

## Study and optimization of polymeric membranes with different siloxanes for development of lanthanide-based optical sensors.

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### Abstract

Lanthanide ion complexes anchored in a polymeric matrix have several applications such as biomarkers and chemosensors. In this work several polydimethylsiloxane were synthesised in order to use in lanthanide-based optical sensors. It was observed in general that higher the concentration of the crosslinking agent lower the flexibility of the membrane and apart from that, for the same polymer, a bulkier crosslinker provides higher flexibility than a less bulky crosslinker.

*Keywords: optical sensors, lanthanide complexes, polymeric membranes*

### Introduction

The inherent optical properties of lanthanides complexes, such as long lifetime and narrow emission bands, are attractive for several applications. The anchoring of these complexes in a polymeric matrix enables their use in several applications, such as biomarkers, optical chemosensors and others<sup>1</sup>. In relation to optical sensors, the incorporation of such complexes in polymeric matrix provides greater resistance and broadens their application. This concept enables the development of optical sensors able to monitor various parameters, such as e.g. temperature, oxygen concentration and relative humidity in several processes. In the present work, the influence of type and concentration of the crosslinking agent to cast the polymeric matrices were evaluated in order to obtain a membrane with optimum mechanical properties with potential application as lanthanide-based optical sensors.

### Results and Discussion

The polydimethylsiloxane was chosen as polymeric matrix due to its high permeability and diffusion coefficient to oxygen ( $200\text{-}400 \cdot 10^{-15} \text{ moles s}^{-1} \text{ N}^{-1}$  and  $1500\text{-}2500 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$ , respectively), besides its chemical, thermal and mechanical stabilities and transparency in the UV-Vis region.<sup>2</sup> In an inert nitrogen atmosphere, using toluene as solvent and a Karstedt catalyst, the following membranes were synthesised: terminal hydride polydimethylsiloxane (PDMS),  $580 \text{ g mol}^{-1}$ , polyhydromethylsiloxane (PMS),  $2450 \text{ g mol}^{-1}$ , and poly(dimethyl)-co-(methylhydro)siloxane (PDMS-PMS),  $2400 \text{ g mol}^{-1}$ , along with the crosslinkers tetravinyl silane (TVS), 2,4,6,8 tetramethyl 2,4,6,8 tetravinylcycletetrasiloxane (D4V) and mixture of 2,4,6,8 tetramethylcycletetrasiloxane (D4I) and divinyltetramethyldisiloxane (DVS), respectively. Aiming to evaluate the influence of different

crosslinking levels on the mechanical properties of the membranes, polymer:crosslink ratios of 1:1, 4:3, 0,5:0,5, 4:1 were used following a factorial design  $3^3$ , by setting the amount of crosslinking agent as  $7,34 \cdot 10^{-4} \text{ mol}$ . After curing and solvent removal, transparent membranes with different mechanical properties were obtained. The malleability of the PDMS-PMS membranes with TVS increases inversely proportional to the concentration of the crosslinking agent. For the same concentration of crosslinker agent, PMDS membranes with TVS and D4V are more flexible and resistant than PMDS-PMS membranes prepared with the same crosslinker, due to different amount of Si-H groups in those polymers. In addition, for a given polymer, membranes with D4V are more malleable than those with TVS, due to the higher volume inherent to D4V. The PDMS membrane with D4V presents a higher malleability and resistance when synthesised in the absence of solvent as there is a higher level of crosslinking.

### Conclusions

It was observed that the increase of the concentration of the crosslinking agent, decreases the flexibility of the membrane. It was also noted that, for the same polymer, a bulkier crosslinker, as D4V, provides higher flexibility than a less bulky crosslinker, such as TVS. As the Si-H groups increase in the polymeric matrix, its malleability decreases. Further studies aiming the optimisation of polymeric membrane are required to assess their influence on the luminescent properties of lanthanide-based optical sensors.

### Acknowledgement

Authors are grateful to CNPq (process 479115/2012-5).

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<sup>2</sup> Wang, X.-d.; Wolfbeis, O. S., *Optical methods for sensing and imaging oxygen: materials, spectroscopies and applications*. *Chemical Society Reviews* 2014, *43* (10), 3666-3761.