Incorporation of fillers in elastomeric composites: impact of the process on the thermomechanical properties

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Adrien Simon, Daphné Berthier[2], Marie-Pierre Deffarges[1], Mathieu Venin[1], Florian Lacroix[1], Yohan Tendron[2], Stéphane Méo[1]

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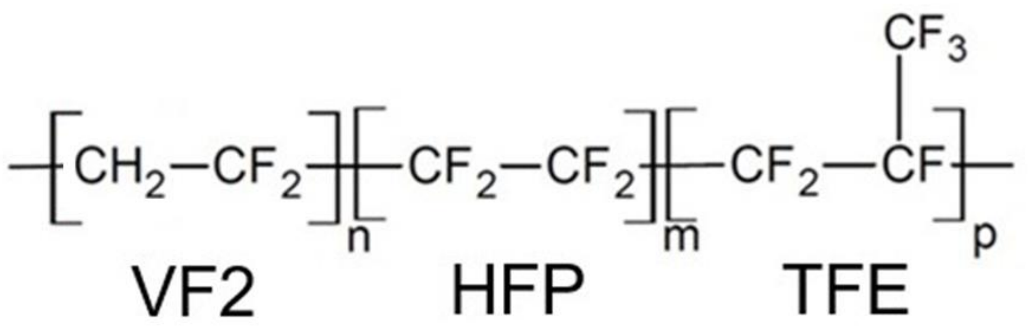
Previous works [1] led to the development of a new formula on the basis of FKM blend reinforced with Polyhedral Oligomeric Silesesquioxanes (POSS). The main objective consists in maintaining thermomechanical properties while changing the process scale. To this end, two new specimen geometries of vulcanized rubber are studied : thin films obtained by coating at laboratory scale through masterbatch and sheets obtained through rubber mill and thermocompression.

Fluorinated rubber: FKM



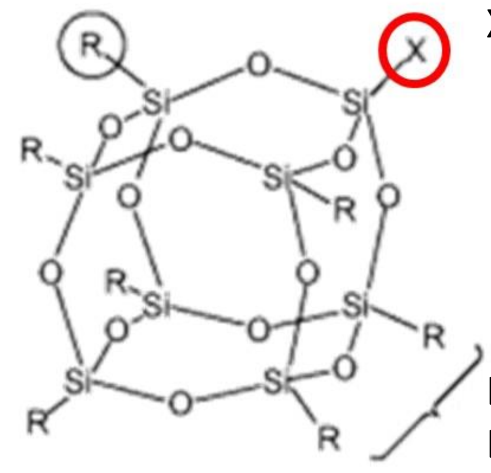
Formula of the terpolymer FKM

- A fourth monomer is incorporated to enhance the crosslinking action, named « Cure Site Monomer » (CSM)
- FKM exhibits good mechanical, chemical and thermal properties

Polyhedral Oligomeric SilSesquioxanes (POSS)

R : non reactive group with R ≥ 1

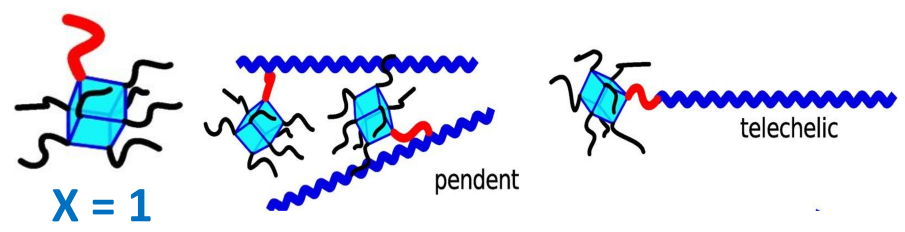
X : functionnal group with X ≥ 1



Length Si-Si 0.5nm
Length R-R 1.5nm

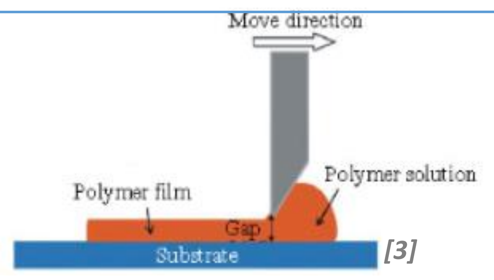
Chemical structure of POSS

- Smallest silica particles (1 to 3nm)
- Hybrid chemical composition
- Role of functionnal groups (X) : chemical interaction with polymers



Possible interactions with a POSS (X=1) [2]

Two studied processes
Main parameters

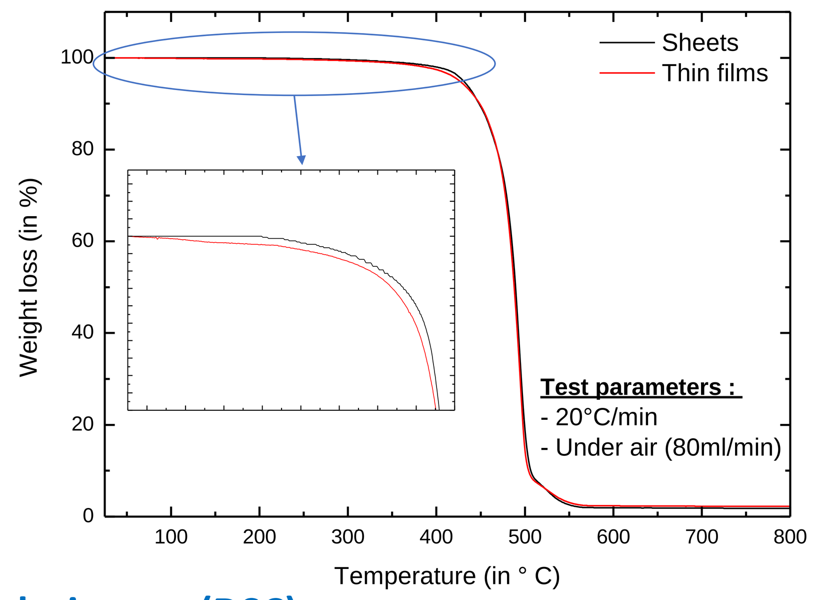
	Coating	Thermocompression
1. Mixing step	 Dispersion in solvent ▪ *Order of incorporation* ▪ *Solvent, temperature, stirring rate* Deposition rate	 Rubber mill ▪ *Order of incorporation* ▪ *Rotation speed* ▪ *Temperature*
2. Vulcanising process (Vulcanization + Post-vulcanization)	▪ Cycles (Temperature, time) ▪ Specimen volume ≈ 0,4 cm^3	▪ Cycles (Temperature, time, pressure) ▪ Specimen volume ≈ 40 cm^3
3. Specimen geometries	Thin films ▪ Dimension: *Thickness : around 400 µm*	Sheets ▪ Dimension: *Thickness : around 2 mm*

Thermal behaviour

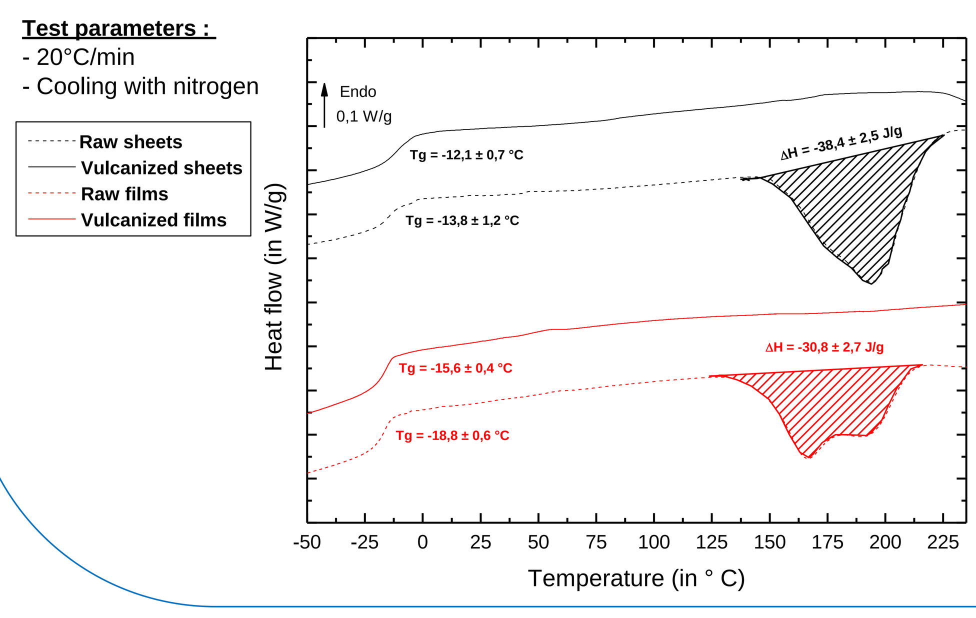
ThermoGravimetric Analysis (TGA)

- Same degradation trends
- For thin films, a slightly weight loss, is supposed to be associated to evaporation of volatile compounds (around 130°C)

$$T_{degradation\ at\ 50\ \%} = 488\ °C$$



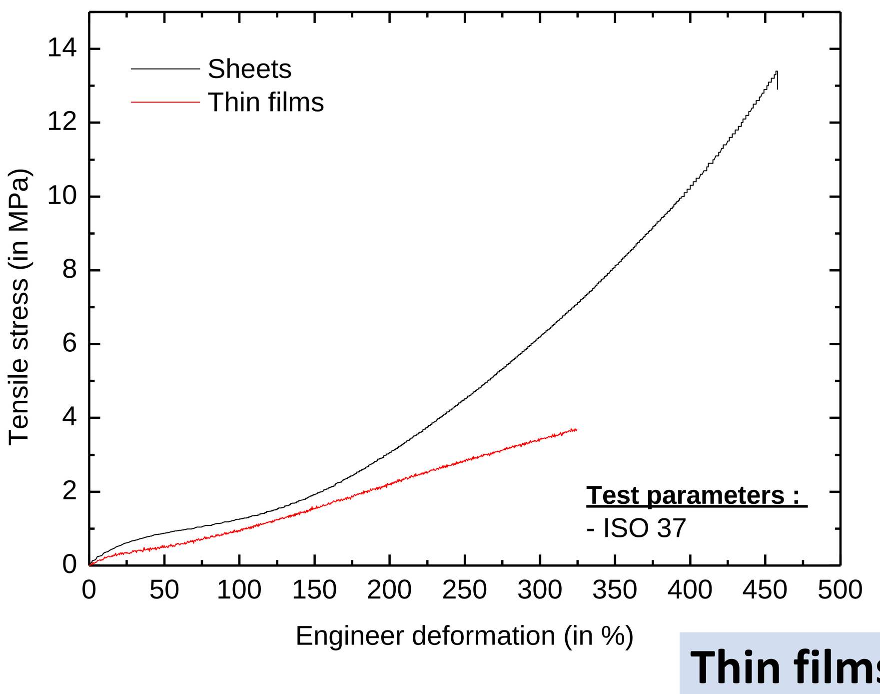
Differential Scanning Calorimetry (DSC)



- The glass transition (for raw and vulcanized samples), the activation temperature and the reaction area of the crosslinking reaction are higher by thermocompression than by coating

Mechanical behaviour

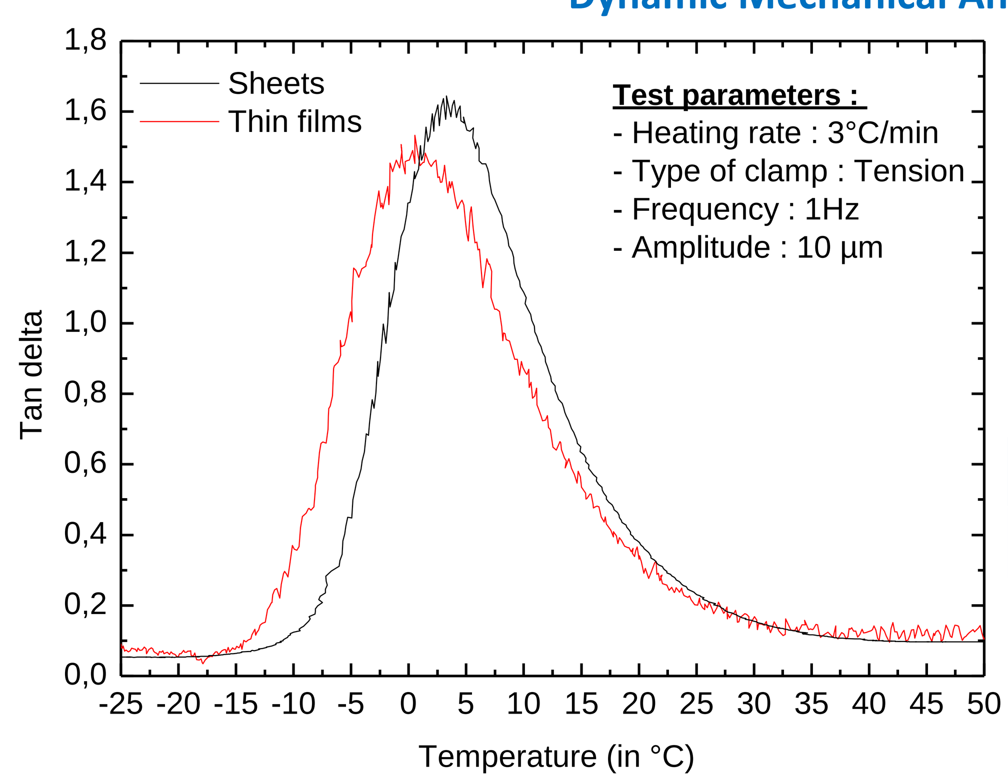
Tensile tests at 23°C



- Curve trends and failure parameters are differents between thin films and sheets

	Modulus at 100% (in MPa)	Tensile at failure (in MPa)	Elongation at failure (in %)
Thin films	0.6 ± 0.05	2.4 ± 0.7	278 ± 45
Sheets	1.24 ± 0.01	11.2 ± 1.5	425 ± 30

Dynamic Mechanical Analysis (DMA)



- Tα: temperature at the maximum of the tan δ in the glass transition zone

	Tα (in °C) at 1 Hz
Thin films	1.4 ± 0.2
Sheets	2.7 ± 0.6

$$T\alpha_{\ Sheet} > T\alpha_{\ Thin\ film}$$

Conclusions

- Impact of the process and of the specimen geometries on the macroscopic mechanical characterisation (by tensile test : underestimation of the materials properties on thin films), on the glass transition and on the cross linking reaction (on activation energy and activation temperature)
- Presence of volatile compounds in thin films but not in sheets (TGA results)
- No impact on degradation behaviour
- Thin films is a cost efficient way to provide thermal informations before sheet fabrication

Perspectives

Processes and geometries

- Impact of a new manufacturing way (tube by extrusion)
- Comparison between the three final products (thin film-sheet-tube)

Upgrade of the formula

- Incorporation of POSS with new functionnal groups
- Characterisation of materials after chemical and/or thermal aging

[1] D. Berthier, M-P. Deffarges, N. Berton, M. Venin, F. Lacroix, B. Schmaltz, Y. Tendron, E. Pestel, F. Tran-Van, S. Méo. "*POSS Nanofiller-Induced Enhancement of the Thermomechanical Properties in a Fluoroelastomer Terpolymer*", Materials, 11(8): 1358, 2018.
[2] K. Raftopoulos, K. Pielichowski, « Segmental dynamics in hybrid polymer/POSS nanomaterials », Prog. Polym. Sci. 52 136–187, 2016.
[3] S.-R. Tseng, H.-F. Meng, K.-C. Lee, and S.-F. Horng, "Multilayer polymer light-emitting diodes by blade coating method," *Appl. Phys. Lett.*, vol. 93, no. 15, p. 153308, Oct. 2008.