Biobased and non-ionic LTTMs composed of fructose and glycerol: *water and temperature impact on the supramolecular organization*

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2nd International Meeting on Deep Eutectic Systems

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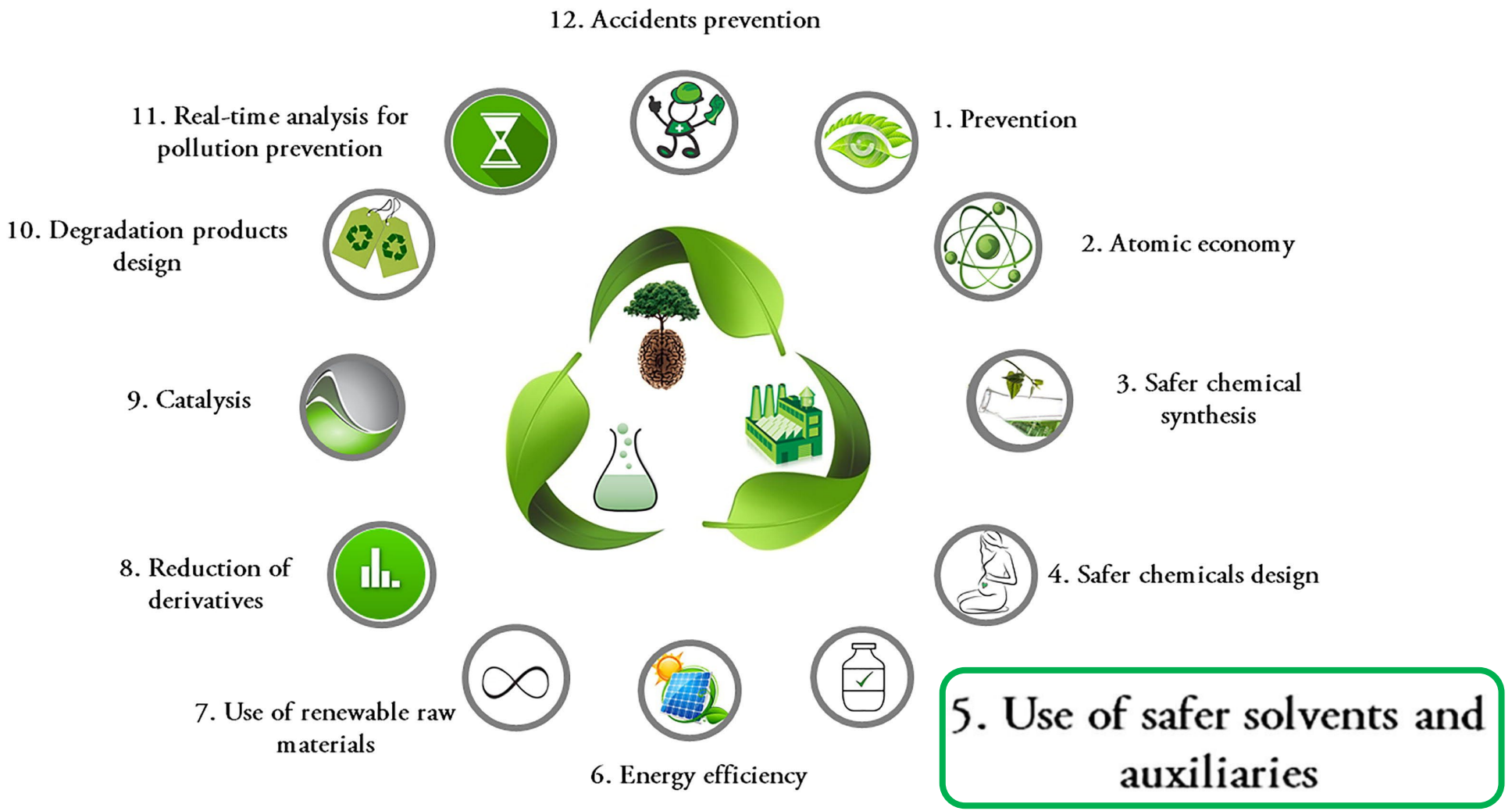
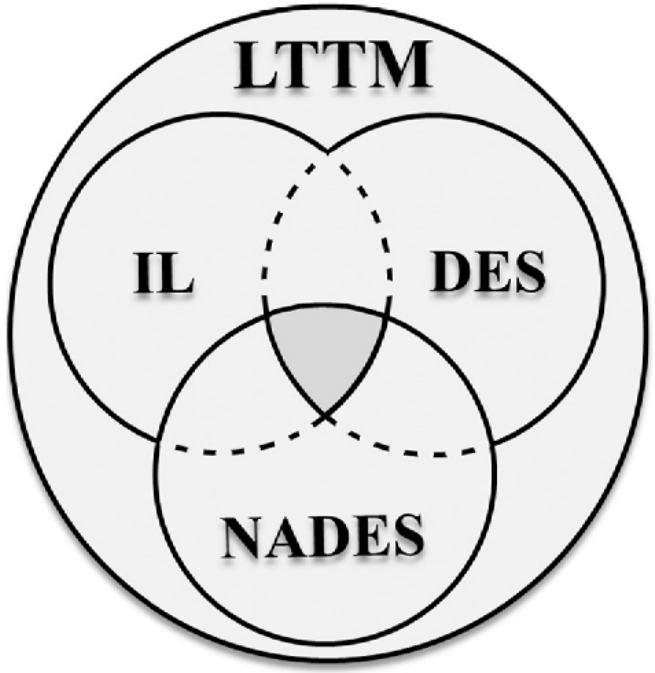
12 principles of Green chemistry[1]



1. Aparecida de Marco B. et al. in Saudi Pharmaceutical Journal, 27, 1, 1-8 (2019)

Appealing classes of solvents



Classification of Low Transition Temperature Mixtures proposed by Durand *et al.*[1]

HBA (Hydrogen Bond Acceptor) + HBD (Hydrogen Bond Donor)

T_m or T_g (DES/LTTM) < T_m or T_g (HBA and HBD)

= most of the resulting systems exhibit a high viscosity

+

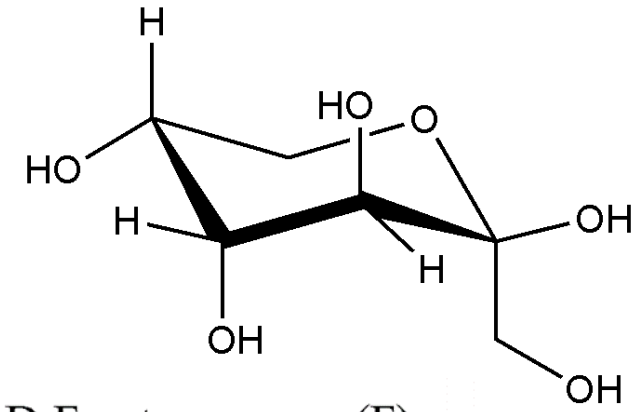
WATER

= addition of water is a simple way to reduce viscosity

The effect of water on the molecular organization of mixtures is an emerging issue[2]

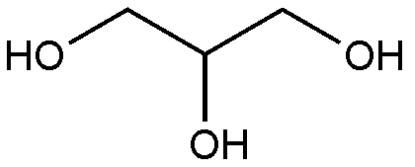
1. *Durand E., Lecomte J., Villeneuve P., in Biochimie, 120, 2016, 119-123*
2. *Roda A., Santos F., Chua Y.Z., Kumar A., Do H.T., Paiva A., Paiva A., Duarte A.R.C., Held C. in Phys. Chem. Chem. Phys., 2021, 23, 1706-1717*

Why exploring Fructose / Glycerol / Water mixtures ?



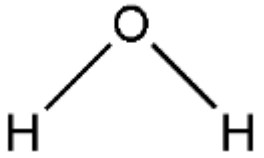
β-D-Fructopyranose (F)

+

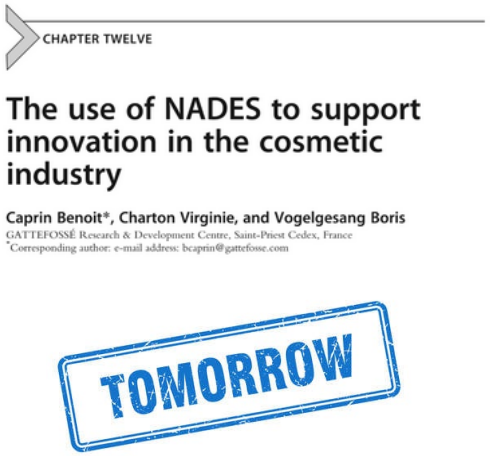


Glycerol (G)

+



Water (W)

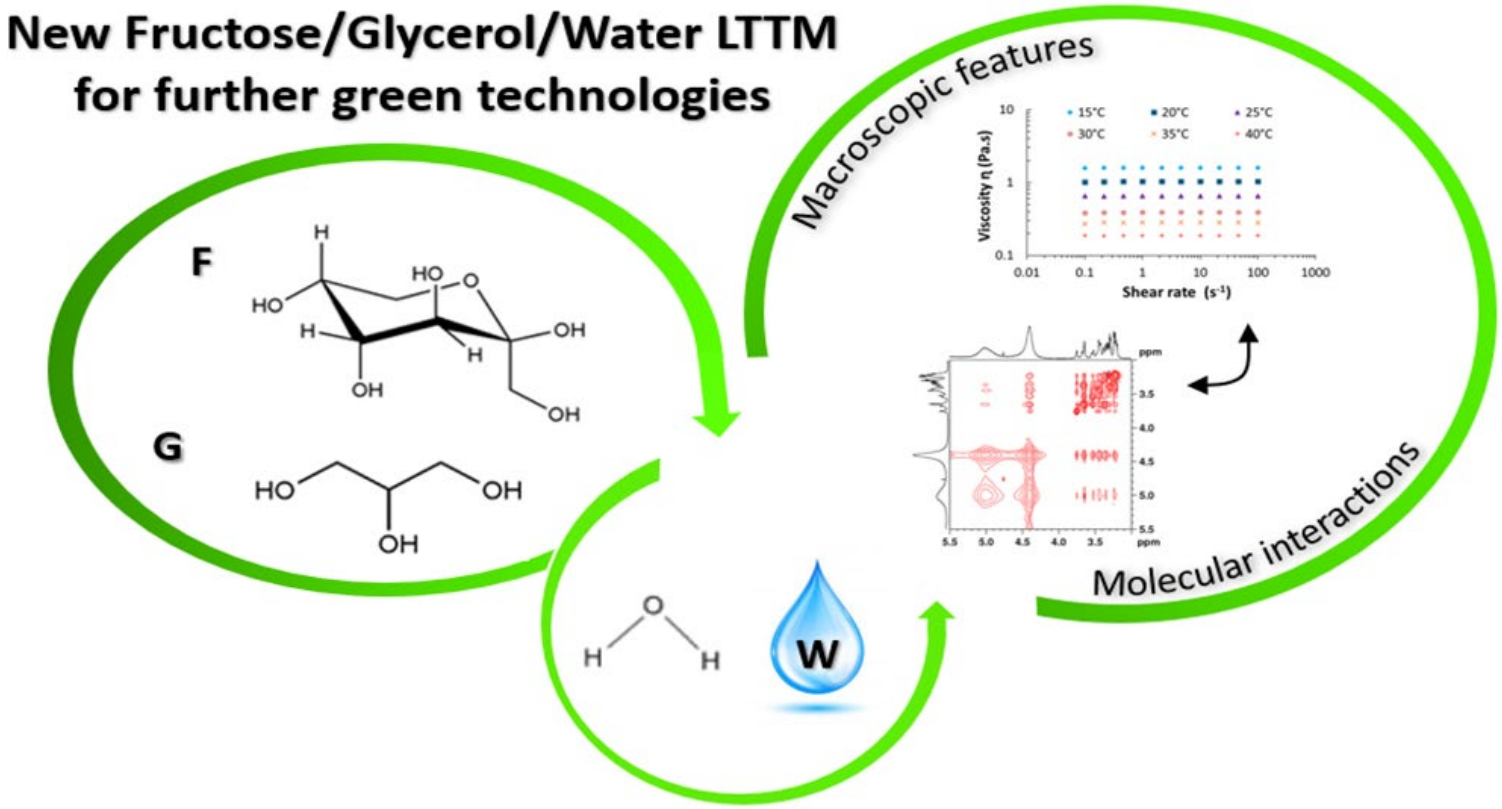


- Natural origin, renewable, safe and low cost
- The concurrent use of fructose and glycerol is scarcely described[1]
- Used for plant extraction at industrial scale[2]

1. Jablonsky M., Skulcova A., Malvis A., Sima J., in Journal of Biotechnology, 282, 2018, 46-66

2. Caprin B., Charton V., Vogelgesang B., in Advances in Botanical Research, Volume 97, Chapter 12, ISSN 0065-2296 (2021)

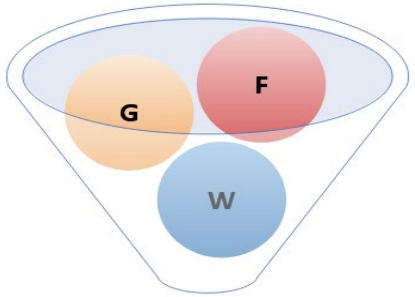
Objectives



1. Understand interactions at the molecular level for various F/G/W mixtures
2. Establish a relationship between their micro and macroscopical features

*Caprin B., Charton V., Rodier J.D., Vogelgesang B., Charlot A., Da Cruz-Boisson F., Fleury E., In Journal of Molecular Liquids, **337**, 2021, 116428*

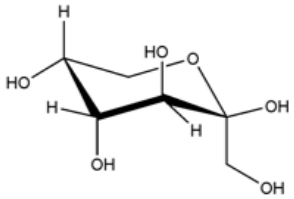
Molar ternary diagram of FGW mixtures / preparation

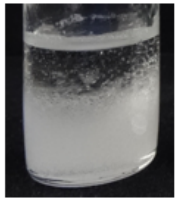


Heating and stirring
at 50°C (1 to 4h)

Optical inspection at 25°C

β-D-fructopyranose (F)





FGW211
(50/25/25 mol%)
(77/20/4 wt%)

FGW115
(14/14/71 mol%)
(50/25/25 wt%)

■ = 2 distinct phases

▲ = homogeneous and transparent liquids

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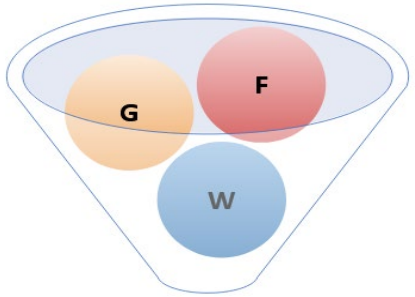
Molar ternary diagram of FGW mixtures / stability

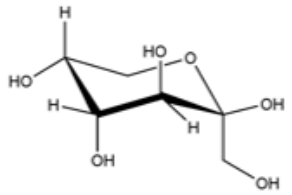


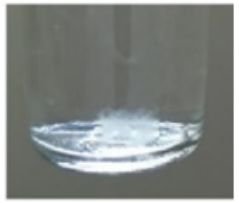
Heating and stirring at 50°C (1 to 4h)

Optical inspection at 25°C

Optical inspection after a storage for one year at 25°C

β-D-fructopyranose (F)

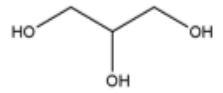




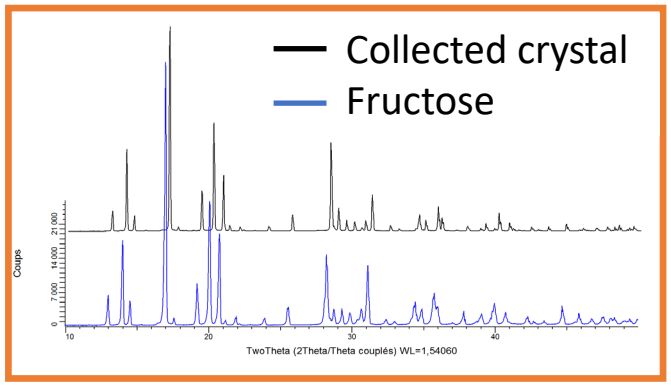
FGW1120
(5/5/91 mol%)
(28/15/57 wt%)

FGW111
(33/33/34 mol%)
(62/32/6 wt%)

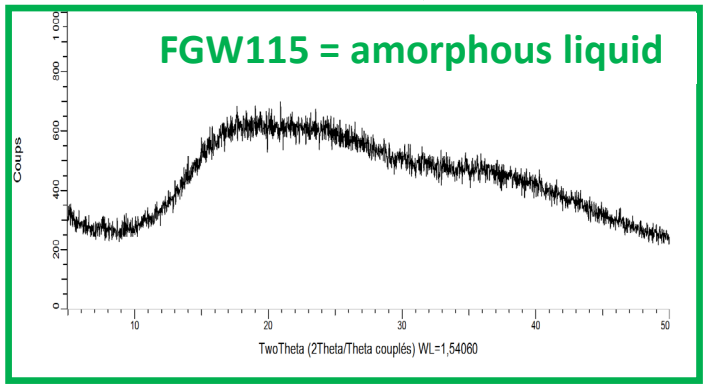
FGW115
(14/14/71 mol%)
(50/25/25 wt%)



Glycerol (G)



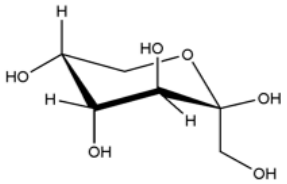
DRX pattern at 25°C of a crystal collected in FGW111



DRX pattern of FGW115 at 25°C

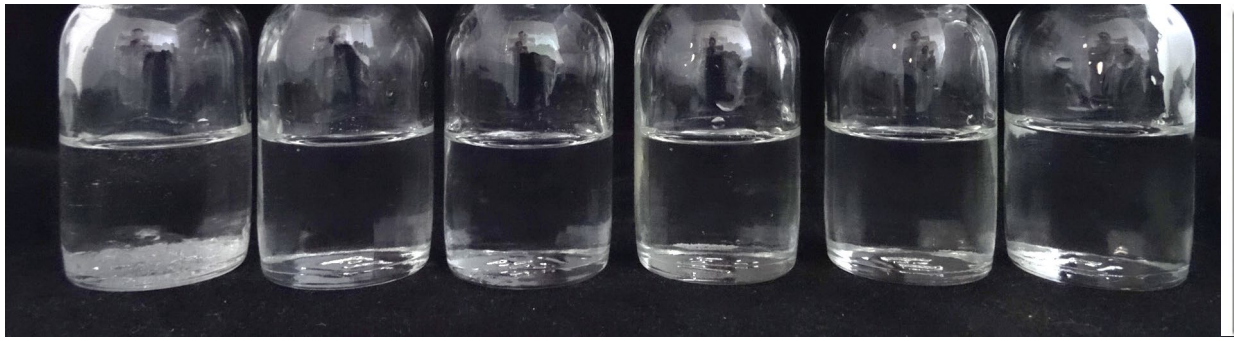
Non-ionic systems to study water inclusion

β-D-fructopyranose (F)



Glycerol (G)

FGW11**1** FGW11**2** FGW11**3** FGW11**4** FGW11**5** FGW11**6** … FGW11**17**



Unstable systems > < Stable, homogeneous and transparent liquids > < Bacteria !

What is the role of water on the molecular organization of these systems ?

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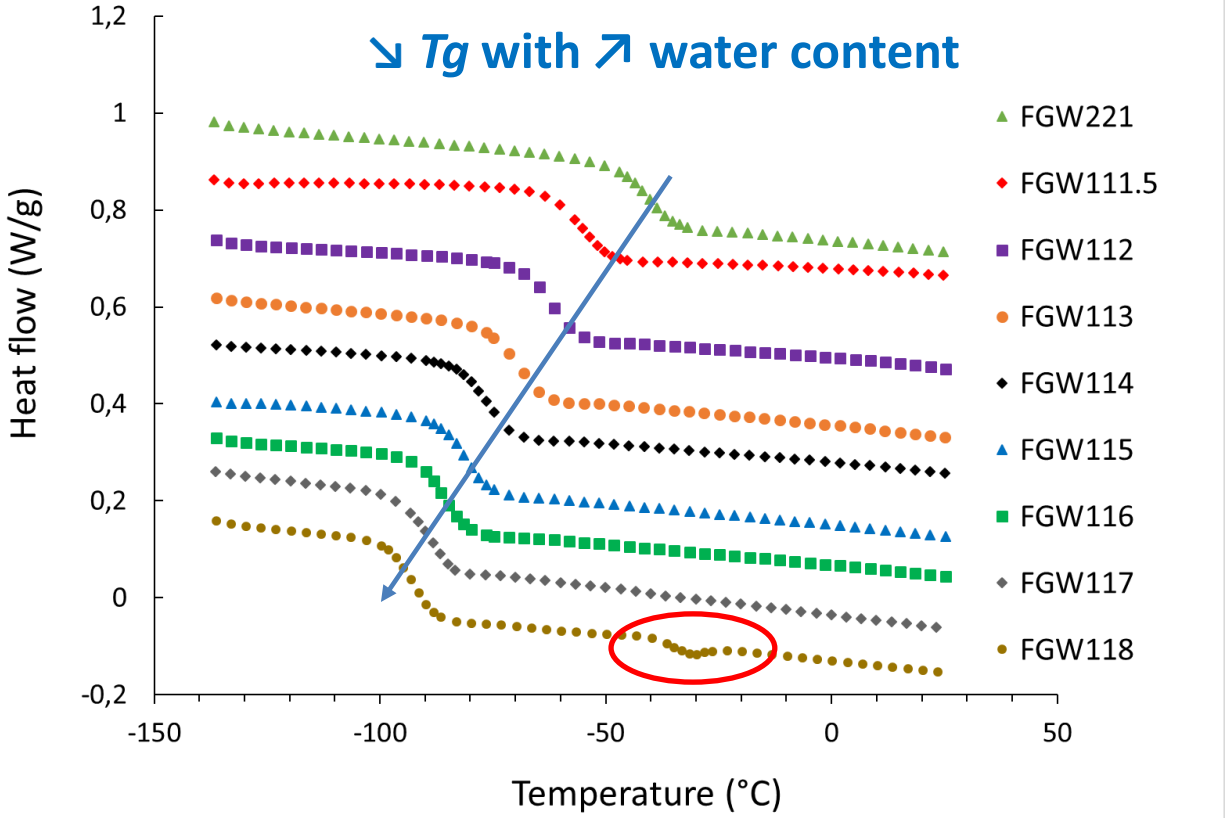
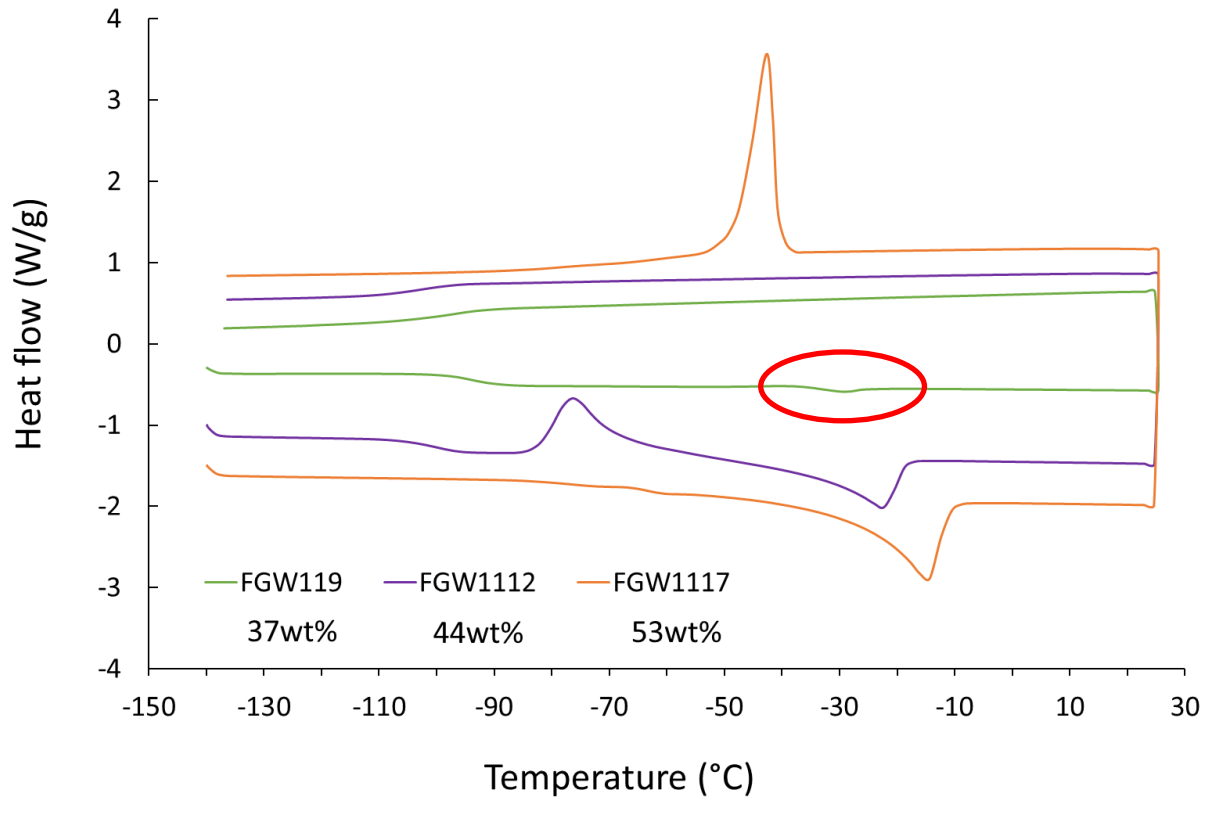
Analysis of the thermal transitions

DSC thermograms of FGW mixtures : from FGW221 to FGW118 (left) and for higher dilutions (right)





only 1 low *Tg* **≤ n_{Water} = 7 >** *Tg* + other thermal transitions

LTTM ~~**LTTM**~~

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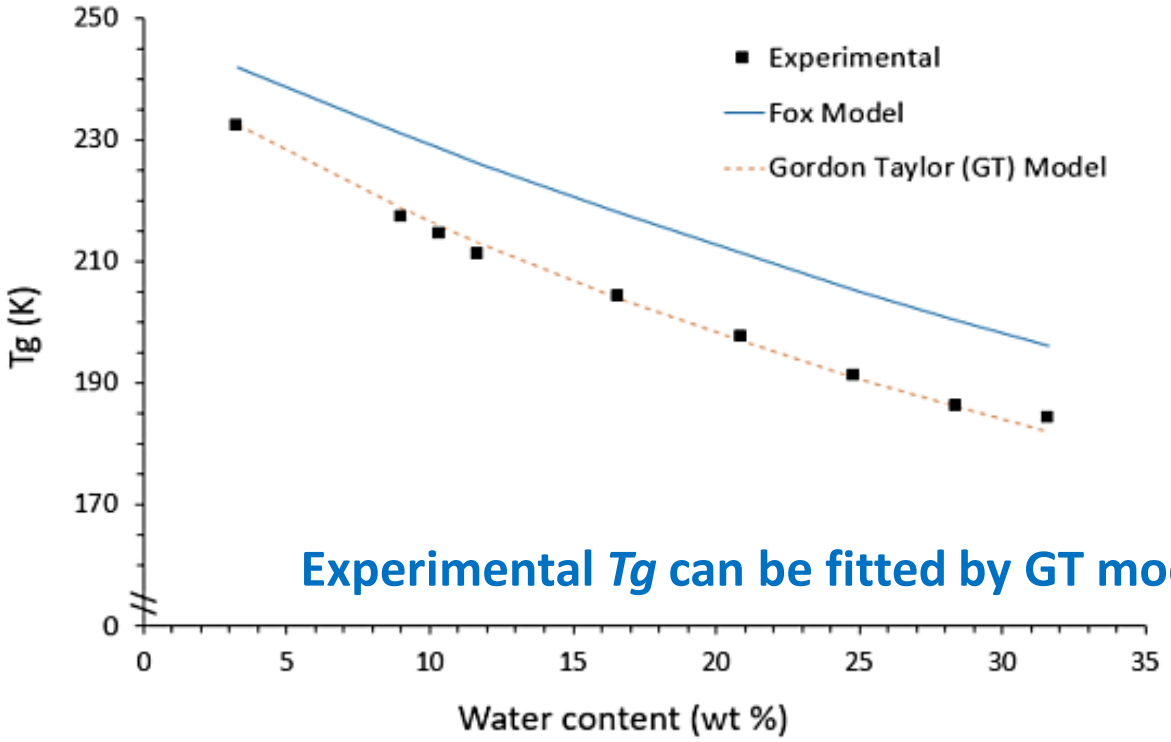
Analysis of the thermal transitions

Comparison of experimental and predicted values of Tg



Experimental *Tg* can be fitted by GT model

Thermal properties obey the GT model which takes into account H-bonds

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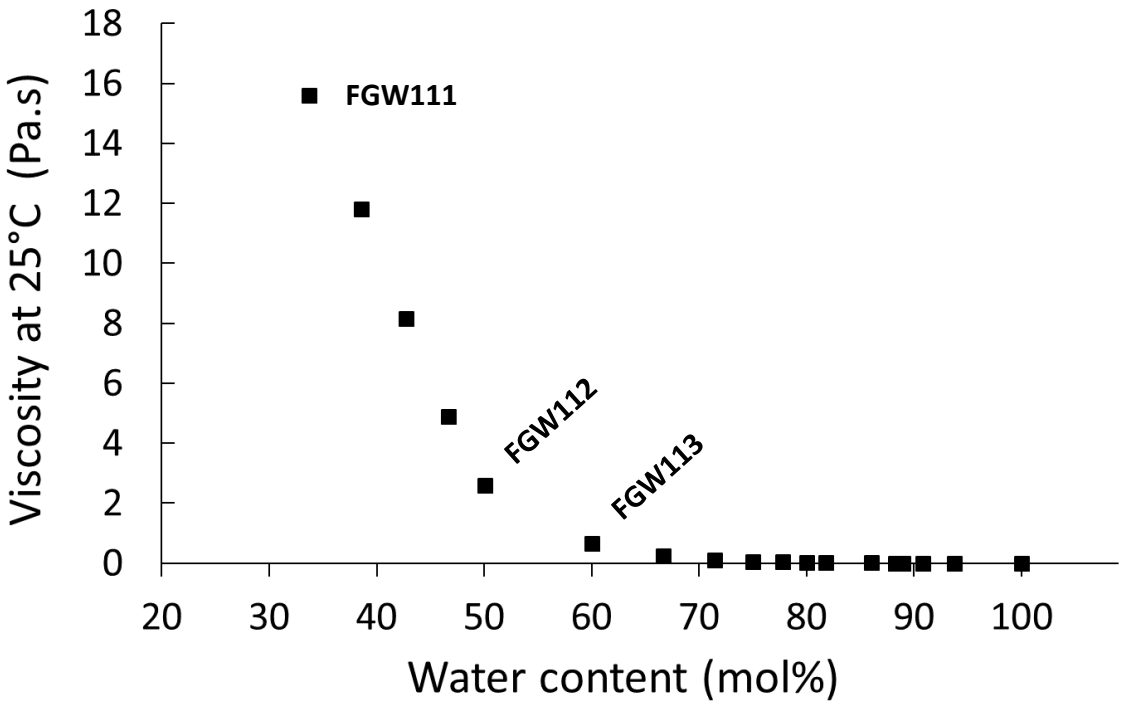
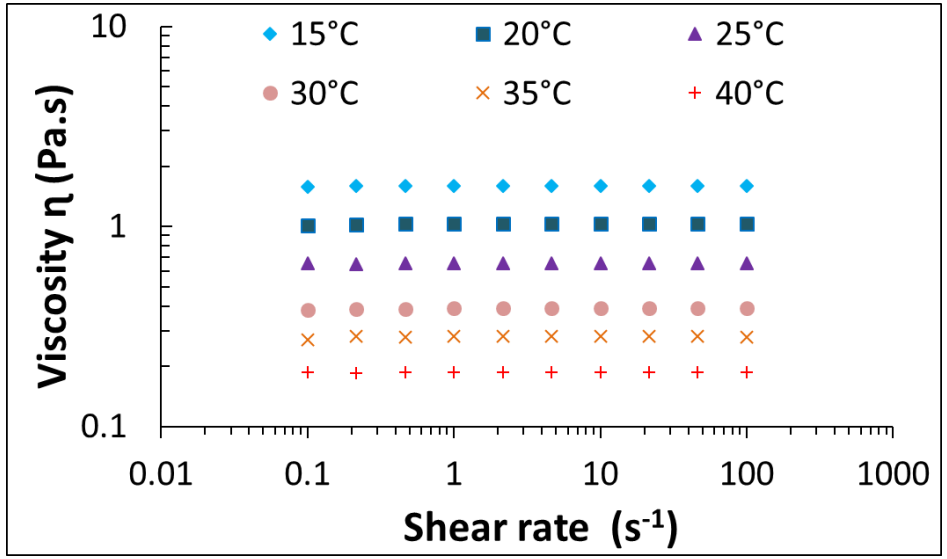
Study of shear rate viscosity : impact of water & temperature

Viscosity of FGW mixtures as a function of water



Flow curves at different temperatures for FGW113



Mixtures	FGW113	FGW115	FGW117	FGW119	FGW1112
Ea (kJ.mol^{-1})	65	49	38	35	30

↘ viscosity with ↗ water content

↘ Ea with ↗ water content

Hydrogen bonds cohesion and cooperativity ↗ when water content ↘

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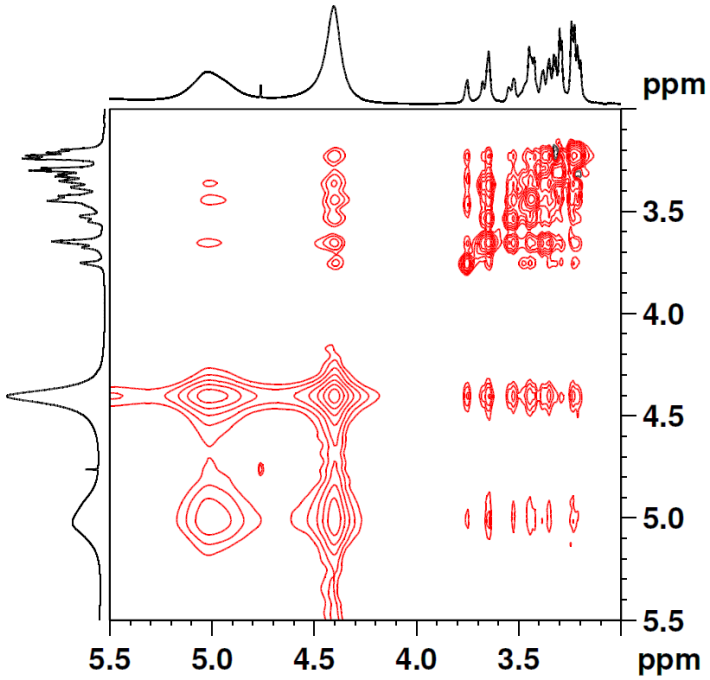
^{1}H-^{1}H NOESY NMR : impact of water content

NOESY spectra recorded at 25°C

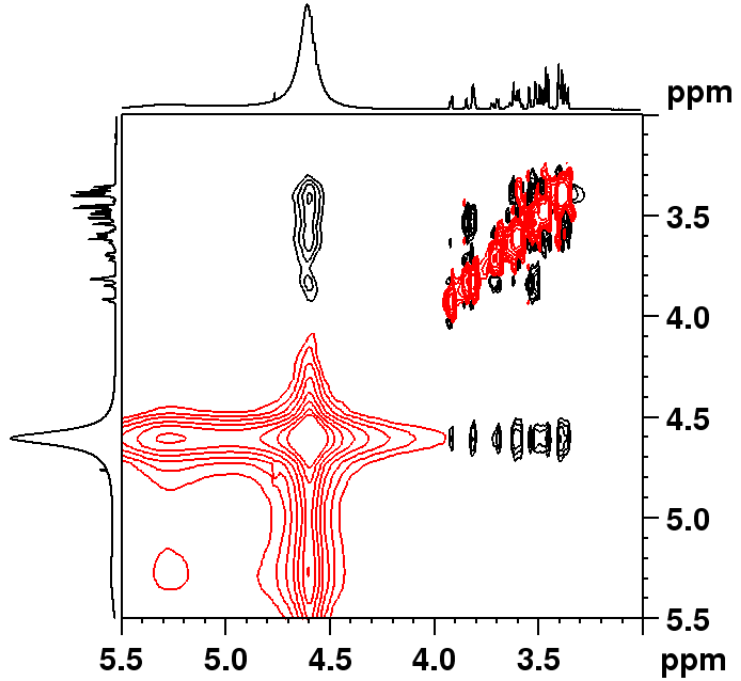
FGW115

n_{Water} = 5



molecules with low τ_c

slow exchange & spatial proximity



FGW1120

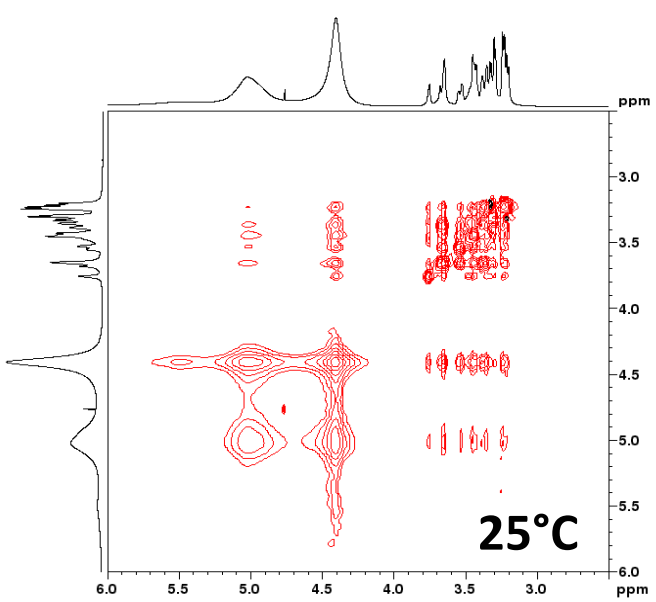
n_{Water} = 20

molecules with high τ_c

faster exchange & ~~spacial proximity~~

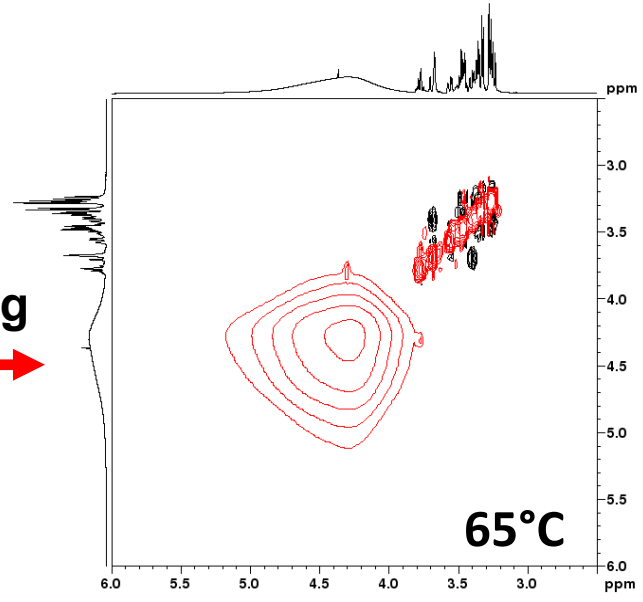
H-bonded network ≤ n_{Water} = 6 > small molecules in water

^{1}H-^{1}H NOESY NMR : impact of temperature on FGW115



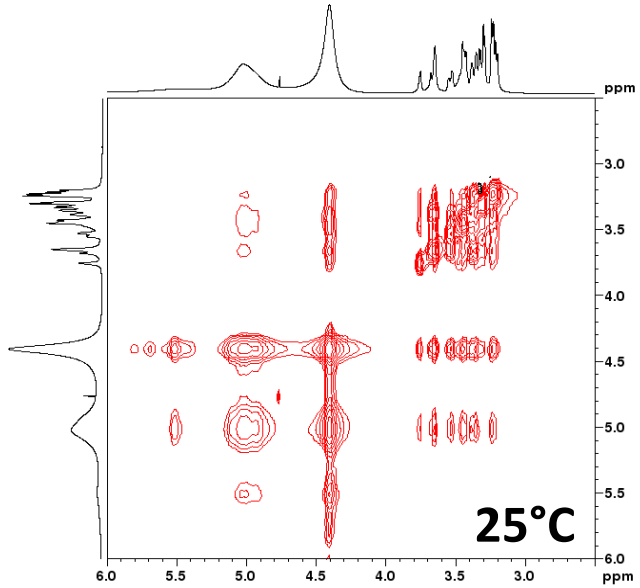
Initial state

Heating



Thermal dissociation of the interactions

Cooling



Recovery of the initial state

Thermal dependency and reversibility of interactions confirm the formation of a hydrogen bonded network

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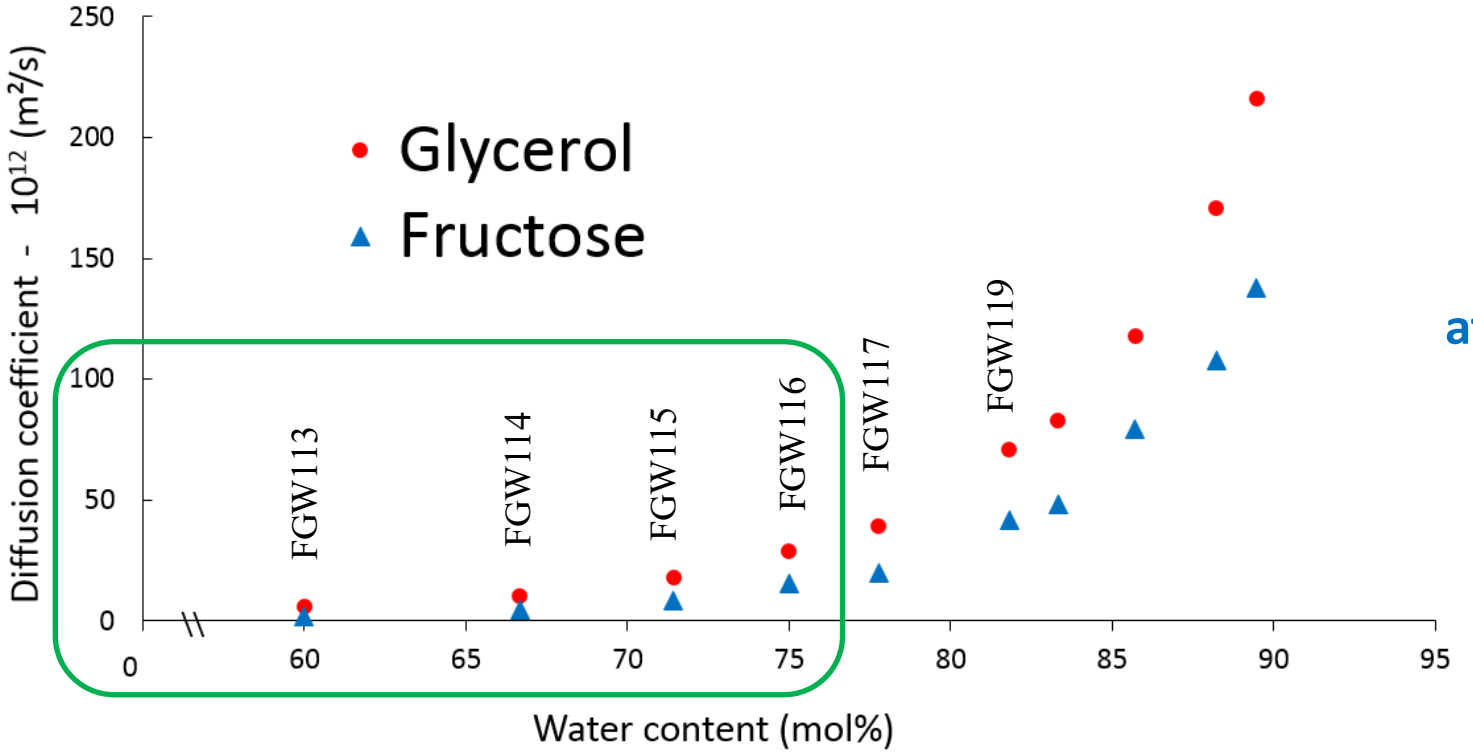
Pulsed Field Gradient NMR & self-diffusion coefficients

$D_F \approx D_G$
at low water content



$D_F < D_G$
at high water content

2 distinct coefficients for all FGW mixtures (D_F & D_G)

Restricted self-diffusion of molecules in LTTM mixtures

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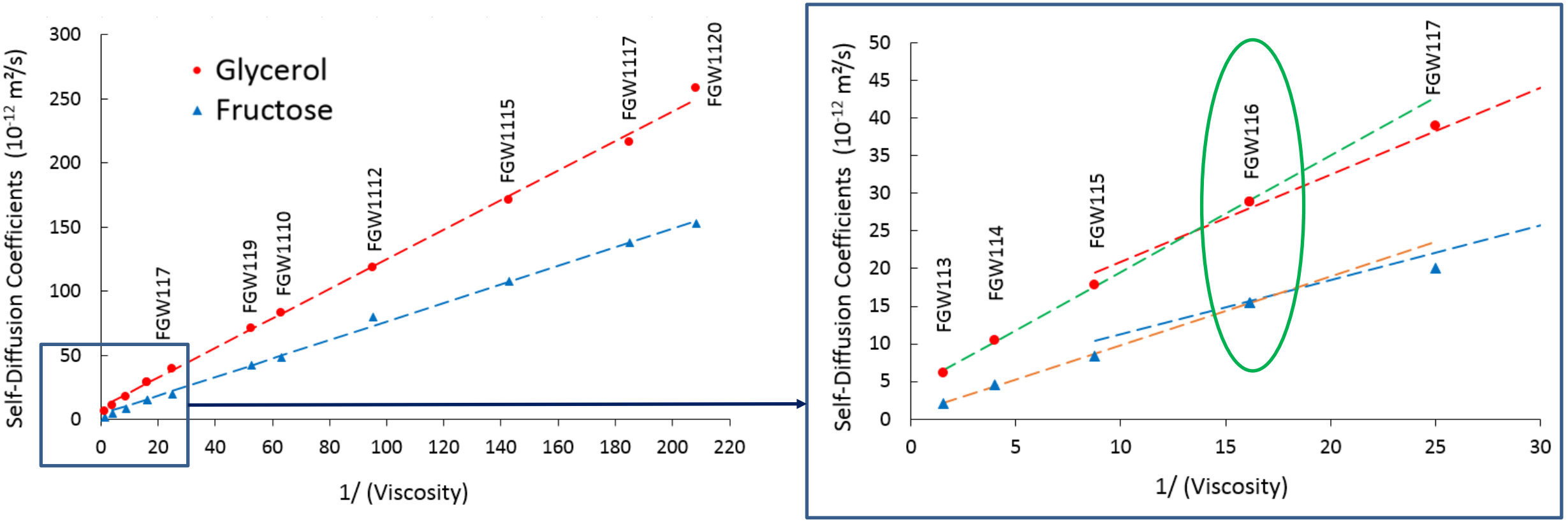
Relationship between micro and macroscopical features

Evolution of self-diffusion coefficients as a function of inverse viscosity



2 distinct diffusion zones

Restricted self-diffusion of F and G ≤ n_{Water} = 6 > free self-diffusion of F and G

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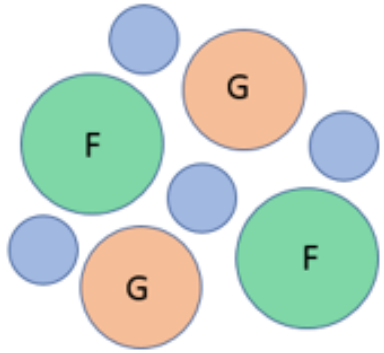
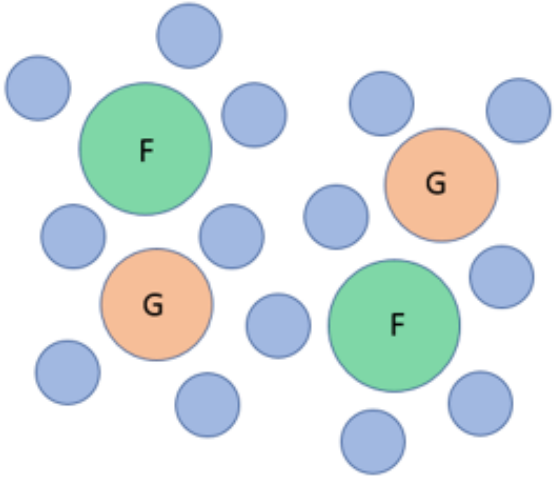
Relationship between micro and macroscopical features

Schematic illustration of molecular organization depending on water content



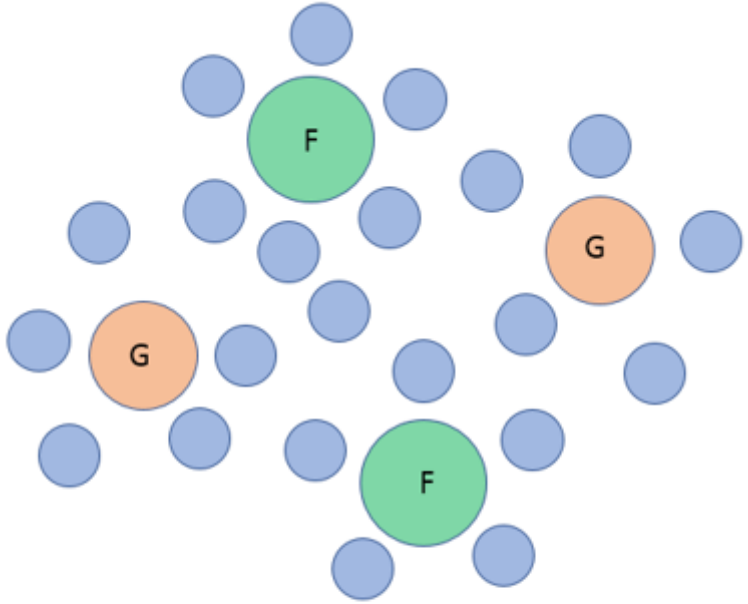
$n_W \leq 6$ moles

H-bonded structured liquid
=> H_2O embedded in LTTM



$6 \leq n_W \leq 9$ moles

Transitory state



$n_W \geq 9$ moles

=> Aqueous solution of F and G

Water content affects both molecular organization & macroscopical features

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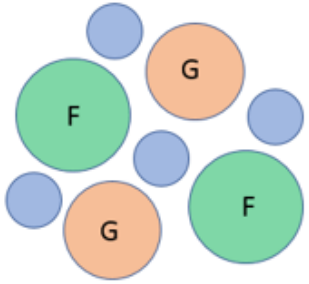
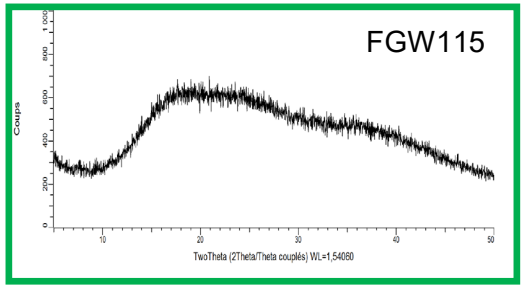
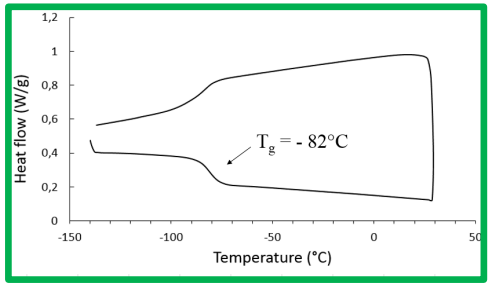
Conclusion

High cohesive forces : formation of a hydrogen bonded network

- Homogeneous, amorphous and viscous LTTM



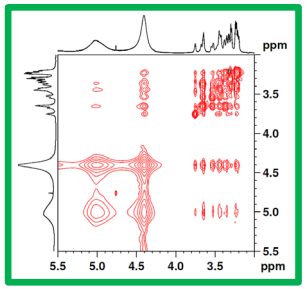


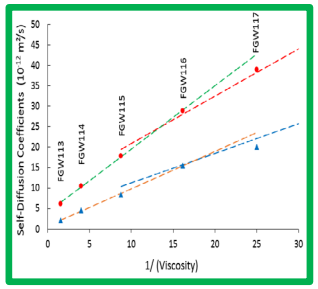


- Mixture with supramolecular structuration since molecules within it
  - are spatially close
  - have low rotational correlation times
  - have restricted translational mobility

$n_W \leq 6$ moles

H-bonded structured liquid
=> H_2O embedded in LTTM





Pave the way to the use of FGW mixtures for further green technologies

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Aknowledgments

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INSA

2nd International Meeting on
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15-17 JUNE 2021
ONLINE

Thank you for your attention