

Tribological behavior of Ionic Liquids and Deep Eutectic Solvents on Silicon surfaces

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MEMs and NEMs

Silicon



- 2018 - the total market value for microsystems was 10 billion euros.
- 2024 - is expected to reach 50 billion euros.

It is necessary to choose a suitable lubricant that can form a thin film between the sliding surfaces.



ILs and DESs

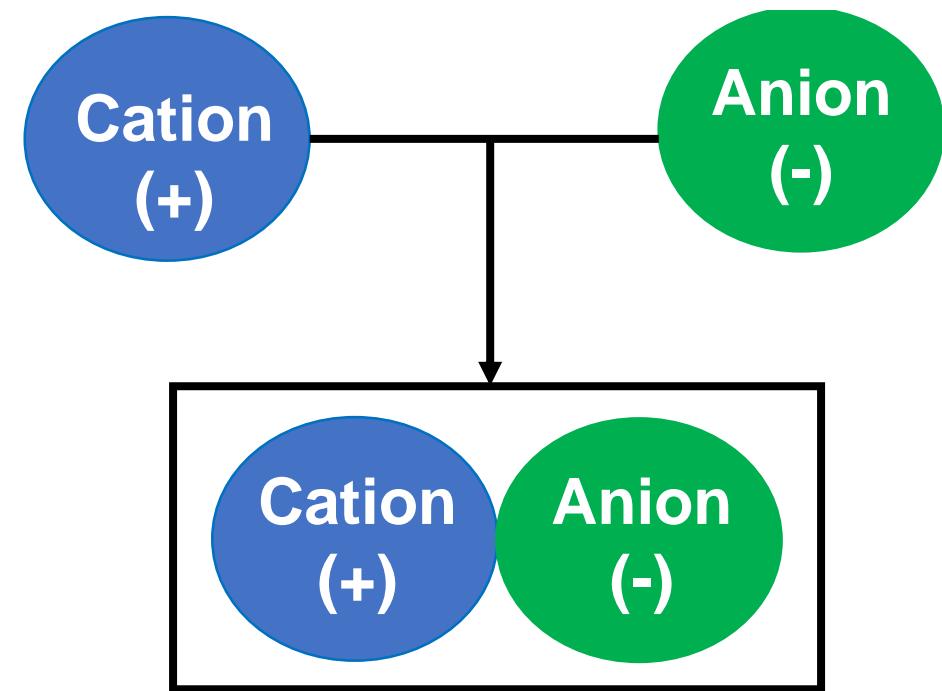
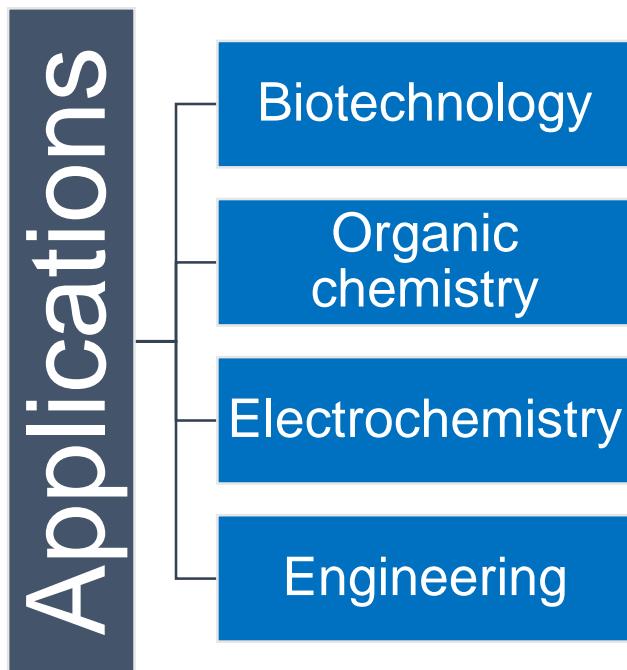
- Moderate to high viscosity.
- Can be designed to a specific tribological systems.
- They are able to form thin films on the surface.
- Since they have high conductivity, they can improve the electrical system on the machine.

Applications:

Electromechanics, medicine, chemistry and biology

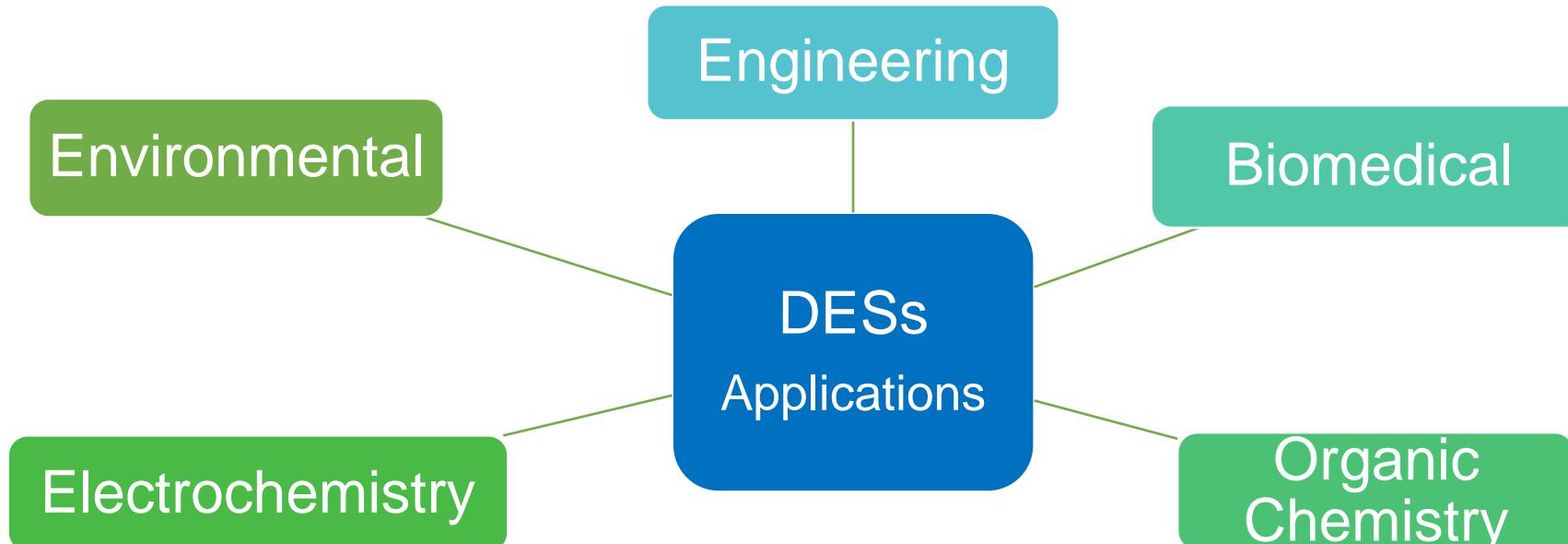
Ionic Liquids (ILs)

- Organic salts with a melting point lower than 100 °C.
- Low vapor pressure, high chemical and thermal stability and high ionic conductivity.
- The cation-anion combination is possible to be design according to the intended application.

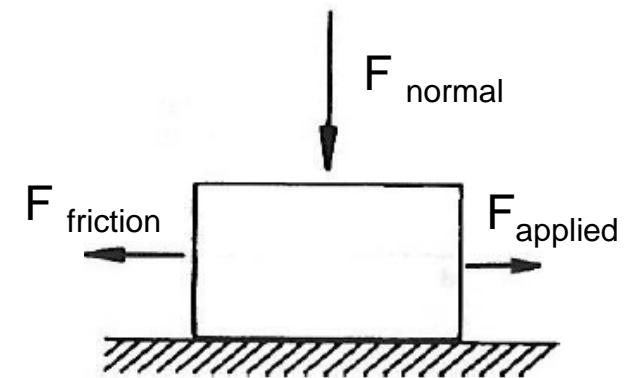
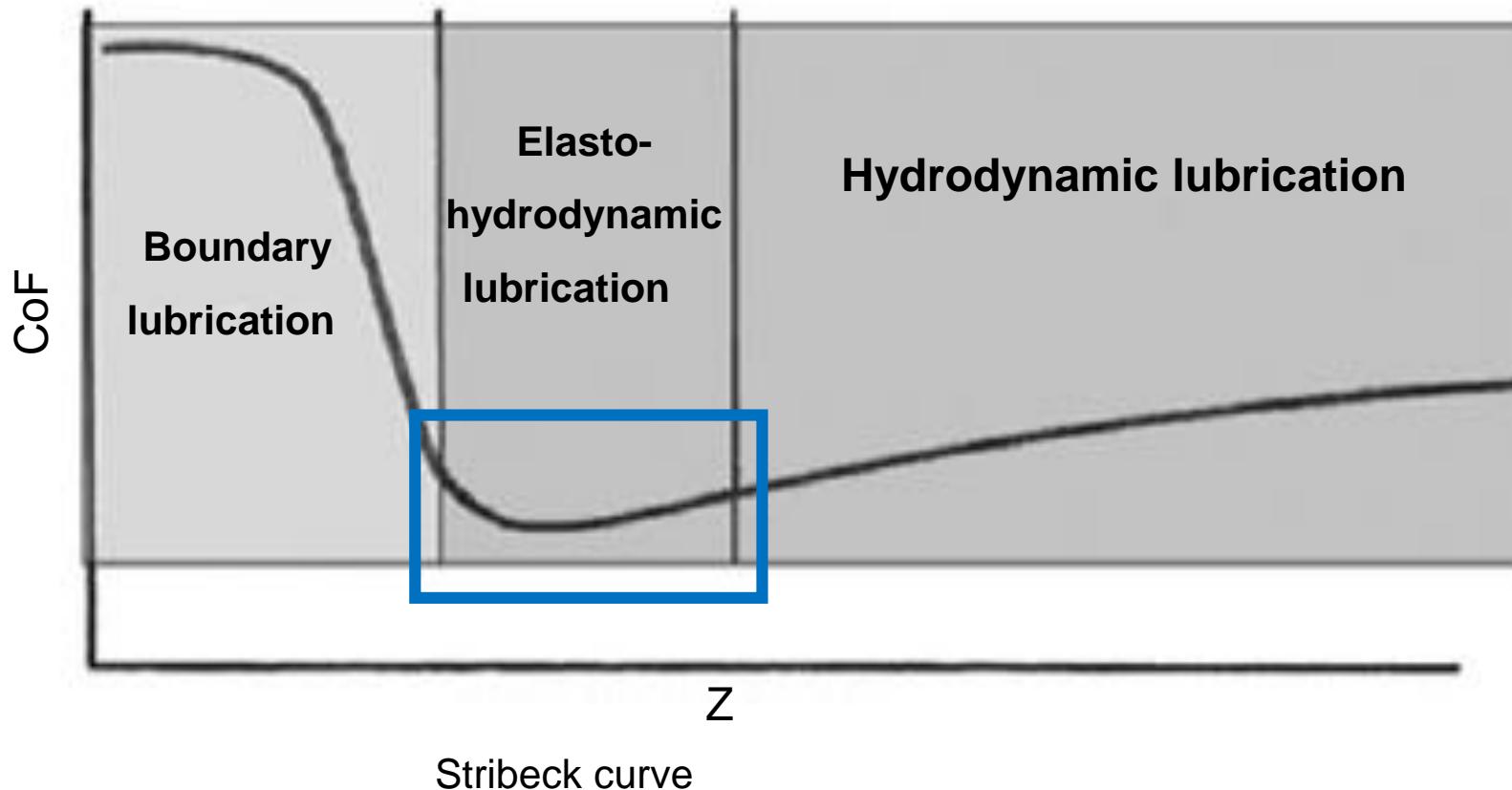


Deep Eutectic Solvents (DES)

- The formation of DESs is due to the interaction between Hydrogen Bond Acceptor (HBA), for e.g an IL, and a Hydrogen Bond Donor (HBD).
- A solution can be defined as a DES if the mixture of the HBD: HBA has a lower melting point than its pure compounds.
- They are easier to prepare and have a more competitive price than ILs



Lubrication Regimes



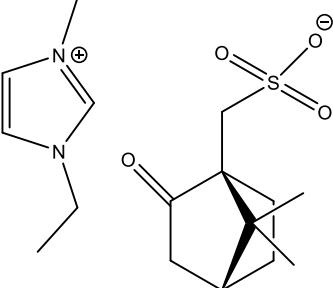
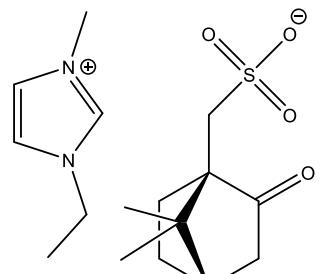
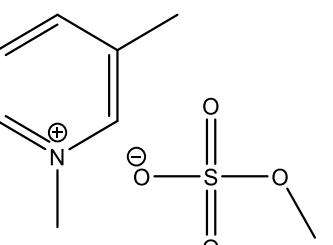
Representação das forças.

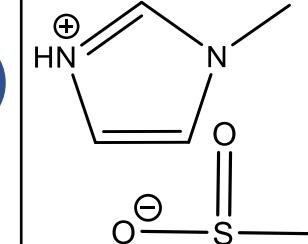
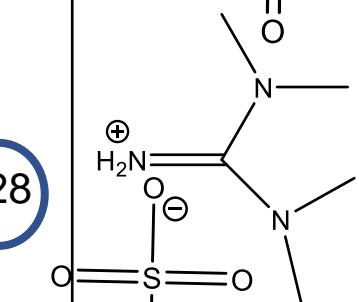
$$CoF = \frac{F_{friction}}{F_{normal}}$$

Sommerfeld number

$$Z = \frac{\eta vr}{N}$$

Synthesized Salts

Salt	Yield (%)	Appearance of the IL	Molecular Structure
[C ₂ MIM][(S)-CSA]	79	 Liquid R.T.	
[C ₂ MIM][(R)-CSA]	84	 Liquid R.T.	
[C ₁ -3-pic][MeSO ₄]	93	 Liquid R.T.	

Salt	Yield (%)	Appearance of the salt	T _f (°C)	Molecular Structure
[HMIM][MeSO ₃]	98	 Solid	134	
[TMG][MeSO ₃]	96	 Solid	128	

Melting point higher than 100° C.
Can not be classified as ILs.

All the salts were
characterized by ¹HNMR

Produced DES

HBA:HBD	Appearance of the DES	Molecular Structure
[C ₂ MIM][(S)-CSA]:PEG200 (1:4)		
[C ₁ -3-pic][MeSO ₄]:PEG200 (1:4)		
[HMIM][MeSO ₃]:PEG200 (1:4)		
[TMG][MeSO ₃]:PEG200 (1:4)		
[S _{4,4,2}][EtSO ₄]:PPG425 (1:4)		

All DESs were characterized by FTIR- ATR and DSC

Characterization of the lubricants

ILs

[C₂MIM][(S)-CSA]
[C₁-3-pic][MeSO₄]
Pures

Additives

All salts were tested
as additives
2%(wt/wt) on
PEG200

DES

Pures

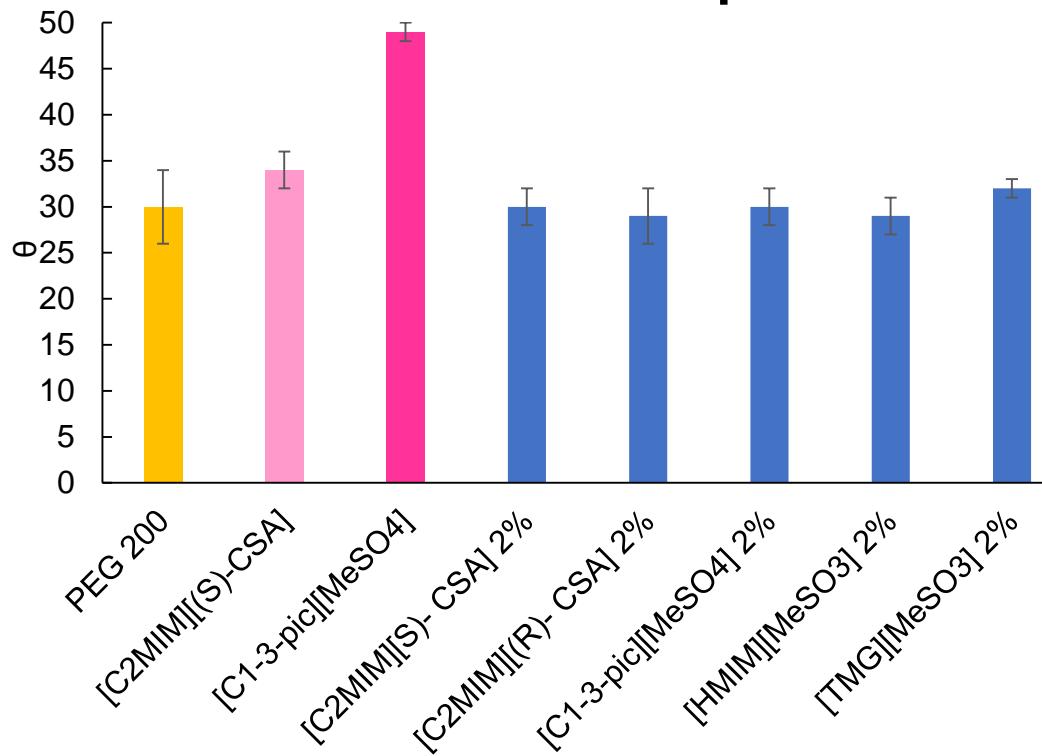
Wettability

Viscosity

Tribological
tests

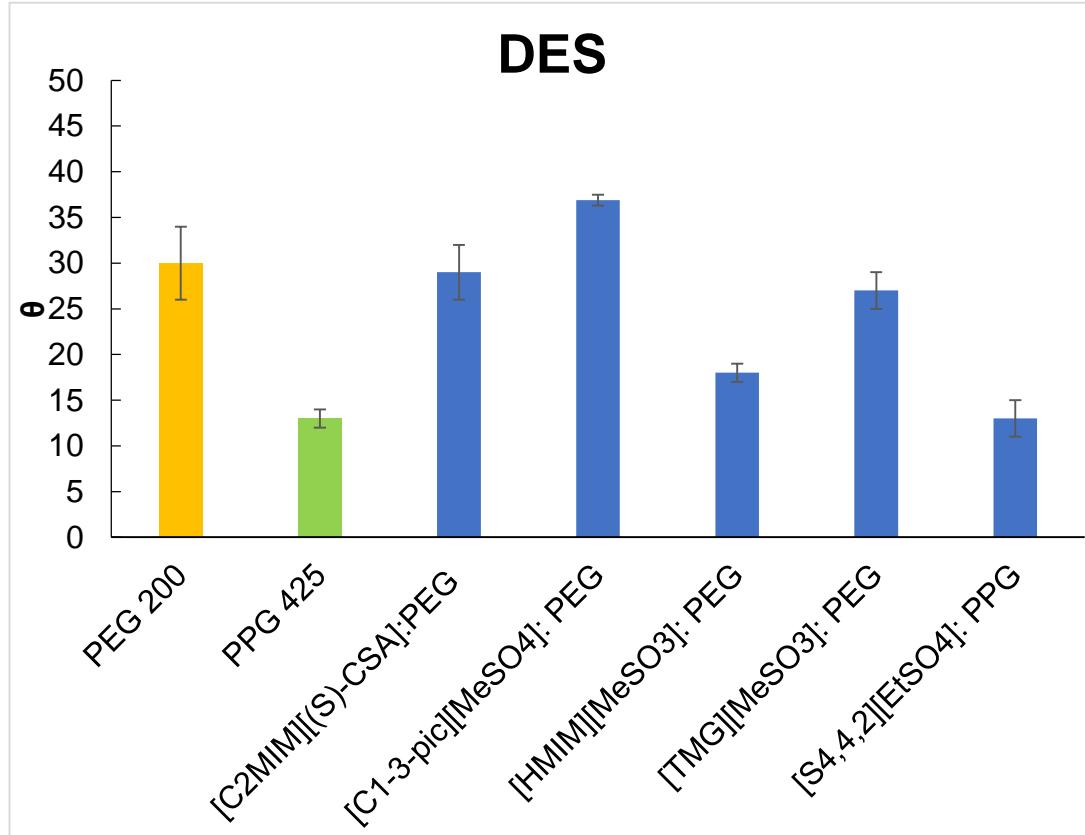
Wettability- Contact Angle

PEG with additive and pure ILs



The additives did not show any alteration relatively the wettability capacity of PEG

DES



In comparison to the HBD, it was only evident a change in the wettability for [HMIM][MeSO₃]:PEG200 and [C₁-3-pic][MeSO₃]:PEG200.

Viscosity

Lubricant	η (mPa.s) 25°C
Pure Liquids	
PEG200	47,5±0,1
PPG425	70 ³
[C ₁ -3-pic][MeSO ₄]	938±95
[C ₂ MIM][(S)-CSA]	11506±20
PEG+Additive	
[C ₂ MIM][(S)-CSA] 2%	50,6±0,2
[C ₂ MIM][(R)-CSA] 2%	50,0±0,4
[C ₁ -3-pic][MeSO ₄] 2%	60,9±0,1
[HMIM][MeSO ₃] 2%	49,9±0,1
[TMG][MeSO ₃] 2%	49±0,1
DES	
[C ₂ MIM][(S)-CSA]:PEG200	94,3±0,5
[C ₁ -3-pic][MeSO ₄]:PEG200	135,1±0,2
[HMIM][MeSO ₃]:PEG200	66,4±0,2
[TMG][MeSO ₃]:PEG200	76,8±0,6
[S _{4,4,2}][EtSO ₄]:PPG425	145,6±0,4

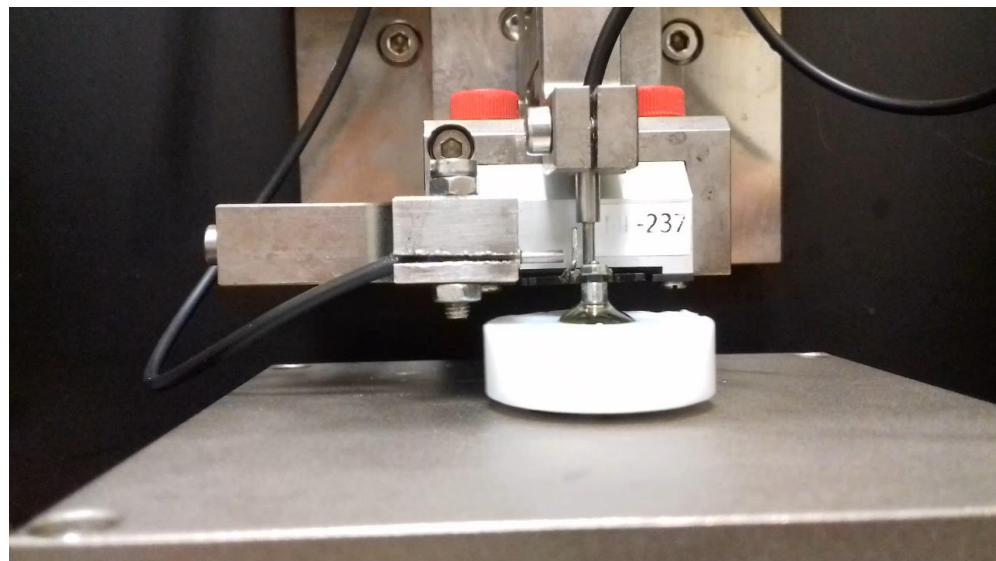


Viscometer Brookfield DV-II+

Newtonian

Tribological tests

Experimental conditions

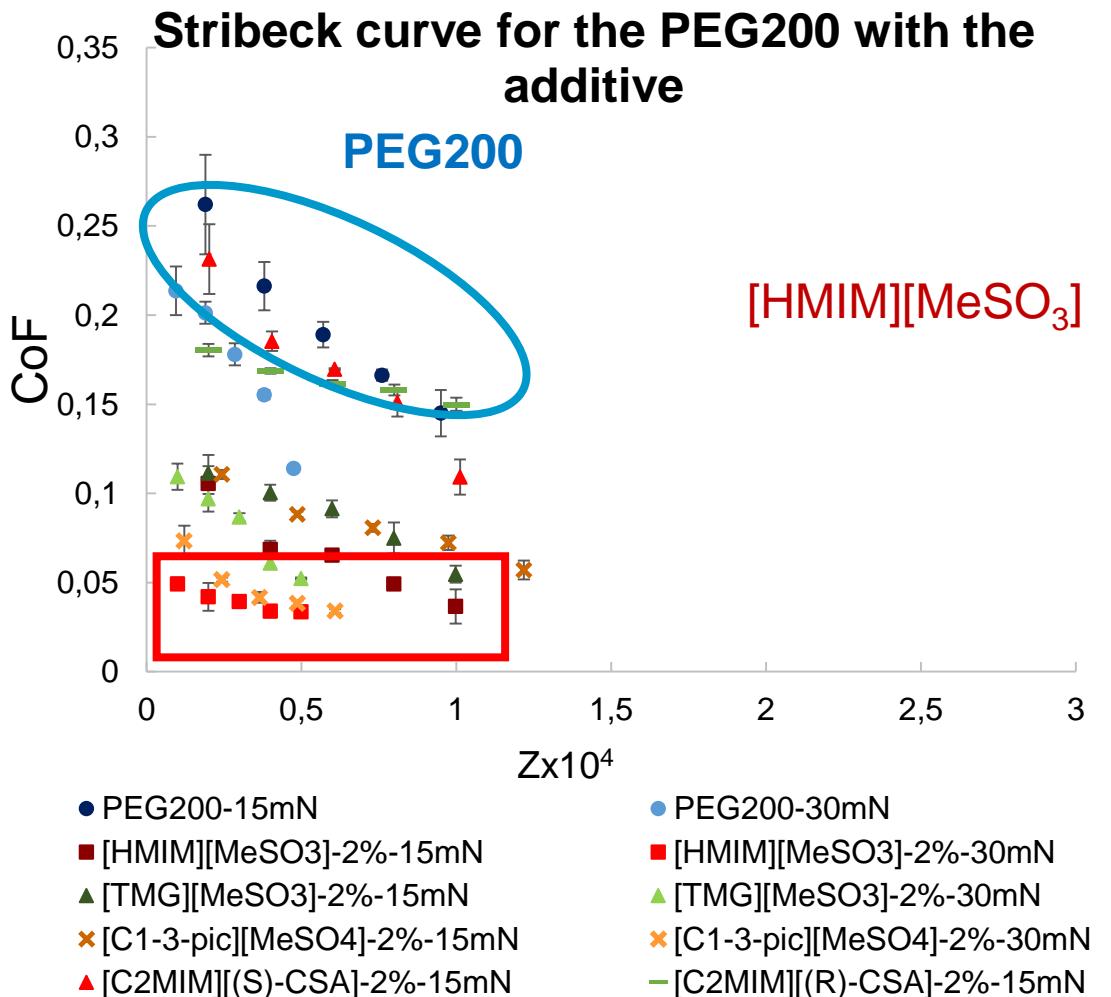


Nanotribometer (CSM Instruments)

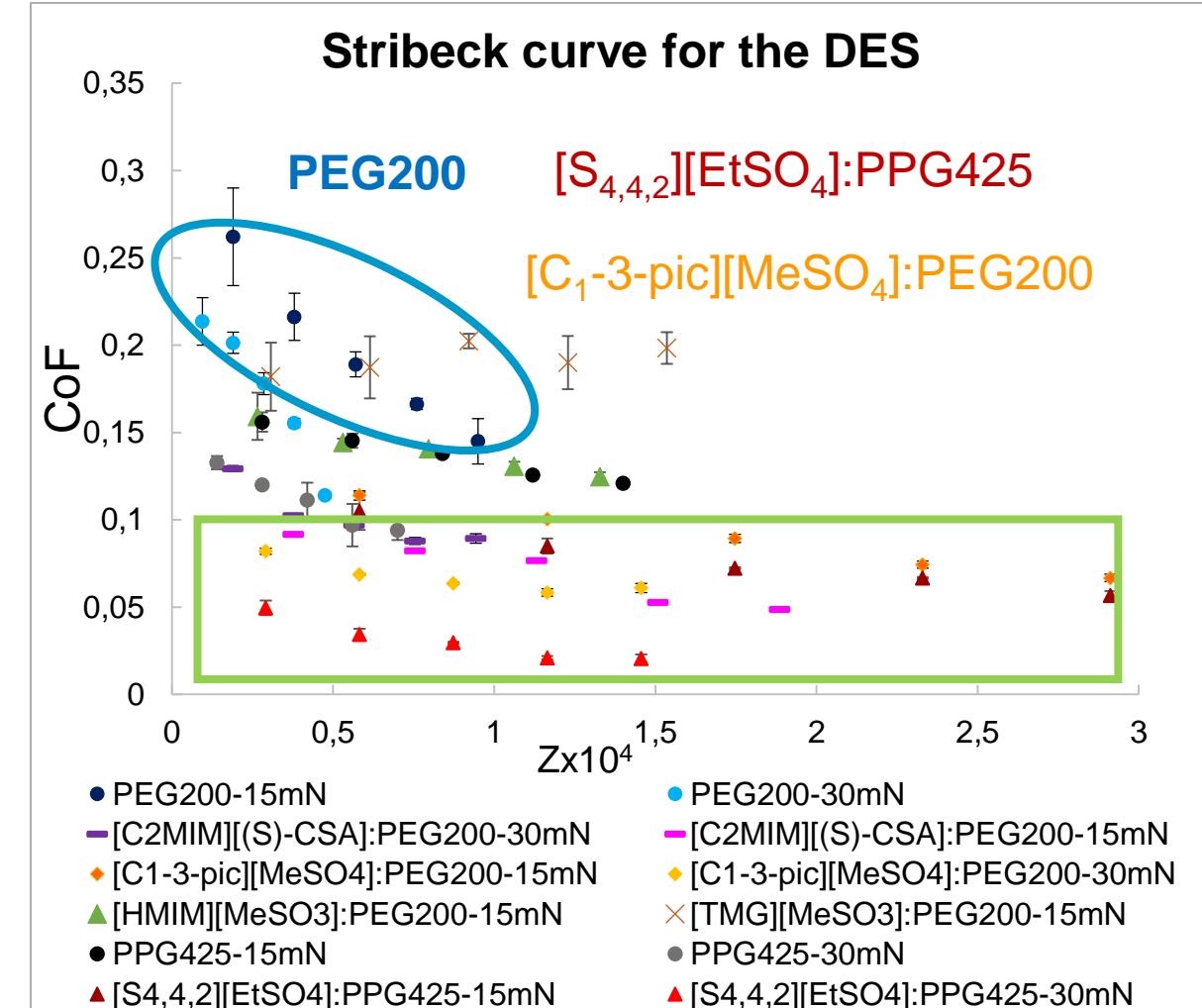
- Sliding velocities - 4, 8, 12, 16 e 20 mm/s
- 400 cycles
- $\frac{1}{2}$ Amplitude- 0,425 mm
- Force- 15 mN

For the best performing lubricants the tests were repeated with a force of 30 mN.

Additives and DESs results

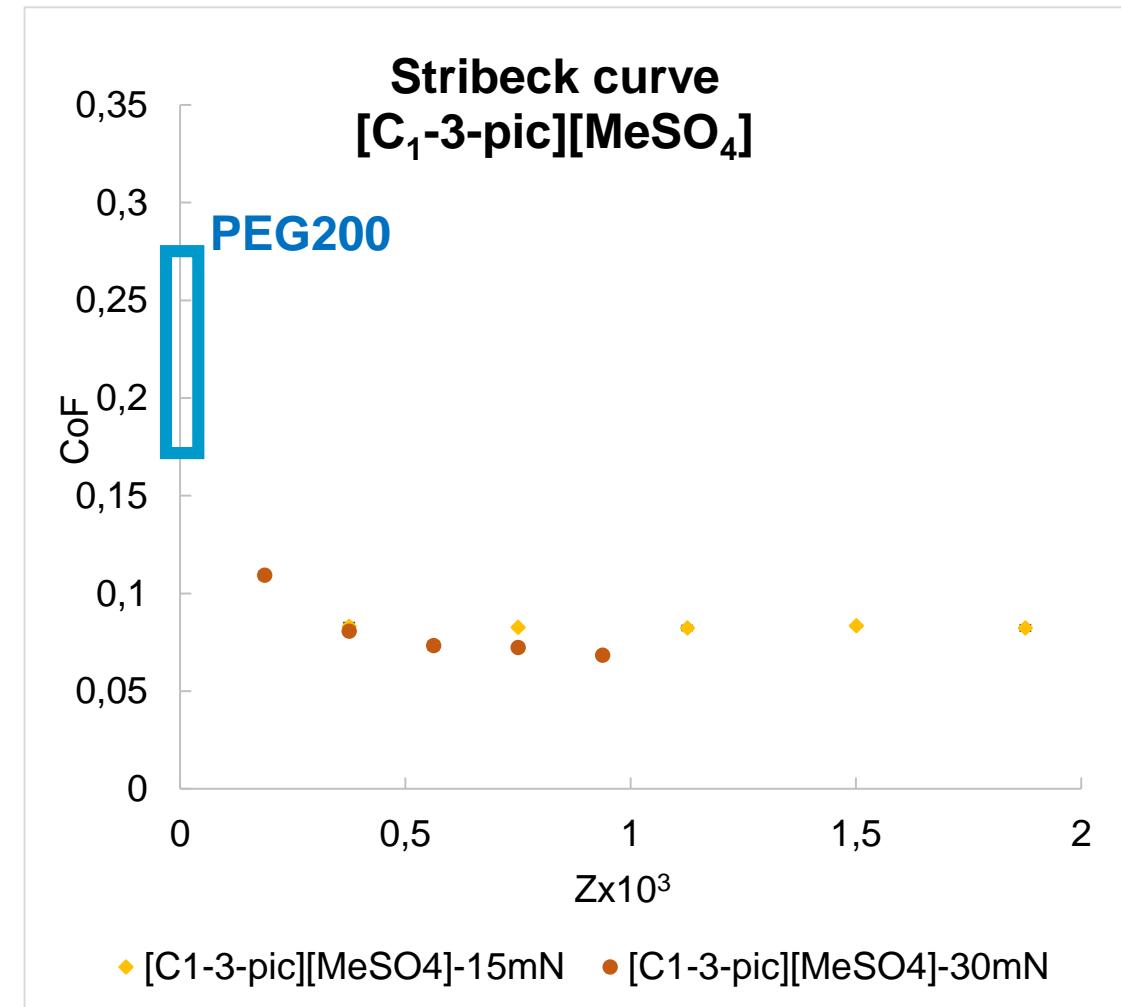
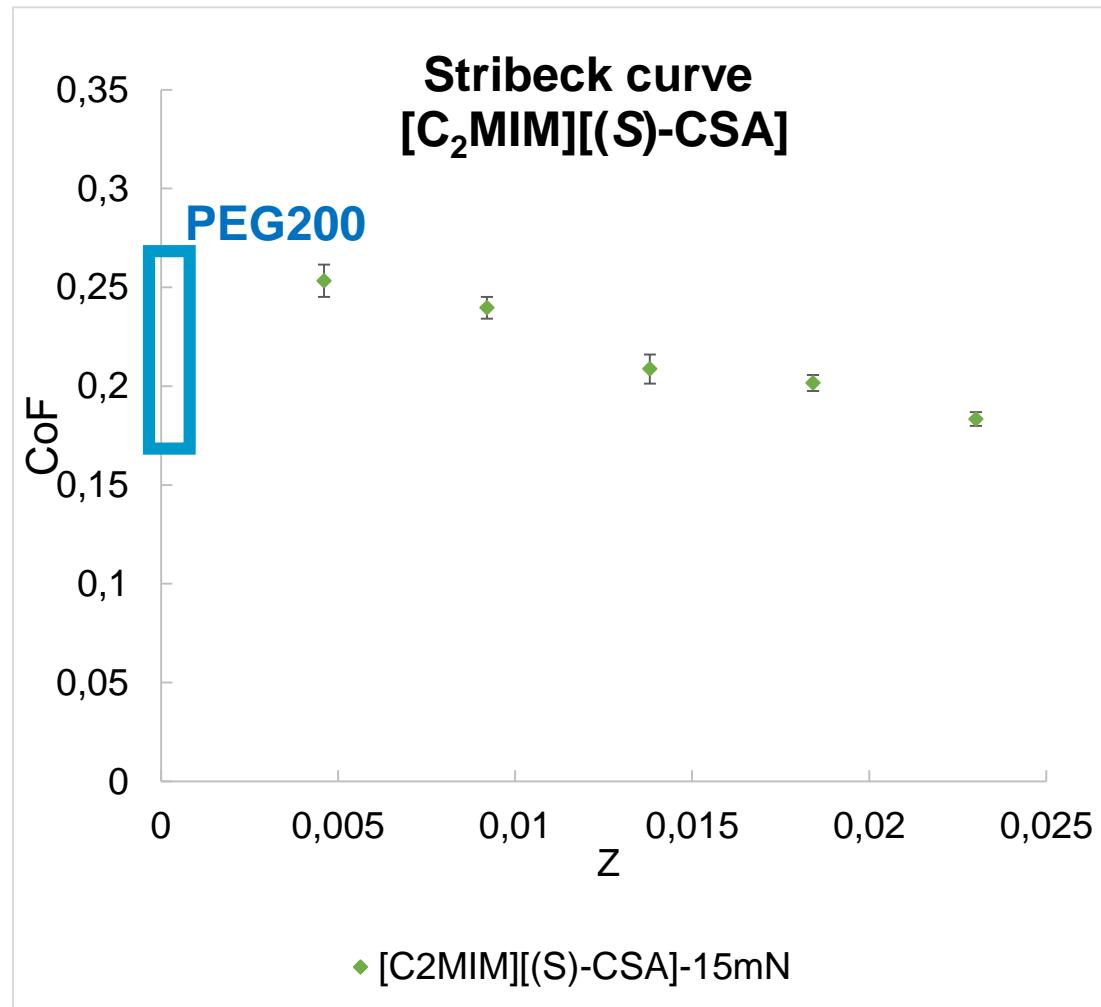


The CoF decreases with the additive

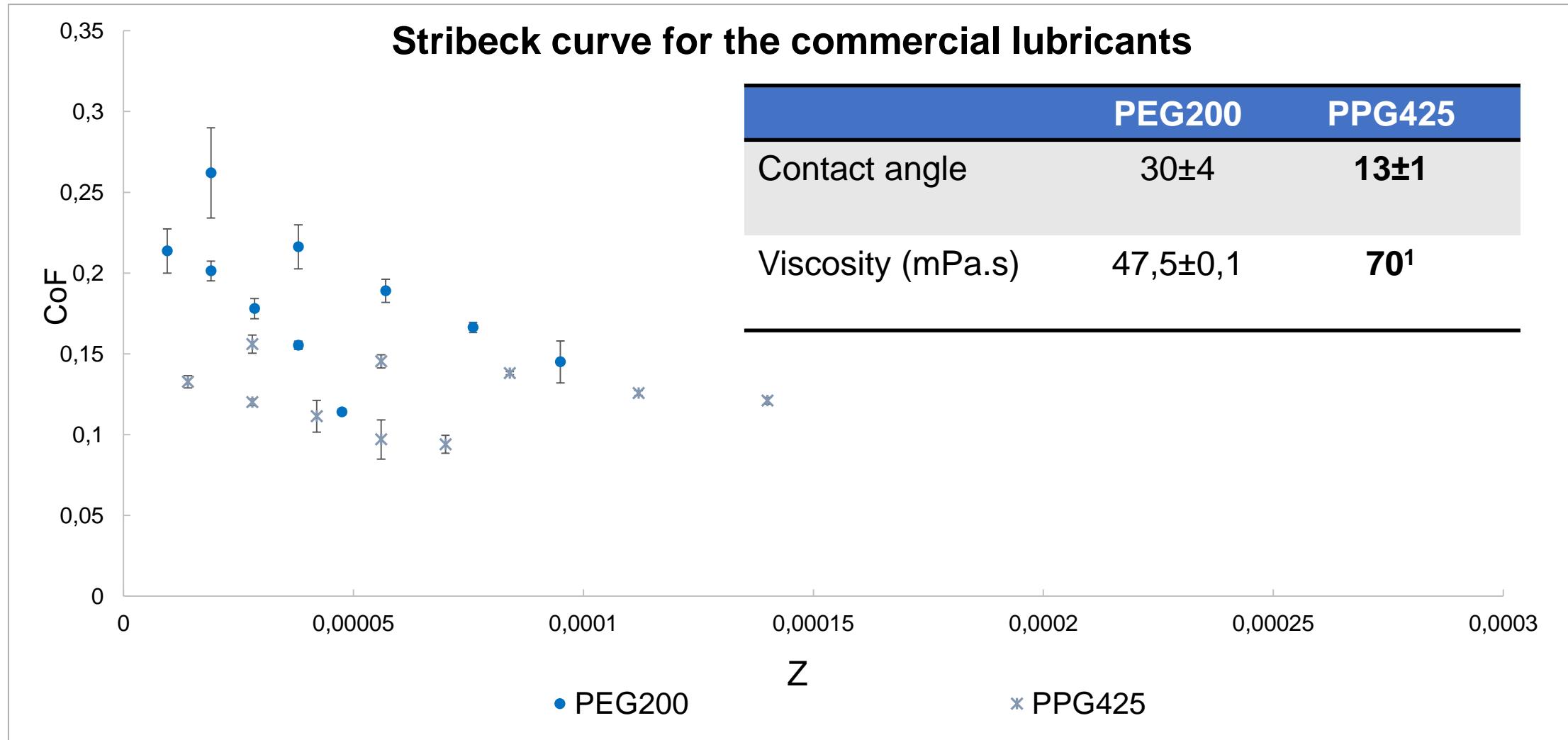


The DES with the best results were
[S_{4,4,2}][EtSO₄]:PPG425 e [C₁-3-pic][MeSO₄]:PEG200

Pure ILs results

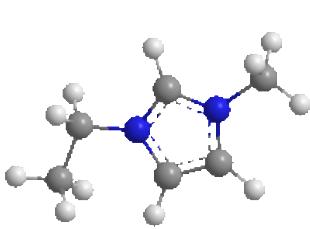
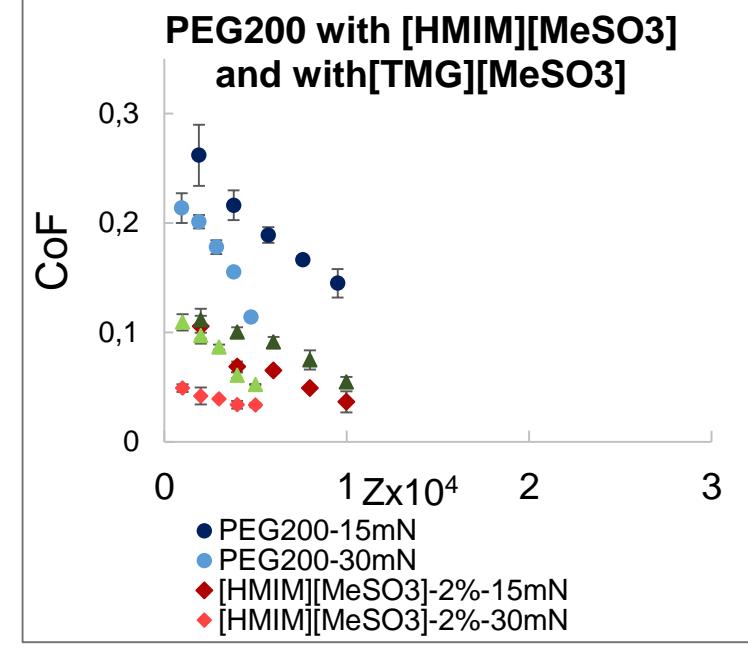
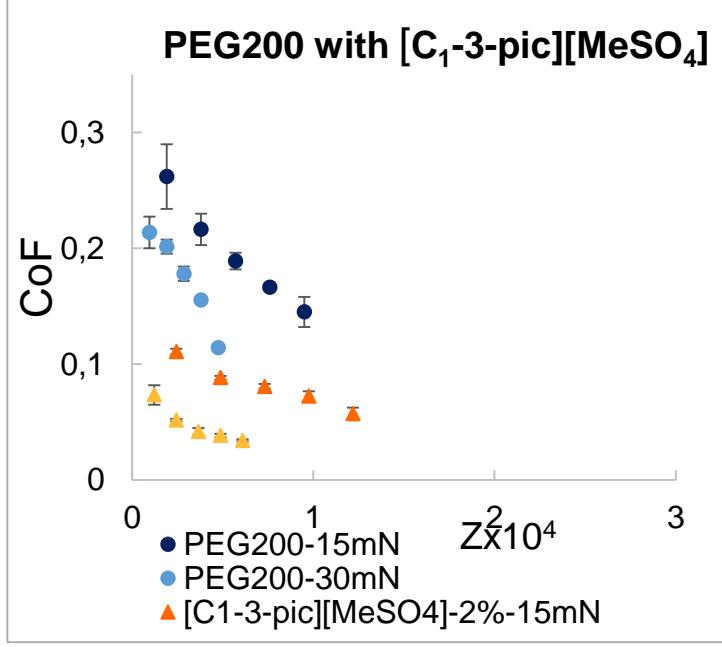
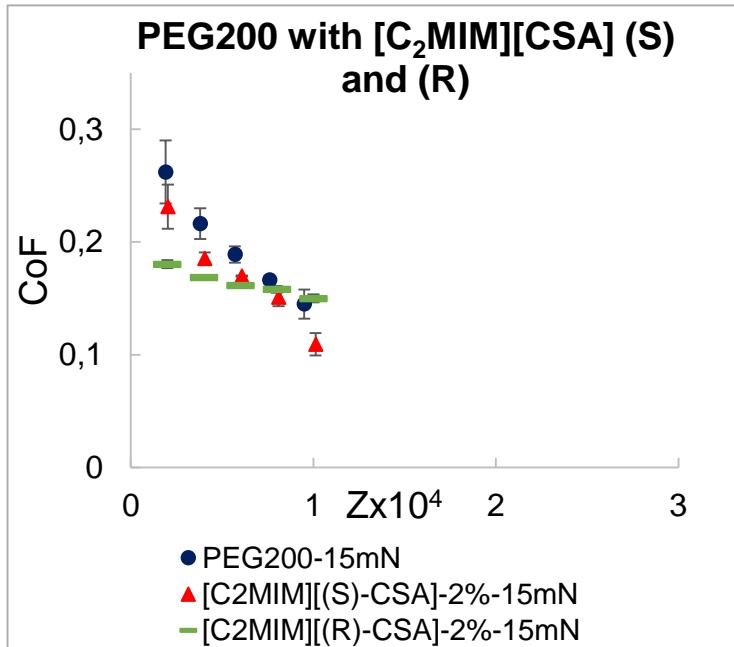


Commercial lubricants comparison

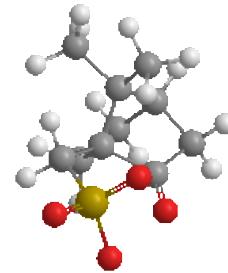


Additives

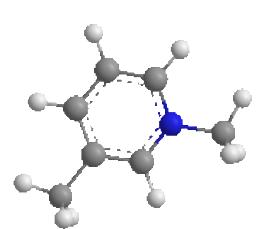
The viscosity and the wettability of PEG200 wasn't significantly modified by the presence of the additives



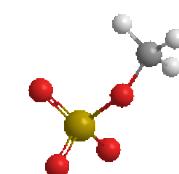
$[C_2MIM]$



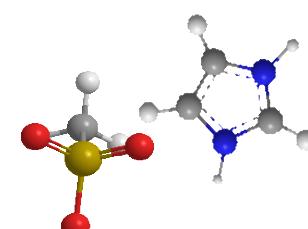
$(S)-CSA$



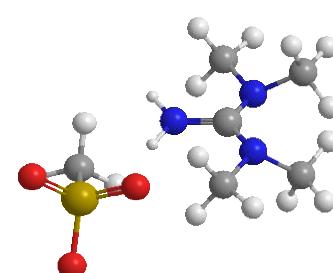
$[C_1-3-pic]$



$[MeSO_4]$



$[HMIM][MeSO_3]$



$[TMG][MeSO_3]$

The structure of the salt affects the lubrication

The protonated cation decreases de CoF

Possible interaction with surface

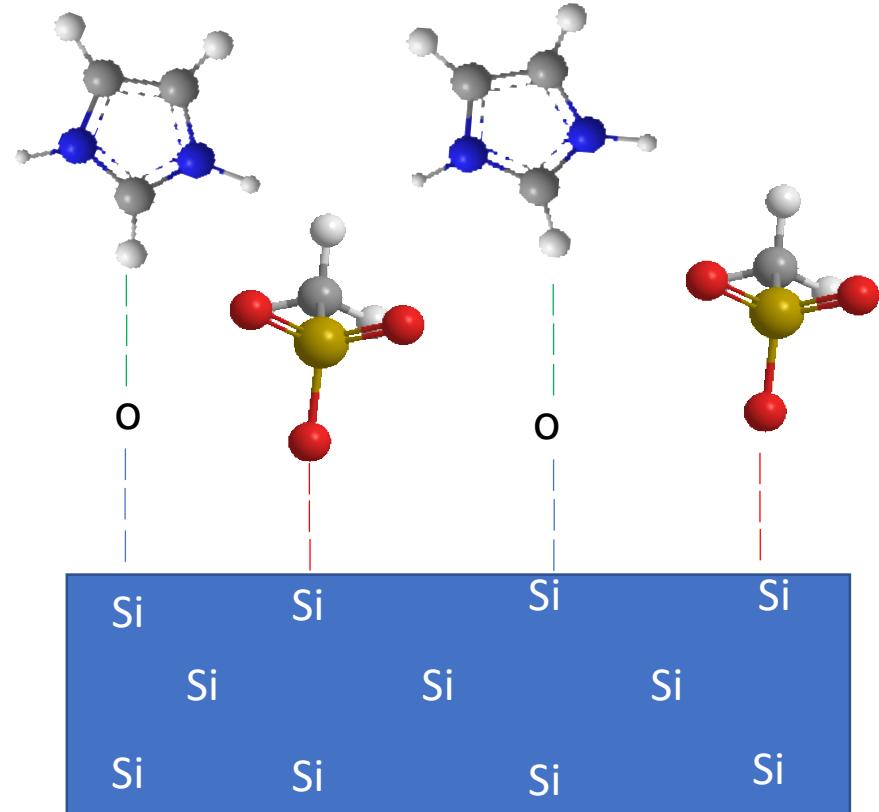
Surface of the silicon wafers spontaneously oxidizes in the presence of air and becomes coated by an oxide layer Si-O.

Previous studies

The C — H bond of the [C₂MIM] cation interacts with the oxygen ².



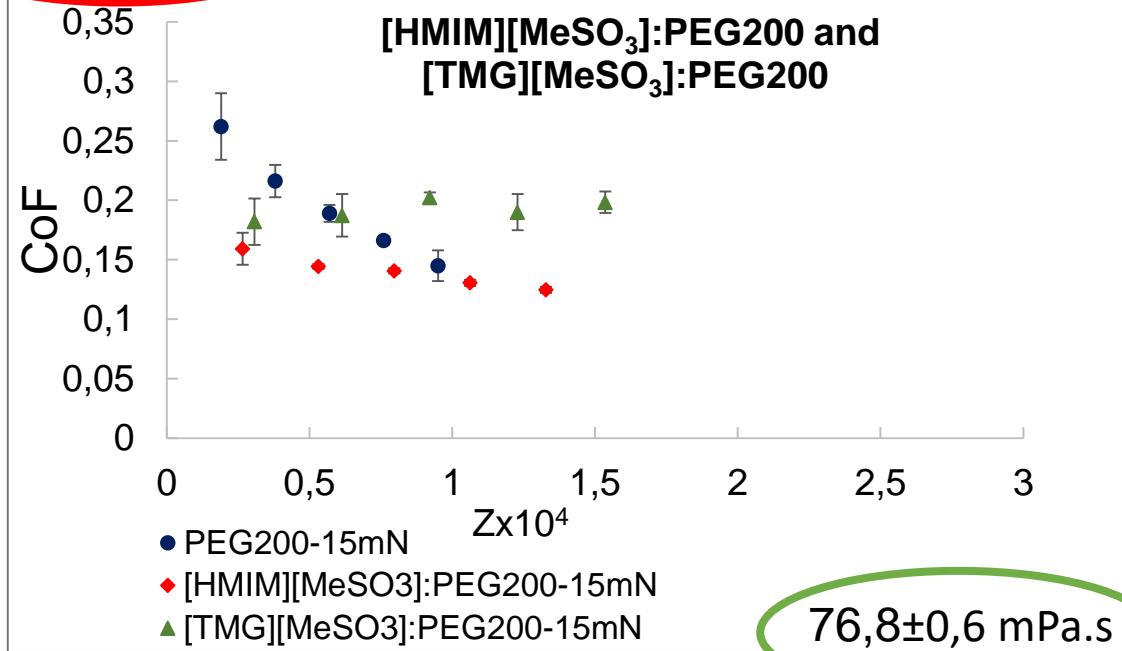
The S—O bond of the anion interacts with the Si surface atoms ³.



Interaction of [HMIM][MeSO₃] with the surface of Si

DES

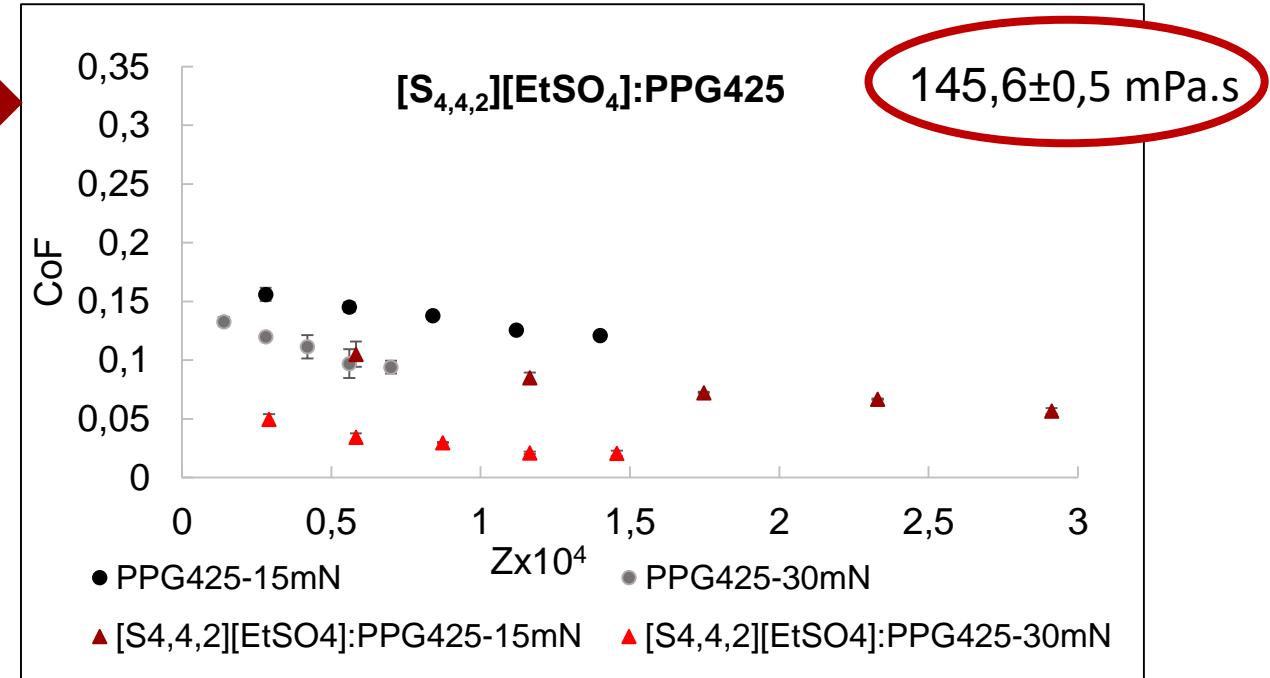
$66,4 \pm 0,2$ mPa.s



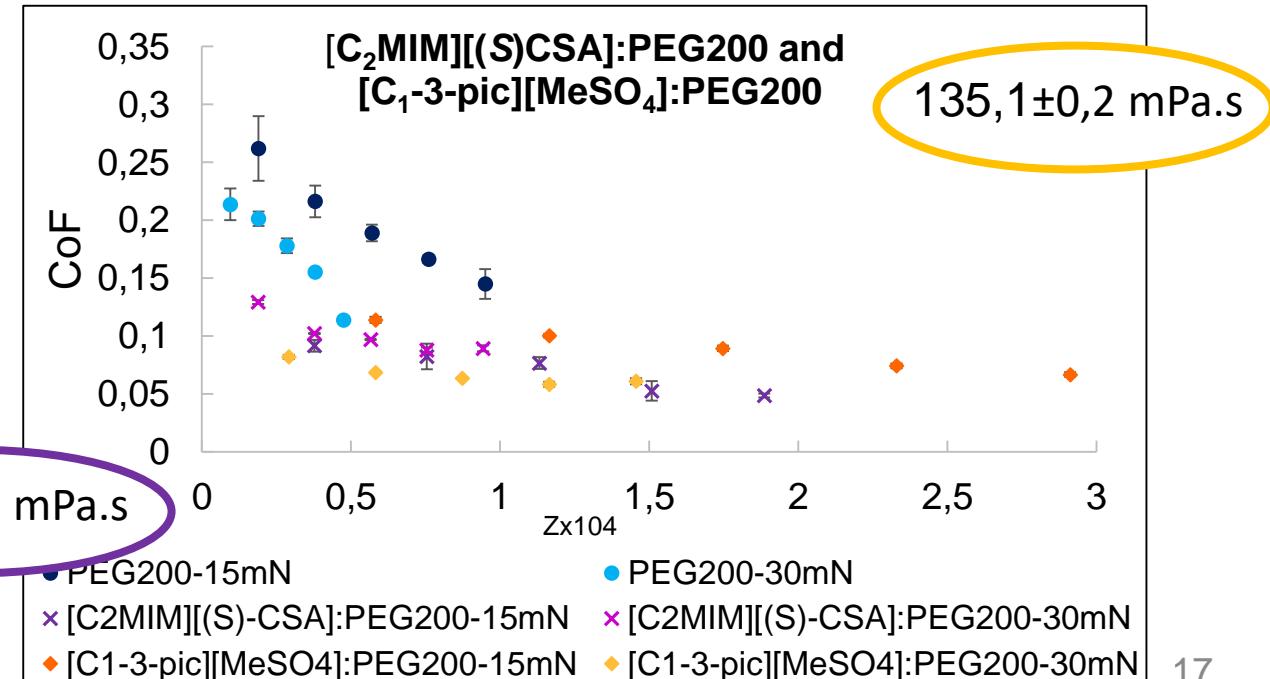
$76,8 \pm 0,6$ mPa.s

The most viscous DES presented the best results

$94,3 \pm 0,5$ mPa.s



$145,6 \pm 0,5$ mPa.s



$135,1 \pm 0,2$ mPa.s

Conclusions

- The properties that had more influence on lubrication were :
 - **Salts as additives:** the ability of the salt to interact with the surface and the structure of the salt.
 - **DESs:** the viscosity and the interaction capability with the surface.
- **Salts as additives :** small cations and anions presented the best results. Particularly, the protic salts led to the lower CoFs due to the good interaction between the protic cations with the Si surface. The best additive was [HMIM][MeSO₃] 2% in PEG200 that is, not only protic, but also has small ions.
- **DESs:** The most viscous DES showed a better lubrication performance. The DES with the lowest CoF was [S_{4,4,2}][EtSO₄]:PPG425.

Perspectives for the future

- Perform further tribological tests with PPG425.
- Study the tribofilm with X-ray photoelectron spectroscopy (XPS).
- Synthesize new protic salts to test their tribological properties.
- Simulate real application conditions used by the micro and nano-machines.

