Stabilization of polydimethylsiloxanes under UV irradiation

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Outlines

Introduction:

❖ Silicone resins, geostationary environment conditions

UV studies:

❖ Solutions proposed, requirements specification & UV ageing process

❖ Summarize of CNC results : Thermal & UV results

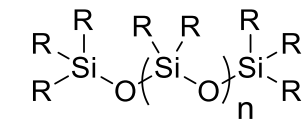
❖ Summarize of catalytic system results : Thermal & UV results

Conclusion and Prospects

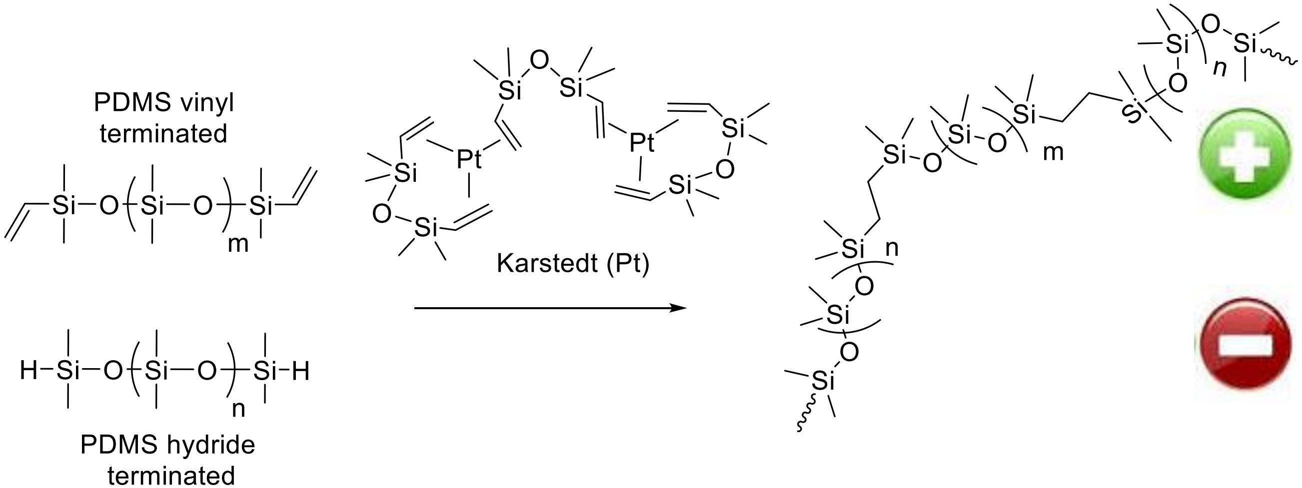
Introduction

Interest of silicone resins: definition, properties.

Chain of silicon/oxygen atoms and side organic groups
Most used silicone: *polydimethylsiloxane* **(PDMS)**



R : CH3, OH, H, CH=CH2



Karstedt's catalyst:

Industrial uses
Ease of utilization
Stable under air
Vs
Formation of colloidal species under UV irradiation

Attractive physico-chemical properties:

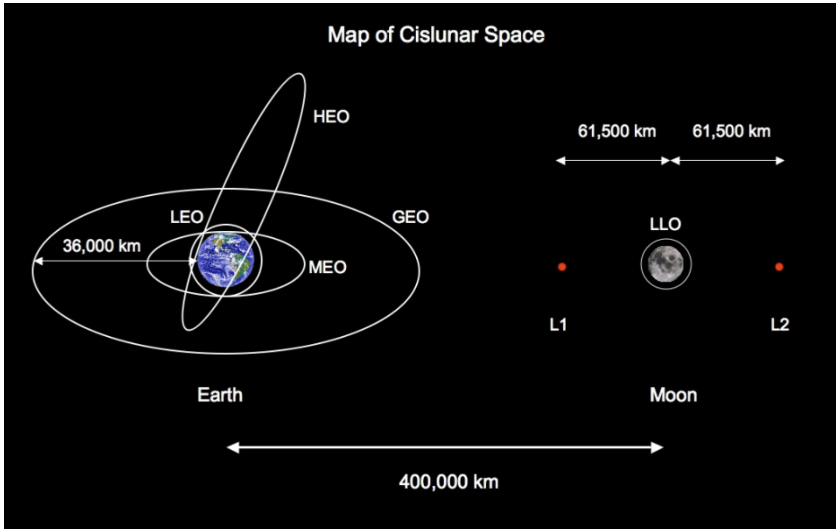
- Inorganic backbones, high energy level of **Si-O** bonding, low glass transition and transparency

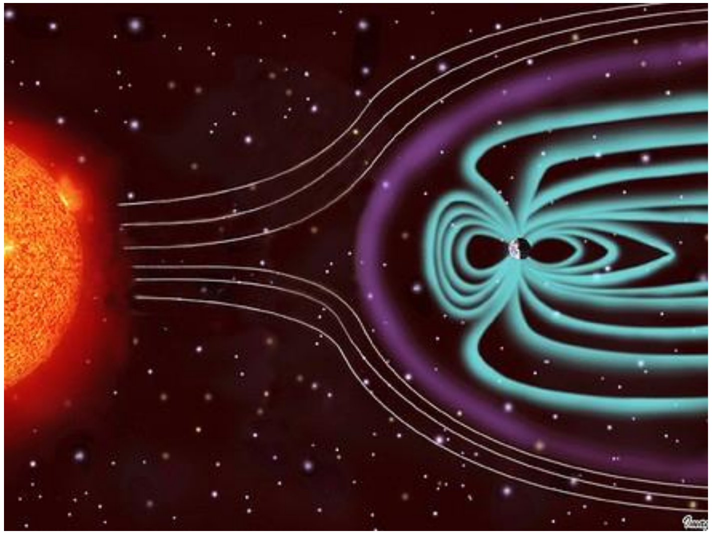
Aerospace applications:

- Paint binder, varnish, encapsulating, sealing, or adhesive

Objective: use PDMS as thermal-control coatings

The geostationary environment conditions





3 different heights for artificial satellites:

- ❖ Low Earth Orbit (LEO): 600 – 1600 km
- ❖ Medium Earth Orbit (MEO): ~10 000 Km
- ❖ **Geostationary Orbit (GEO) : 36 000 km**

Components of GEO:

❖Temperature between -170°C and 130°C
❖Height vacuum: low pressure <10^{-13} mbar
❖Electromagnetic irradiations (electrons, protons, neutrons…)

✓ *Focus on UV irradiation*

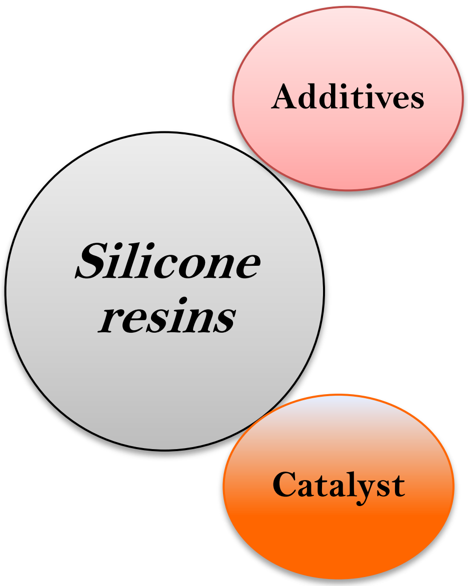
Impact on the lifetime and performance of any satellite in orbit

UV studies

Limits of silicone resins under UV irradiation: solution to improve the UV stability

Degradation of polysiloxane under UV irradiation:

- Homolytic cleavage bonds leading to the formation of free radicals
- Inter-and/or intra-molecular rearrangement
- Presence of different mechanisms: depending on the UV wavelength range and the atmosphere composition



Two ways to limit the evolution of properties:

Add additives in the PDMS matrix: Cause some interactions stabilizing the silicone resins & absorb the UV irradiation in place of the polymer chain

Replace the Karstedt's catalyst: Limit the formation of colloidal species under UV irradiation

MAP/CNES Requirements:
Keep the industrial features of cross-linking process
Transparency> 90% from 250 to 1000 nm

LCPO Laboratoire de Chimie des Polymères Organiques

Simulation of UV irradiation/Ageing process

Vacuum chamber & Oriel solar simulator (UV)

Vacuum chamber

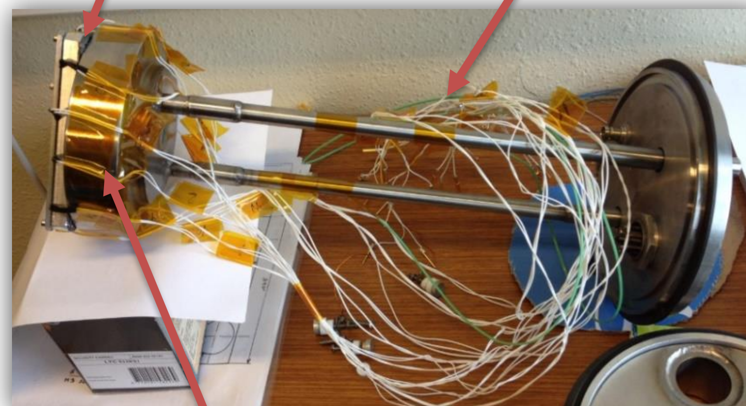
Oriel Solar Simulator

Specifications:

- Temperature: ~ 30° C
- Pressure chamber < 10^{-5} mbar
- UV simulator: up to 1.5
- Time of irradiation: 450-500 ESH

Sample holder

Water cooling system



Thermo couples

New sample holder:

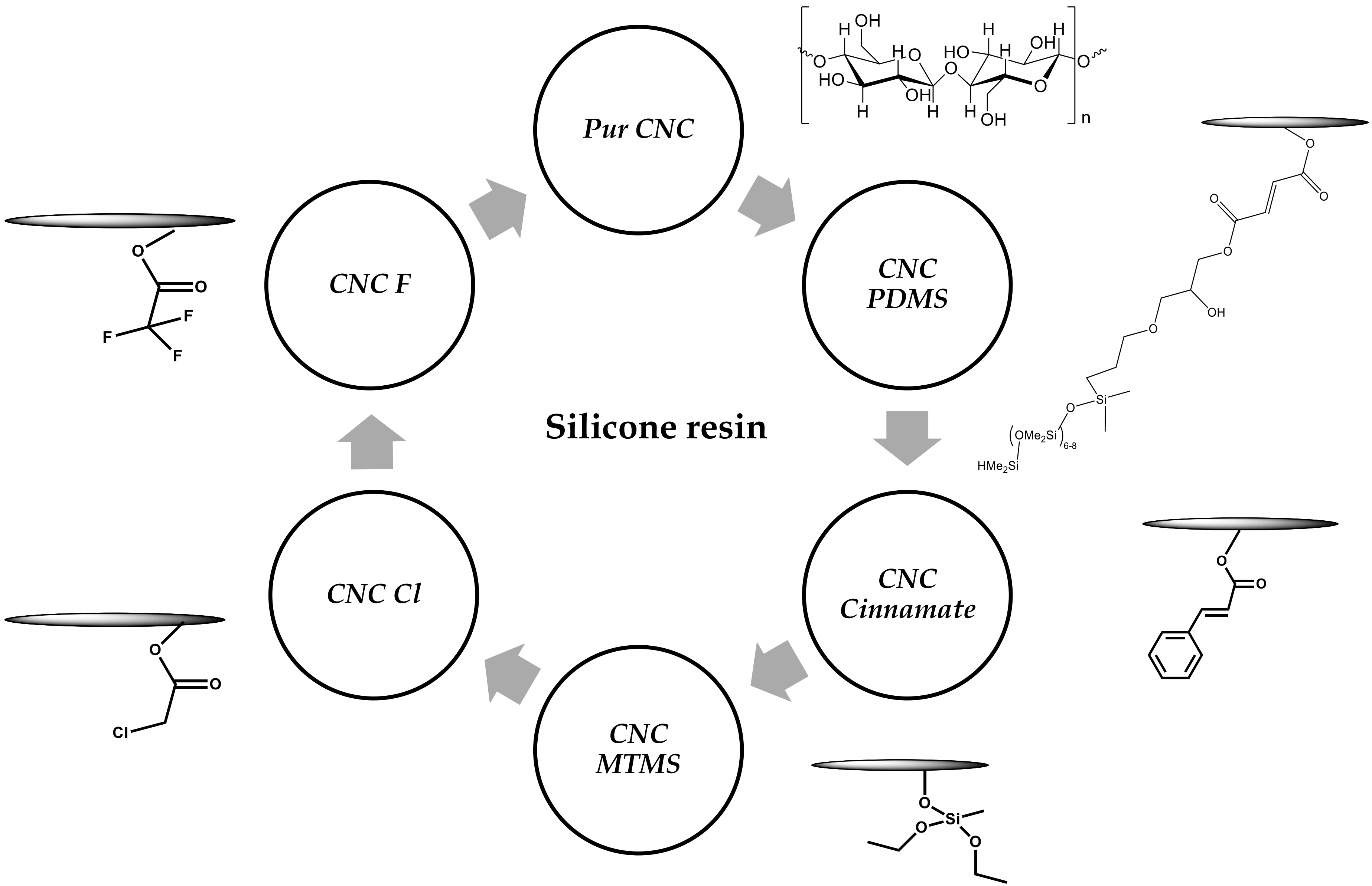
Regulate and monitor the temperature

Control the aging of the material & improved reproducibility

Summarize of CNC studies

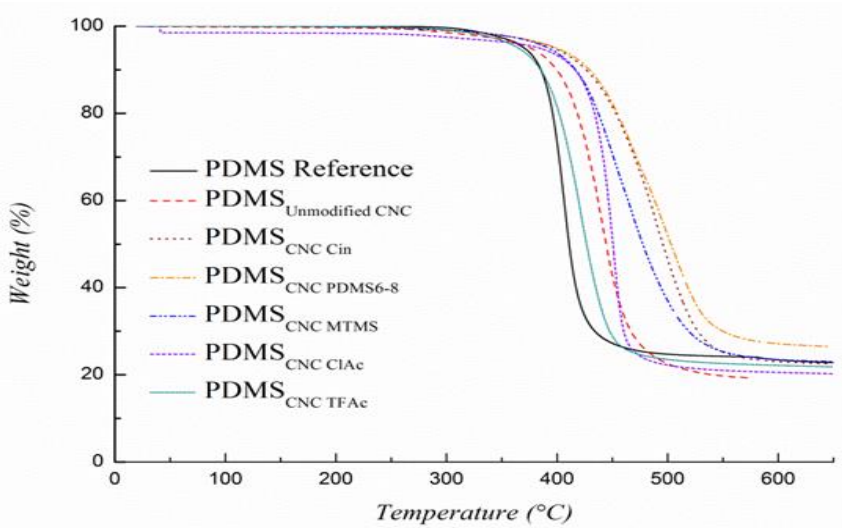
Laboratoire de Chimie des Polymères Organiques

Different structures of CNC studied

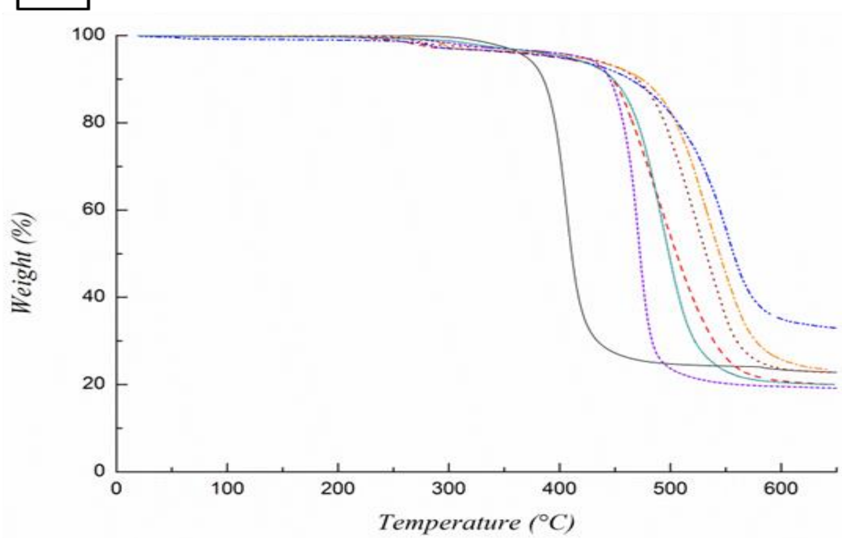


Influence of CNCs structures on the thermal degradation

a 0.5 wt.% of fillers



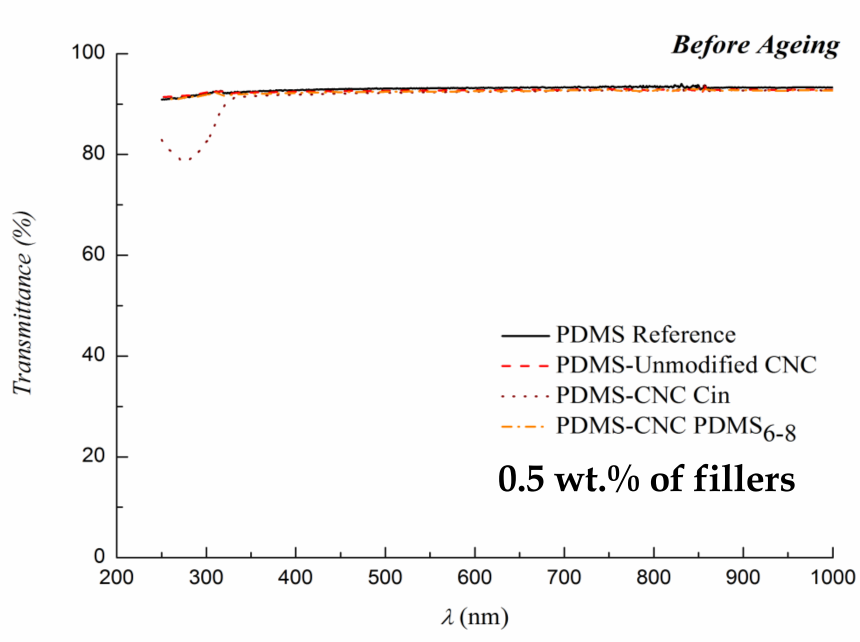
b 4.0 wt.% of fillers

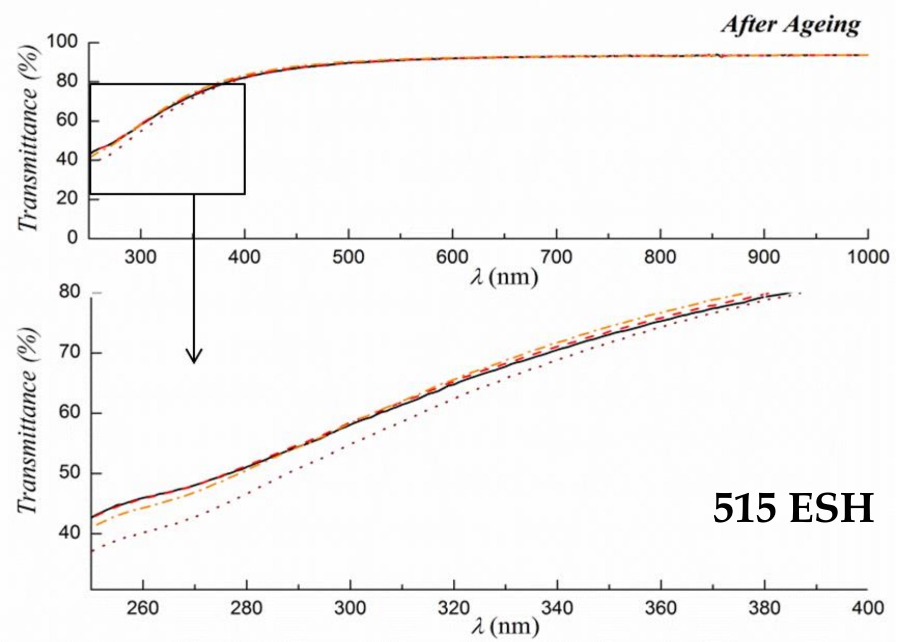


Samples	$T_{5\%}$ [°C]	T_m [°C]
PDMS	360	405
PDMS with 0.5 wt% of CNCs		
$PDMS_{CNC}$	**420**	**460**
$PDMS_{CNC-MTMS}$	**400**	**470**
$PDMS_{CNC-PDMS6-8}$	**400**	**490**
$PDMS_{CNC-Cin}$	**400**	**510**
$PDMS_{CNC-ClAc}$	**390**	**460**
$PDMS_{CNC-TFAc}$	**370**	**430**
PDMS with 4 wt% of CNCs		
$PDMS_{CNC}$	**410**	**500**
$PDMS_{CNC-MTMS}$	**405**	**550**
$PDMD_{CNC-PDMS6-8}$	**420**	**535**
$PDMS_{CNC-Cin}$	**425**	**525**
$PDMS_{CNC-ClAc}$	**425**	**475**
$PDMS_{CNC-TFAc}$	**410**	**450**

Improvement of thermal stability regarding the percentage and the nature of CNC added

Evolution of the optical properties during photo-ageing for CNC

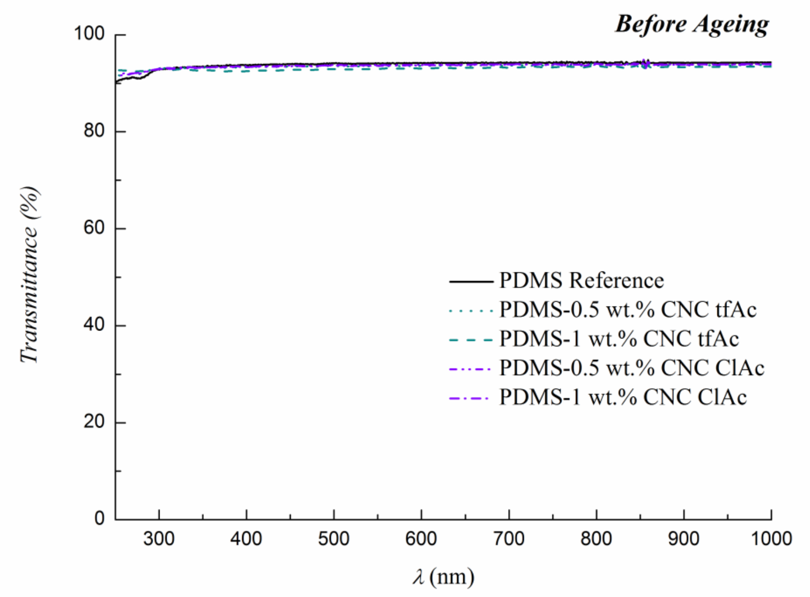


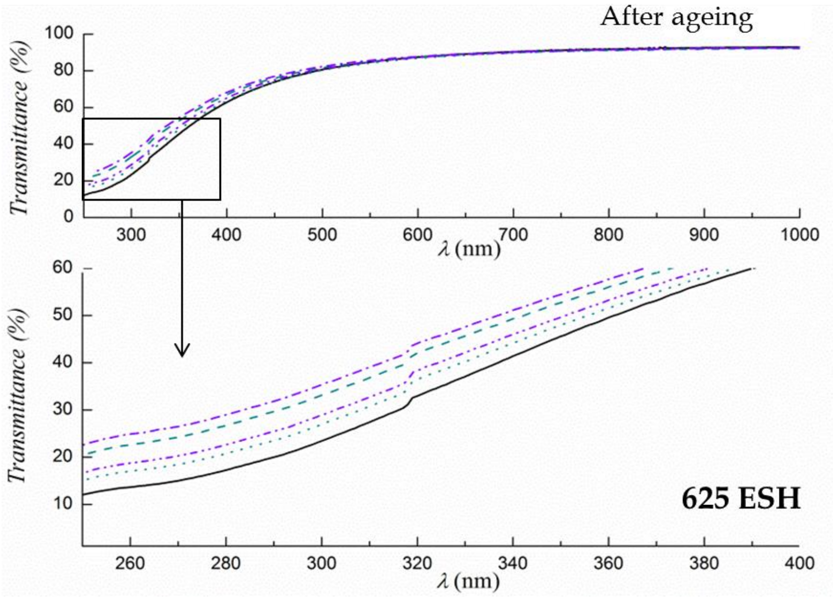


Wavelength range (nm)	ΔG% : (ΔTs ref - ΔTs CNC-Unmodified)	ΔG%: (ΔTs Ref - ΔTs CNC-Cin)	ΔG%: (ΔTs Ref - ΔTs CNC-$PDMS_{6\text{-}8}$)
[250-1000]	0.5	0.9	1.0
[250-400]	0.6	1,20	1.45

Transparency before irradiation similar between PDMS-CNC Unmodified & PDMS-CNC $PDMS_{6\text{-}8}$ Vs PDMS Ref
Initial transparency different for PDMS-CNC Cin due to the aromatic function
Small increase of UV resistance against UV irradiation

Evolution of the optical properties during photo-ageing for CNC



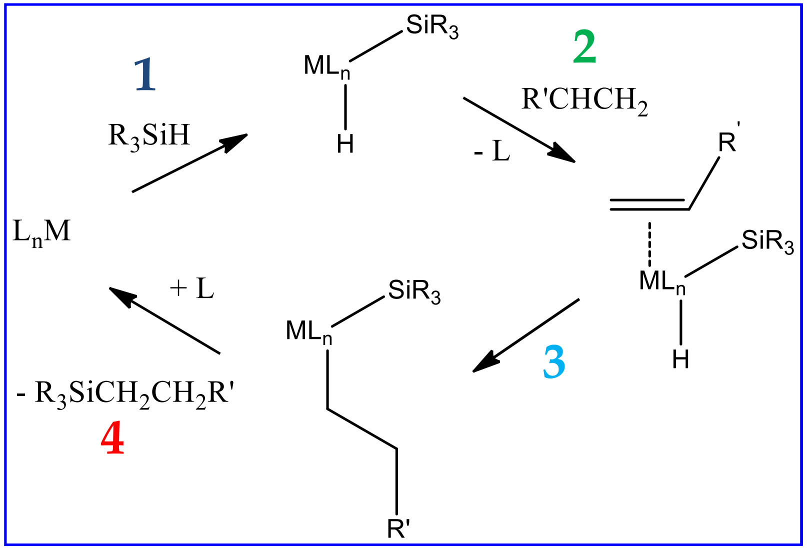


Wavelength range (nm)	Filler content (weight %)	Δg %: (ΔTs Ref - ΔTs CNC-TFAc)	Δg %: (ΔTs Ref - ΔTs CNC-ClAc)
[250-1000]	0,5	0,3	0,8
	1,0	2,0	2,0
[250-400]	0,5	1,75	3,5
	1,0	6,6	8,2

Transparency before irradiation similar between PDMS-CNC TFAc & PDMS-CNC ClAc Vs PDMS Ref
Small increase of UV resistance against UV irradiation
UV Stability depending of the filler content

Summarizes of catalytic approach

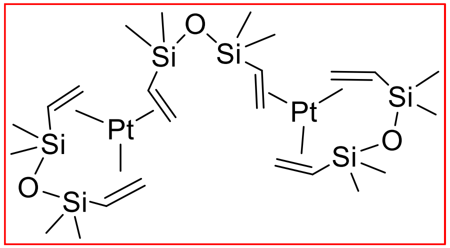
Mechanism of hydrosilylation: Aim of the catalyst



Catalyzed hydrosilylation by VIII metals

Chalk and Harrod mechanism: 4 Steps

(1) Oxidative addition of Si-H to the metal center
(2) Coordination of the alkene to the metal
(3) Insertion of the alkene into the M-H bond
(4) Reductive elimination of Si-C product



Karstedt's catalyst

Under UV:

Colloidal species formation leading to yellowing

Karstedt's catalyst:

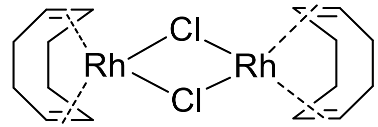
Number of valence electrons = 16, $5d^96s^1$

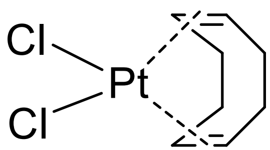
Ligand L present on the metal: ***Trigonal plane geometry***

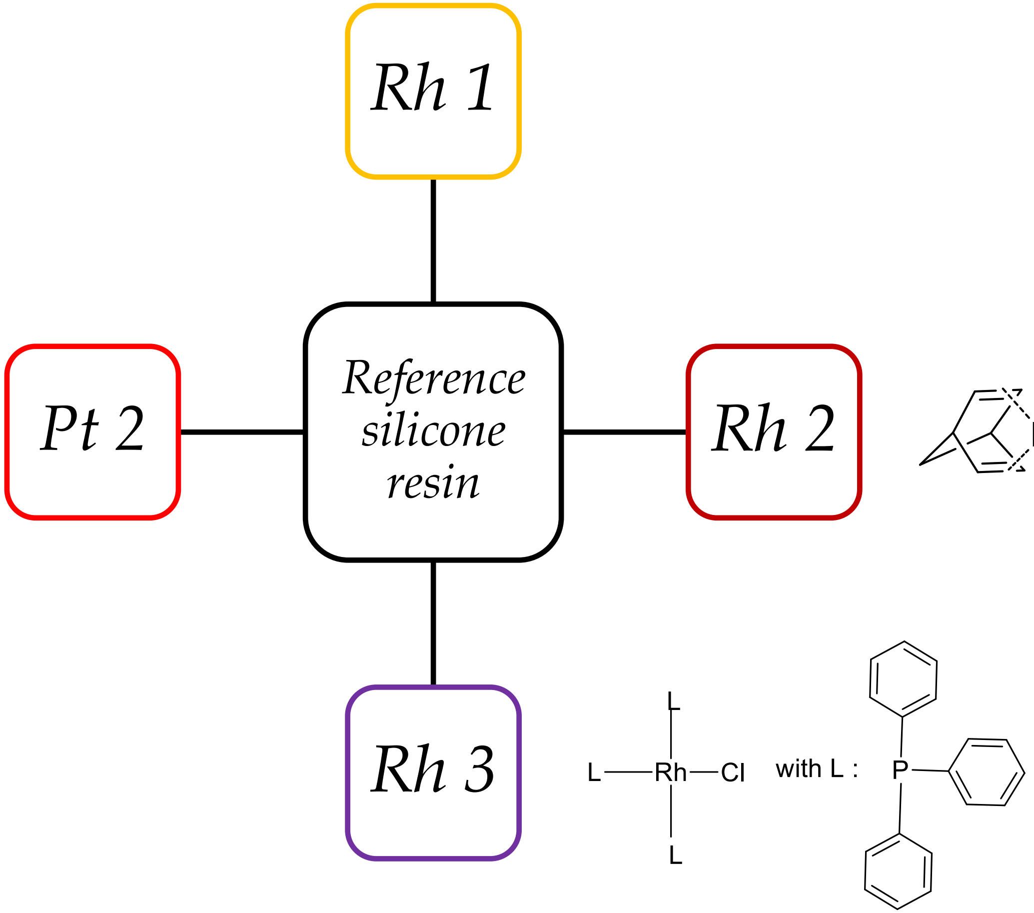
Paramagnetic complex: attracted by a magnetic field

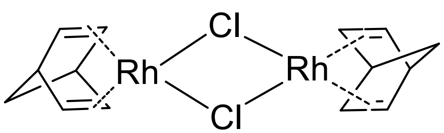
Change catalytic system by conserving the number of valence electrons

Different structures of studied catalyst

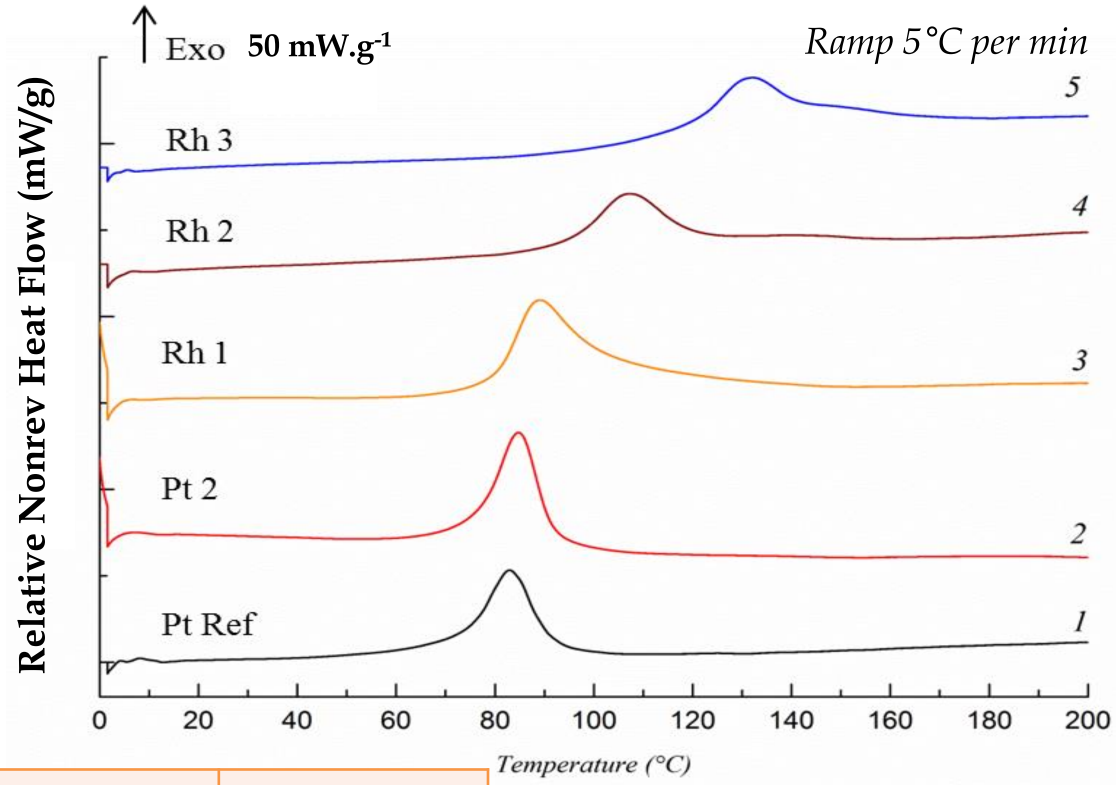








Check the cross-linking features



$$Q_{Heptane} = 1 + \left(\frac{m_f}{m_i} - 1\right)\left(\frac{\rho_{PDMS}}{\rho_{sol}}\right)$$

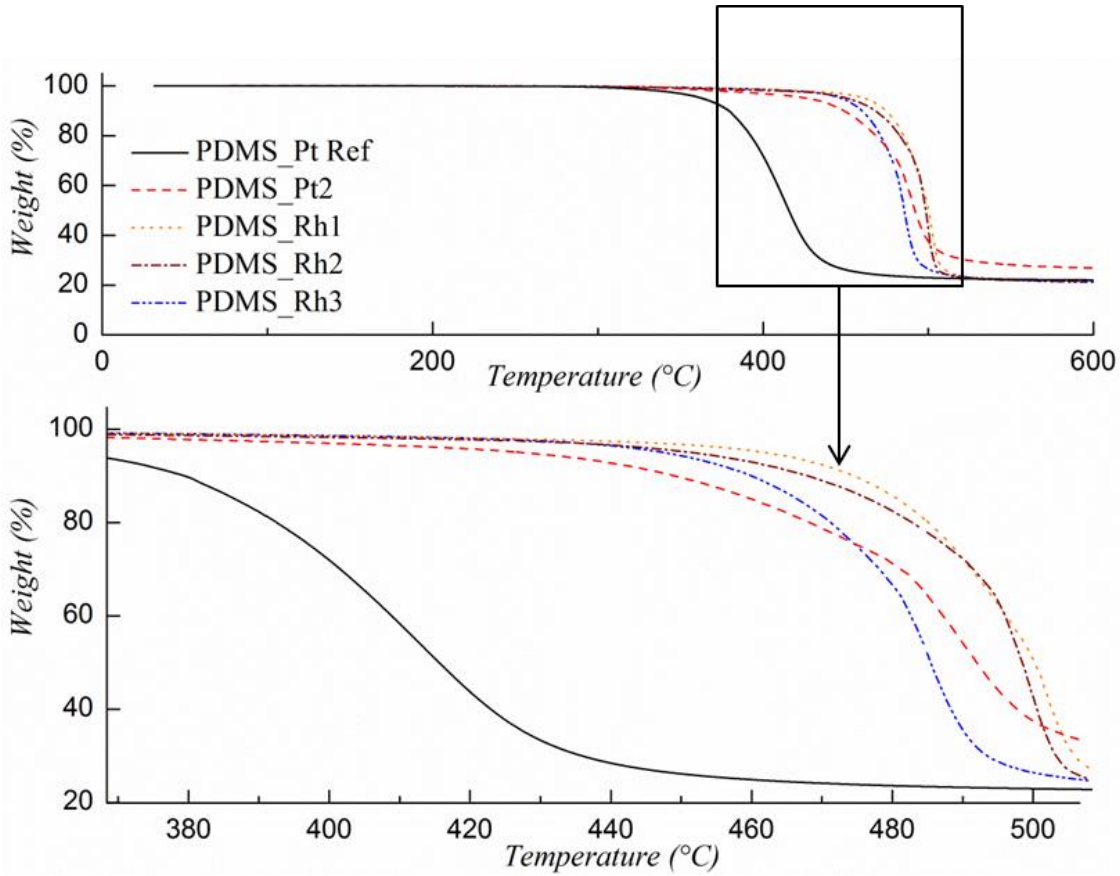
Swelling % in heptane for 72 hours:

Catalytic system	Swelling percentage (q)
Pt ref	2,05
Pt 2	2,18
Rh 1	2,43
Rh 2	2,73
Rh 3	2,92

Catalytic system	$T_{\text{optimal of cross-linking}}$ (°C)
Pt ref	83
Pt 2	85
Rh 1	90
Rh 2	110
Rh 3	130

Influence of the organometallic derivatives on the cross-linking temperature
E′ for each catalytic systems close to the reference E′ at 1,60 Mpa except for the Rh 3
Industrial cross-linking process efficient regarding the catalytic system

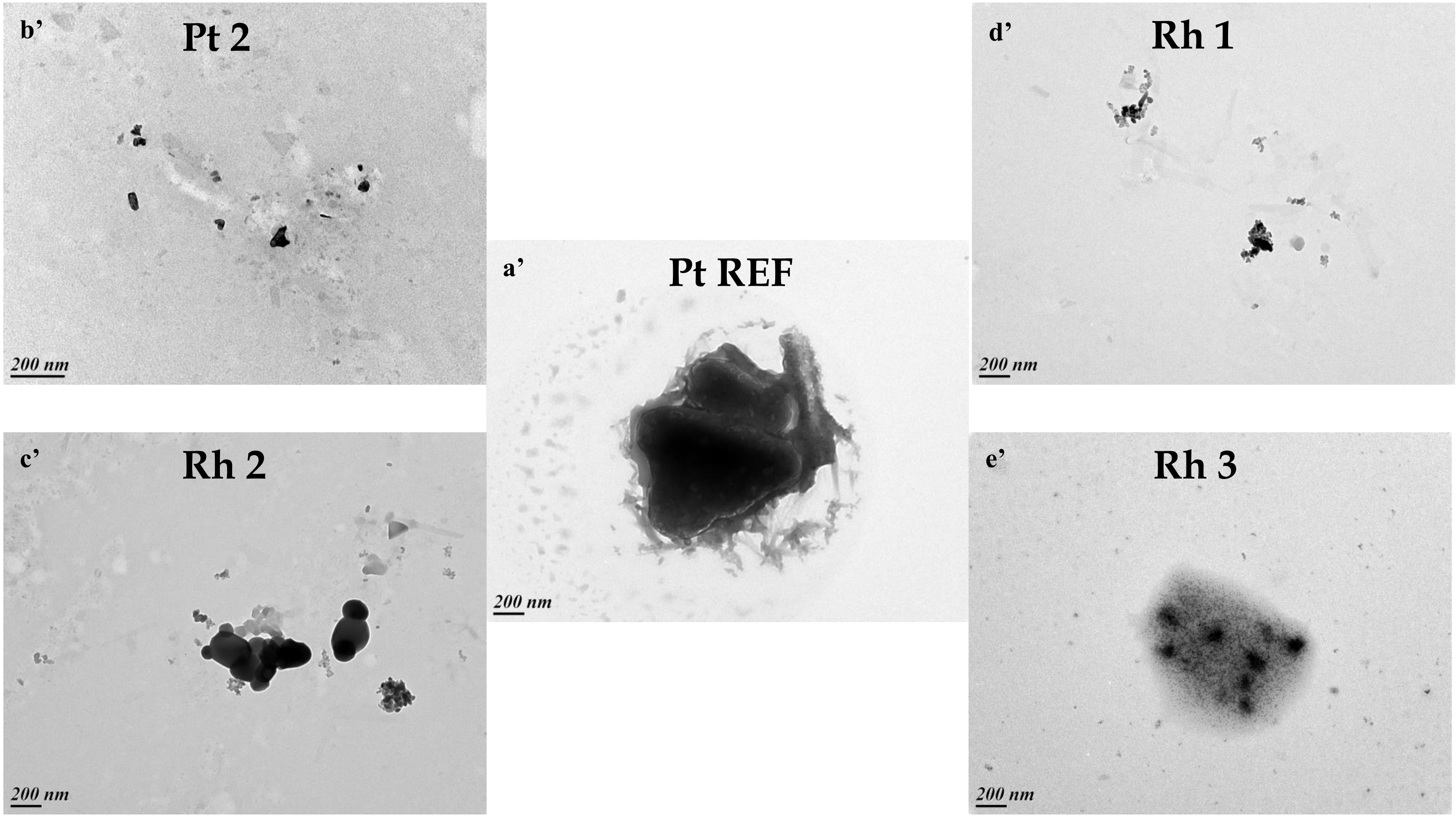
Thermal results for new catalytic systems



System catalytic used	$T_{d\,5\,\%}$ (°C)	T_d (°C)
Pt Ref	360	405
Pt 2	430	470
Rh 1	460	480
Rh 2	450	480
Rh 3	450	465

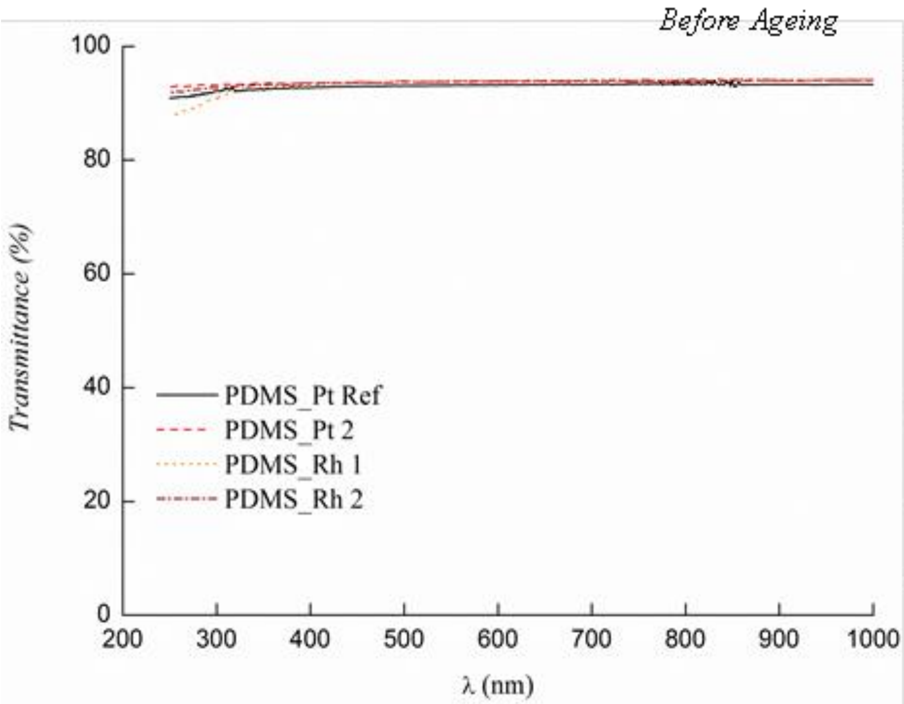
Thermal stability improved for all new organometallic derivatives
Influence of halogens ligands on the thermal behavior : limit the PDMS depolymerization

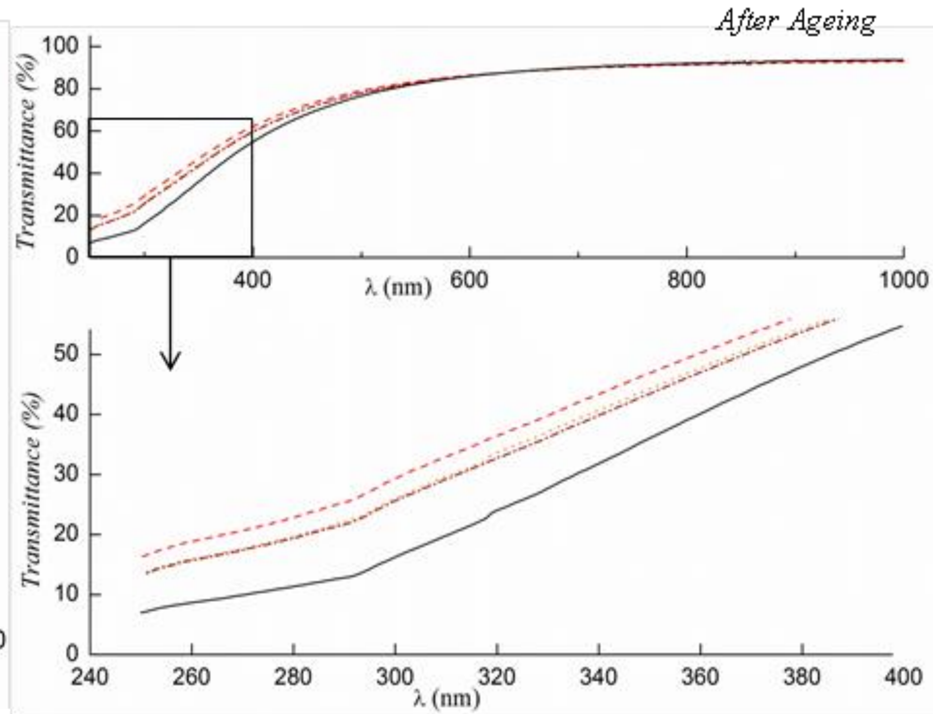
TEM analyses on each PDMS materials



Presence of larger object and colloidal species participant to the UV degradation for the reference system as compare to the new one studied

Optical performances under UV irradiation





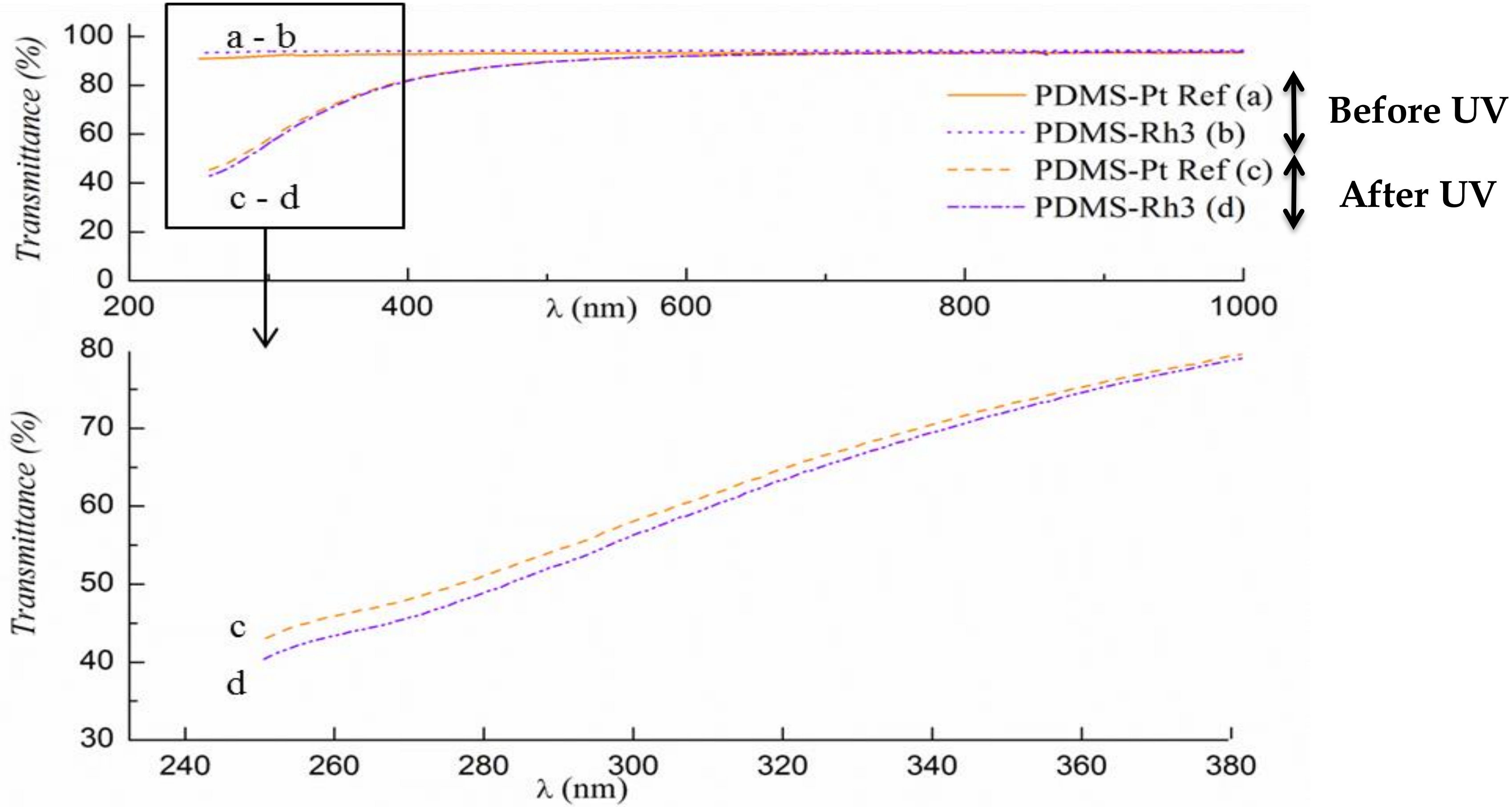
$$Ts = \frac{\int_{250}^{1000} Ts(\lambda).Is.d(\lambda)}{\int_{250}^{1000} Is.d(\lambda)}$$

T: spectral transmittance of the material & **Is**: spectral irradiance of the sun

Wavelength range (nm)	Δg Pt 2	Δg Rh 1	Δg Rh 2
250-1000	4.0	2.9	2.7
250-400	12.2	9.7	9.3

Optical properties before UV irradiation similar between Pt 2, Rh 1, Rh 2 and Pt Karstedt
Better resistance to UV irradiation for new catalytic system

Optical performances under UV irradiation



Optical properties before UV irradiation similar between Rh 3 & Pt Karstedt
Same loss of transmittance between these two systems
Influence of the cross-linking density as compare to the other new catalytic derivate

Conclusion & Prospects

CNC as UV stabilizers:

- Thermal stability increased regarding the structure of CNC studied up to 150 °C for the CNC-MTMS
- UV stability improved on the wavelength range 250-400 nm up to 8 % for the CNC-ClAc

Replacement of Karstedt catalysts

- Thermal stability increased regarding the structure of catalyst studied: around 80 to 100 °C
- UV stability improved on the wavelength range 250-400 nm up to 12 % for the Pt 2
- Large catalytic species observed for Karstedt catalyst

General perspective:

Last generation: Combine CNC additive and catalyst on the same formulation

Inherent limitation due to PDMS chemical structure

Thank you for your attention

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