Effect of molecular weight on PDMS coatings networks

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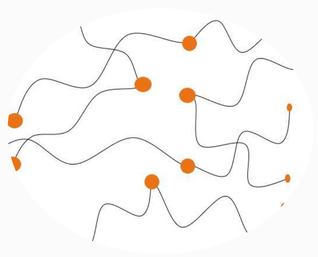
Introduction

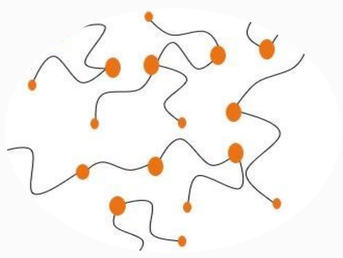
Silicone elastomers such as poly(dimethylsiloxane) (PDMS) have received great attention regarding their potential use as anti-bioadhesion coatings[1]. It is widely used to reduce or prevent bioadhesion in biomedical and marine fields. The main properties responsible for its efficiency are low surface tension, low roughness and a Young's modulus of a few MPa[2]. To date, only a few studies have looked at the relationship between the network structure, the coatings properties and the anti-bioadhesion efficiency. Our previous work has shown the influence of PDMS molecular weight on anti-bioadhesive properties coatings with no variation in surface properties[3] with molecular weights ranging from 800 g.mol^{-1} and 10 000 g.mol^{-1}. PDMS were modified to have trimethoxysilane end-groups and coatings were prepared by condensation reaction. Ellipsometry analysis in hexane and AFM measurements were carried out to evaluate the network structure. In addition, the chemical and mechanical surface properties were evaluated by contact angle and nanoindentation measurements.

Objectives

Network of long chains

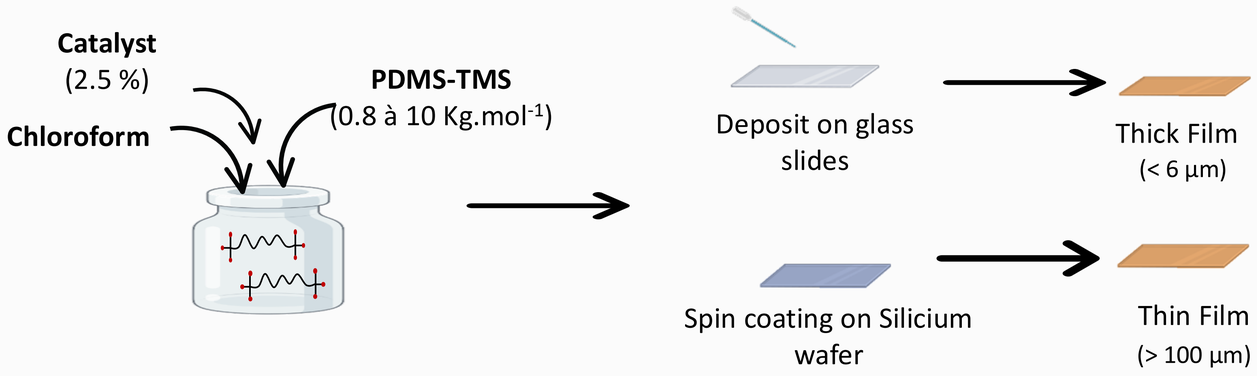


Network of short chains



- Determining the cross-linking density of PDMS networks
- Determination of mesh size and elastic modulus
- Calculation of surface energy

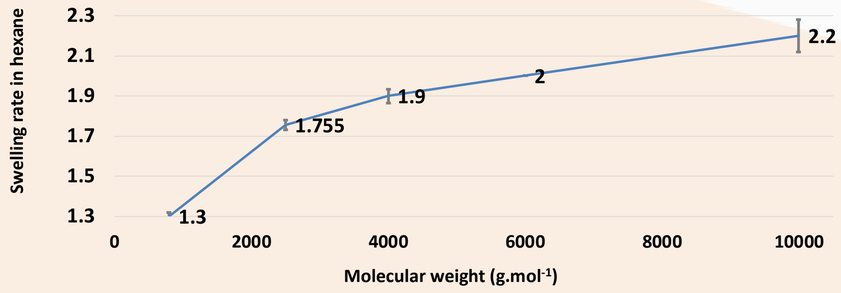
Material & Method



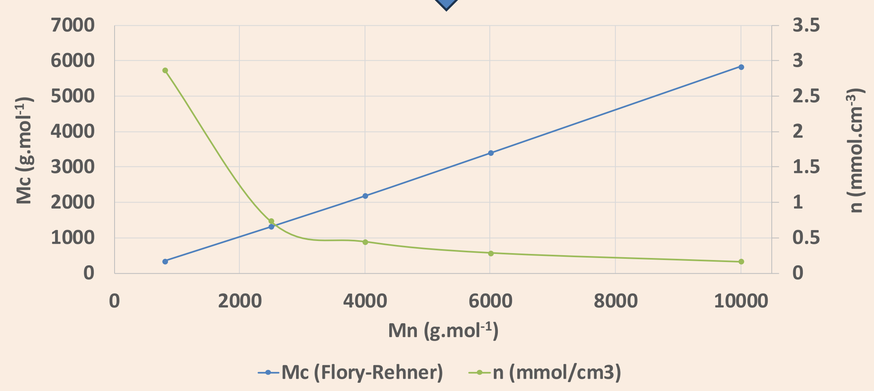
Polymers	Theoritical Molecular weight	Molecular weight (NMR ^{1}H)
PDMS-TMS0.8K	800 g.mol^{-1}	860 g.mol^{-1}
PDMS-TMS2.5K	2 500 g.mol^{-1}	2 800 g.mol^{-1}
PDMS-TMS4K	4 000 g.mol^{-1}	3 800 g.mol^{-1}
PDMS-TMS6K	6 000 g.mol^{-1}	5 200 g.mol^{-1}
PDMS-TMS10K	9 400 g.mol^{-1}	9 000 g.mol^{-1}

Results and discussion

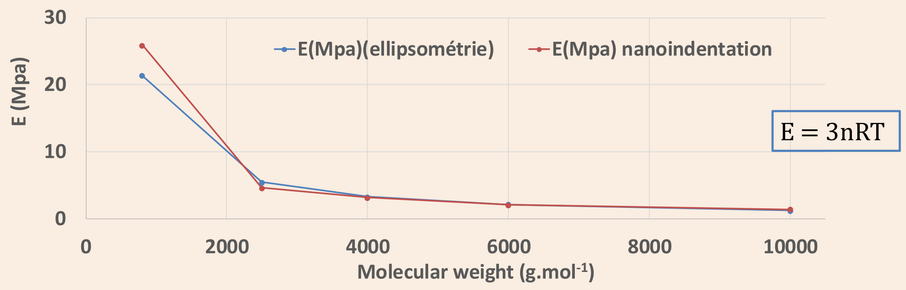
Ellipsometry : network structure and properties[2]



Flory-Rehner Equation[2] $$M_c = \frac{V_H \rho_p M \left(\alpha - \frac{1}{2\alpha}\right)}{2V_H \rho_p \left(\alpha - \frac{1}{2\alpha}\right) - M\left[ln(1-\emptyset_p) + \emptyset_p + \chi\phi_p^2\right]} \qquad n = \frac{\rho(p)}{Mc}$$



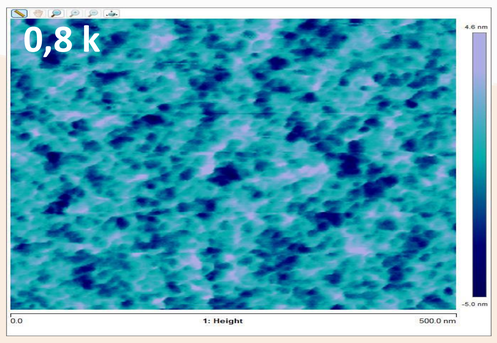
- The critical molar mass (Mc) of films is proportional of the PDMS molecular weight
- Decrease of the reticulation nodes (n) with the molecular weight of PDMS



$$E = 3nRT$$

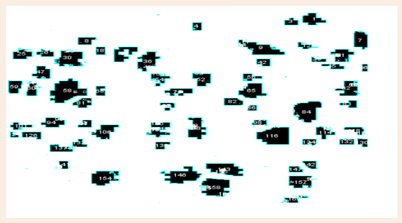
- Decrease of the elastic modulus
- Same results for nanoindentation measurement and calculation with n obtain by ellipsometry

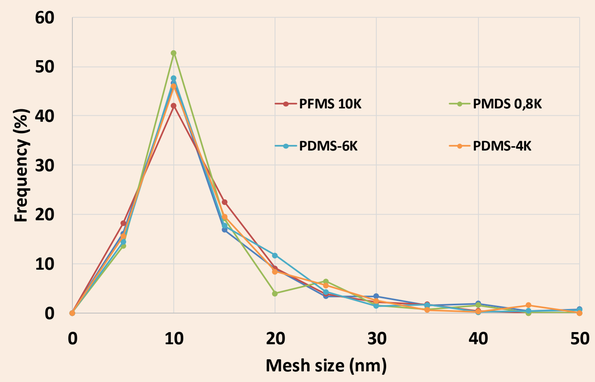
AFM : Determination of mesh size[3]



- Typical mesh-like network structure of PDMS

RMS = 8-11 nm (1µm²)





- No impact of the molecular weight on the mesh size
- Same result than the litterature[3]

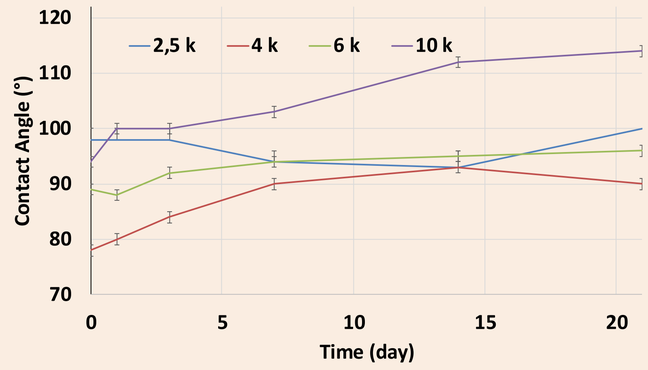
Contact Angle : Surface chemical properties

- Surface energy was calculated using LWAB, Owens-Wendt and Wu models[4]

PDMS (g.mol^{-1})	Surface Energy γ (mN.m^{-1})			
	LWAB	Owens-Wendt		WU
		γs	R²	
0,8k	24,39	18,57	0,81	26,67
2,5k	30,51	23,37	0,42	29,75
4k	29,87	21,4	0,72	29,87
6k	36,56	23,86	0,58	32,92
10k	36,85	23,48	0,47	32,24

- Wu model seems the only one suitable for PDMS films
- Influence of the cross-linking density on the surface chemical properties ?

Captive bubble : Evolution of the surface in water



- Modification of the surface chemical properties during immersion in water
- Water absorption/adsorption?

Conclusion

The molar mass of PDMS influences the structure of networks obtained condensation reaction, the elastic modulus, and the surface chemical properties. However, it does not explain the differences in performance observed during *in situ* immersion. This raises the question of how the properties and structures evolve during immersion in a marine environment.

References

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