

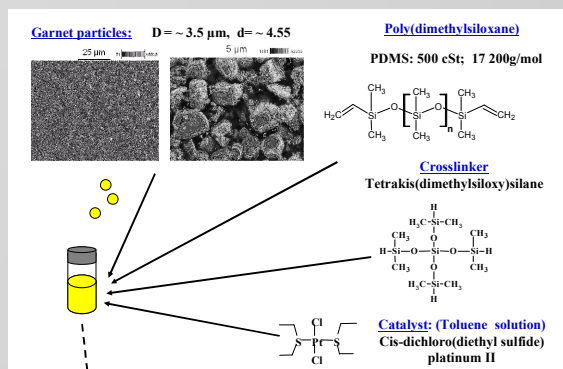
## INTRODUCTION

Silicone based materials have been widely used in coatings, sealants and adhesives for different technological fields.<sup>[1]</sup> Cross-linked Poly(dimethylsiloxane) (PDMS) in particular, is well known for its biocompatibility, good resistance to high temperature, light irradiation and chemical attack, and has been extensively used i.e. in coatings for biomedical devices.<sup>[2]</sup>

Typically, PDMS-based formulations contain fillers in order to improve their rheological<sup>[3]</sup>, mechanical<sup>[4]</sup> or thermoelastic<sup>[5]</sup> properties. These fillers can interact with other components of the system by for instance decreasing the cross-linking rate or promoting unwanted reactions. Ultimately, these effects can give some problems in coatings such as colouring, brittleness, or phase-segregation.

Herein, we report a new IR approach to follow the cross-linking of PDMS composite materials, in the presence of inorganic oxide particles (garnet). For this purpose ATR-FTIR *in situ* Spectroscopy was used to study different conditions for the cross-linking reaction, in the presence and absence of particles.

## MATERIALS



## IN-SITU ATR-FTIR APPROACH

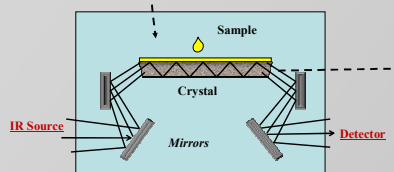


Fig. 1: Scheme of the ATR-FTIR spectrometer. MCT detector, air atmosphere, resolution 2 cm<sup>-1</sup>, typical thickness probed: ~ 3 μm

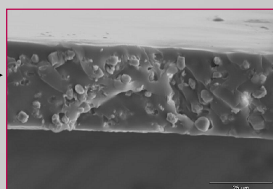


Fig. 2: SEM image of the cross-section of a thin PDMS coating, containing 20% v/v of garnet

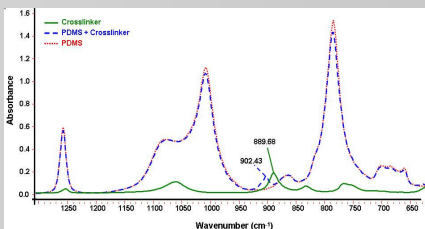
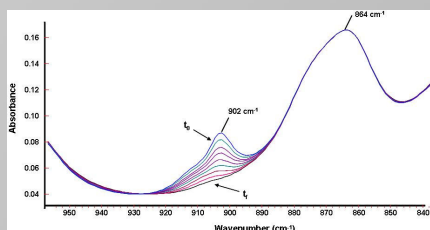


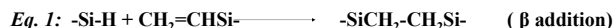
Fig. 3: ATR-FTIR spectra of pure cross-linker, initial PDMS polymer, and a mixture of the two. Si-H bending<sup>[5]</sup> band at 902 cm<sup>-1</sup> is used to monitor the cross-linking reaction.

Fig. 4: ATR-FTIR spectra of different times of the cross-linking reaction showing the gradual decrease of the total integration area of the Si-H bending band at 902 cm<sup>-1</sup>.



## RESULTS AND DISCUSSION

The new ATR-FTIR approach allows to follow *in situ* the cross-linking of PDMS vinyl-terminated polymers with a multifunctional Si-H cross-linker, through hydrosilylation (Eq. 1)



### Cross-linker concentration effect

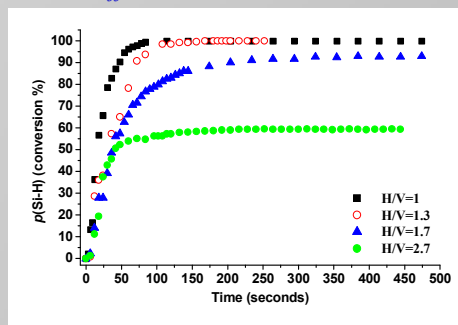
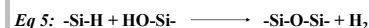
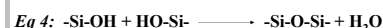
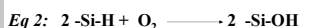


Fig. 5: Si-H total conversion *versus* time of cross-linking for PDMS samples with different concentrations of cross-linker (H/V=Si-H/ Vinyl ratio), at 60 °C.

- H/V < 1.3, complete conversion of the Si-H groups. The main reaction is hydrosilylation, and full conversion of the double bonds is expected<sup>[6]</sup> (Eq. 1).
- H/V > 1.3, slower and incomplete consumption of the Si-H groups.
- Excess of reactive groups from the cross-linker are consumed by the secondary reactions which play a major role (Eq. 2 to 5)



### Garnets concentration effect

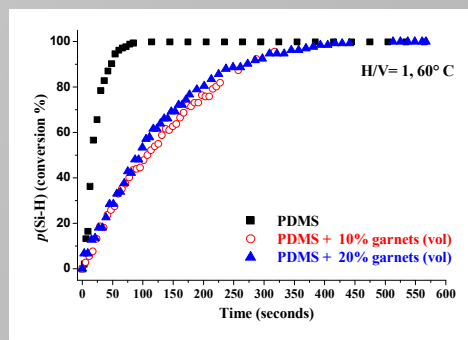


Fig. 6: Si-H total conversion *versus* time of cross-linking for PDMS sample with different concentrations of garnets, H/V=1 and at 60 °C.

- Clear influence of the garnets on the cross-linking reaction which can be related with a combination of several factors: viscosity increase, interaction with cross-linker or with catalyst...

## FUTURE WORK

Investigate in depth the cross-linking of PDMS in the presence of the garnet, through a better understanding of the interactions between: catalyst, garnet and cross-linker.

Optimize the formulations and reduce the amount of leftover residues, in order to avoid undesired reactions on the coatings.