

A Comparative Study on the Influence of the Platinum Catalyst in Poly(dimethylsiloxane) Based Networks Synthesis

Anca Gabriela Bejenariu¹, Julie Öblom Poulsen², Anne Ladegaard Skov¹, and Lars Henriksen²

¹ The Danish Polymer Center, Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

² PoLight AS, P.O.Box 163, N-3192 Horten, Norway

ABSTRACT

The aim of the project is to find the best of three Pt catalysts and their appropriate quantity in order to obtain soft networks in one hour at room temperature. How the choice of catalyst influences the final elastomeric properties is also evaluated. The differences between the catalysts are the solvent and the platinum concentration.

INTRODUCTION

Silicone gels have been widely used in the industrial fields of optical components¹⁻³, electronics and automobile because of their excellent optical and mechanical properties (high resistance, relatively unchanged elastic properties over a wide temperature range) and chemical stability at high temperatures. Their use is also widespread in the pharmaceutical field⁴, medical and cosmetic area due to their biocompatibility (biomedical electronics⁵, medical implants⁶ and cancer treatments⁷), softness and barrier properties against water⁸. Poly(dimethylsiloxane) (PDMS) $[\text{OSi}(\text{CH}_3)_2]_n$ is a very used silicone polymer in both medical and nonmedical applications. It is an indispensable part of many controlled drug delivery devices, such as Norplant⁹.

Hydrosilylation is the addition process of Si-H bond to a carbon-carbon double or triple bond between the silicone chains.

These reactions are driven under a catalyst complex action; successful results were obtained under the rhodium action and also with platinum complexes¹⁰⁻¹². The first use of platinum in silicone synthesis was announced by Speier in 1957¹³. Since then, numerous other platinum compounds, complexes of other metals, free radical initiators, nucleophilic–electrophilic catalysts¹⁴ and even strong acids¹⁵⁻¹⁷ have been used as catalysts for the silicon–carbon bond forming reaction.

A neutral complex in which the platinum atom is stabilized by vinyl containing silicones (vinylsiloxanes) is specially used as platinum catalyst for the synthesis of crosslinked silicones for biomaterials. These complexes are named “Karstedt’s catalyst”¹⁸ and they are made from chloroplatinic acid by addition of an appropriate siloxane and reducing agent. Other stable platinum-containing catalysts such as Speier^{19,20} or Lamoreaux^{21,22} are well known and used.

The paper presents a comparative behaviour study of identically synthesized network using three different platinum catalysts, in presence or absence of a reaction inhibitor. Three types of platinum containing catalyst are compared in this study: two Karstedt catalysts (Cat 500 and Cat 510) and a platinum divinyl tetramethylsiloxane complex (PC072).

No other studies, to our knowledge, have performed a comparative study of catalyst systems for the PDMS networks since a general conception or maybe rather assumption is that the catalyst is inactive in that sense that it does not influence the final properties of the network as long as it is used in the concentration recommended from the supplier (usually with a concentration of 8-20 ppm).

MATERIALS AND METHODS

A linear, endlinked vinyl poly(dimethyl siloxane) (DMS-V22, $M_n = 9400 \text{ g}\cdot\text{mol}^{-1}$, $\rho = 0.97 \text{ g}\cdot(\text{cm}^3)^{-1}$) is obtained from Gelest Inc. As crosslinker the (15-18% methylhydrosiloxane)-dimethylsiloxane copolymer-trimethylsiloxane (HMS-151, $M_n = 2000 \text{ g}\cdot\text{mol}^{-1}$, $\rho = 0.97 \text{ g}\cdot(\text{cm}^3)^{-1}$) is used and purchased from Gelest Inc. In addition, a linear PDMS oil ($M_n = 2000 \text{ g}\cdot\text{mol}^{-1}$) obtained from Dow Corning is used (50-75 % (w/w)) in the resulting PDMS network in order to enhance softness. The hydrosilation reaction is carried out in presence of the Pt catalyst.

The three types of commercial available catalysts and their Pt concentration (ppm) are presented in the Table 1.

Table 1. Commercial platinum catalysts and their concentrations in the mixture catalyst.

Name	Solvent	Pt [ppm]
PC072	xylene	20000
Catalyst 500	PDMS	500
Catalyst 510	PDMS	5000

The first catalyst (PC072) is a homogenous platinum catalyst purchased from United Chemicals Technologies. It is a neutral platinum divinyltetramethylsiloxane ($\text{C}_8\text{H}_{18}\text{OSi}_2$) complex in xylene (C_8H_{10} ($\text{C}_6\text{H}_4\text{C}_2\text{H}_6$)), with 2% Pt concentration. It gives the highest reactivity for the neutral complex at room temperature addition cure²³.

From Hanse Chemie are provided the two Karstedt's catalysts: Catalyst 500 and

Catalyst 510 dissolved in PDMS ($(\text{C}_2\text{H}_6\text{OSi})_n$). Platinum concentrations (ppm) in complexes are shown in Table.

Hanse Chemie also provided the Inhibitor 600. This is an alkinol which makes a chemical block on the platinum in the catalyst complex and thereby decreases the Pt catalytic action. The active part of the inhibitor will evaporate and thereby it should have no effect on the final chemical network. The recommended concentration is 0.1 to 0.5 w/w %.

Samples synthesis

The crosslinking reaction result is a three-dimensional network. The reaction is activated by a small amount of a Pt catalyst²⁴. The reaction is presented in Fig. 1. The reaction mixture is prepared using 2 premixes: premix A contained PDMS and catalyst, while the premix B contained PDMS, PDMS oil and HMS. This allows the premixes to be mixed thoroughly and afterwards stored until use.

The A:B mass ratio is always maintained constant 1:1 in the reaction mixture. The quantities of the two premixes are weighed and mixed for 2 minutes before letting the network form.

Rheological tests

The rheological experiments are made at SINTEF, Norway, using a modular compact rheometer (Physica-MCR-300) with the parallel plate geometry (50 mm). The measurements are run at 25°C using a constant strain (4 %) and frequency (1 Hz) which are evaluated not to affect the final structure of the material. The curing time is determined as the time where the plateau of the elastic modulus is reached. Consequently, a frequency sweep experiment is run as a post-curing measurement in order to get the G' evolution with the frequency (0.1-100Hz) as a characterising method of the network.

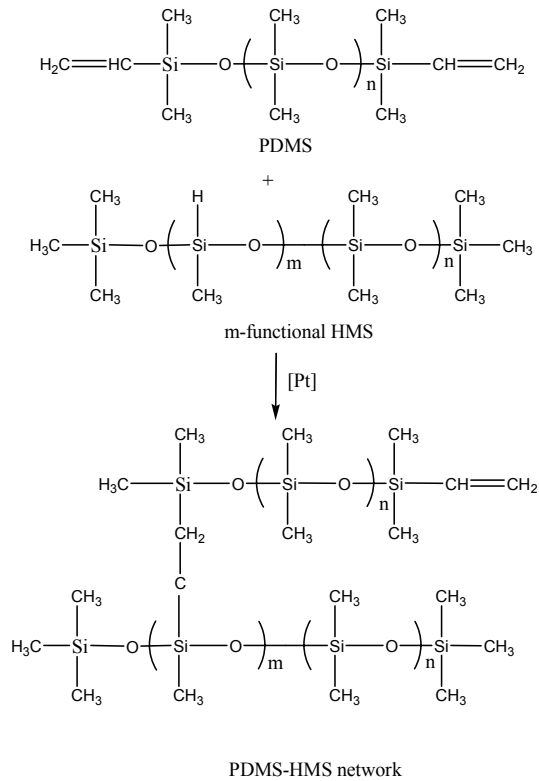


Figure 1. The PDMS-HMS reaction

Table 2. Platinum concentrations for each type of catalyst.

Catalyst type	Catalyst concentration [ppm]
Cat 500	200
	400
	1000
	2000
	4000
Cat 510	100
	200
	400
PC072	25
	50
	100
	200
PC072 + inhibitor (0.5%)	250
	500
	1000
	1250
	2500

RESULTS AND DISCUSSIONS

Networks synthesis

In order to find the best Pt catalyst and its optimal amount for the PDMS-HMS network synthesis, several experiments are made varying the catalyst and inhibitor concentrations.

Using the same 1:1 mass ratio between the 2 premixes, networks are synthesized. The concentration of the catalyst and the presence of the inhibitor are varied as in Table 2.

The system has not been investigated beforehand so a screening has been performed and the most interesting networks have been chosen for further investigations.

Rheological experiments

The curing profiles are achieved using a time sweep procedure applied to the reaction mixtures in order to obtain the time value from when the gel point is attend and the elastic modulus variation is constant within 1% for 2 minutes. The post-curing phenomenon is registered after the curing time, for one hour, through a frequency sweep procedure.

Curing time values

The curing times values (t_{cure}) are obtained for every sample as the point from where the storage modulus reached the plateau. The type of the catalyst, the platinum concentration and the presence of the inhibitor are varied as showed in Table 3. Generally, when the Pt concentration is under 0.3 ppm any curing time value is not recorded within 48 hours (Table 3).

Picking t_{cure} values for every catalyst type and following their variation with Pt concentration, Fig. 2 is obtained. A mathematical derivation is made (Eq. 1-5) in order to explain the exponential dependency between the two parameters. The t_{cure} values are increasing exponentially by decreasing the Pt concentration in the catalyst Fig. 2) and the linear regression equations are listed in Table 4.

Table 3. Platinum and inhibitor concentrations, with corresponding curing time for different samples using the three types of catalysts.

Catalyst type	[Pt] [ppm]	t _{cure} [min]
Cat 500	0.26	-
	0.27	-
	0.19	-
	0.6	65
	1.02	34
	0.54	114
	1.75	26
Cat 510	1.15	32
	2.76	14
	0.86	42
	2.24	18
	1.18	47
	0.6	101
PC072	5.27	22
	2.66	27
	4.51	24
	2.3	42
	1.18	56
PC072 + inhibitor (0.5%)	52.32	34
	26.47	47
	21.19	54
	10.6	101
	5.29	350

$$\frac{d[x]}{dt} = k \cdot [Pt]^l \cdot [x_i]^m \cdot [y_i]^n \quad (1)$$

$$\frac{d[x]}{dt} = k' \cdot [Pt]^l \quad (2)$$

$$\int_0^{x_f} d[x] = \int_0^{t_{cure}} k' \cdot [Pt]^l dt \quad (3)$$

$$x_f = k' \cdot [Pt]^l \cdot t_{cure} \quad (4)$$

$$t_{cure} = \frac{x_f}{k'} \cdot [Pt]^{-l} \quad (5)$$

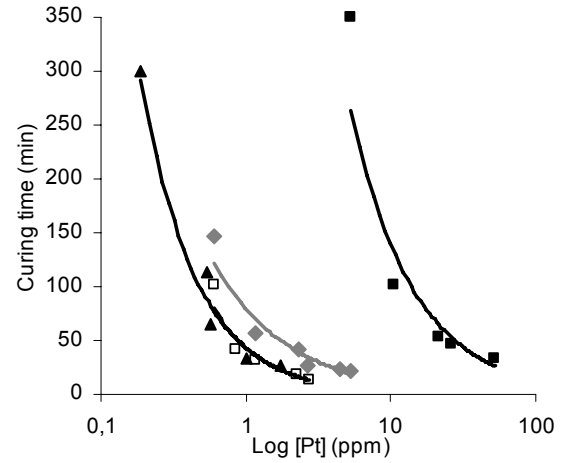


Figure 2. The curing time variation with Log [Pt] concentration for the three catalysts at 25°C (◆CatPC072, ▲cat500, □Cat510) and the inhibitor influence (■CatPC072+inhibitor).

Table 4. The equations gave by the linear regression of t_{cure} as function of [Pt].

Catalyst type	Equation
Cat 500 Cat 510	$t_{cure} = 43.419 \cdot ([Pt])^{-1.1982}$
PC 072	$t_{cure} = 79.57 \cdot ([Pt])^{-0.8475}$
PC072+ inhibitor	$t_{cure} = 1413.2 \cdot ([Pt])^{-1.0081}$

In general, a one hour curing time is obtained using a 1-2 ppm [Pt] for all the three types of catalysts. The presence of a larger quantity of catalyst in the reaction mixture will initiate the network synthesis faster. Using PC072 with 2-5 ppm [Pt] it is possible to obtain a network in ~30 min at 25°C. Using the inhibitor is possible to use an even higher amount of Pt. Hence, the adjusted Pt quantities were higher than 10 ppm in order to obtain sufficiently long t_{cure} values (10 ppm Pt - t_{cure}~100 min, 20ppm Pt - t_{cure} ~50 min) (Fig. 2). The different behaviours may be explained by the compatibility of the networks with the solvents of Pt. The PDMS solvent gives an eventual opportunity to form new bonds and

to hurry the network synthesis, while the xylene makes difficult this interaction .

In order to achieve long t_{cure} the use of PC072 is indicated. To avoid errors and to weigh quantities higher than 10 ppm Pt, is indicated its use in presence of the inhibitor (0.5 %).

Post-curing networks behaviour

In addition to the catalyst concentration optimization, it was found interesting to investigate the post-curing behaviour of the synthesized networks at 25°C and high temperatures (100°C). After the systems reached the plateau modulus, further experiments are performed: firstly, the elasticity development (G') in time and its variation at 100°C for more than 50 minutes (Fig. 3) and secondly the G' variation at 25°C with frequency (0.1-100Hz) for the fully developed network.

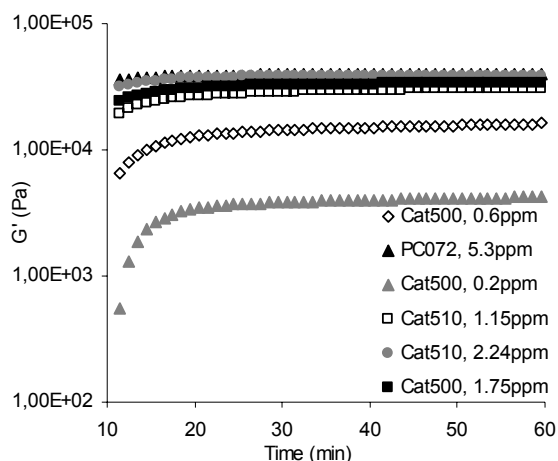


Figure 3. Behaviour of the networks at 100°C using the catalysts (Cat 500, Cat 510 and PC072) in different concentrations.

According to the Arrhenius equation ($k = A \exp(-E_a/RT)$), the curing time evolves with the same tendency at 100°C as at 25°C but with faster reaction rates. The G' variation in time for the networks is investigated in absence of the inhibitor (Fig. 3). For Cat 500 low Pt concentrations are used (0.2 and 0.6 ppm) in order to have long

t_{cure} values. The obtained G' values ($<10^4$ Pa) are a technical requirement regarding the mechanical application of the synthesized materials. Using Cat 500 and 0.2 ppm [Pt], even after 100 min (100°C) the G' do not stabilize. The impossibility to form a network is induced by the low quantity of catalyst wrapped in an excess of PDMS (compatible with the surrounding network), compared to the xylene that evaporates very quickly and able the network appearance.

The G' values at 100°C for the systems which are using PC072 in presence of the inhibitor (0.5 %) are presented separately in Fig 4. The points are presented from 20 min time for clarity reasons.

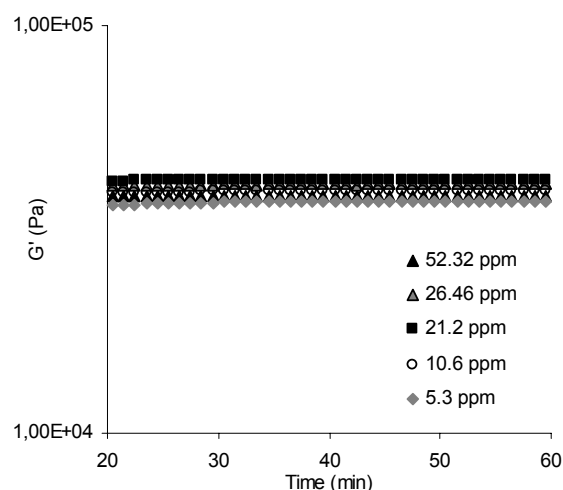


Figure 4. The G' values at 100°C for the systems which are using PC072 in presence of the inhibitor (0.5 %).

The network with the slowest G' stabilisation is the one during which the catalyst is used in 5.3 ppm concentration and when t_{cure} is high (350 min).

If the reactions follow same statistics the steric hindrance problem should be of same magnitude at a given extent of reaction for all the systems. The systems will undergo different types of reactions where the last one is a 'breathing' dominated region in the case where the catalyst is present in sufficient concentration²⁵. The reactive parts will be mainly included within the three-

dimensional network structure and therefore they will no longer be able to relocate by diffusion but their motion will rather be so-called 'breathing'. The breathing motion really limits the mobility of the reactive end and if all the system is governed by breathing motion, the catalyst may experience very low mobility too. Therefore at very low catalyst concentrations we may experience a completely shut-down of the reaction (or rather a reaction approaching infinity).

Consequently to experiments at 100°C, frequency sweeps are performed at 25°C. Decreasing oscillatory frequencies (100-0.1 Hz) at constant strain (4%) are applied on the synthesized networks.

The G' values increase with Pt concentration and it can be observed, for almost all the samples, that a quasiconstant evolution of G' with frequency is obtained indicating that the systems were very ideally crosslinked. Fig. 5 presents the frequency sweep spectra for the systems with Cat 500 and different Pt concentrations. The G' values exceed 10^4 Pa when more than 1ppm [Pt] is used.

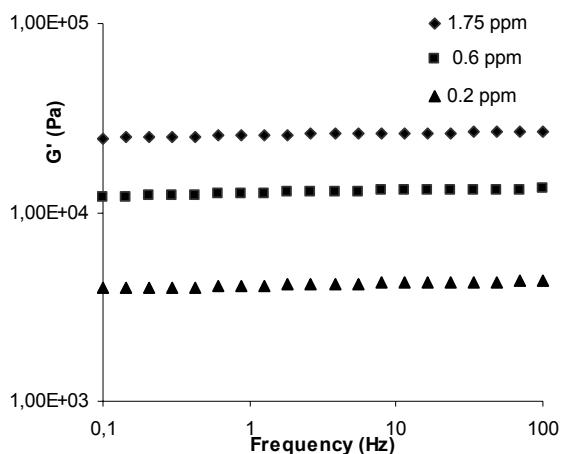


Figure 5. Frequency sweep measurements at 25°C on samples using Cat 500 as catalyst.

The network using Cat510 as catalyst give the disadvantage of curing too fast (18 min), so it is more interesting to have the frequency tests on the systems using PC072

as catalyst in presence of the inhibitor (Fig. 6).

The G' values are consistent with the data for the high concentration. From these results it is clear that in order to have 'theoretical action' of the catalyst, i.e. that the catalyst influences on the curing time only, one needs a sufficiently high concentration of catalyst. Otherwise the catalyst concentration should be regarded as a reaction parameter in the same manner as the amounts of PDMS and HMS.

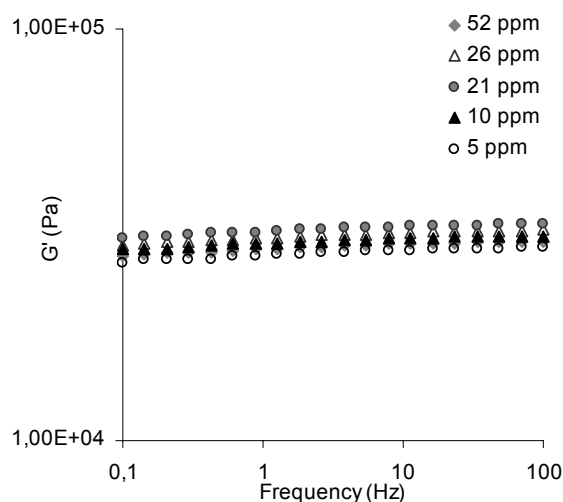


Figure 6. Frequency sweep measurements at 25°C on samples using PC072 as catalyst in presence of an inhibitor.

CONCLUSIONS

Model silicone network are synthesized through a hydrosililation Pt catalysed reaction. Two Karstedt catalysts (Cat 500 and Cat 510) and a platinum divinyl tetramethylsiloxane complex (PC072) are investigated in order to find the right type and quantity for a PDMS network synthesis within $t_{\text{cure}} = 1$ hour at room temperature, without significant post-curing evolution. In general it is found that no significant network structure was formed when the platinum concentration did not exceed 0.3 ppm. Good results are obtained using [Pt] 2-5 ppm, when it seems that adding additional catalyst does not influence the structure of

the network, but the curing time. Regarding the aim of the work paper and the obtained results, it is appropriate to reveal that in order to synthesise a silicone network characterized by a high elastic modulus ($>10^4$ Pa) within an hour at room temperature is indicated the use of catalyst with Pt solved in xylene and the presence of an inhibitor.

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