NATIONAL TECHNICAL UNIVERSITY OF ATHENS
SCHOOL OF CHEMICAL ENGINEERING
Laboratory of Polymer Technology

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Robust self-lubricating poly(urea-formaldehyde) microcapsules designated for thermal spaying coating applications

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OPERATIONAL PROGRAMME
COMPETITIVENESS ENTREPRENEURSHIP INNOVATION
ΕΣΠΑ 2014-2020
Partnership Agreement 2014 - 2020
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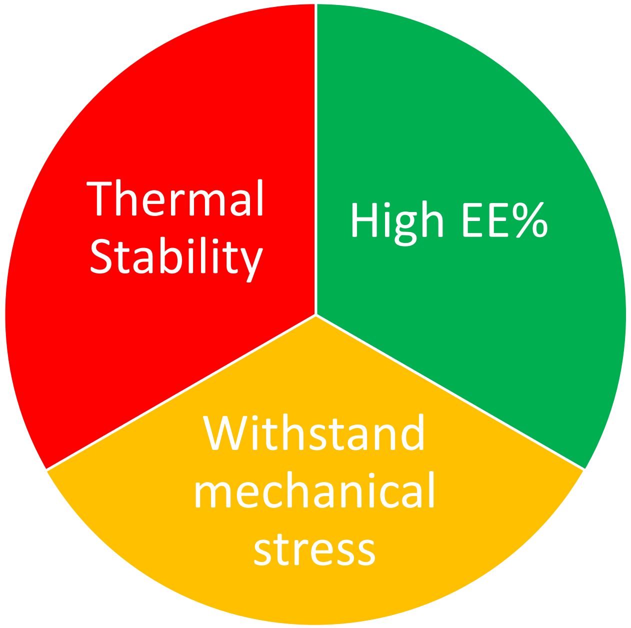
Friction and Lubrication

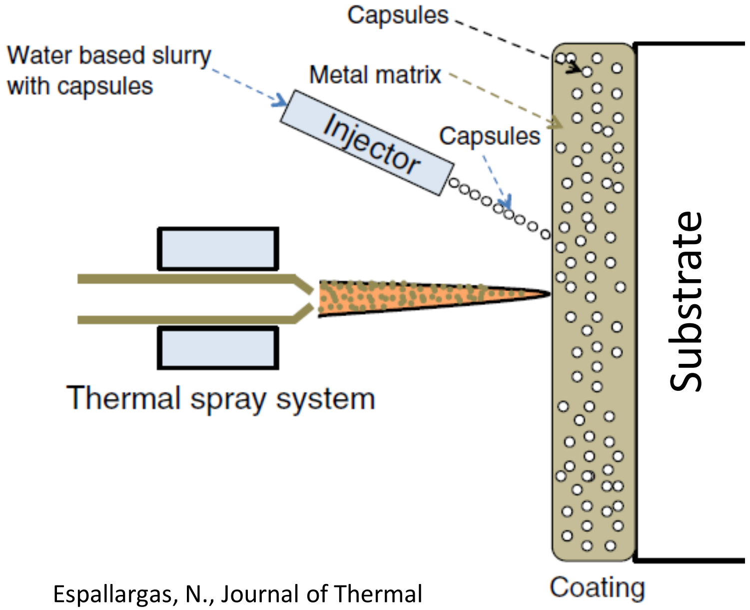
Resistance to motion between two surfaces is called **friction**

Friction leads to:
- Wear and tear
- Heat generation
- Energy loss

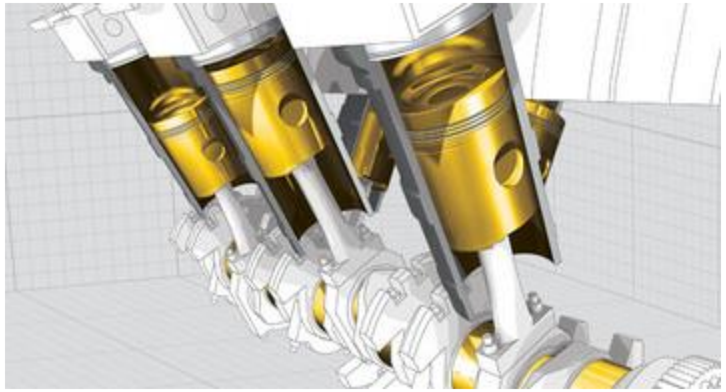
Lubrication is the process used to **reduce friction** between moving parts
- Reduces wear and tear
- Reduces maintenance and running costs
- Increases efficiency
- Acts as coolant

Microcapsules containing a liquid **lubricant** to be used in **metal coatings** produced *via* **thermal spraying** and offer **self-lubrication** properties





Espallargas, N., Journal of Thermal Spray Technology 2015;24:215-233



Self-lubricating microcapsules

Polyurea

Poly(urea-formaldehyde)

Poly(melamine-formaldehyde)

Polyurethane

Polysulfone

Polystyrene

What 's been studied…

What we chose…

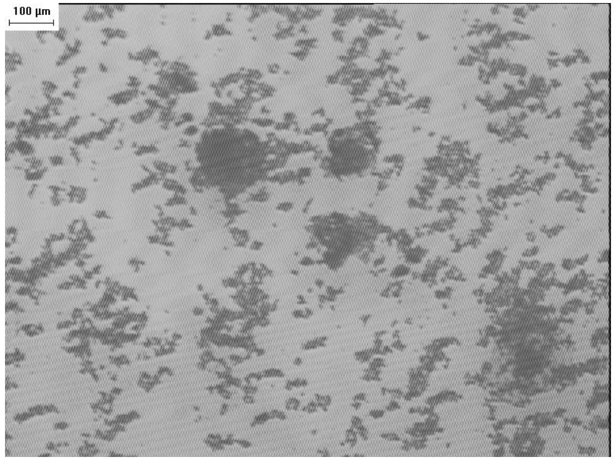
Poly(urea-formaldehyde) — *via in situ* polymerization

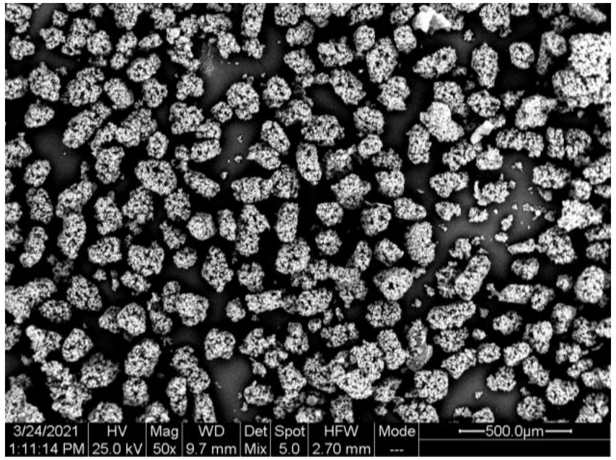
Polysulfone — *via solvent evaporation*

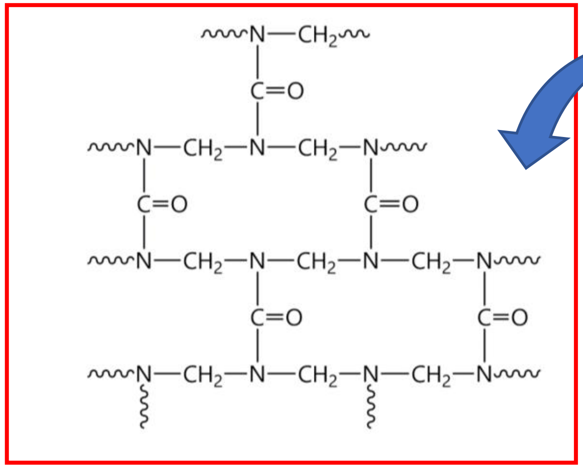
→ **SAE30 Lubricant as core material**

Correlate each encapsulation technique **parameters** to **microcapsule characteristics**

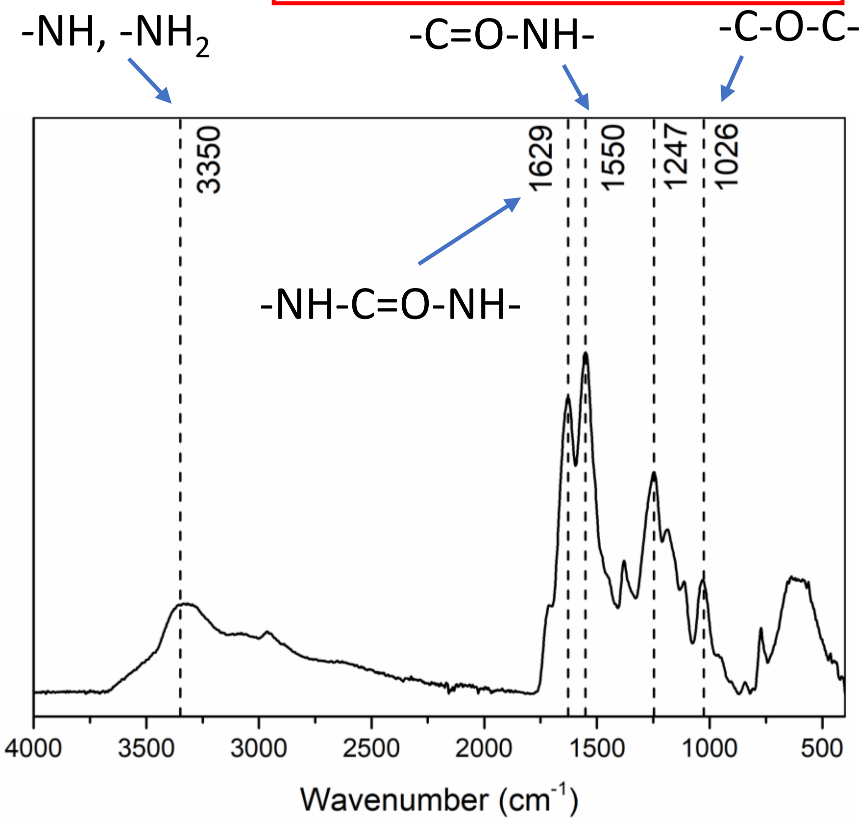
PUF reference experiment

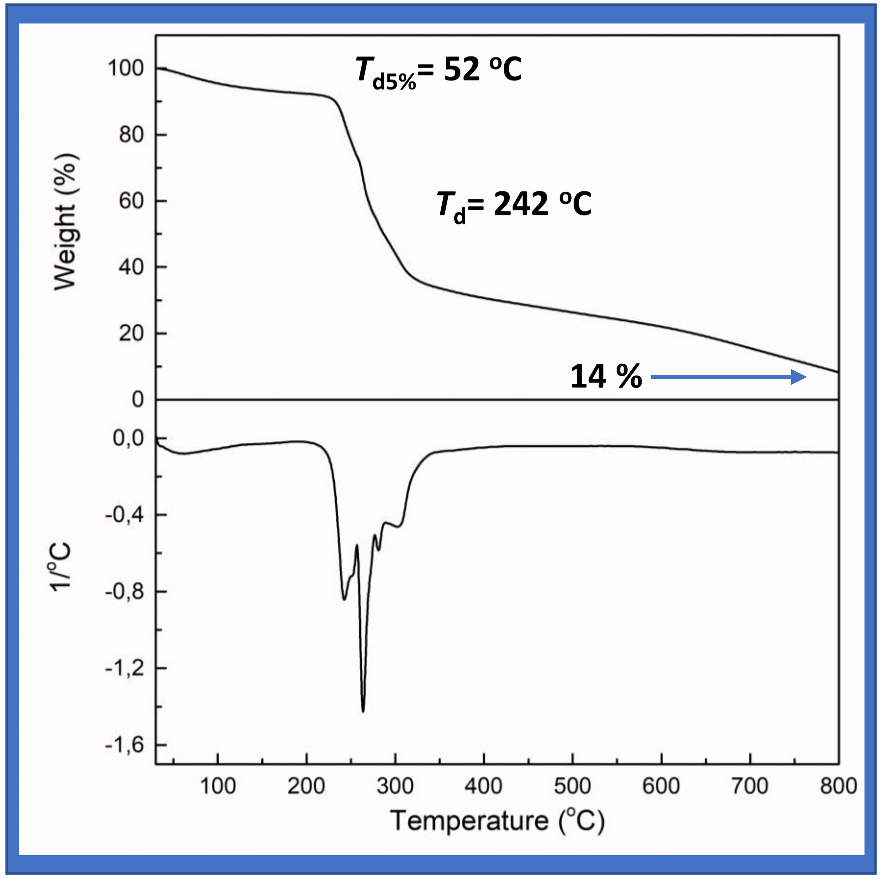






Crosslinked poly(urea-formaldehyde)





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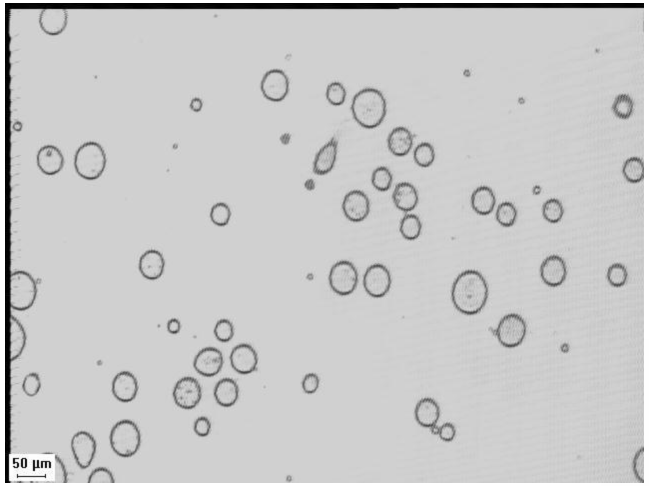
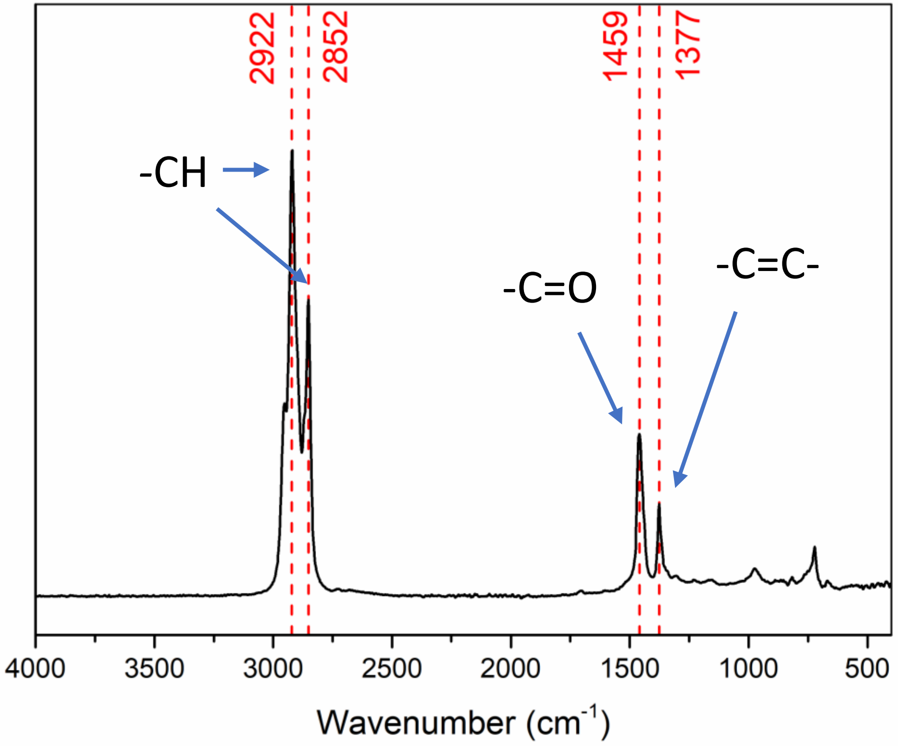
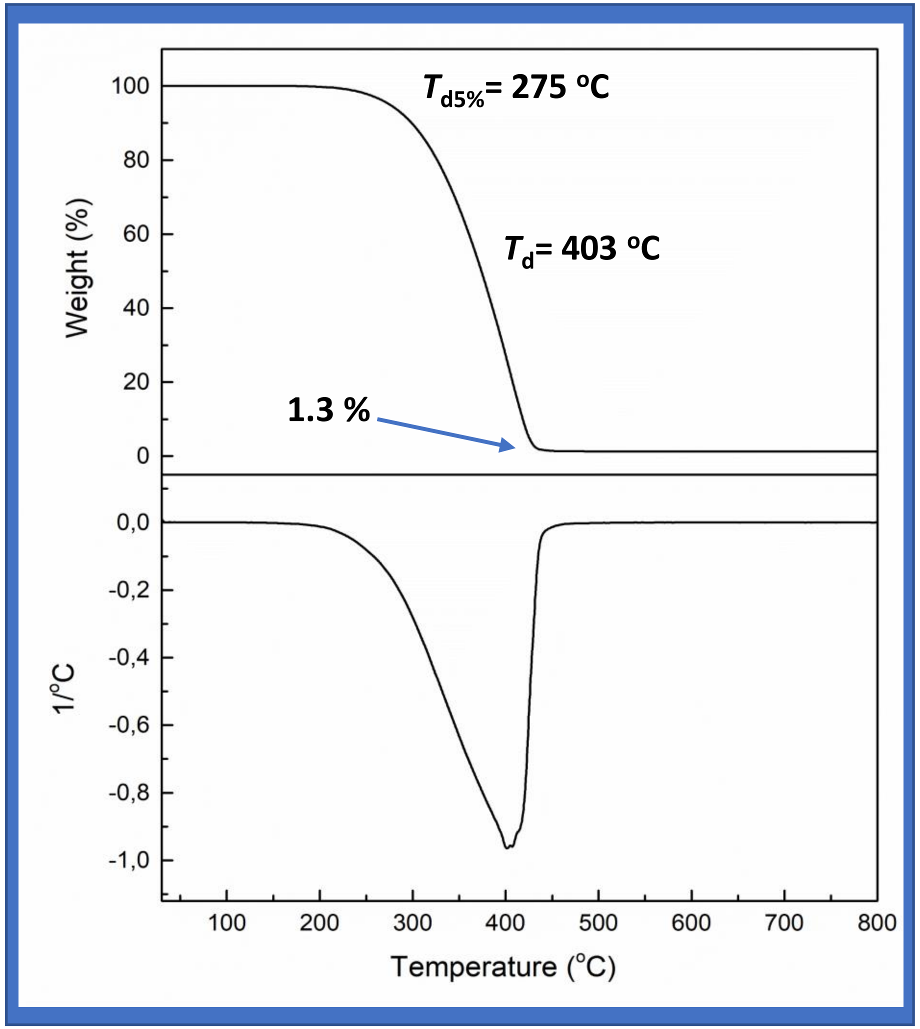
SAE30 Lubricant properties



Properties	SAE30 Lubricant
Kinematic Viscosity @40°C (mm^2/s)	93
Kinematic Viscosity @100°C (mm^2/s)	11
Density @15°C (kg/L)	0.89
Flash Point (°C)	242





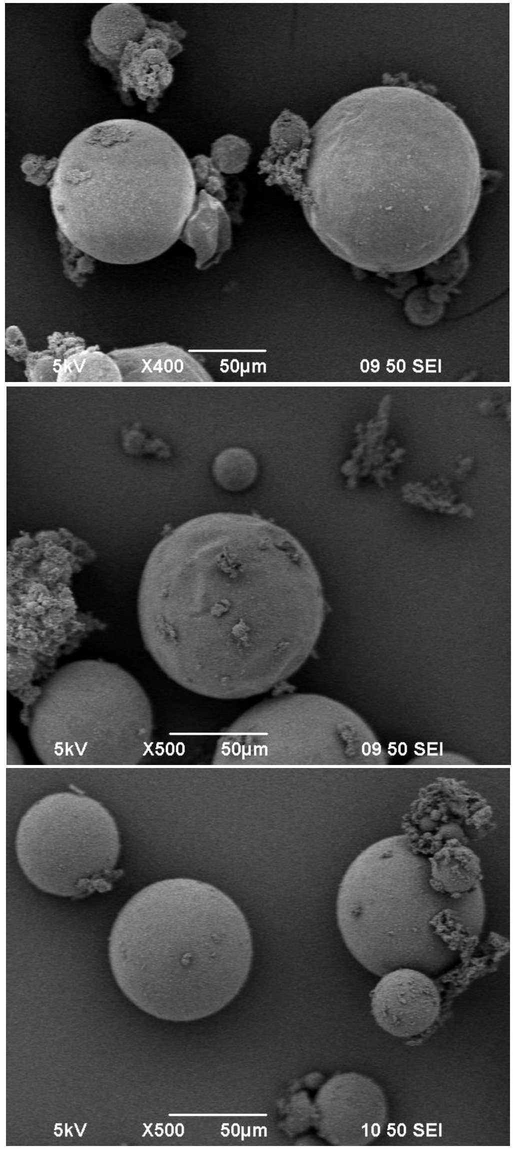
Reproducibility of in situ polymerization

Sample	Core material	Core:Wall mass ratio	Emulsifier content	Stirring rate
RE	DGEBA	2:1	0.5	1000 rpm

RE1

RE2

RE3



- ✓ Macroscopical morphology
- ✓ SEM
- ✓ Chemical structure
- ✓ Microcapsule size
- ✓ Encapsulation efficiency
- ✓ Thermal properties

ARTICLE

Applied Polymer WILEY

Epoxy loaded poly(urea-formaldehyde) microcapsules via in situ polymerization designated for self-healing coatings

Sofia Tzavidi | Christos Zotiadis | Athanasios Porfyris | Dimitrios M. Korres | Stamatina Vouyiouka

ELSEVIER

Progress in Organic Coatings

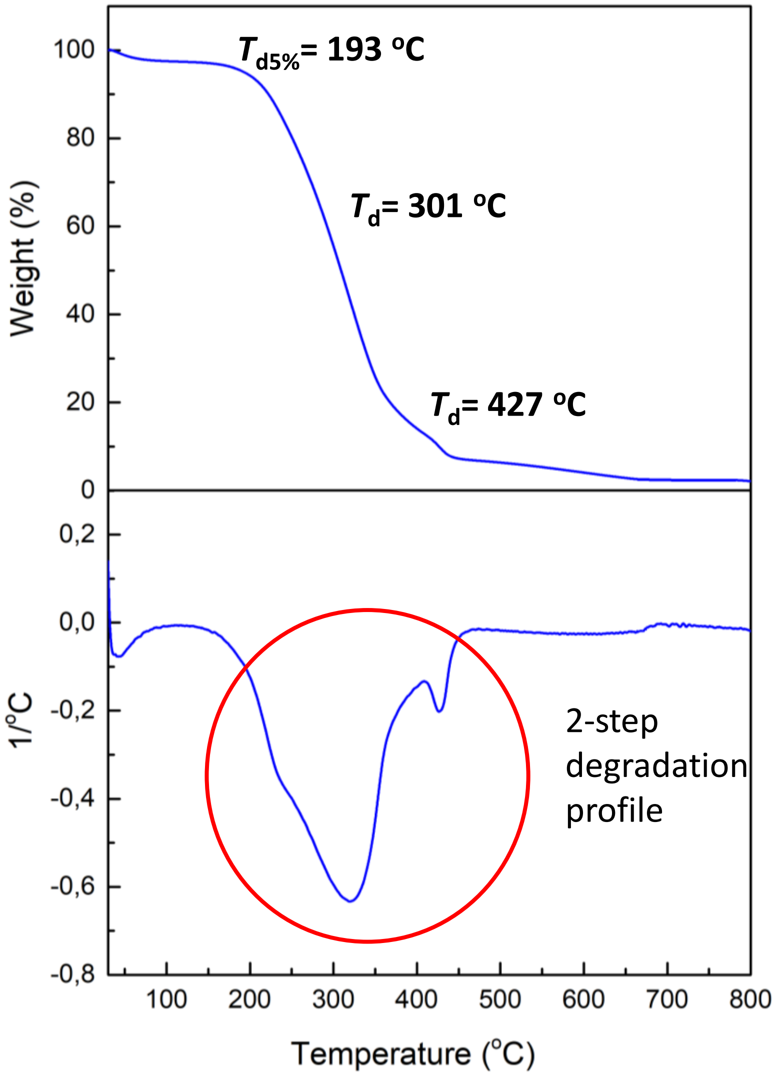
journal homepage: www.elsevier.com/locate/porgcoat

Self-healing coatings based on poly(urea-formaldehyde) microcapsules: *In situ* polymerization, capsule properties and application

Christos Zotiadis [a], Ioannis Patrikalos [a], Vasileia Loukaidou [a], Dimitrios M. Korres [a], Antonis Karantonis [b], Stamatina Vouyiouka [a,*]

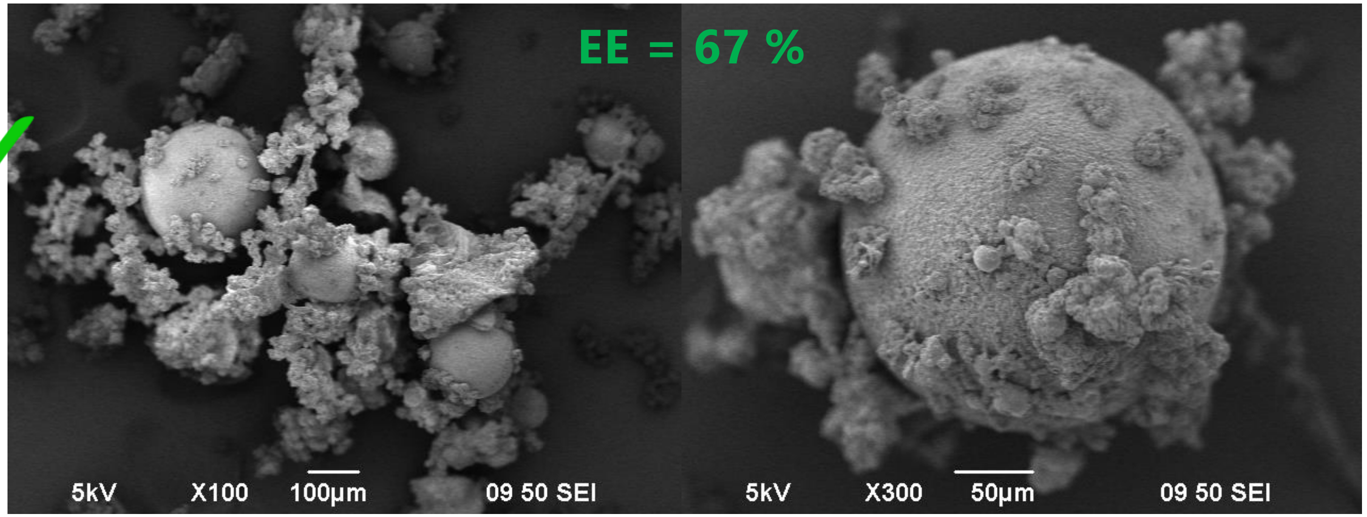
Sample	D[4,3] (μm)	$T_{d5\%}$ (°C)	T_d shell (°C)	T_d core (°C)	EE (%)
RE1	68	222	302	409	80
RE2	54	221	301	401	72
RE3	65	221	296	398	78

Apply the epoxy resin encapsulation conditions on lubricant MCs

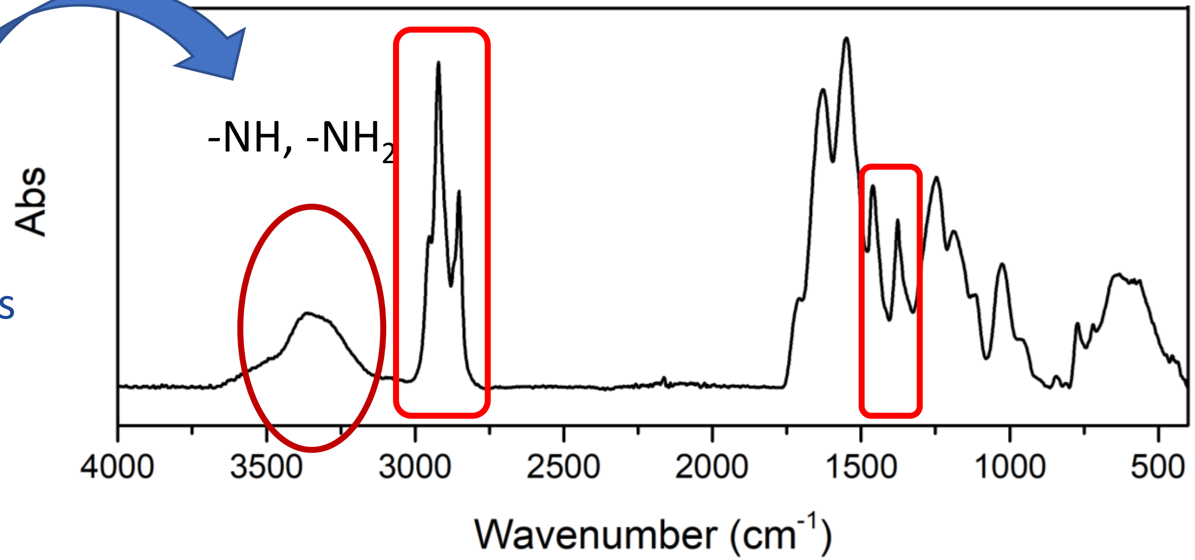


MCs formation ✓

BUT



PUF precipitates



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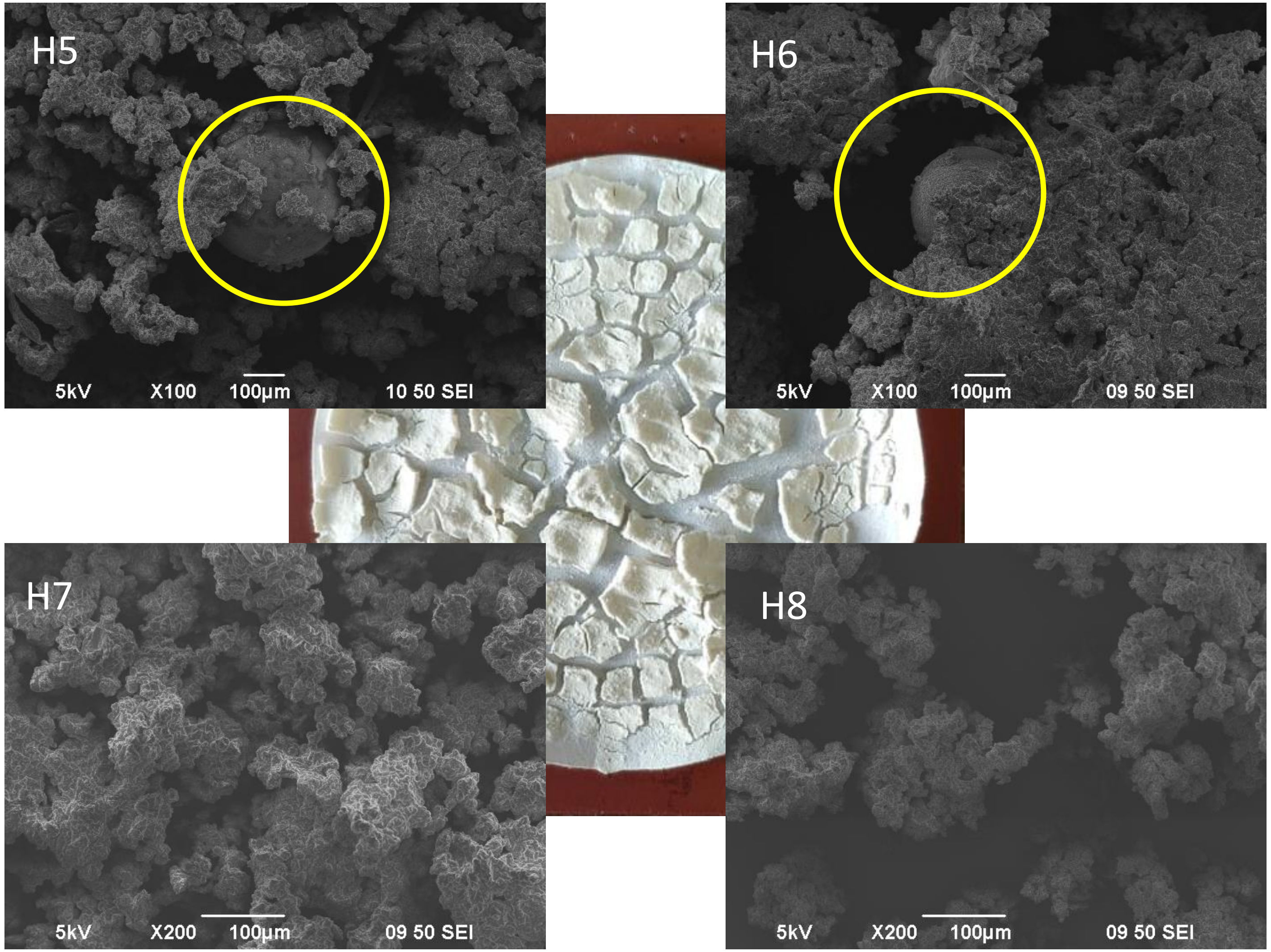
Core:Wall mass ratio effect on self-lubrication MCs

Large, fragile capsules
Excess core material

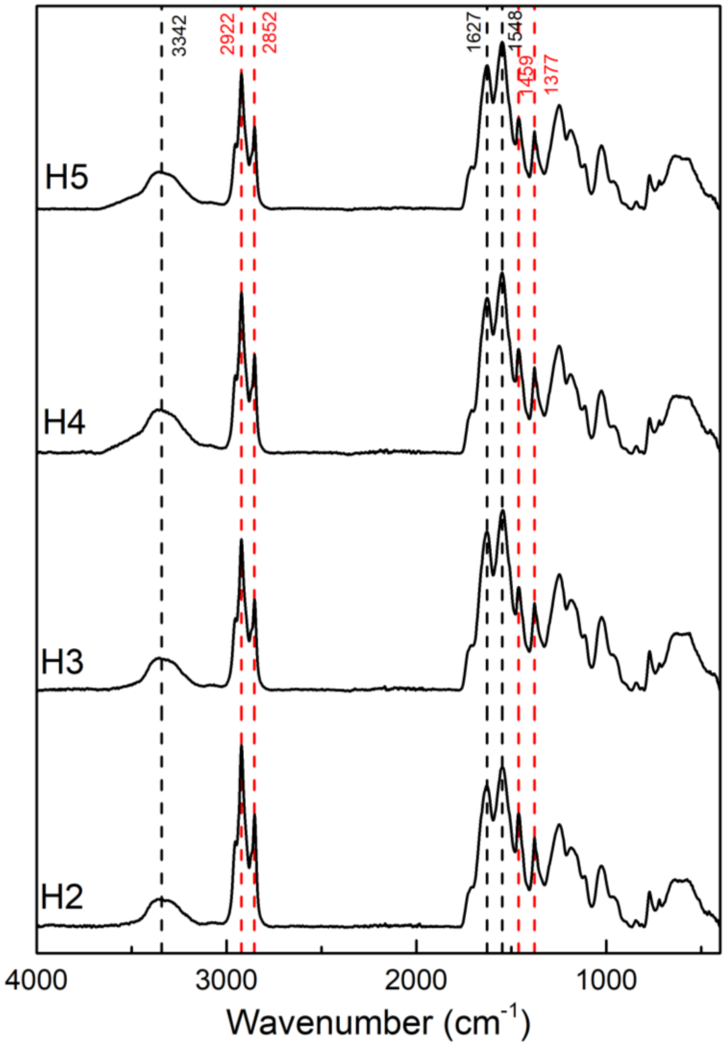
✓ Suitable ratio

Sample	Core:Wall
H5	3.5:1
H6	3:1
H7	2.5:1
H8	2:1

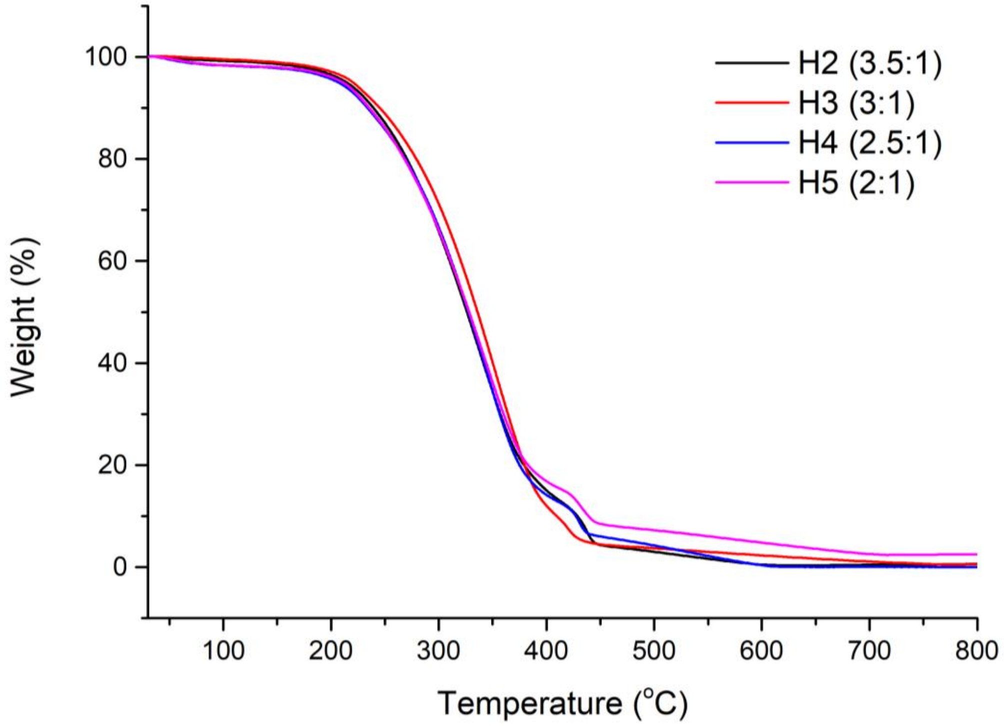
Lack of core material,
PUF precipitation



Core:Wall mass ratio effect on self-lubrication MCs



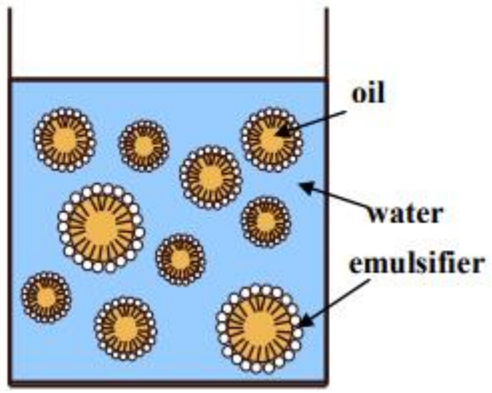
No significant difference between each core:wall ratio

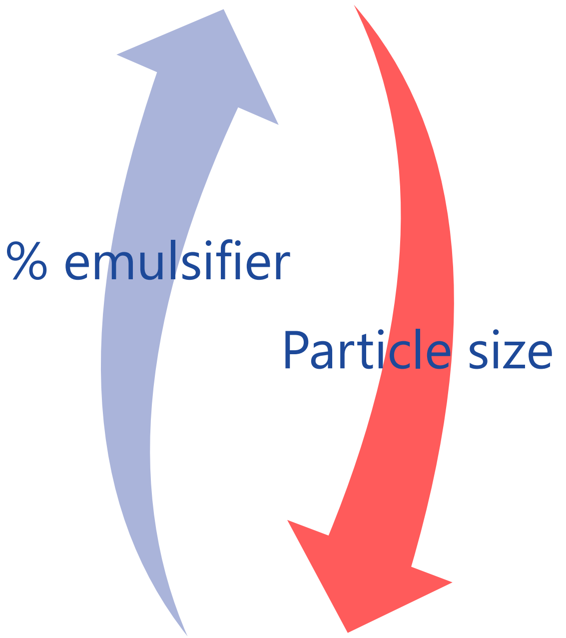


Sample	$T_{d5\%}$ (°C)	T_d (°C)	T_d (°C)	Residue (%)
H2	214	337	437	0.6
H3	220	353	419	0.6
H4	207	343	430	0.1
H5	211	343	432	2.5

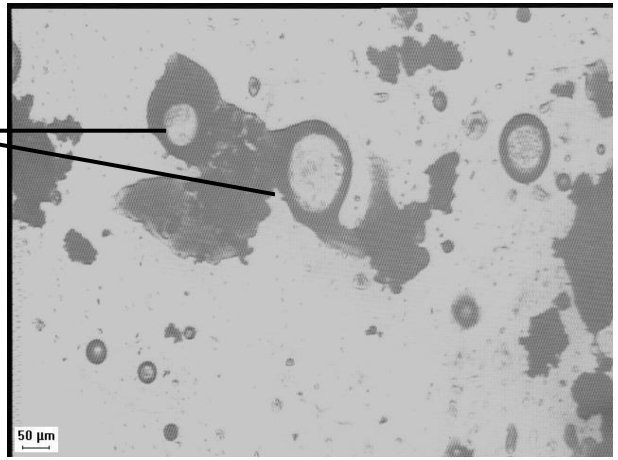
Emulsifier content effect

- Acceleration of core phase dispersion
- Stabilization of the emulsion
- Promotion of wall formation
- Stabilization of microcapsules

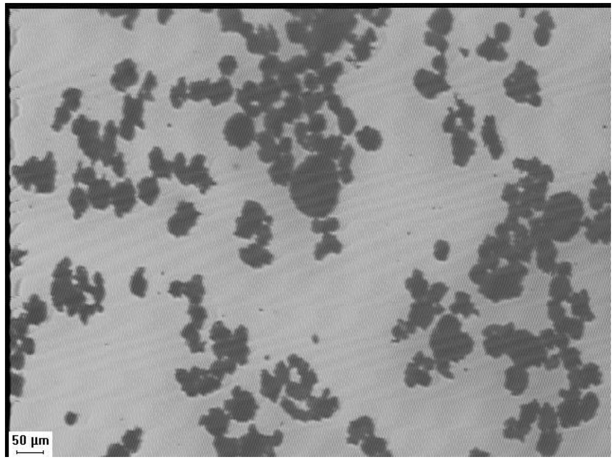




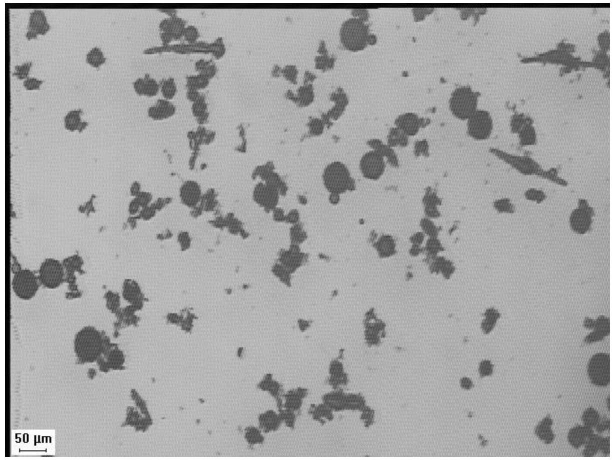
Free lubricant



H6 → 0.2 %, PS: 70 µm

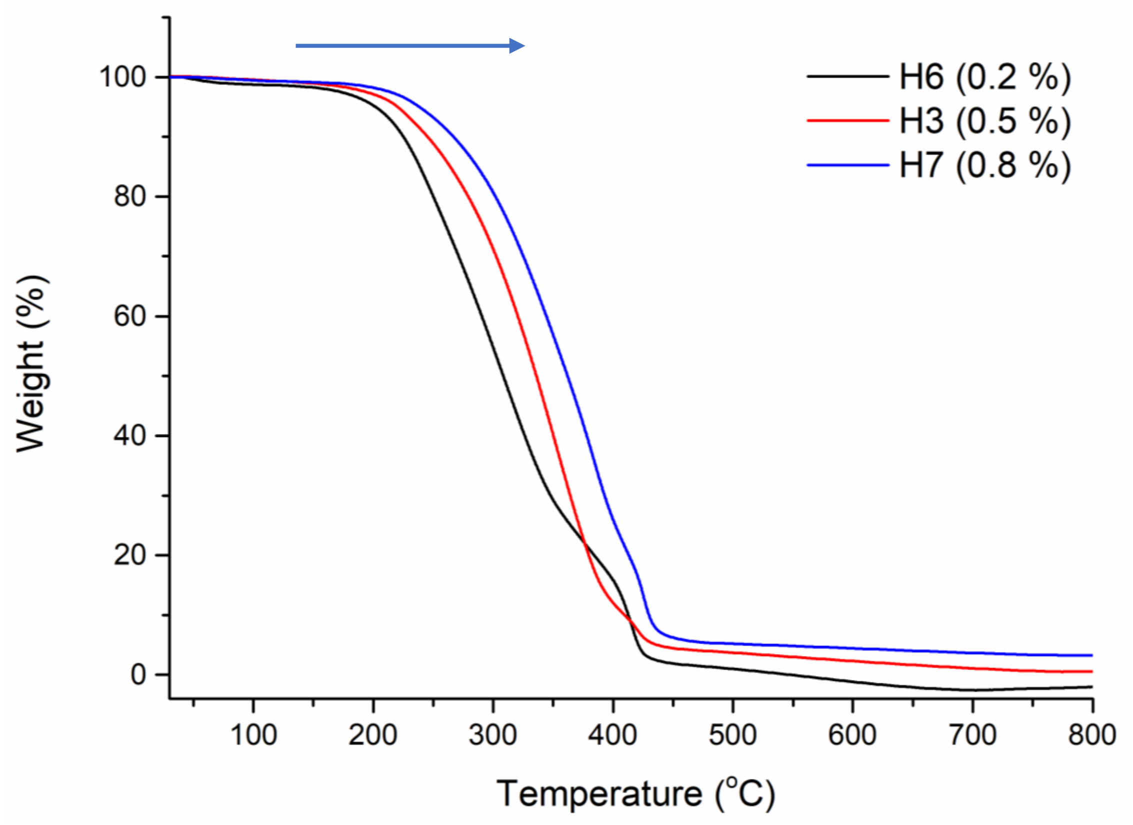


H3 → 0.5 %, PS: 51 µm

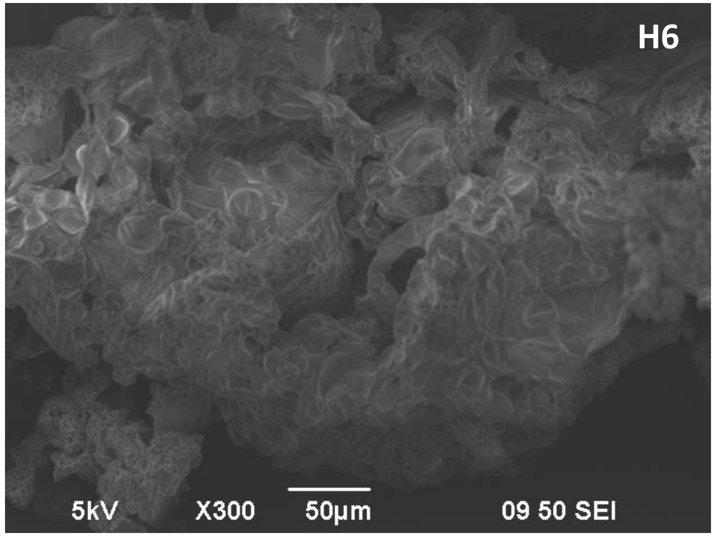


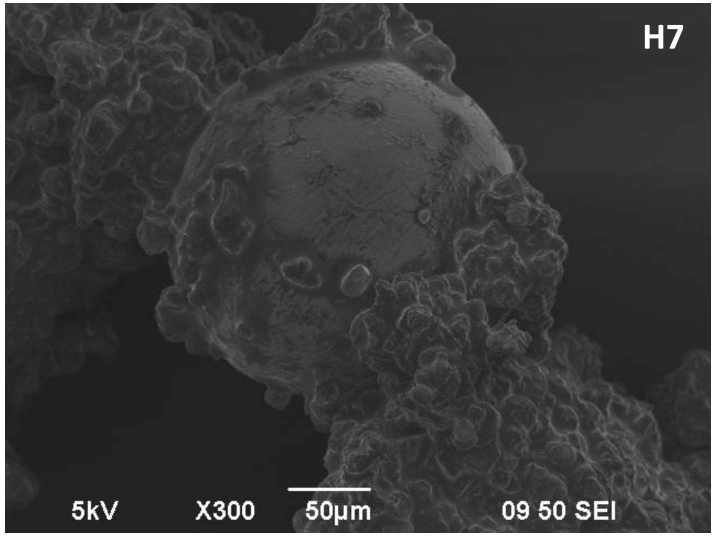
H7 → 0.8 %, PS: 41 µm

Emulsifier content effect



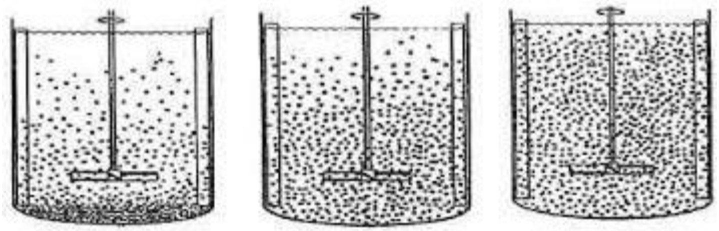
Sample	Emulsifier content (%)	$T_{d5\%}$ (°C)	T_d (°C)	T_d (°C)
H6	0.2	202	310	415
H3	0.5	220	353	419
H7	0.8	238	384	425

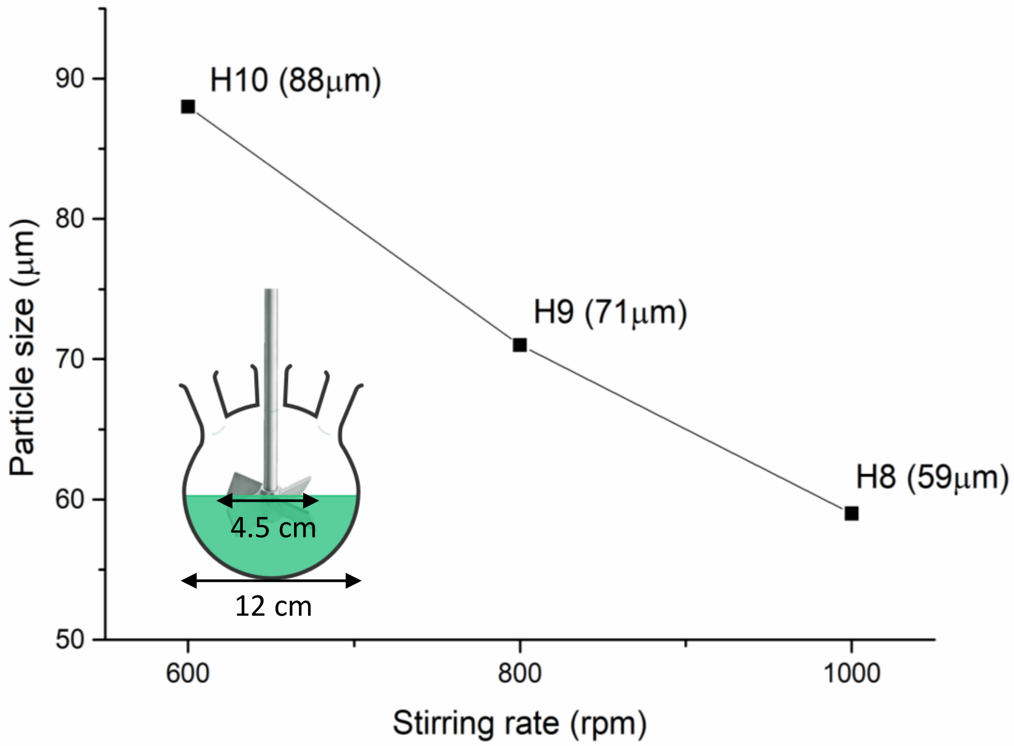


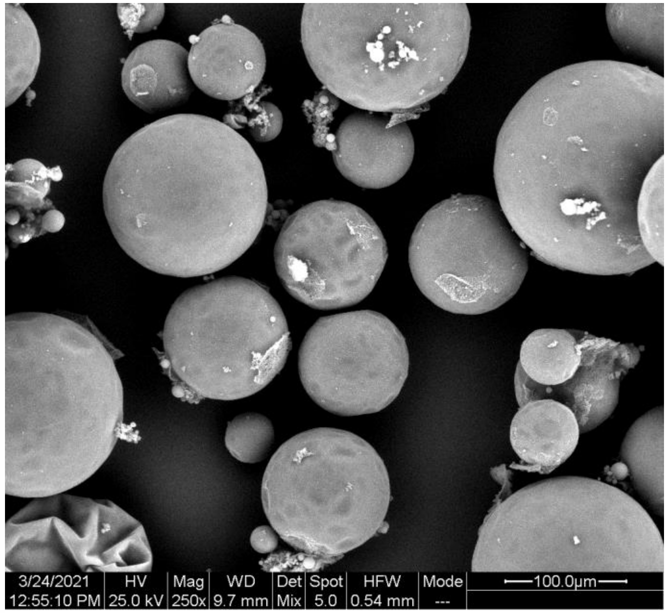


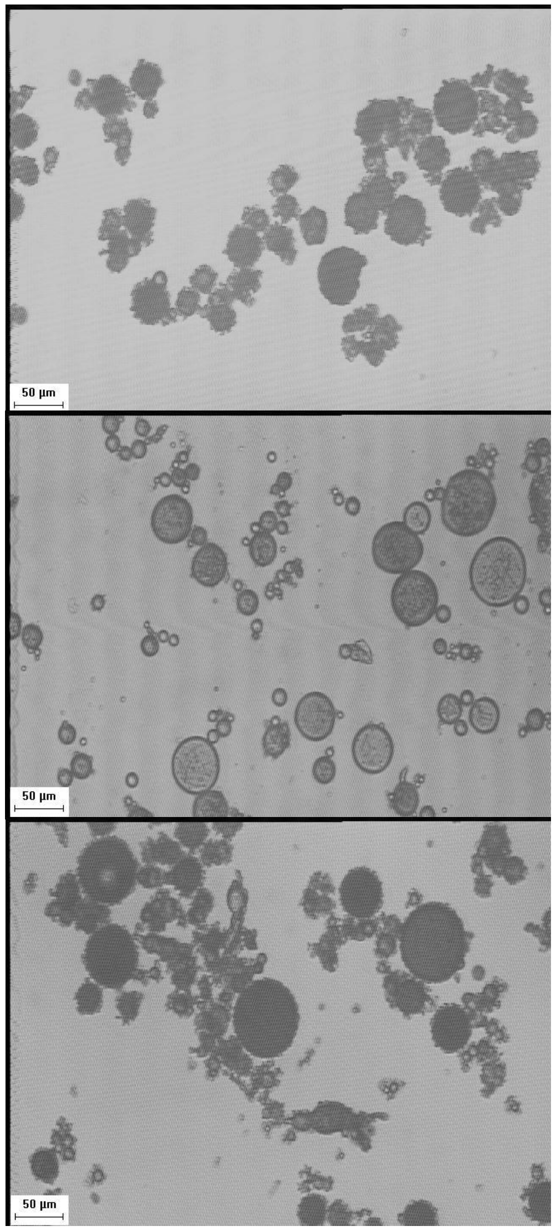
Stirring rate effect for self-lubricating PUF MCs

↑ RPM ⇨ ↓ Particle size







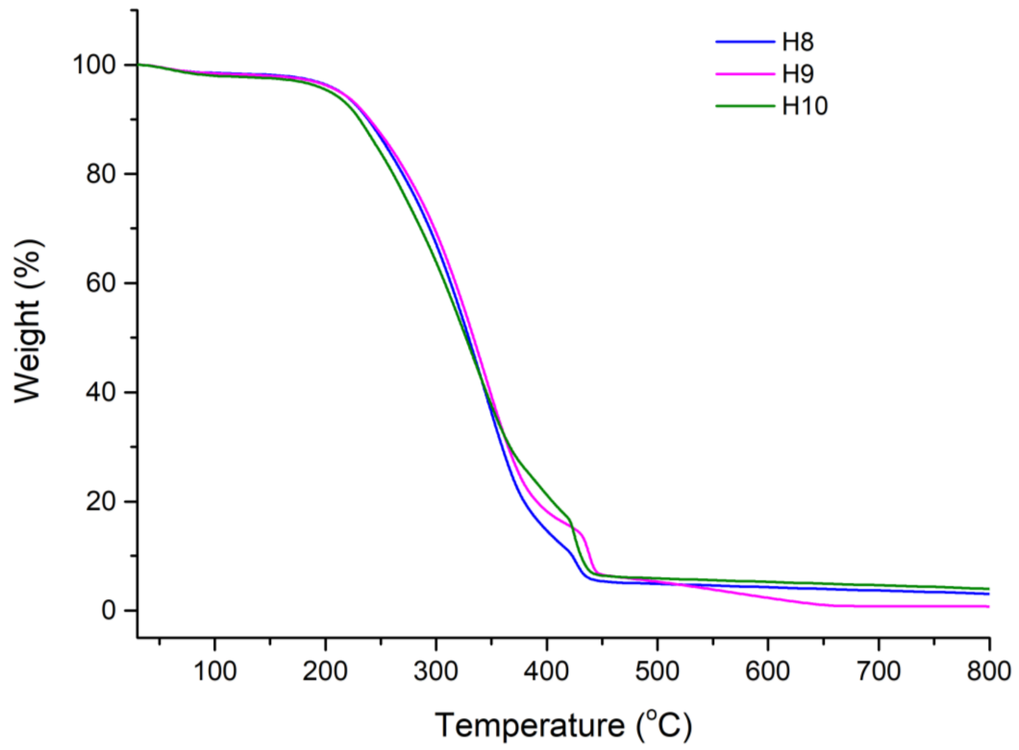


H8:
1000 rpm

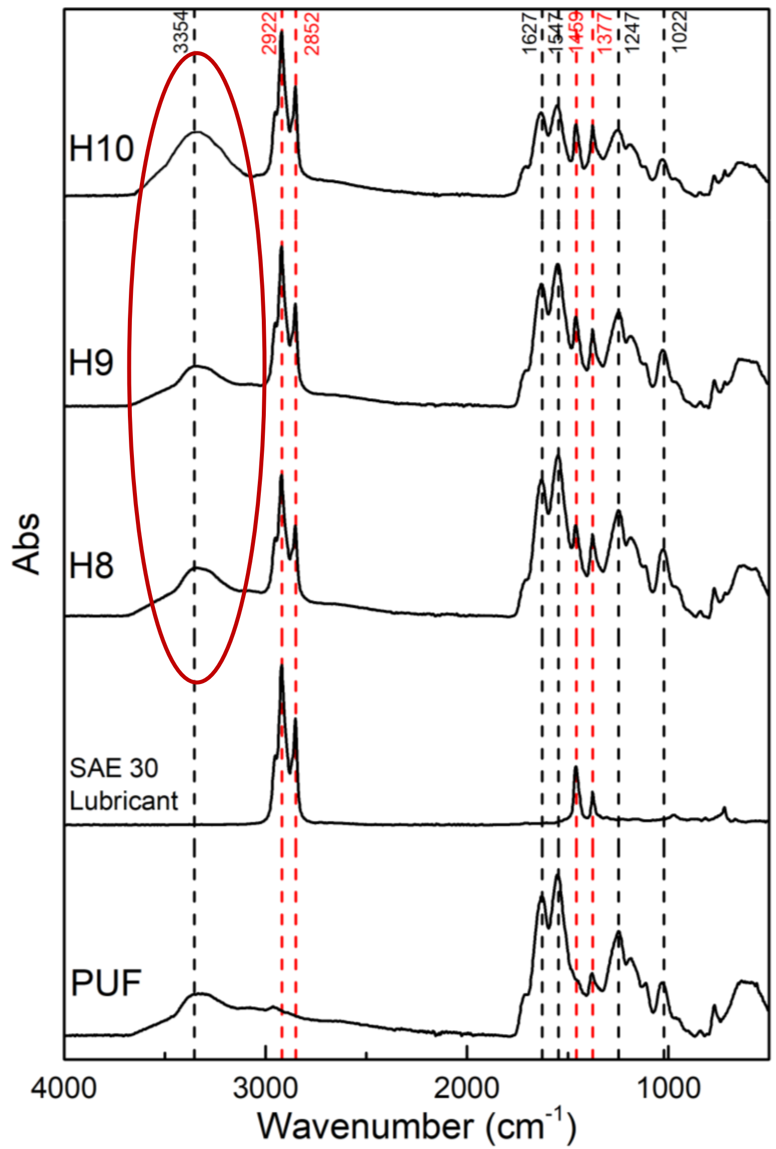
H9:
800 rpm

H10:
600 rpm

Stirring rate effect for self-lubricating PUF MCs



Sample	$T_{5\%}$ (°C)	T_d (°C)	T_d (°C)	Residue 800°C (%)	EE(%)
PUF	52	242	-	14	-
SAE30 Oil	275	-	403	1.3	-
H8	213	345	426	3	79
H9	228	362	428	1,6	76
H10	205	334	425	4	65



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Polysulfone (PSF) MCs via emulsification-solvent evaporation

$\overline{MW}: 60{,}000$

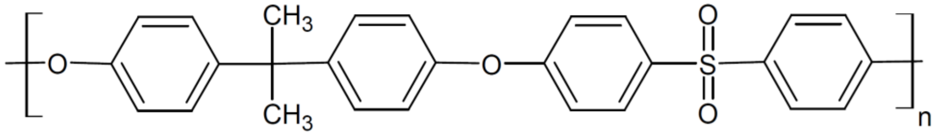
+ Increased thermal stability

− Lower Encapsulation Efficiency

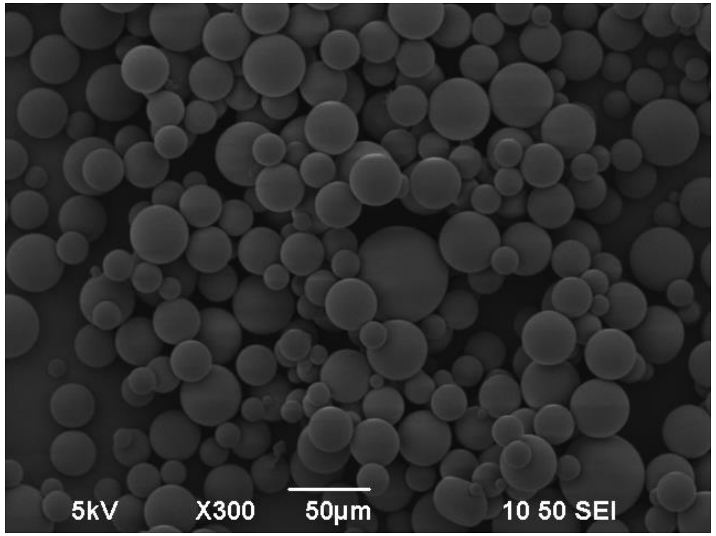
− Price

Study the encapsulation **parameters** and **correlate** them to **MCs properties**

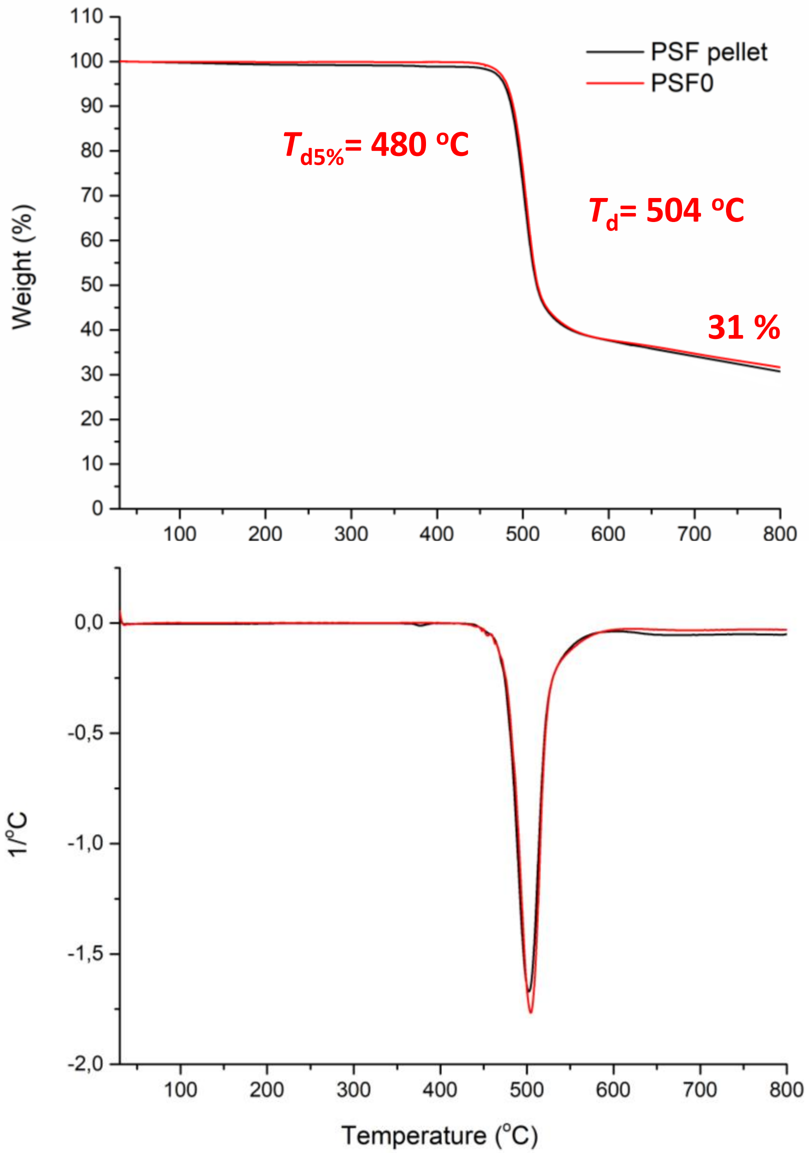
Parameter	PSF0	PSF1	PSF2	PSF3
Core material	-	SAE30	SAE30	SAE30
Core:Wall	-	1.2:1	2:1	1.2:1
Stirring rate (rpm)	700	700	700	1000

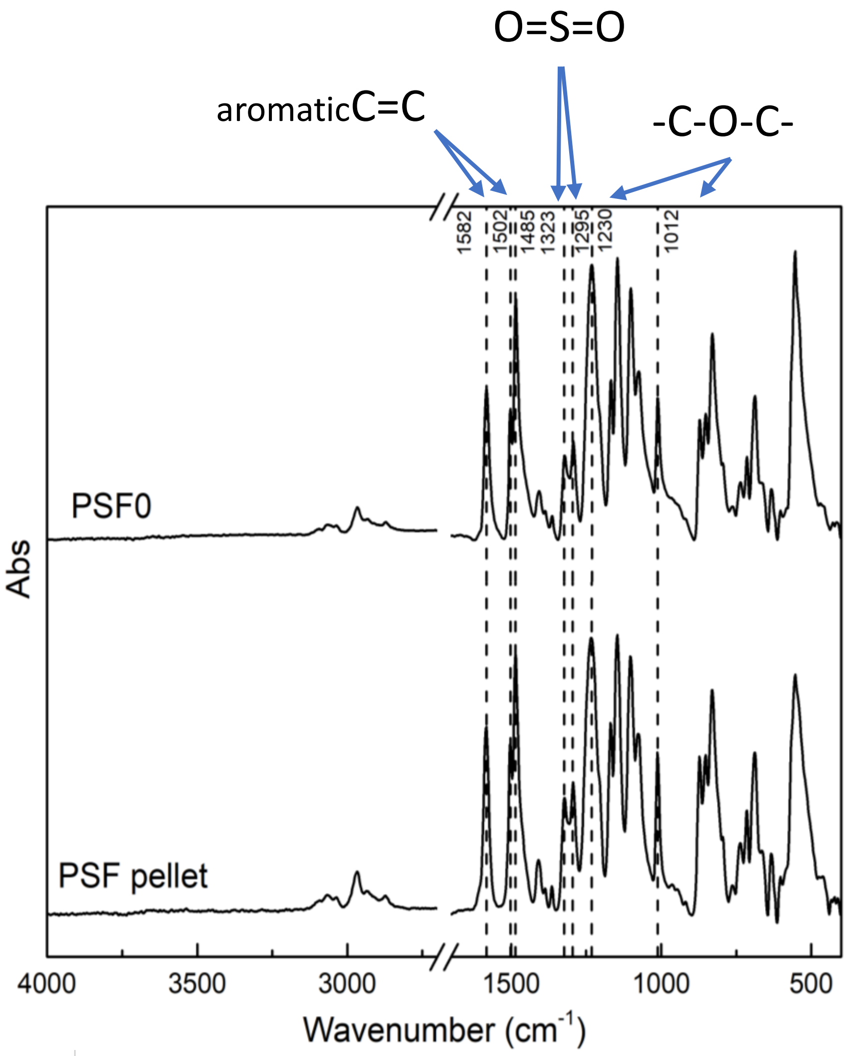


PSF0-reference unloaded



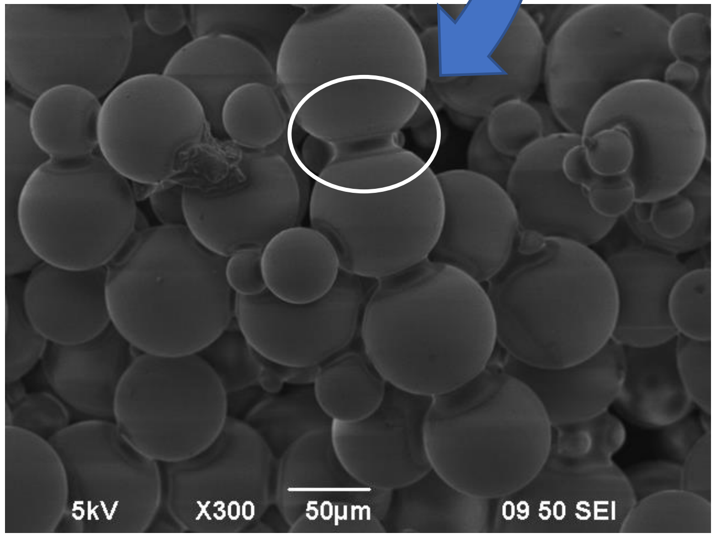
PS: 22 μm, STDEV: 10.1 μm



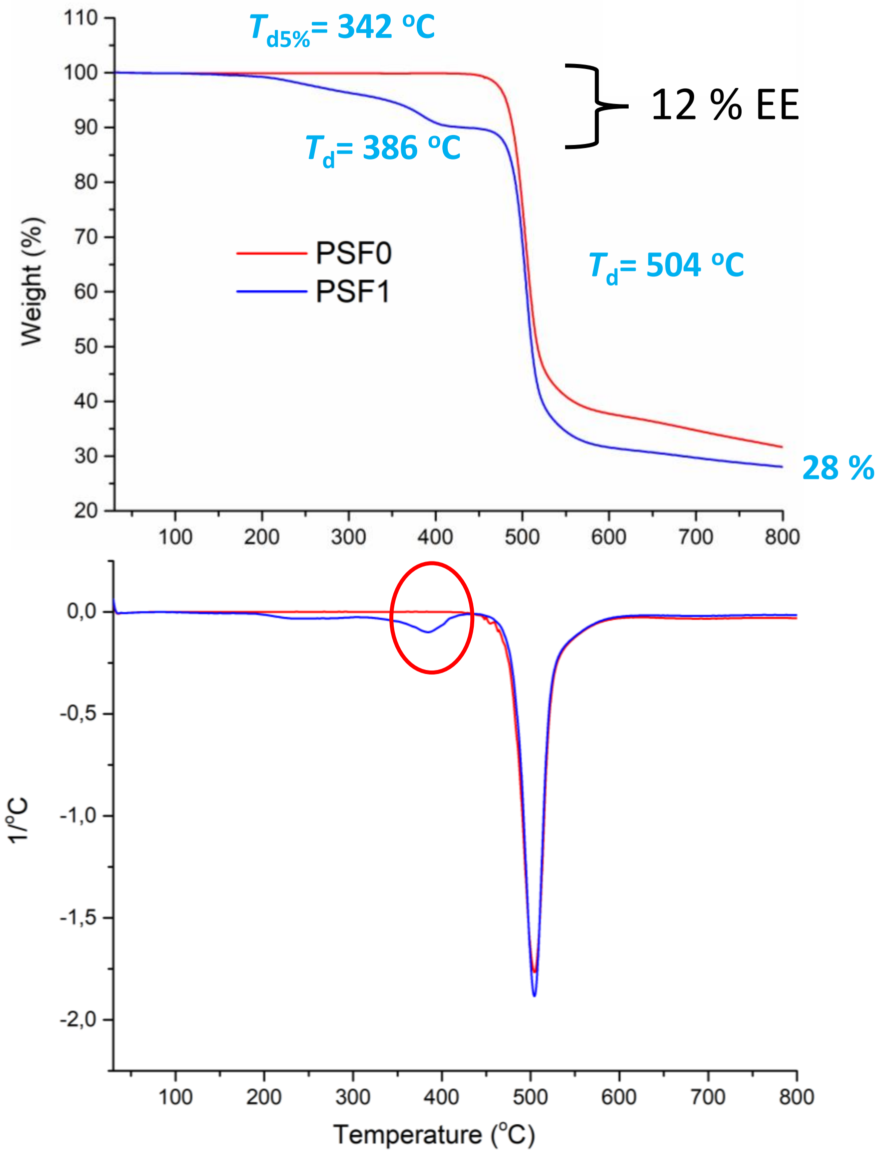


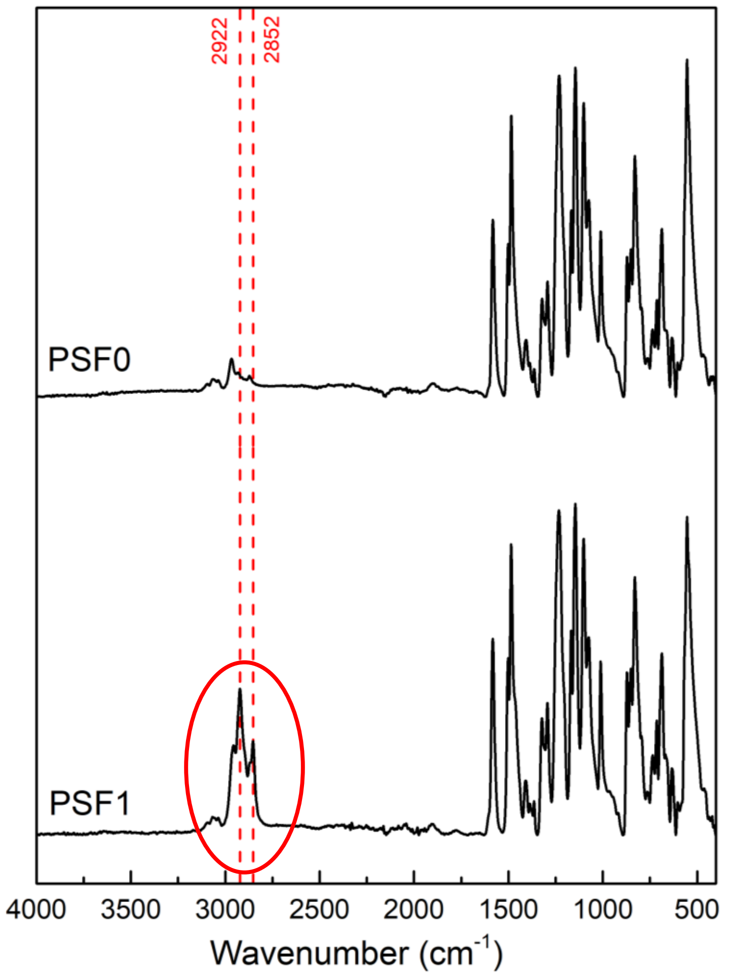
PSF1-SAE30 Lubricant encapsulation

Unencapsulated lubricant

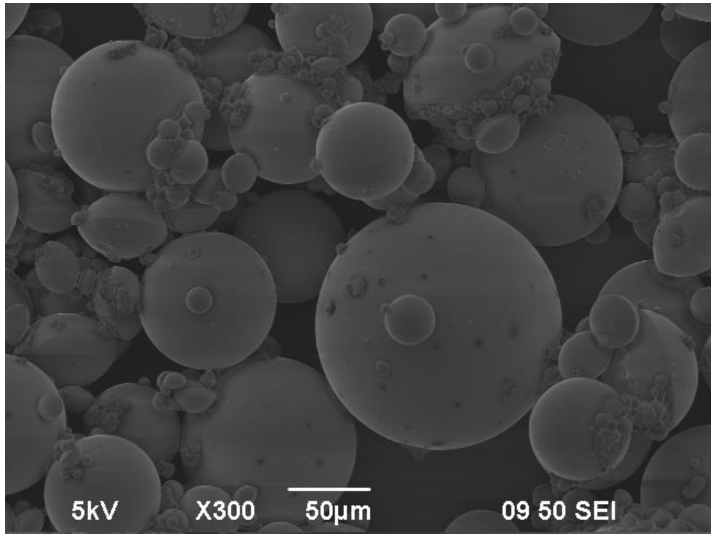


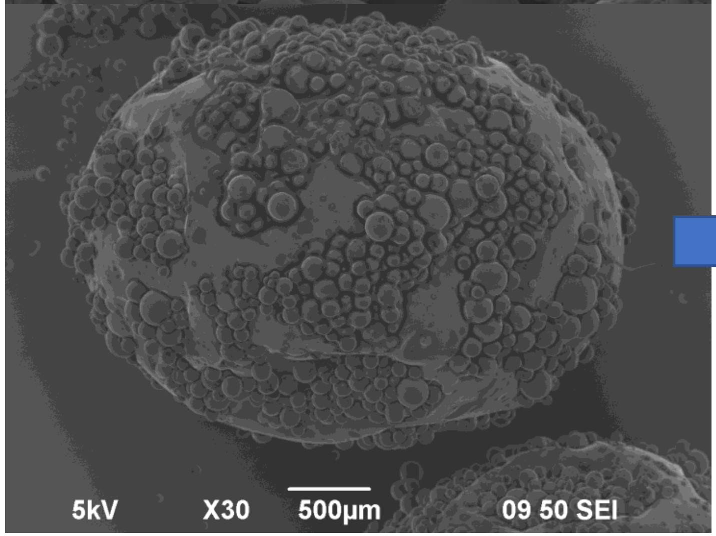
PS: 61 µm, STDEV: 21.5 µm
Shell thickness: 19.5 µm





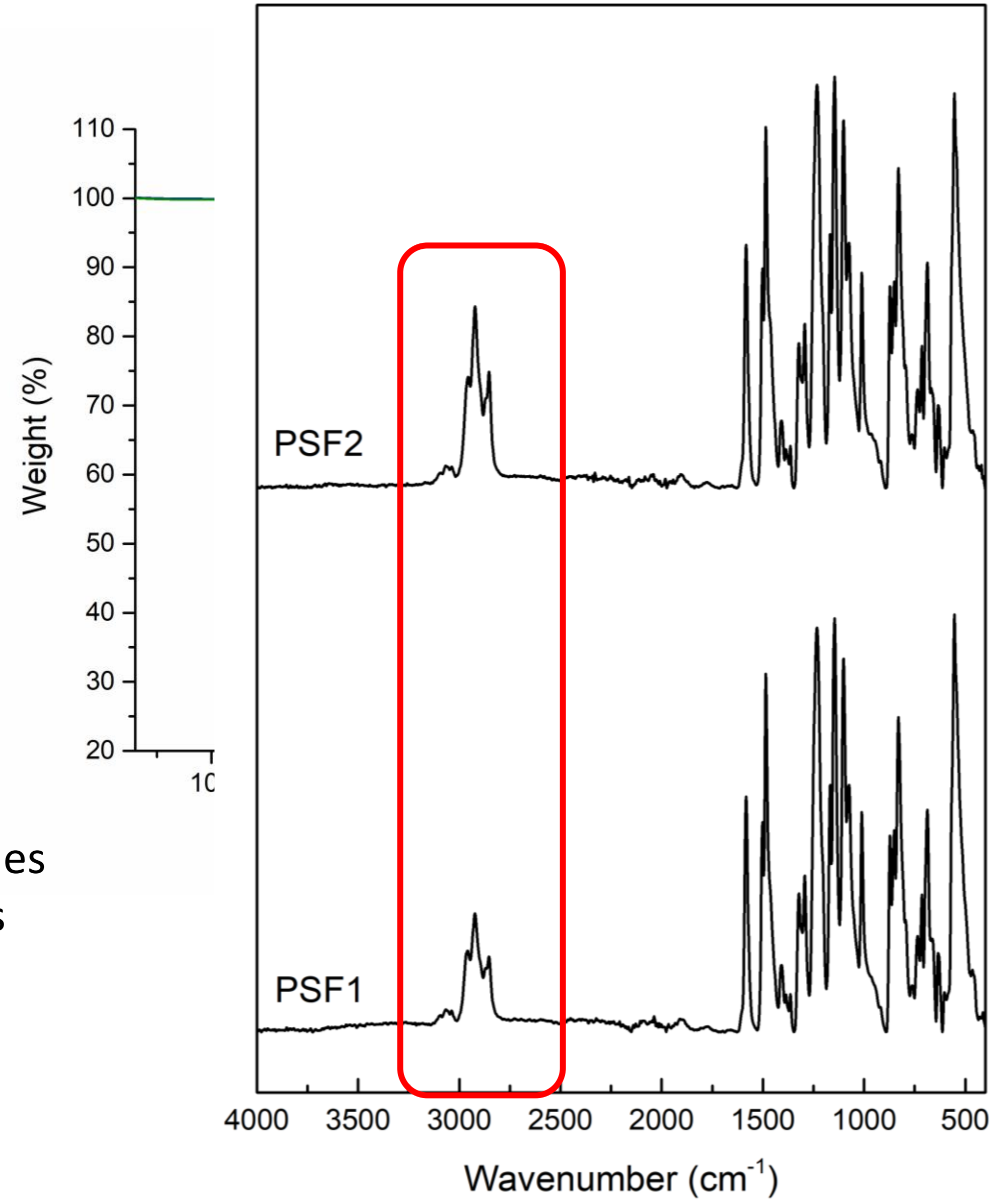
PSF2-Increased Core:Wall ratio (2:1)



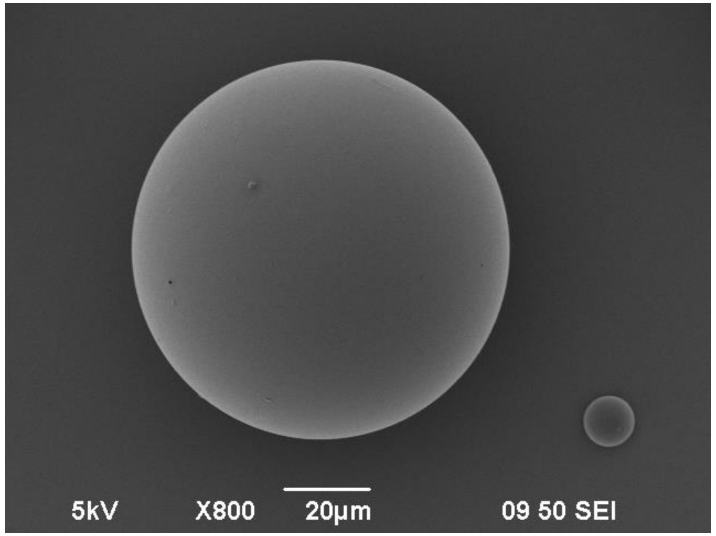


PS: 61 μm,
STDEV: 34.2 μm
Shell thickness: 18 μm

Large PSF-Oil particles covered with MCs

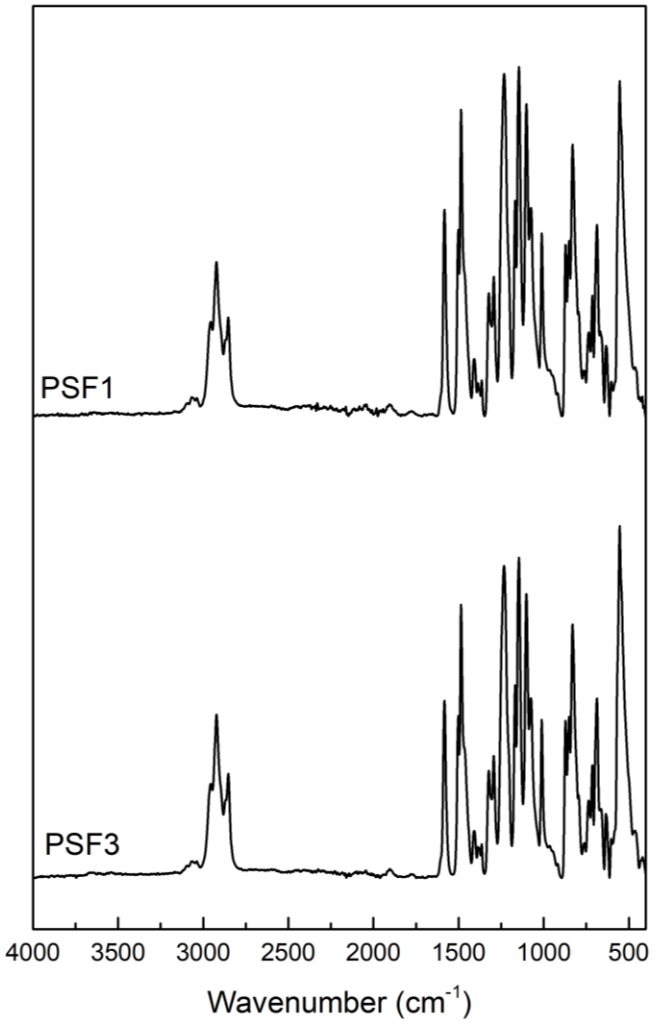


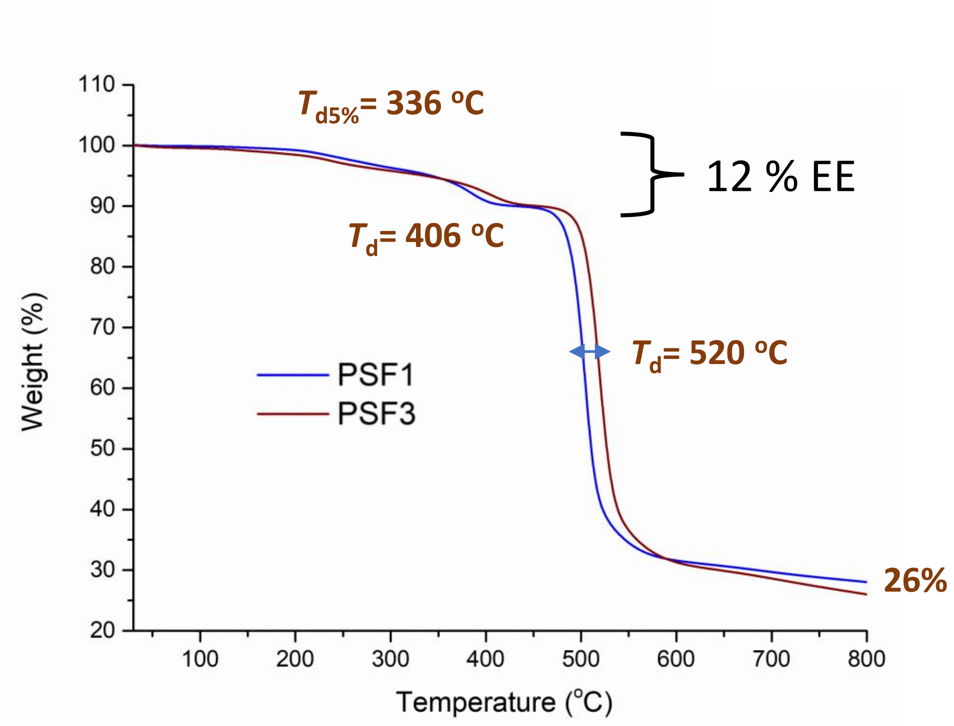
PSF3-Increased stirring rate (1000 rpm)



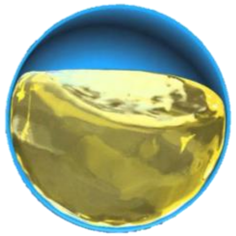
PS: 55 μm, STDEV: 19.5 μm
Shell thickness: 17 μm

↑ RPM ⇨ ↓ Particle size





Conclusions



PUF microcapsules

- Successful application of ***in situ*** **polymerization** for the **encapsulation of active ingredients →** **self-healing** and **self-lubricating** microcapsules
- **Key process parameters**: the initial core:wall mass ratio, the stirring rate during the emulsification stage and the emulsifier quantity
- Effect on **MCs morphology, particle size and size distribution, encapsulation efficiency and thermal properties and chemical structure**
- Most **promising sample** was H9 at **800 rpm**, **3:1** ratio and **0.5 %** emulsifier and presented a PS of **71 μm, 76 % EE** and was thermaly stable up to **230 °C**

PSF microcapsules

- Successfully produced **PSF microcapsules** *via* the **emulsification-solvent evaporation** technique
- Both **reference** and **SAE30 lubricant encapsulated** capsules were produced
- **Process parameters (**initial core:wall mass ratio, and stirring rate) **correlated to MCs properties**
- **Thermally more stable** (>500 °C), smooth and uniform capsules **BUT lower EE** compared to PUF MCs
- Most **successful sample** was PSF3 at **1000 rpm**, **1.2:1** ratio (PS: **55 μm, 12 % EE,** $T_{d5\%}$**= 336 °C,** T_d**= 406°C,** T_d**= 520°C)**

Acknowledgments

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European Union
European Regional Development Fund

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ΕΣΠΑ 2014-2020
ανάπτυξη - εργασία - αλληλεγγύη
Partnership Agreement
2014 - 2020

Co-financed by Greece and the European Union