X Workshop Italiano Sol-Gel

UNIVERSITÀ DI TRENTO
Dipartimento di Ingegneria Industriale

INTERNATIONAL SOL-GEL SOCIETY
ISGS
materials through chemistry

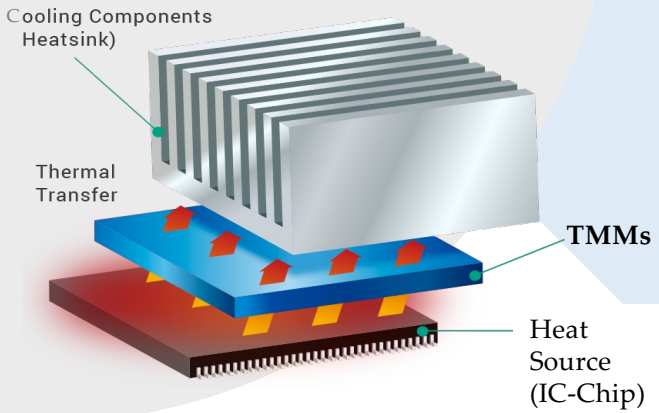
Engineering the Hybrid Interfaces in Ladder-Like Polysilsesquioxane-Al_2O_3 Nanocomposites for Enhancing Thermal Conductivity

Sandra Dirè

Introduction

Advanced electronics (microelectronics, flexible robotics)

- **High power density** ⟶ **Thermal management issues** (electronic packaging)

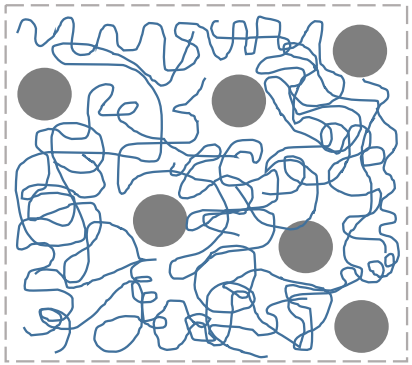


Thermal Management Materials (TMMs)

- ✓ High thermal conductivity (TC)
- ✓ Electrical insulation
- ✓ Flexibility (flexible electronics)
- ✓ Thermal stability

➢ **Polymers** (PB, Si rubber,..)

→ **Electrical insulation**
→ **Flexibility**
→ Easy processing
→ Light weight
→ **Low TC**

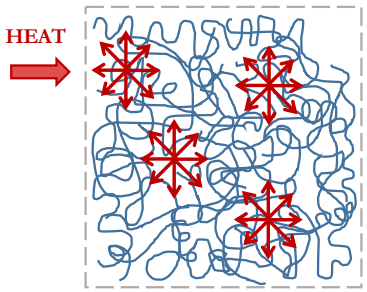


Polymer-ceramic nanocomposites (NCs)

➢ **Ceramics** (BN, SiC, Al_2O_3)
➢ **Metals** (Au, Cu, Ag)
➢ **C** (graphene, CNT)

→ **High TC**

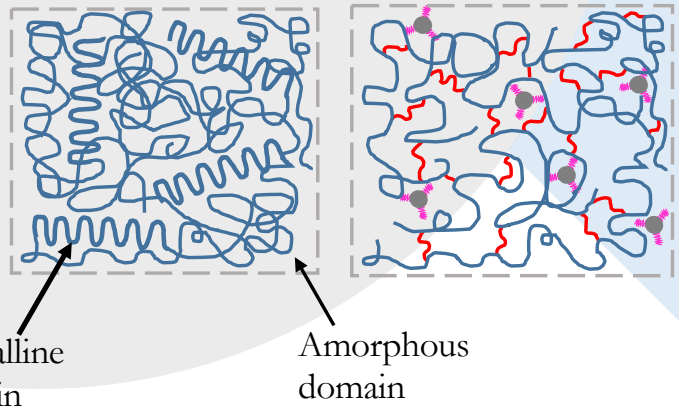
Introduction & Aim



Phonon scattering

To limit phonon scattering:

- ➢ **chain-chain interactions**
- cristallinity
- crosslinking
- weak interactions (H-bonding, π-π)
- ➢ **ceramic-polymer interface**
- particles functionalization

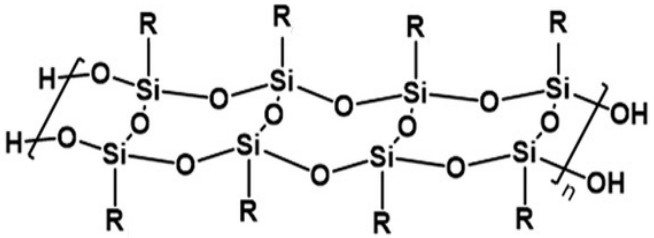


✓ **Innovative polymeric TMMs**
→ **Ladder-like polysilsesquioxanes (LPSQs)**

✓ **Design of NCs hybrid interfaces by tuning covalent and weak interactions**
→ **Different methacrylate/phenyl ratio in LPSQs**
→ **Al_2O_3 NPs funcionalization : methacrylate and amino groups**

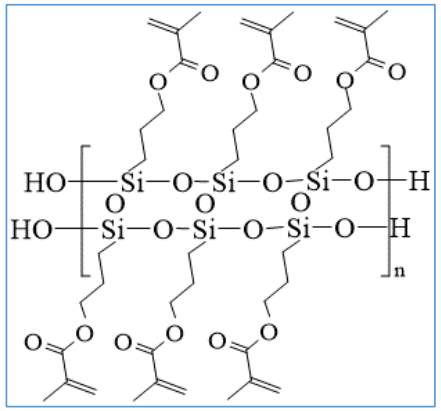
Ladder-like polysilsesquioxanes: synthesis of matrices

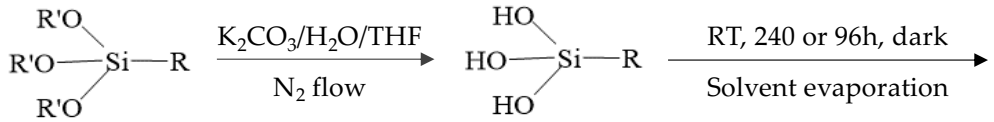
Double-stranded ribbons with organic side chains R



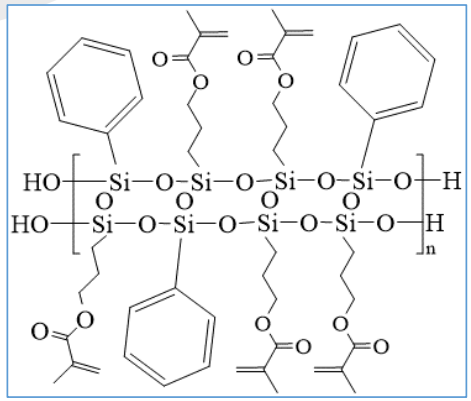
LPSQs

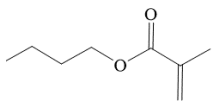
- ✓ High Thermal Stability (up to 400°C)
- ✓ Tunable Properties (reactive or non reactive R group)
- ✓ Low Thermal Expansion (rigid backbone Si-O-Si)
- ✓ Excellent Dielectric Properties
- ✓ Compatibility with polymers





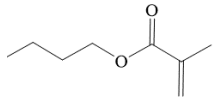
Sol-gel synthesis of LPSQs

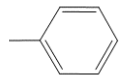


R (100%) = 

➢ **LPMASQ (L)**

➢ **MAPSQ (M64 & M46)**

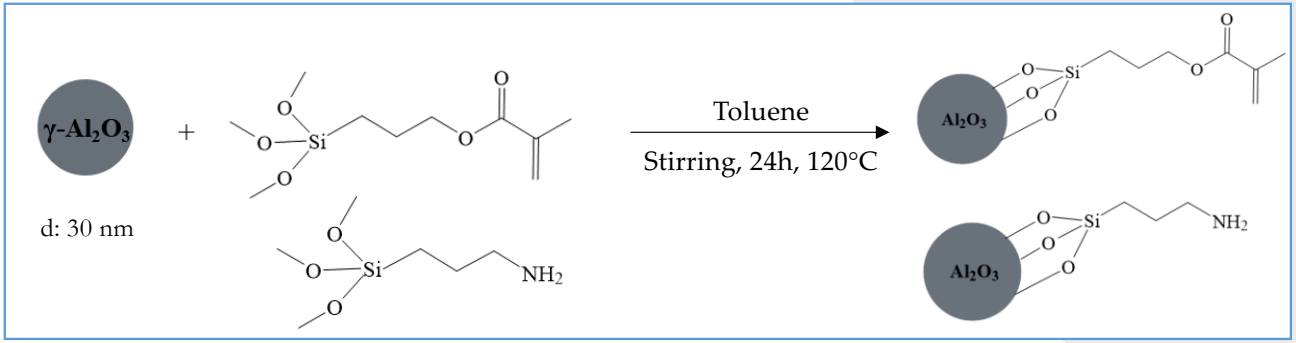
R^1 (60 or 40 %) = 

R^2 (40 or 60%) = 

A. Lee, et al. *J. Mater. Chem.* A 2014, 2, 1277−1283.

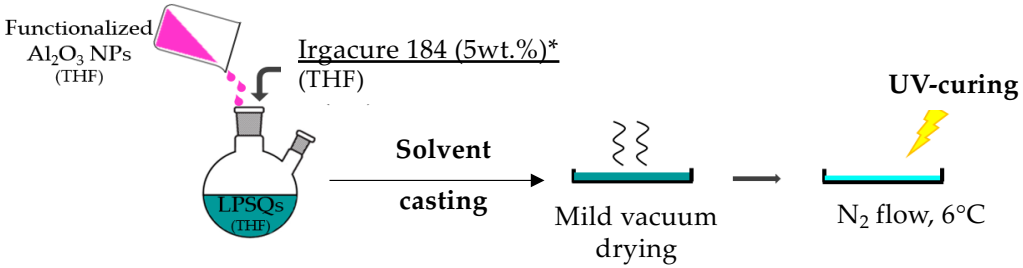
M.D'Arienzo, et al. *ACS Appl.NanoMater.* (2018) 1, 3817-3828

γ-Al_2O_3 NPs functionalization & NCs production



- **Methacryloxypropyltrimethoxysilane → MPTMS@Al_2O_3 → MA**
  (grafting density : 1.5 molecules/nm²)
- **Aminopropyltrimethoxysilane → APTMS@Al_2O_3 → AA**
  (grafting density : 3.94 molecules/nm²)

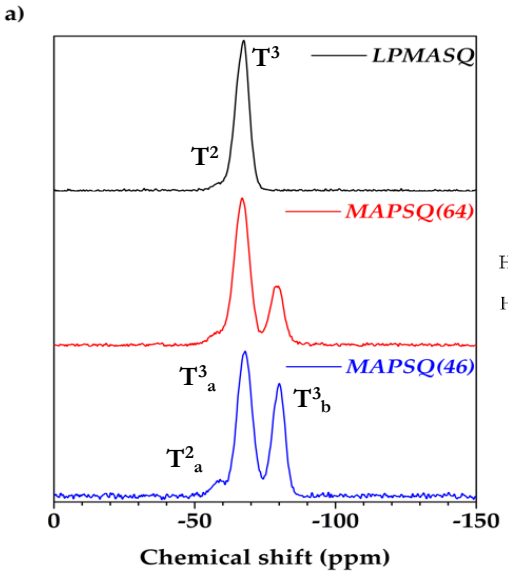
Nanocomposites: solvent casting and photopolymerization

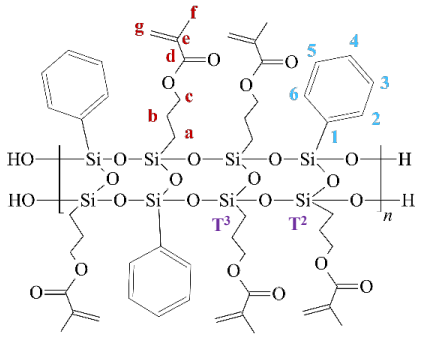


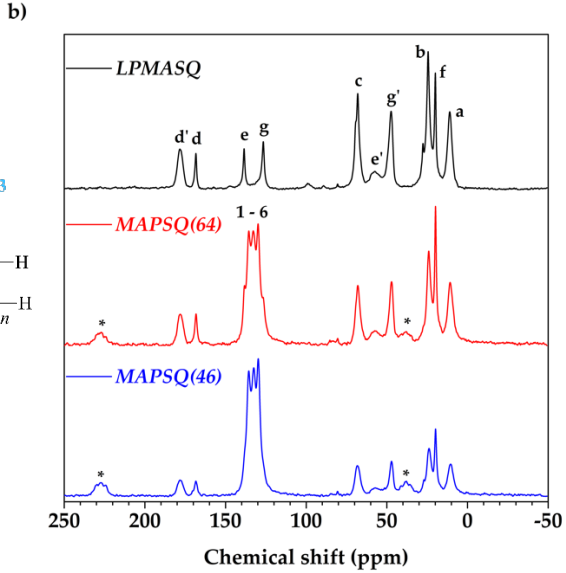
	MA (20-120wt%)	AA (20-120 wt%)
LPMASQ (L)	MA_L	AA_L
MAPSQ (M64, M46)	MA_M64 , MA_M46	AA_M64 , AA_M46

*C. Romeo et al.,J. Compos. Sci. (2024) 8, 295
P. Mingarelli et al., Gels (2023) 9, 810
S.Dirè et al., J.Sol-Gel Sci. Technol., (2025) 114, 1–13
C. Romeo et al., Composites Communications, (2025), 00, 00

Effect of phenyl groups on photo-crosslinked LPSQs







29Si & 13C NMR

- almost fully condensed siloxane network
- nominal composition confirmed
- phenyl addition → decrease of conversion of methacrylate double bond (L 75%, M64 67%, M46 65%)

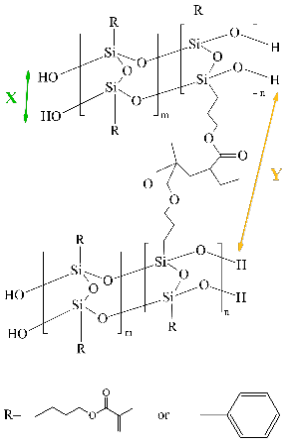
XRD

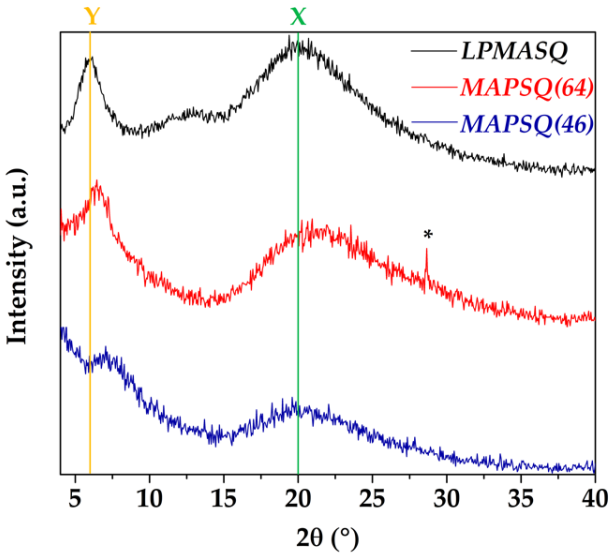
With phenyl addition:

- decrease of d_Y → increase of chain packing density
- increase in linewidth → random copolymer

- increase of R → Ph groups affect structural regularity

Sample	d_Y, nm (FWHM, °)	R (I_Y/I_X)
LPMASQ	1.45 (1.7)	0.70
MAPSQ(64)	1.37 (2.0)	0.90
MAPSQ(46)	1.21 (2.7)	0.75





Effect of phenyl groups on photo-crosslinked LPSQs

LPSQs with mixed methacrylate – phenyl side chains:

- decrease of crosslinking degree (methacrylate % and conversion)
- insoluble fraction L 99%, M64 & M46 90-92% (gel content exp. in THF)
- contribution of π-π stacking on molecular packing

29Si & 13C NMR

- almost fully condensed siloxane network
- nominal composition confirmed
- phenyl addition → decrease of conversion of methacrylate double bond (L 75%, M64 67%, M46 65%)

XRD

With phenyl addition:

- decrease of d_Y → increase of chain packing density
- increase in linewidth→ random copolymer

NCs: effect of interface interactions on photo-crosslinking

Real time FTIR (C=C band, 10 μm thick samples)

NCs with 80 wt % of filler

LPSQs matrices.

With addition of Ph side groups

→ **increase of matrix stiffness and viscosity**

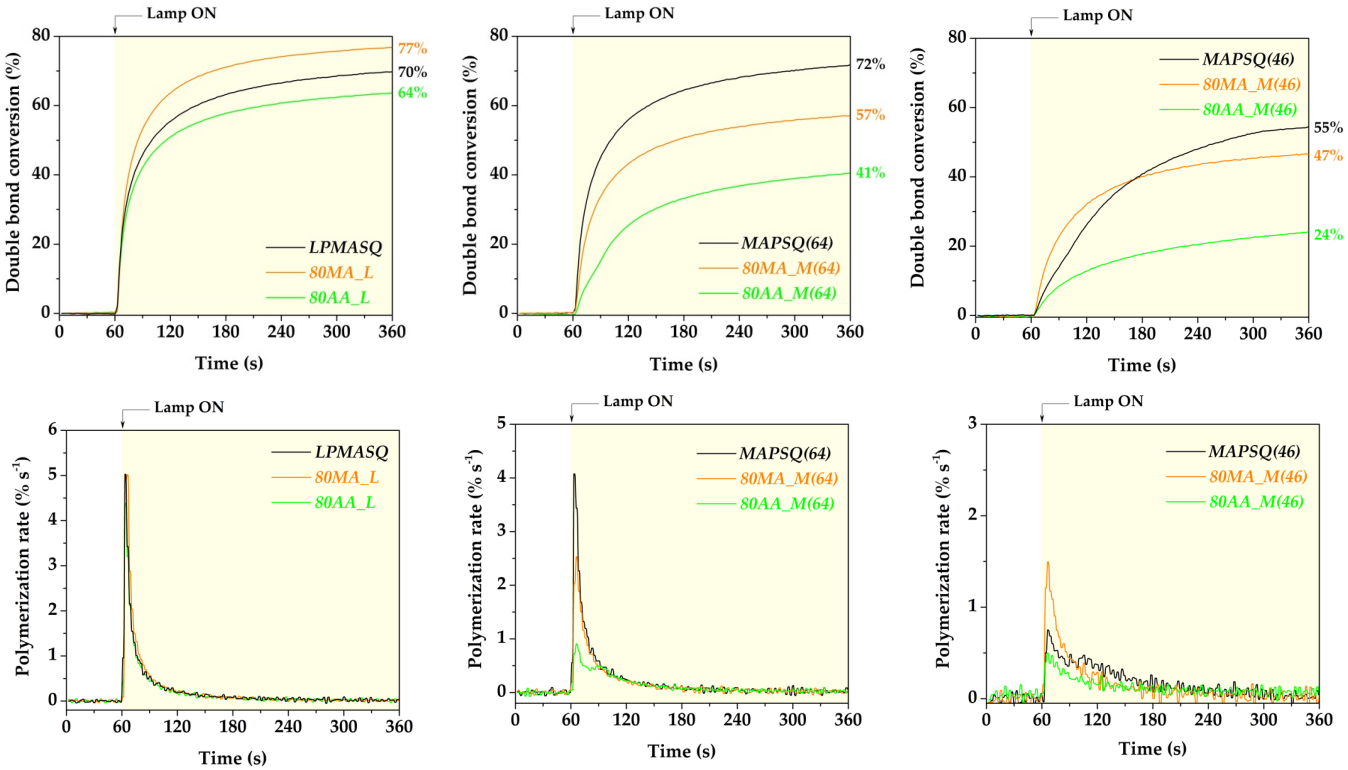
Methacrylate –based NCs (L)

Polymerization rate unaffected by NPs

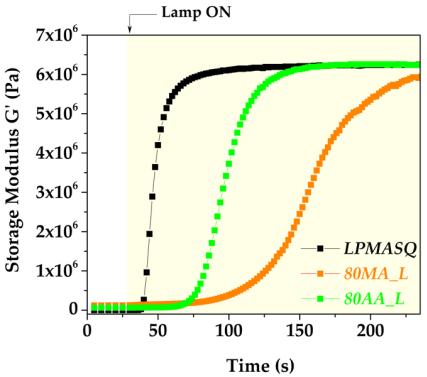
With AA decrease of methacrylate conversion (filler-filler interactions)

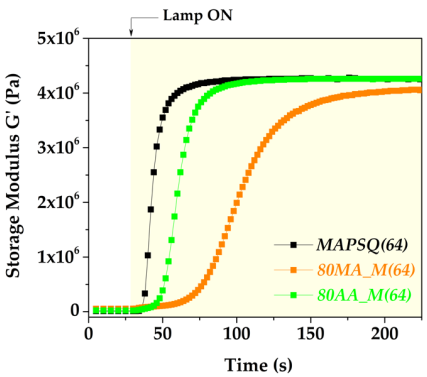
Methacrylate-phenyl –based NCs (M64, M46)

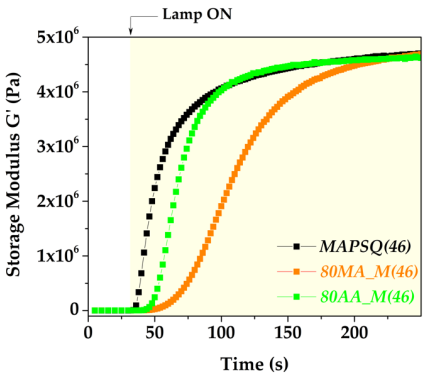
Decrease of methacrylate conversion and polymerization rate, in particular with **AA**



NCs: effect of interface interactions on photo-crosslinking







Real time photorheology

Viscoelastic properties during UV-curing influenced by conversion degree and physical interactions among chains

Samples with 80 wt % of filler

LPSQs matrices

M46: slower increase of G' vs. time (medium viscosity) **but final G' value similar to L and M64**

π- π stacking contribution in mixed ladders (despite of lower crosslinking)

NCs

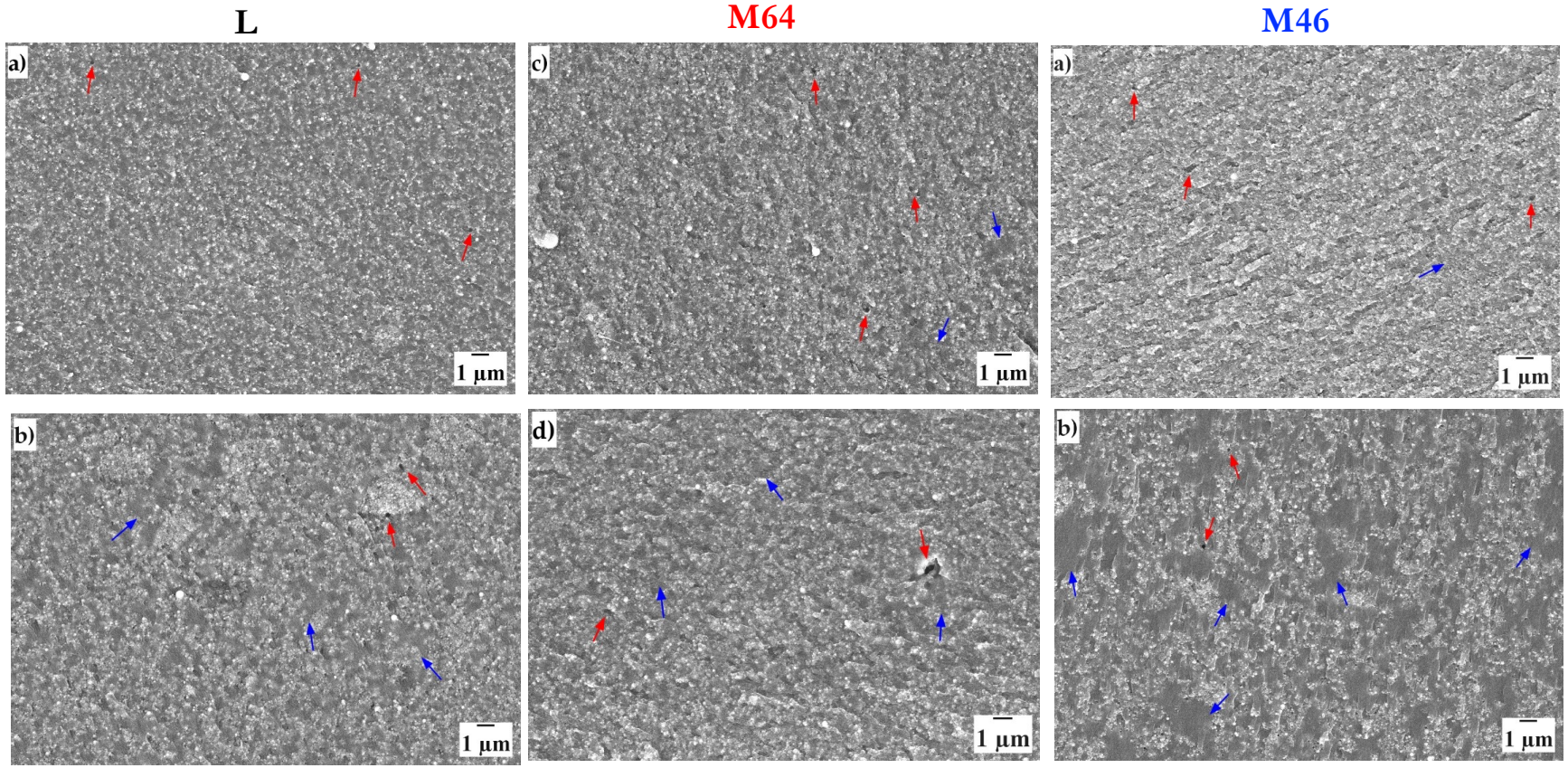
Delay in the increase of G' with respect to LPSQs matrices, larger with MA than with AA:

light shielding by NPs

- **Slower increase of G' vs. time: reduced chain mobility, larger with MA than with AA**

→ **Covalent vs. weak interactions**
→ **NPs dispersion (matrix – filler and filler-filler interactions, viscosity)**

NPs dispersion in LPSQs-based NCs (SEM, cross-sectional surface)



Red arrows: pores
Blue arrows: depleted regions

Filler amount : 80% wt

- NPs embedded in the matrices
- Few pores

- **MA: more homogeneous distribution (particularly in L)**
- **AA : large regions devoid of filler/agglomeration: M46 > M64 > L**

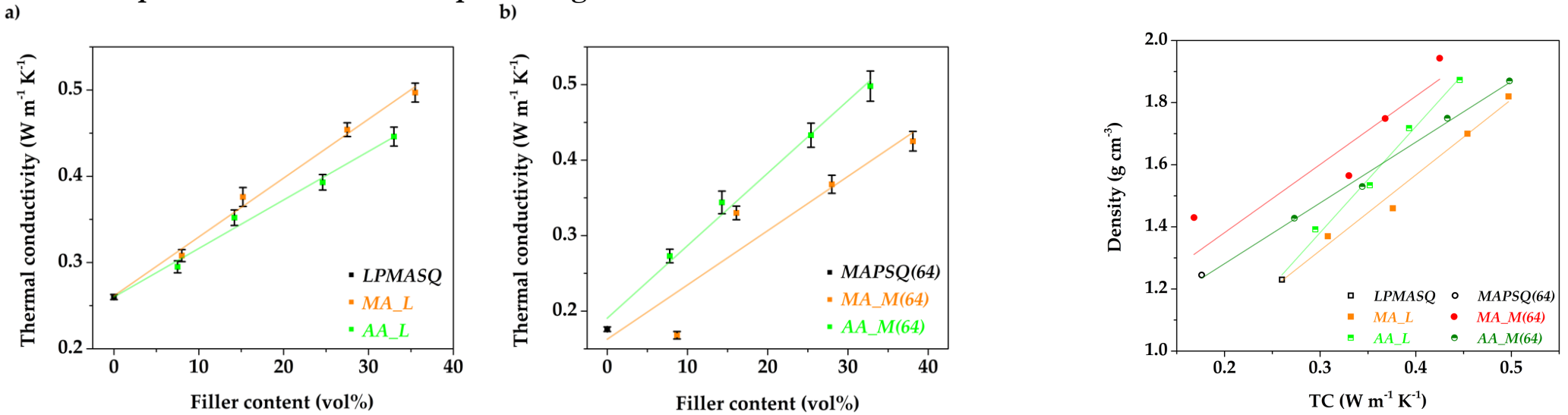
Thermal Conductivity (k) of LPSQs matrices and NCs

$$k = \rho \cdot c_P \cdot \alpha \qquad \left[\frac{W}{m \cdot K}\right]$$

- Density (ρ) (He picnometry)
- Specific heat capacity (c_P) (ASTM E1269)
- Thermal diffusivity (α) (LFA)

- **TC evolution of (a) L-based and (b) M64-based composites with respect to alumina volume percentage**

Systematic study for L and M64 based NCs (filler vol %)



- **Linear increase of TC with filler content**
- **Larger improvement for L with MA**
- **Larger improvement for M64 with AA**

- **Density higher for M64 than for L (π- π stacking)**
- **Reduced free volume → heat transport**

Thermal Conductivity (k) of LPSQs matrices and NCs

- **Matrices**

→ **L: highest TC , crosslinking**

→ **M46 : π-π interactions, chain packing**

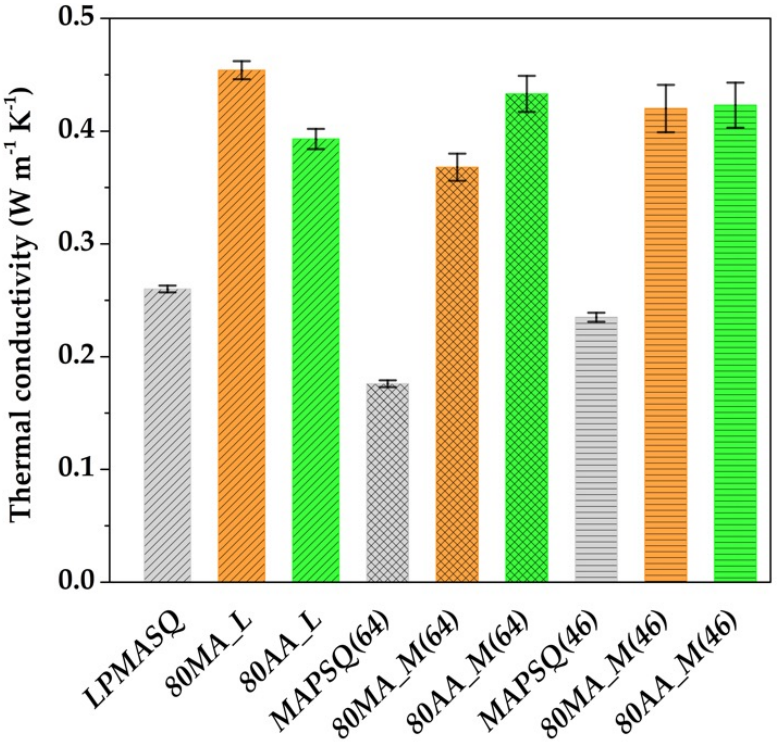
- **L-based NCs with MA NPs**: **crosslinking**

  0.260 → **0.497** W/m·K (120 wt%) (gain +91.2%)

- **M-64 based NCs with AA NPs**: **weak interactions**

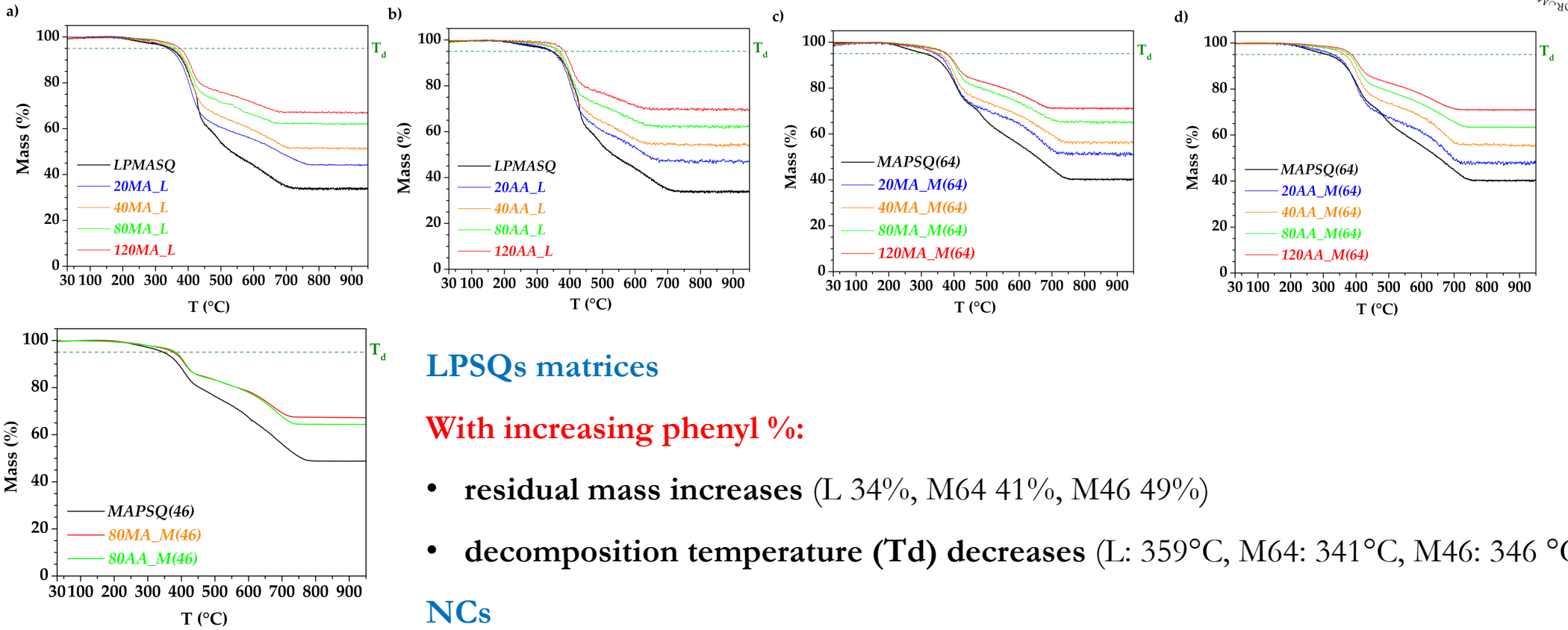
  0.176 → **0.498** W/m·K (M64, 120 wt%, gain +183%)

- **M46-based NCs**: **sinergy between weak interactions (high) and crosslinking (low)**



- **Covalent vs. weak interactions**
- **NPs dispersability**

Thermal stability of LPSQs and NCs (TGA, air)



LPSQs matrices

With increasing phenyl %:

- **residual mass increases** (L 34%, M64 41%, M46 49%)
- **decomposition temperature (Td) decreases** (L: 359°C, M64: 341°C, M46: 346 °C)

NCs

With increasing filler % (independently on functionalization)

- **net weight loss decreases** (down to 30%) **and Td increases** (up to 395°C)

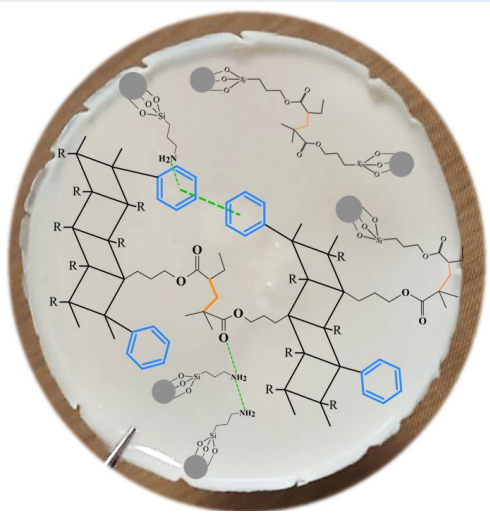
Conclusion & perspectives

- **LPSQs-based NCs with high alumina loading** and **high thermal stability as novel polymeric TMMs**
- **Effect of LPSQs organic side groups and Al_2O_3 functionalization:**

  Complex interplay between TC, molecular interactions, crosslinking behavior

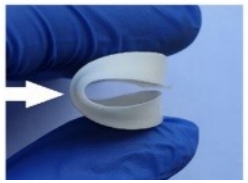
  Covalent bonds : network crosslinking (L), filler-matrix interactions (MA)

  Weak interactions : chain packing (π-π stacking) (M) , filler-filler/ filler-matrix interactions (AA)



✓ **TC increase by balancing covalent and weak interactions : engineering NPs surface and organic side-chains in LPSQs**

- **For flexible electronics: blends of LPSQs and organic polymers (PB)**



Gels (2023) 9, 810

Acknowledgements

UNIVERSITÀ DI TRENTO
Dipartimento di Ingegneria Industriale


Chiara Romeo (PhD)


Emanuela Callone


Riccardo Ceccato


Francesco Parrino


Giulia Fredi

POLITECNICO DI TORINO


Alessandra Vitale


Ignazio Roppolo


Roberta Bongiovanni

UNIVERSITA' DEGLI STUDI DI MILANO BICOCCA

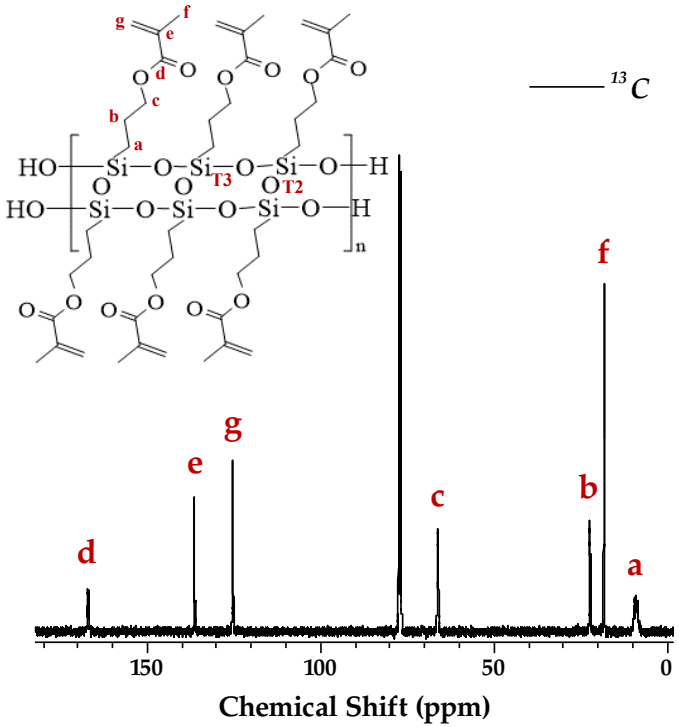

Massimiliano D'Arienzo

2023-2027 DIPARTIMENTO DI ECCELLENZA MUR

Departments of Excellence 2023-2027 (MUR)

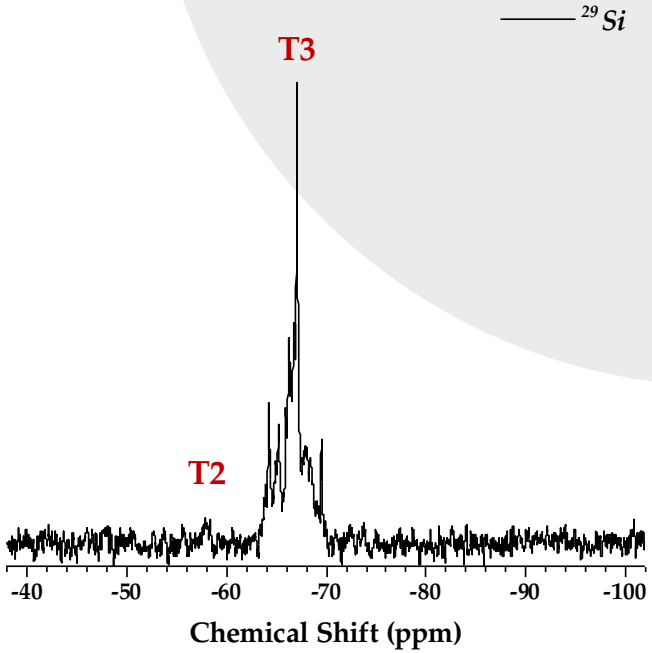
Thank you!

Synthesis of LPMASQ



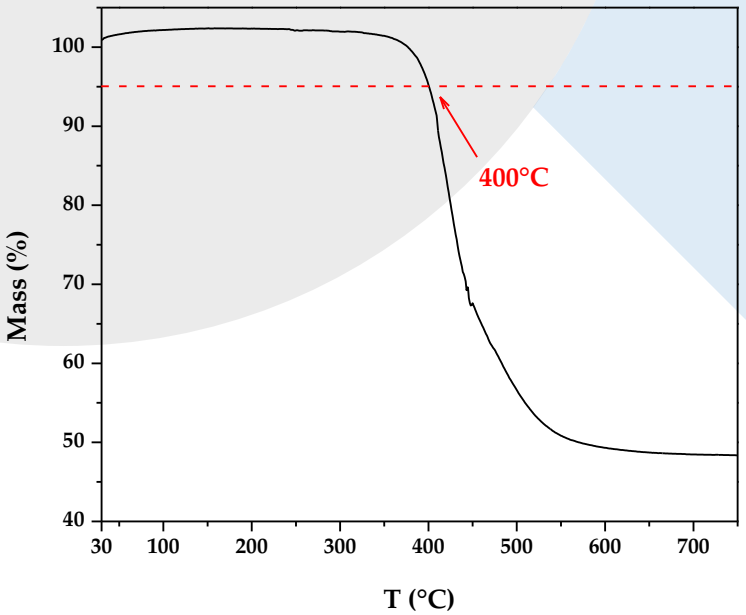
^{13}C NMR (in $CDCl_3$)

Successful hydrolysis and condensation.



^{29}Si NMR (in $CDCl_3$)

Fully condensed T^3 units with a 2% of terminal T^2 units.

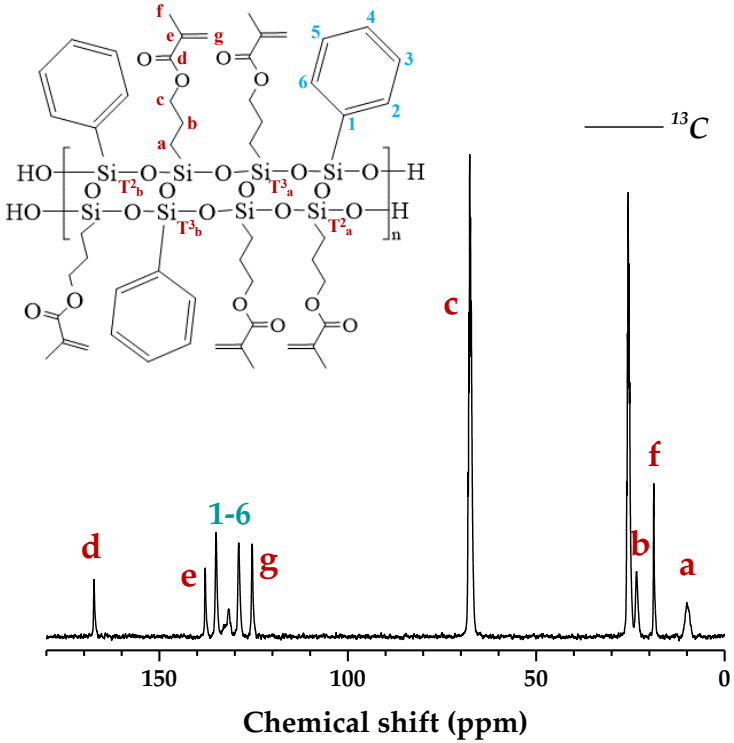


TG analysis

Td = 400 °C (at 5% weight loss)
Net weight loss 52%

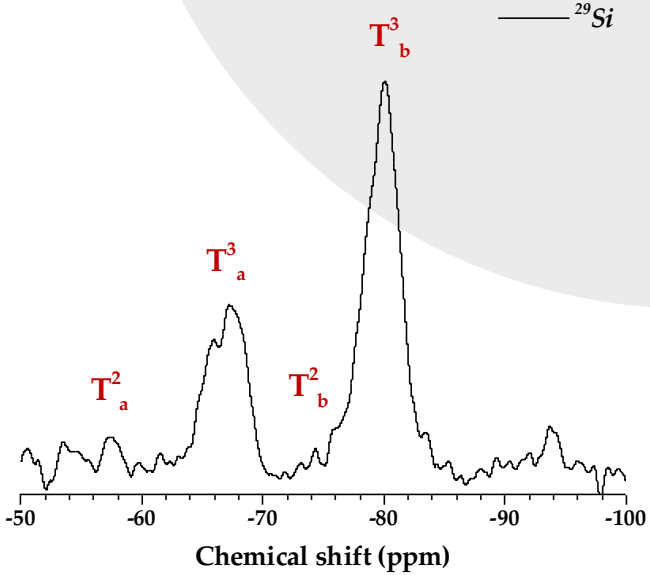
A. Lee, et al. "Novel Polysilsesquioxane Hybrid Polymer Electrolytes for Lithium Ion Batteries." *J. Mater. Chem.* A 2014, 2, 1277−1283.

Synthesis of MAPSQ



^{13}C NMR (in THF-d8)

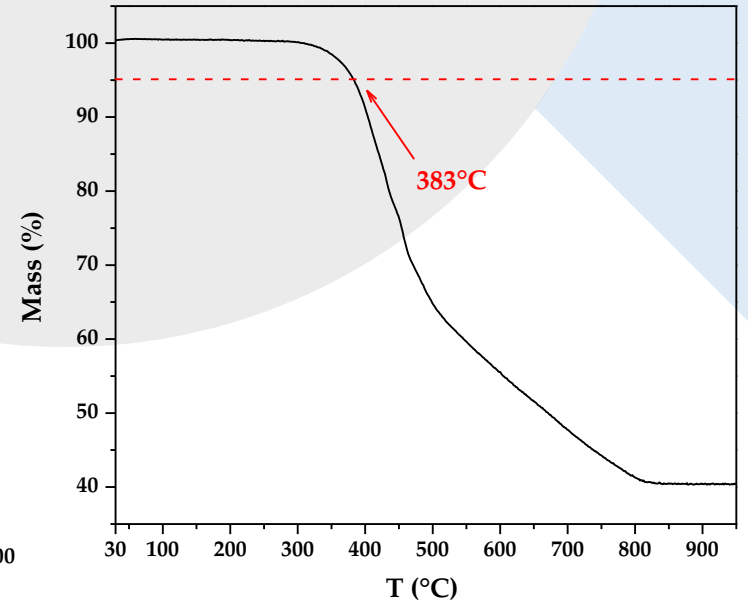
Successful hydrolysis and condensation.



^{29}Si NMR (in THF-d8)

Fully condensed T^3 units (98%).

MPTMS/PTMS = 6/4



TG analysis

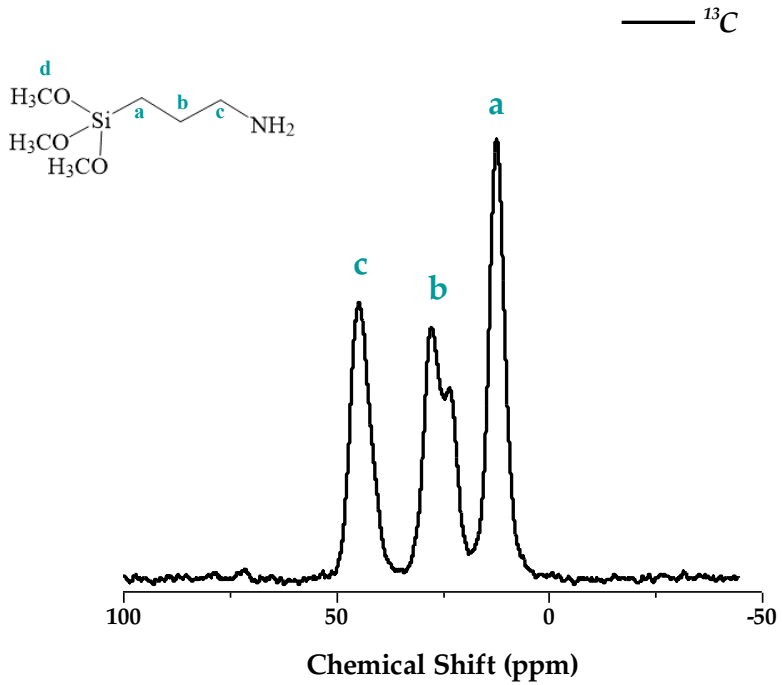
Td = 383 °C (at 5% weight loss)

Net weight loss 60%

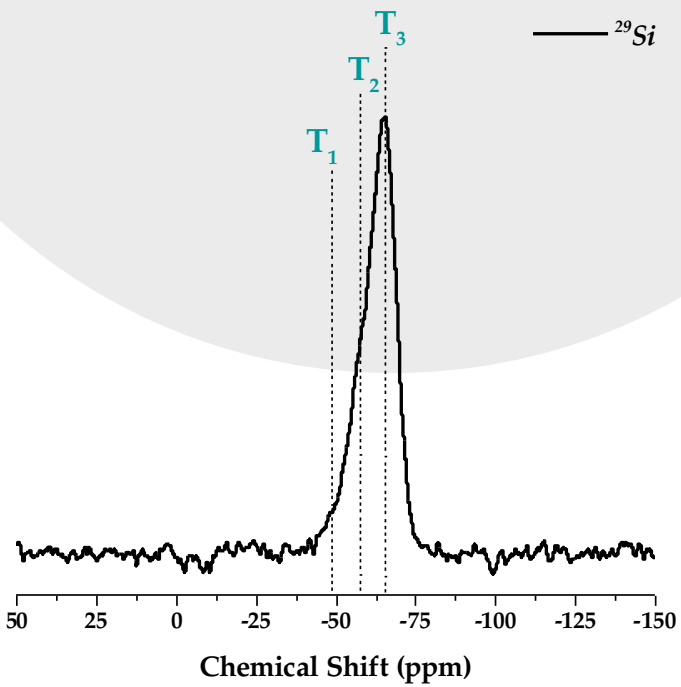
A.Lee, et al. "Novel Polysilsesquioxane Hybrid Polymer Electrolytes for Lithium Ion Batteries." *J. Mater. Chem.* A 2014, 2, 1277−1283.

Nano-alumina functionalization

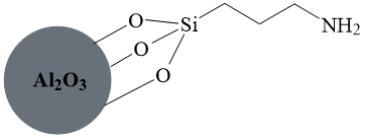
APTMS@Al_2O_3



^{13}C CPMAS NMR



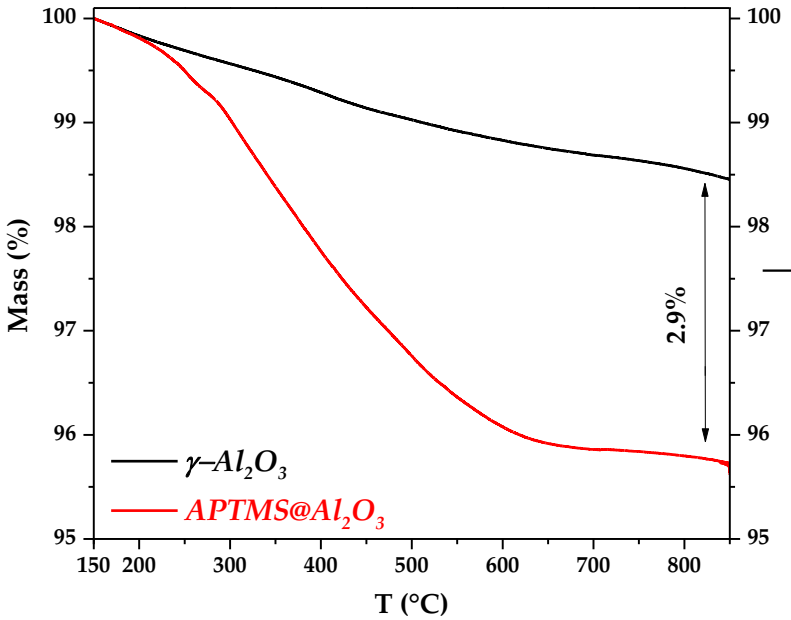
^{29}Si CPMAS NMR



- Absence of **d** → **Fully hydrolysed organosilane**
- Downfield of **a** → **Successful condensation**

Nano-alumina functionalization

$APTMS@Al_2O_3$

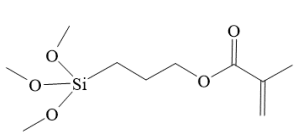


Grafting density

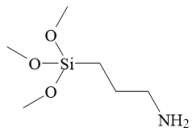
$$\sigma = \frac{X_{wt}}{100 - X_{wt}} \cdot \frac{N_A}{MW_{sil} \cdot SSA} \qquad [molecules/nm^2]$$

X_{wt} = % weight loss
N_A = Avogadro number
MW_{sil} = organosilane MW
SSA = specific surface area

Sample	X_{wt} [%]	σ [molecules/nm²]
$MPTMS@Al_2O_3$	1.7	1.46
$APTMS@Al_2O_3$	**2.9**	**3.94**



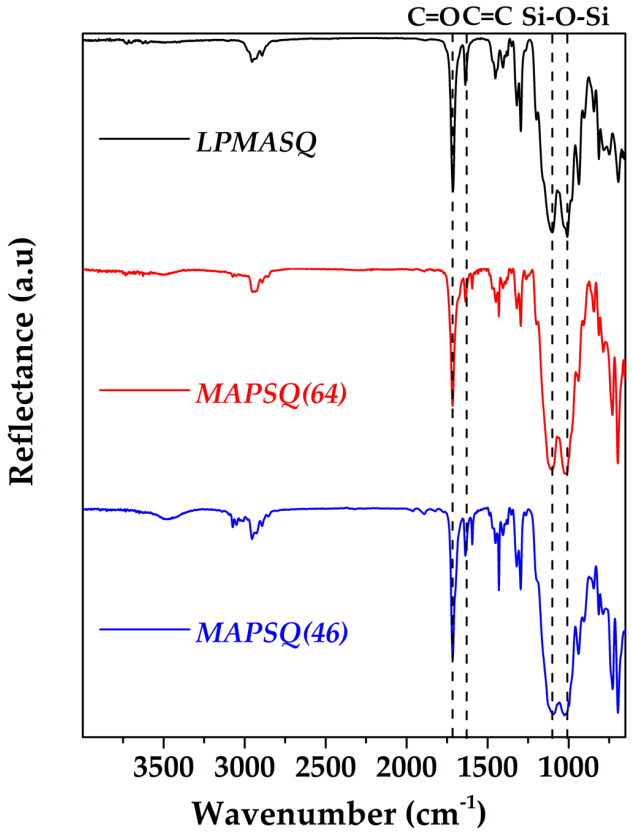
MPTMS

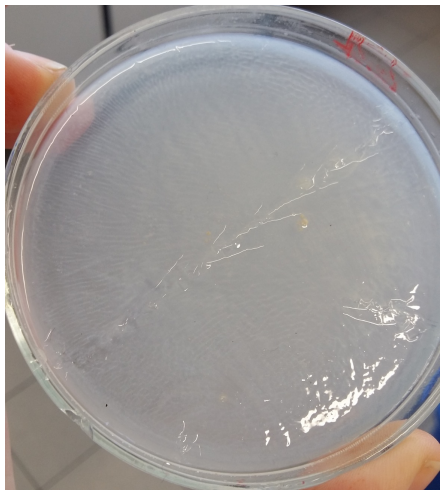


APTMS

ATR ladders

Typical two bands of ladders centered at 1100 cm^{-1} and 1000 cm^{-1}.





NCs: ^{13}C CPMAS NMR