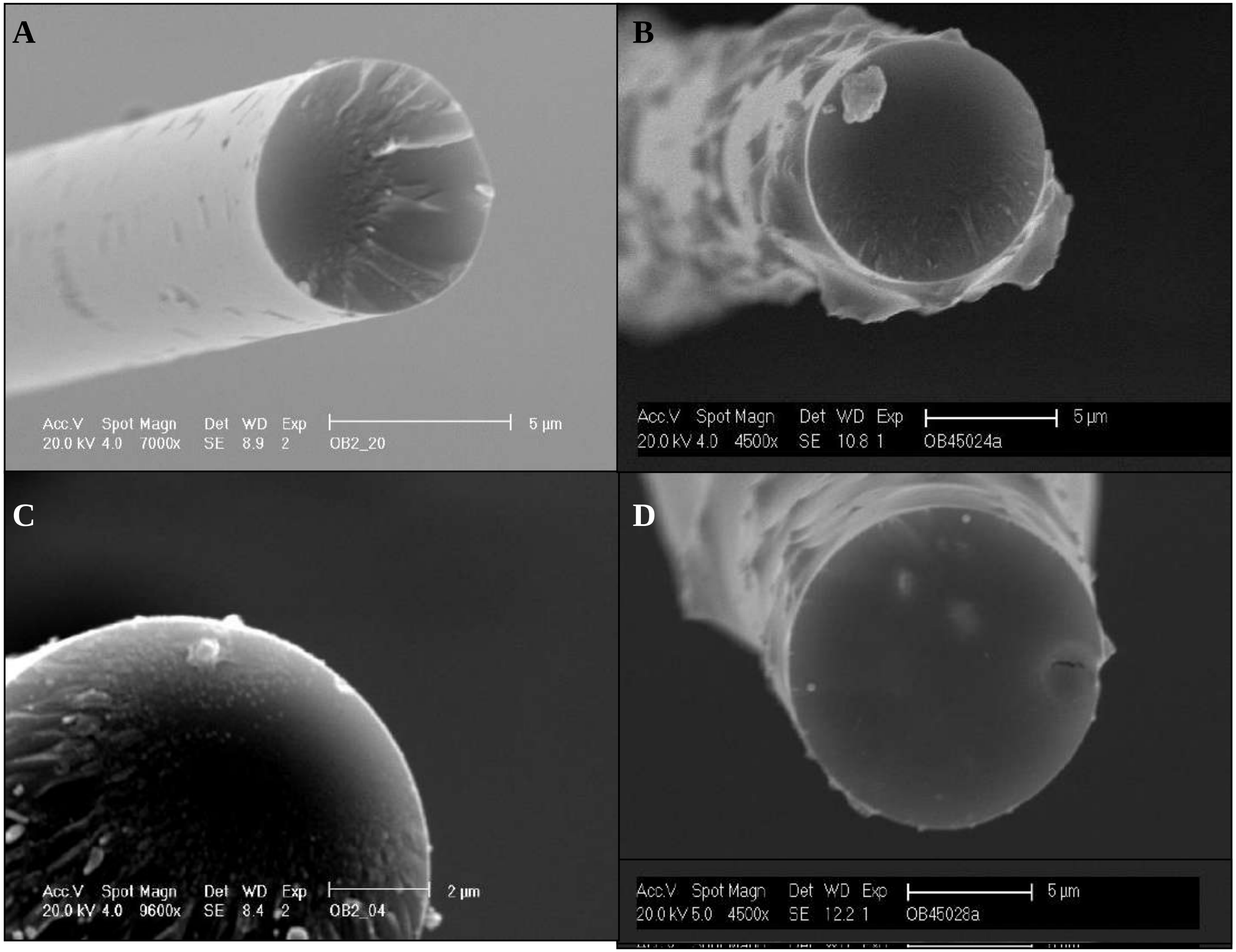
Continuous fibers

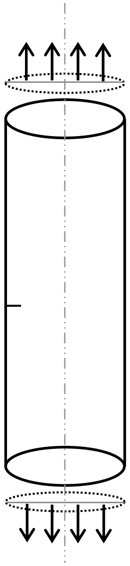


Smaller axial drawing force →
Lower orientation degree of defects (striae, bubbles) → More stress concentration →
Lower strength

Larger axial drawing force →
→Higher degree of orientation of defects → Less stress concentrations
Higher strength

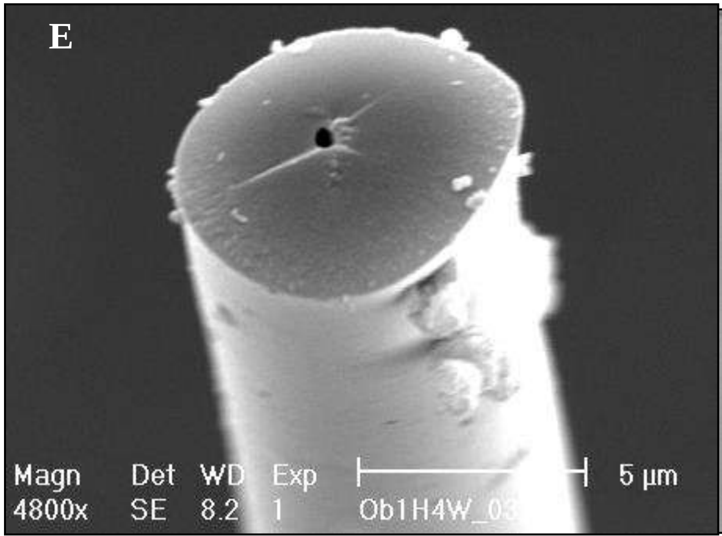
How do the fracture surfaces of basaltic wool fibers look?

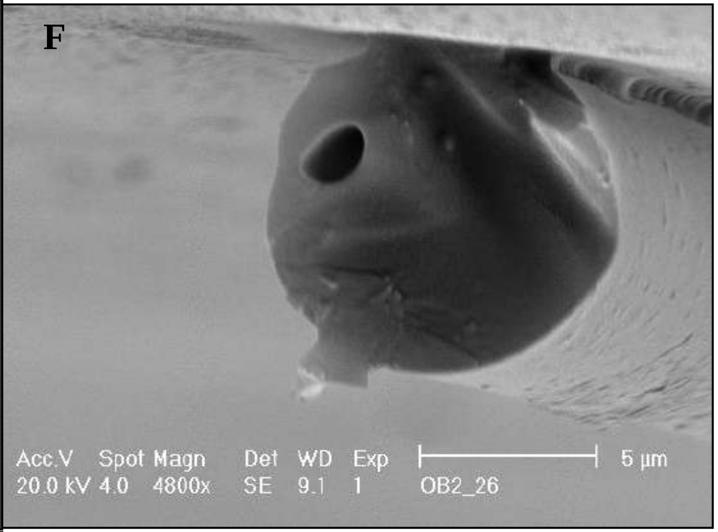


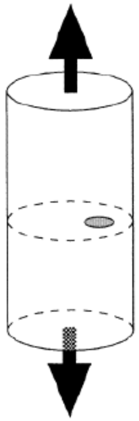


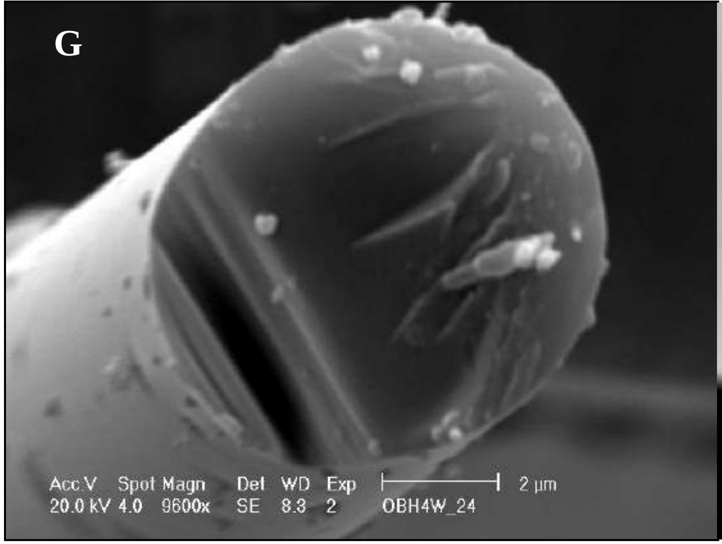
Defects as initiating points of fracture of stone wool fibers?

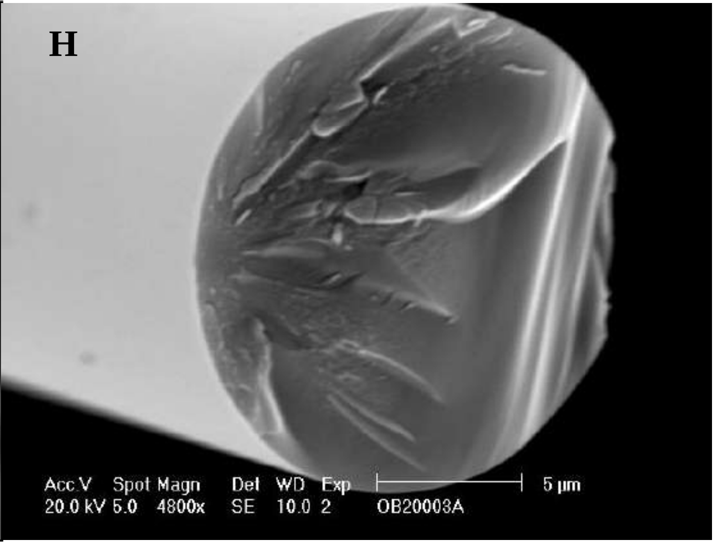
(*The fracture surfaces are not so smooth as defect-free fracture surface*)

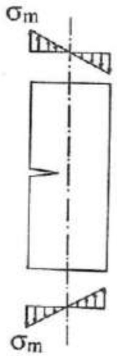




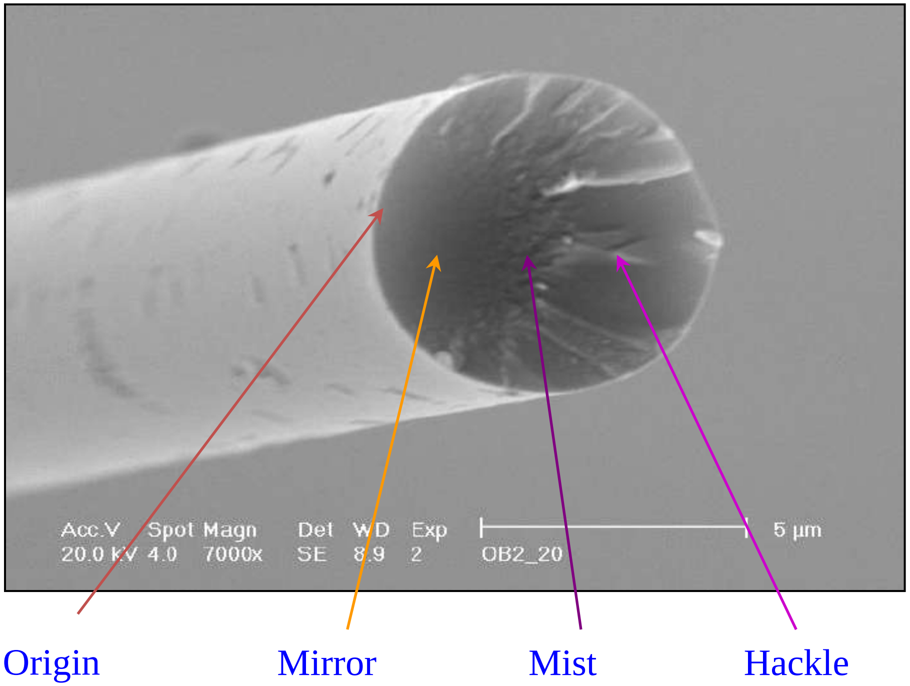


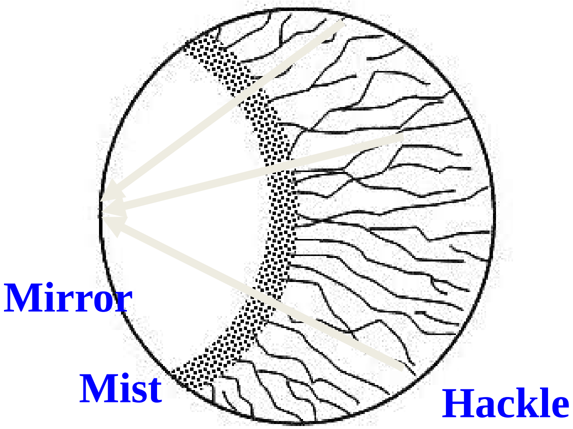






Typical fracture pattern of the fibers



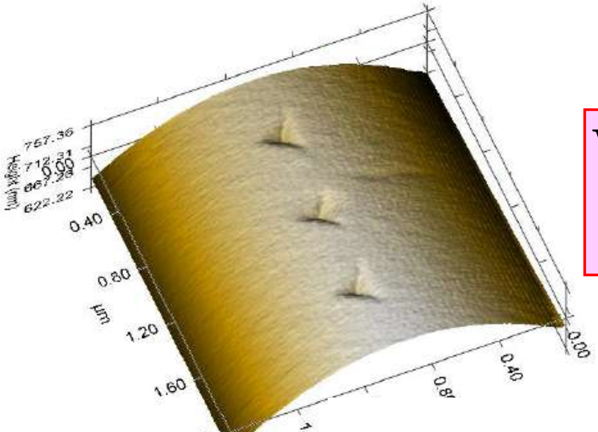


- Self-cracking process
- Fracture speed and stability determine the fracture surface roughness.

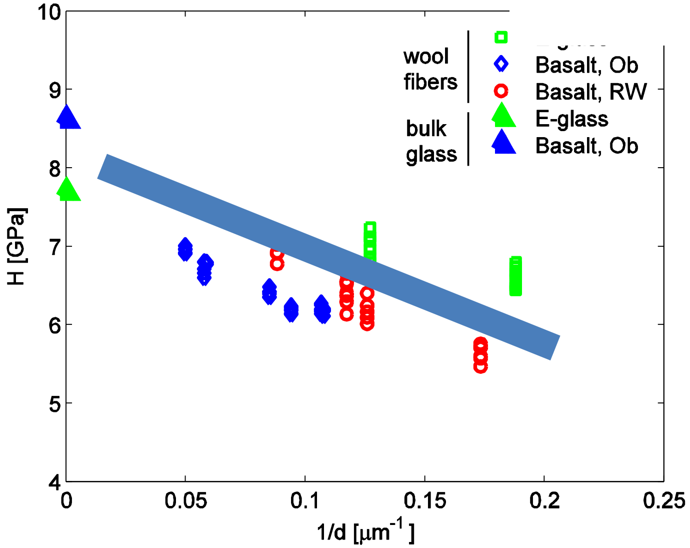
Lund, Yue, *J. Ceram. Soc. Japan* 2009

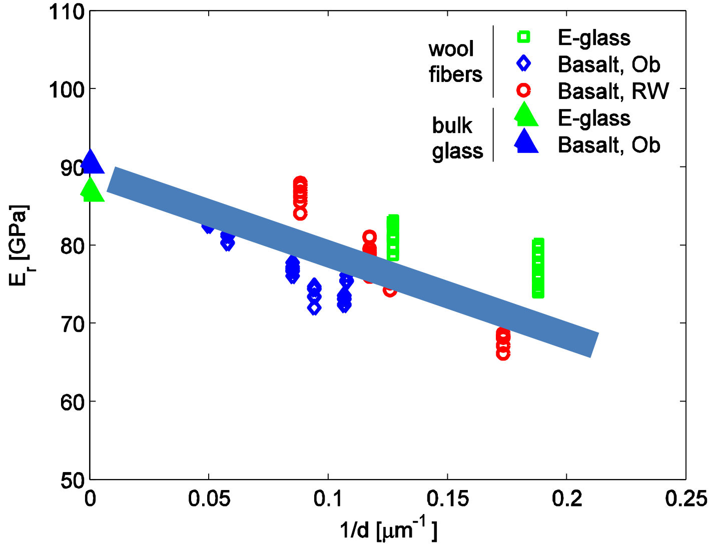
Diameter dependence of hardness (H) and elastic modulus (E_r) by nano-indentation

All indents were made with 1 mN load.



Wool fibers from E and basalt glass



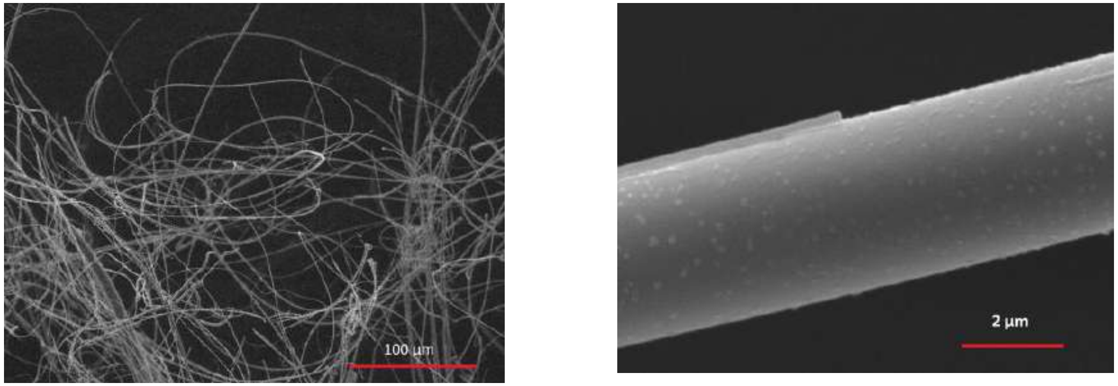


Lonnroth, Muhlstein, Pantano, Yue, J. Non-Cryst. Solids (2008)

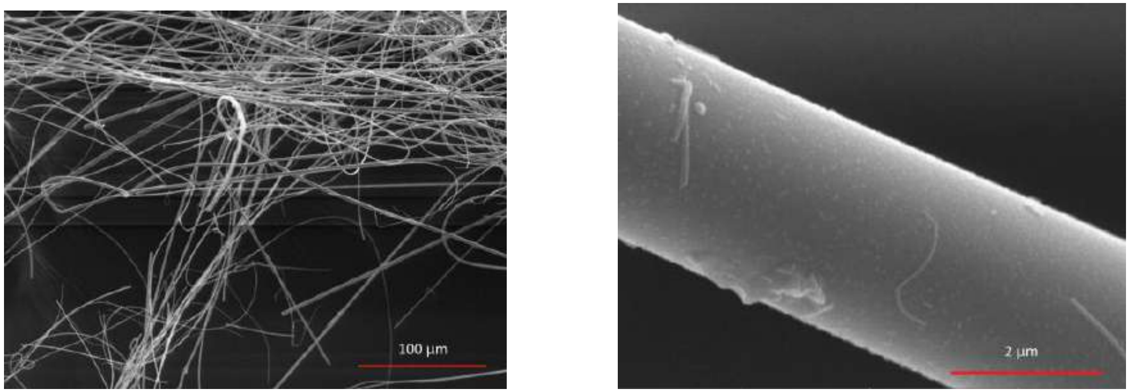
Dependence of the tensile strength of the filtration mat of glass fiber wool on fiberizing techniques

(in collaboration with Hollingsworth and Vose Company, PSU and QLUT)

Rotary Spinning



Flame spinning

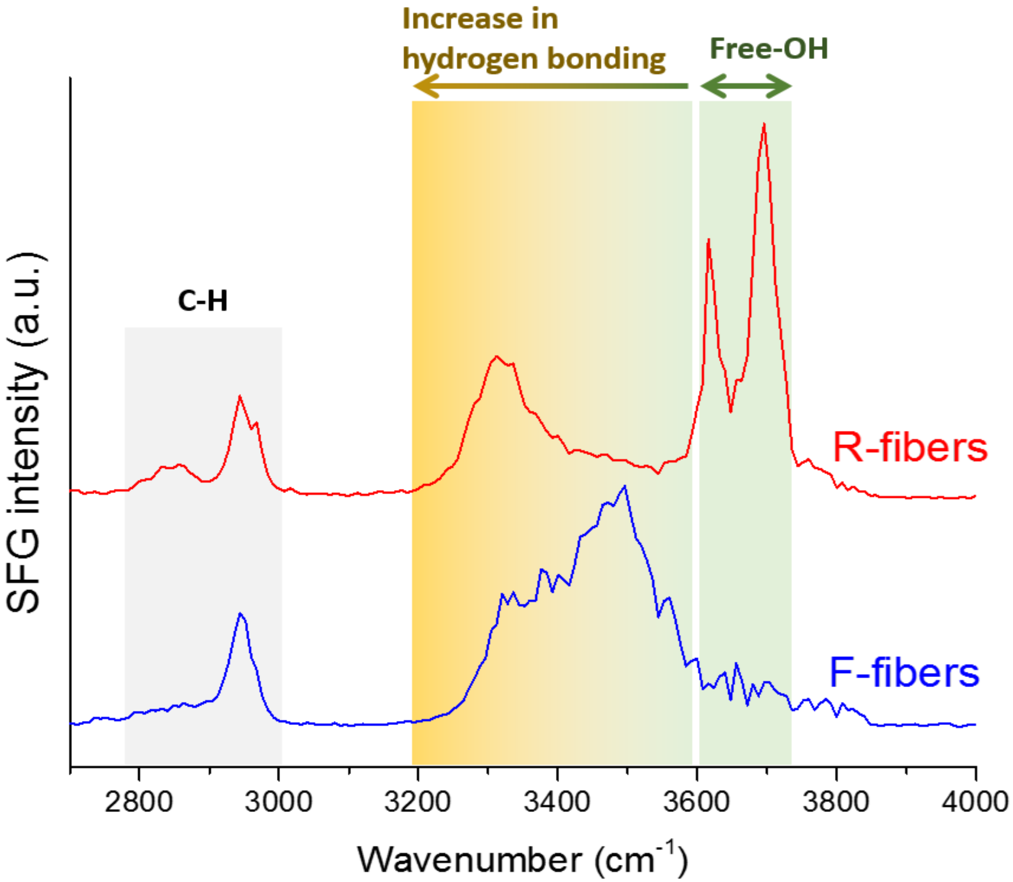


Mat of F-fibers have higher strength than R-fiber mat.

Both have same chemical composition

Zhang, Vulfson, Zheng, Luoc, Kim, Yue, *J. Non-Cryst. Solids* 476 (2017) 122-127

Difference in the number of surface hydrogen bonds between Fibers R and F

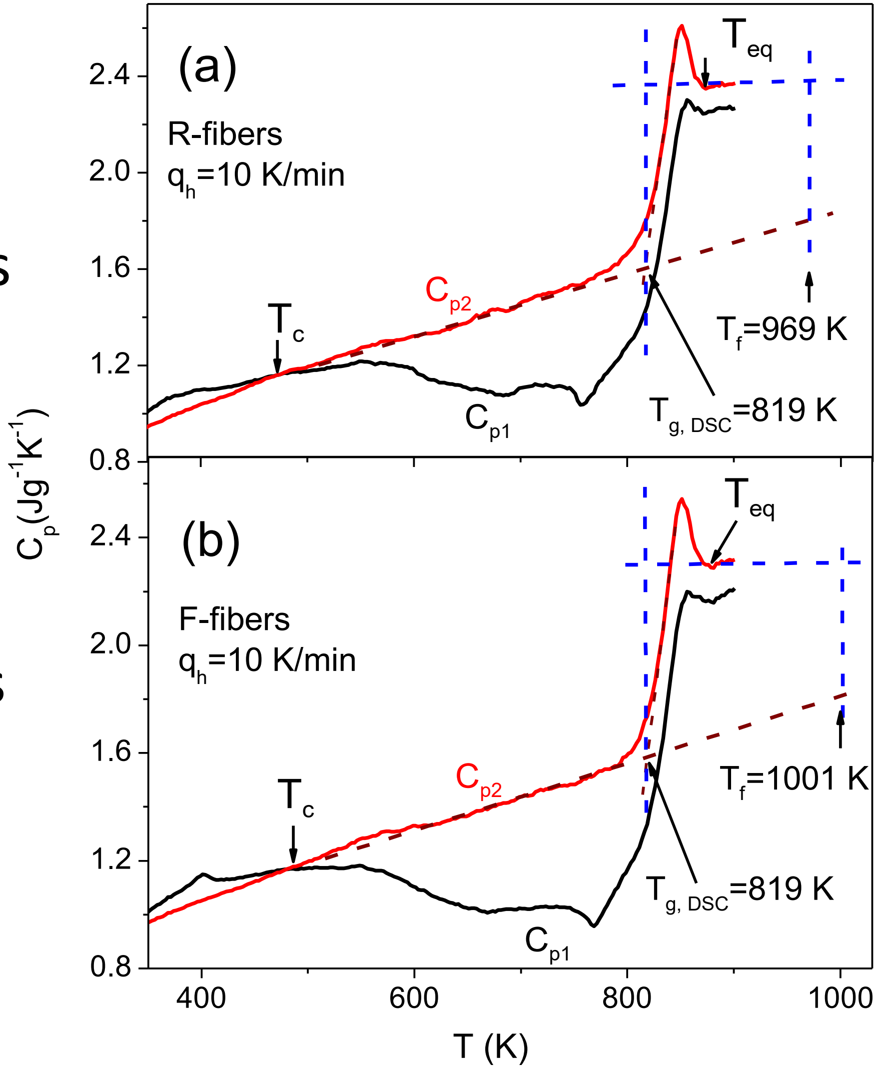


Large difference in H-bonding can be identified:
The surface of F-fibers has more H-bonds than R-fibers.
Thus, F-fiber mat exhibited higher strength.

Comparison in T_f between R- and F- fibers

R-fibers

F-fibers



T_f: 969 K
Cooling rate: 20000 K/s

T_f: 1001 K
Cooling rate: 90000 K/s

Implications:
F-fibers are thinner, undergo larger drawing force, higher anisotropy
Hence, higher strength

Question: which factor is dominant, OH or drawing force?

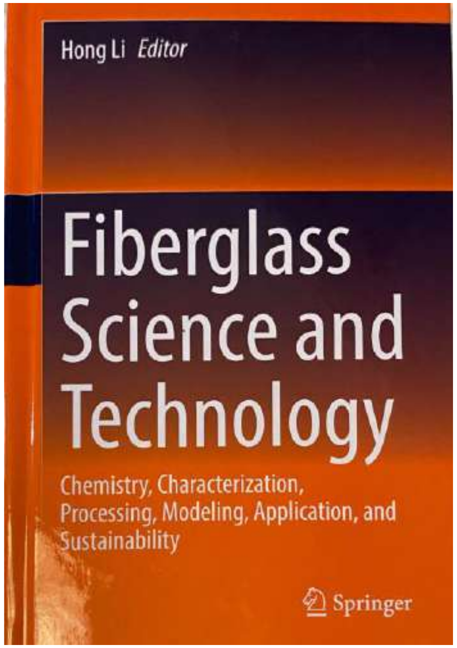
Outline of my talk

1. Background
2. Fiber spinnability of a melt
    - I. Glass-forming ability
    - II. Melt dynamics (liquid fragility and viscosity)
    - III. Glass fiber spinnability
3. Fracture of fibers and fiber mat
4. **Challenging questions….**

Challenging questions

- We gained some insights into fiberizing window, fiber spinnability and fiber mechanical properties.
- But what is the physics behind fiber spinnability?
- It is known that glass fiber modulus affects the performance of the fiber-reinforced composite.
- But it is less known about **HOW**. How is the composite performance affected through fiber modulus?
- What is the maximum modulus for an oxide composition to reach?

Some references

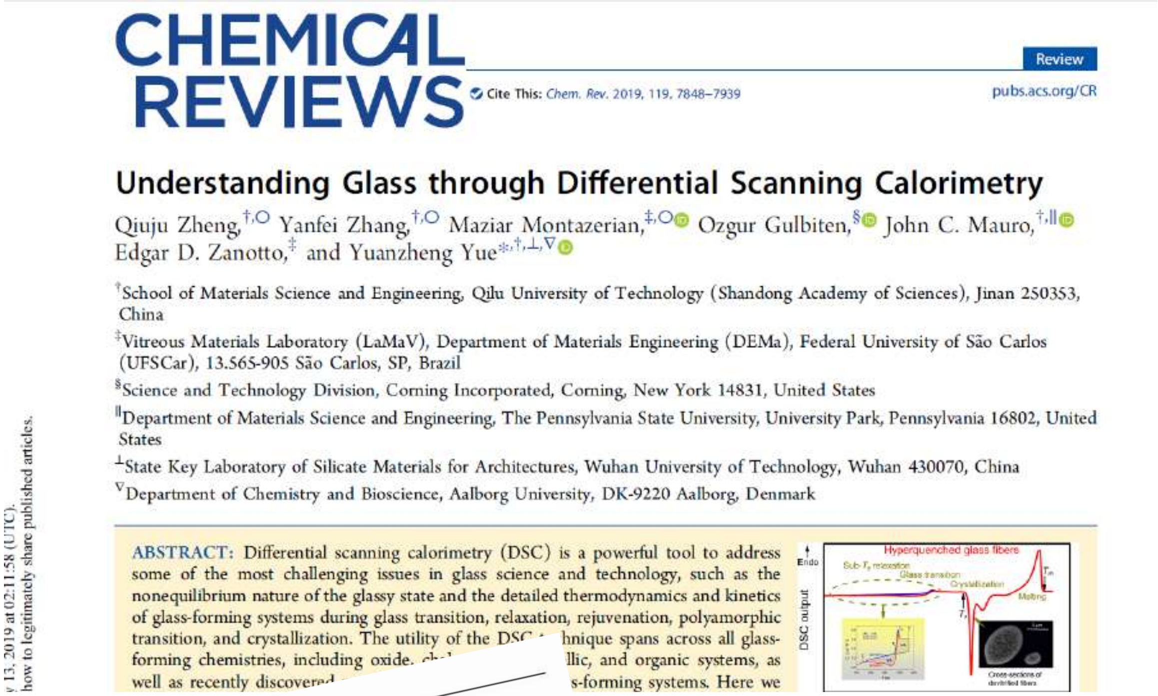


Hong Li *Editor*

Fiberglass Science and Technology

Chemistry, Characterization, Processing, Modeling, Application, and Sustainability

Springer



CHEMICAL REVIEWS

Review

Cite This: *Chem. Rev.* 2019, 119, 7848−7939

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Understanding Glass through Differential Scanning Calorimetry

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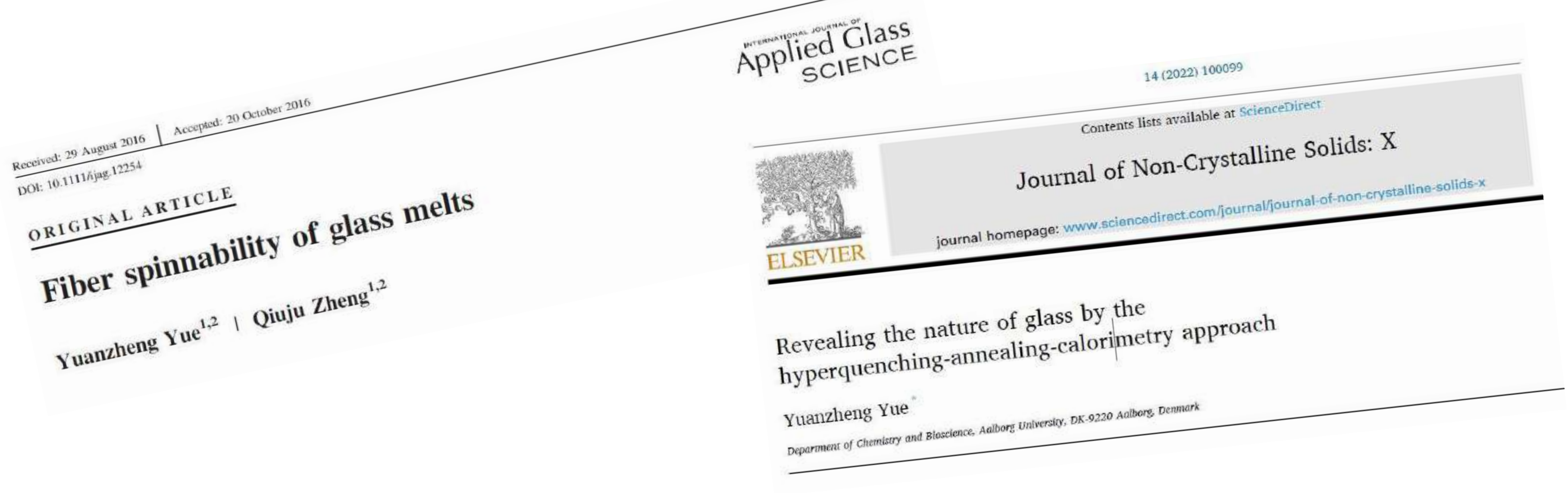
ABSTRACT: Differential scanning calorimetry (DSC) is a powerful tool to address some of the most challenging issues in glass science and technology, such as the nonequilibrium nature of the glassy state and the detailed thermodynamics and kinetics of glass-forming systems during glass transition, relaxation, rejuvenation, polyamorphic transition, and crystallization. The utility of the DSC
hnique spans across all glass-forming chemistries, including oxide,
llic, and organic systems, as well as recently discovered
s-forming systems. Here we



INTERNATIONAL JOURNAL OF Applied Glass SCIENCE

Received: 29 August 2016 | Accepted: 20 October 2016

DOI: 10.1111/ijag.12254

ORIGINAL ARTICLE

Fiber spinnability of glass melts

Yuanzheng Yue[1,2] | Qiuju Zheng[1,2]

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14 (2022) 100099

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids: X

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ELSEVIER

Revealing the nature of glass by the hyperquenching-annealing-calorimetry approach

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Thanks all my co-authors and collaborators!
Thanks for your attention!