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Optimization of the Synthesis Parameters for Obtaining PDMS Samples Suitable for Filament Stretch Rheometer Measurements

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ABSTRACT

The filament stretch rheometer (FSR) can be used for large amplitude oscillatory elongation measurements (LAOE) on polymer networks. During sample formation the shape and integrity of the samples can be affected. This research paper presents the results of an optimization study concerning the synthesis parameters for obtaining silicone samples suitable for FSR.

INTRODUCTION

Elastomers exhibit large reversible deformabilities with distinctly low elastic modulus due to the entropic elasticity. Extensive research on elastomers has been conducted over the years[1,2], and today, elastomers are widely utilized as commercial products[3,4]. Elastomeric networks are very interesting and have obtained attention in the biomedical field due to their biocompatibility and biodegradability[5,6].

Poly(dimethylsiloxane) (PDMS) $[OSi(CH3)_2]_n$ is known as one of the most flexible polymers due to the structural features of the Si–O bonds[7]. PDMS is a low-cost polymer characterized by excellent optical and mechanical properties (high resistance, relatively unchanged elastic properties over a wide temperature range and one of the lowest glass transition temperatures of any polymer ($T_g \approx -120°C$). Furthermore it has chemical stability at high temperatures. These features amongst other of PDMS are beneficial for fundamental studies of rubber elasticity. PDMS is very often applied as precursor in model end-linked elastomer networks[8,9].

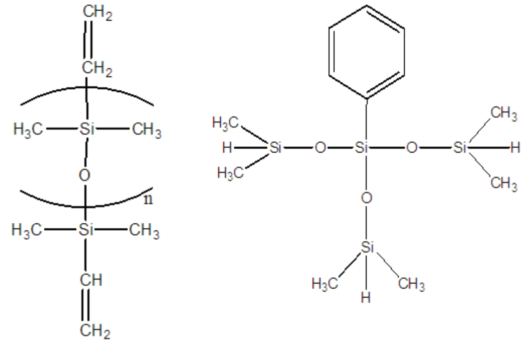
PDMS based networks are considered a model system for studying the development of elasticity and modelling studies of both structural development and resulting properties[8-10]. The resulting materials present both viscous and elastic characteristics and the dominating character usually depends on the applied frequency. The softness of the networks is a result of the dangling substructures and soluble structures and these may influence the general dynamics of the systems.

Extensional rheometry is widely used as characterization method due to its applicability in industrial processes which are involving extensional deformation such as extrusion of polymeric materials.

In order to utilize and verify the LAOE measurements on FSR as an analytical method for elastomeric networks, a new sample fixture with special 3D dumbbell shaped samples is required. Soft silicone networks are usually materials with fast initial curing times and high adhesivity to steel. Problems related to the synthesis parameters such as the PDMS molecular weight, the stoichiometric imbalance or the Pt catalyst concentration arise during sample preparation. All these parameters are varied and their influence on the properties of the final samples is verified rheologically. The final materials need to cure into soft networks without high adhesivity to the steel mould. The shape of the samples is 3D dumbbells in order to obtain the best geometry to be applied in the FSR and to perform large amplitude oscillatory elongation measurements.

MATERIALS AND METHODS

Two different molecular weights of vinyl endlinked poly(dimethyl siloxane) (Fig. 1, PDMS) are obtained from Gelest Inc (DMS-V35, DMS-V31). The analytical characterization of the molecular weights revealed M_n of DMS-V35, $M_n = 49500$ g·mol^{-1}, and DMS-V31, $M_n = 28000$ g·mol^{-1} The crosslinker is a trifunctional phenyl tris (dimethyl siloxy)silane (SIP6828, $M_n = 330.68$ g·mol^{-1}) (Fig. 1, HMS) also purchased from Gelest Inc. The reaction is catalyzed by a platinum cyclovinylmethyl-siloxane complex (511), provided by Hansechemie AG.



PDMS HMS

Figure 1. Chemical formula for the main polymer (PDMS) and the crosslinker (HMS).

Analytical characterization of the polymers

Molecular weights and polydispersity indices were estimated by size exclusion chromatography (SEC) on Viscotek 200 instrument using two PLgel mixed-D columns (Polymer Laboratories (PL)), assembled in series, and a refractive index detector. SEC samples were run in THF at room temperature (1 mL/min). Molecular weights were calculated using polystyrene (PS) standards from PL using TriSEC software.

^{1}H NMR spectra have been obtained on Bruker 300 MHz spectrometer in $CDCl_3$ (Aldrich) at room temperature. NMR spectra were recorded for both polymers as well as for the crosslinker, in order to investigate its possible degradation, and consumption throughout the course of the reaction.

Samples preparation

PDMS networks are prepared by weighting two ready-made mixes in different mass ratios: PDMS and crosslinker (mix A) and PDMS and catalyst (mix B). The mixtures are stable since the crosslinker and the catalyst are separated. The catalyst concentration varies slightly in the experiments.

The test samples are prepared in different mass ratios (A:B) corresponding to different stoichiometric imbalances values (r). The molar ratio of crosslinking sites to precursor polymer ends is called stoichiometric imbalance and is defined as:

$$r = \frac{\text{no. of silane groups}}{\text{no. of vinyl groups}} = \frac{f\left[A_f\right]}{2\left[B_2\right]} \qquad (1)$$

where A and B denotes the crosslinker and the polymer, respectively, with their functionalities as subscripts (f and 2)
In order to be ensure that all the crosslinker is consumed during the synthesis reaction and that a soft network is formed, an excess of the polymer and consequently an excess of double bonds is ensured.

In order to synthesize very soft silicone networks the chosen values of r should be close to the critical crosslinking degree (r_c, Eq. 2).

$$r_c = \frac{1}{f-1} \qquad (2)$$

where f is the functionality of the crosslinker[11-13].

Rheological experiments

In order to determine the synthesis parameters for soft silicone networks using the proposed materials, the systems are evaluated in simple linear oscillatory flow. The linear viscoelastic parameters are determined using the parallel plate geometry of a controlled strain rheometer (AR2000, TA Instruments) and small oscillatory amplitude time sweeps procedures performed at 25°C. The development of the elastic modulus (G') and the viscous modulus (G") during curing are followed and the curing time value is picked at the crossover point between G' and G" (G' = G"). For the very soft materials, characterized by a low value of r, the rheological tests are run for more than 5 hours, but for clarity reasons only a part of the results are presented.

In order to verify the accuracy of the obtained results, the reproducibility of PDMS networks curing profiles is investigated. The curing time of the same PDMS based network is determined a couple of times following the same experimental procedure within few hours interval.

RESULTS AND DISCUSSIONS

Polymer characterization

The molecular weight of DMS-V31 has been estimated via ^{1}H NMR by comparing the integrals of the resonances at 5.73 ppm, which corresponds to the vinyl chain end, and 0.07 ppm, which originates from the methyl group in the repeating unit. However, this approach has not been exercised in case of DMS-V35 due to its relatively high molecular weight.

The crosslinking reaction has been monitored to gain some insight about the r value that facilitates network formation. At r = 0.55 (which is close to the critical stoichiometric ratio) all of the crosslinker has been engaged in the reaction: the resonance peak at 4.77 ppm, which is ascribed to Si-H proton, disappears completely (Fig. 2). However, the network formation can not be detected by rheological experiments. This indicates that it is not the hindered diffusion process of the crosslinker obstructing the network formation; hence, increasing the reaction time is not necessary.

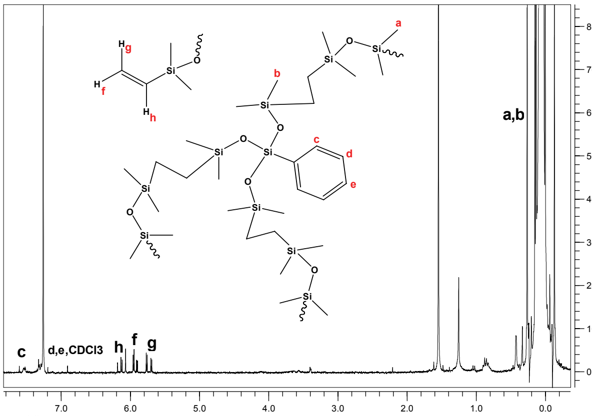


Figure 2. The ^{1}H NMR spectra for the r = 0.55 PDMS network.

The pure crosslinker has also been analyzed before and after exposure to air for 24 h. Loss of the functional groups has not been detected; thus, speculations about the crosslinker degradation have been discarded.

Networks synthesis

For the uniaxial measurements performed on PDMS based networks using filament stretch rheometer (FSR), a new sample fixture is proposed. The new fixture presents 3 holes in each end-plate in order to enhance the adherence of the networks to the geometry and finally to form the 3D dumbbell shaped samples (Fig. 3). The moulding process will be performed in a steel mould (Fig. 3) and a curing time of 10 minutes would be the appropriate time. If the curing time is higher than 10 minutes it is possible for the mixture to flow through the holes of the set geometry and hence not to have the final cylindrical 3D dumbbell shape. Curing time values less than 10 minutes would not be recommended because the mix will not have time to penetrate the holes of the geometry and therefore remain unattached to it. It is also possible that the mix crosslinks in a different shape than the wanted one.

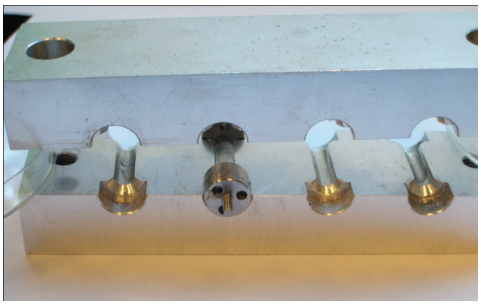


Figure 3. Picture of the steel mould and the new sample fixture.

In order to synthesize PDMS networks the evaluated parameters are: the PDMS molecular weight (DMS-V35 with M_n = 49500 g·mol^{-1} and DMS-V31 with M_n = 28000 g·mol^{-1}), the crosslinker concentration and the catalyst concentration [Pt] (0.1 or 1 ppm).

A series of PDMS networks are prepared using the A and B premixes in different mass ratios (A:B). The weighted polymers quantities for the initial premixes are presented in Table 1. Using Eq. 1 the r values are determined for every network.

Table 1. Polymer quantities used for the two premixes.

Component	Premix A (g)	Premix B (g)
PDMS	196.06	106.8
Crosslinker	4	-
Catalyst	-	3.31

A previous study was made by Larsen and al. regarding the influence of the r values on the PDMS networks kinetic [8]. Applying Eq. 2 the critical stoichiometry value is $r_c = 0.55$. The systems characterized by a value of r closed to r_c are not recognized as networks from a rheological point of view, even if the NMR shows that the entire quantity of crosslinker is consumed. Hence, the stoichiometric threshold is higher than 0.55[14], this situation disagreeing the traditional idea that the optimal network forms when the reactants are reacted stoichiometric.

The final PDMS networks, suitable for the new FSR geometry, should be soft and characterized by an optimal adhesivity to the steel mould.

Reproducibility tests

To validate the accuracy of the rheological measurements, the curing profiles of the same silicone network are repeated with a constant as possible experimental procedures. PDMS network based are synthesized using DMS-V35, r = 0.9 and [Pt] = 1 ppm.

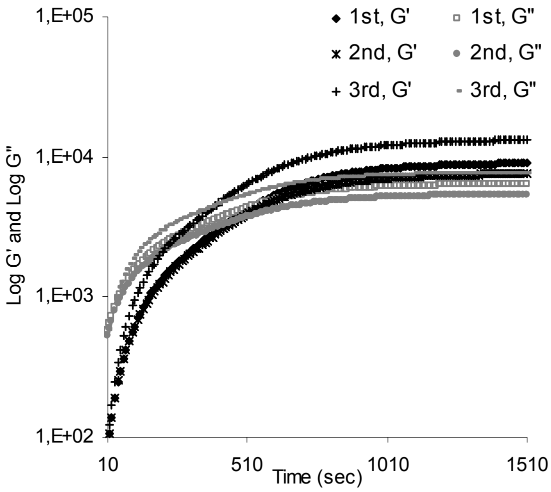


Figure 4. Reproducibility of PDMS (DMS-V35) based network curing profiles.

The curing profiles are obtained for several hours of curing but for clarity reasons only the first part of the G' and G" plateau is presented (Fig. 4)

The graphical results of the reproducibility test are presented in Fig. 4. The curing profiles shape is similar in all 3 measurements and the obtained curing time values are within experimental errors: t_{cure} = 7.7, 8 and 9 min respectively (Fig. 2). The obtained values of reproducibility test give the confidence to further results.

Curing experiments

The curing profiles are registered as G' and G" variation in time applying a time sweep procedure at 25°C and the G', G" crossover point is taken as the curing time value (t_{cure}).

In order to find the appropriate synthesis parameters for different PDMS networks, the variable parameters are: the polymer molecular weight, the crosslinker concentration and the platinum concentration. The selected curing profiles are presented in Fig. 5 to 8 and the registered t_{cure} values are listed in Table 2.

The Si-H of the crosslinker reach the vinyl double bonds of the long PDMS chains (DMS-V35) quickly, comparing with reaching the short ones (DMS-V31). The future PDMS based networks, characterized by a high M_n value of the main polymer (DMS-V35, M_n = 49500 g/mol) will crosslink from a lower r value (r = 0.8), taking though long time. Concurrently, the networks based on PDMS with M_n = 28000 g/mol will begin to form a network from r = 0.95 in shorter times.

It is obvious that increasing the catalyst concentration, decreases the curing time values and using 0.1 ppm Pt concentration the networks take more than 10 minutes to form. The registered values in Fig. 5, 6, 7 and 8 are presented in Table 2.

Table 2. T_{cure} values for different PDMS networks.

Polymer DMS-V35	t_{cure} (min) when [Pt]=0.1	t_{cure} (min) when [Pt]=1
r =0.8	70	15
r=0.9	16.5	5.5
r=1	12	5
Polymer DMS-V31	**t_{cure} (min) when [Pt]=0.1**	**t_{cure} (min) when [Pt]=1**
r=0.95	26	10
r=1	22	6.6
r=1.1	9	3

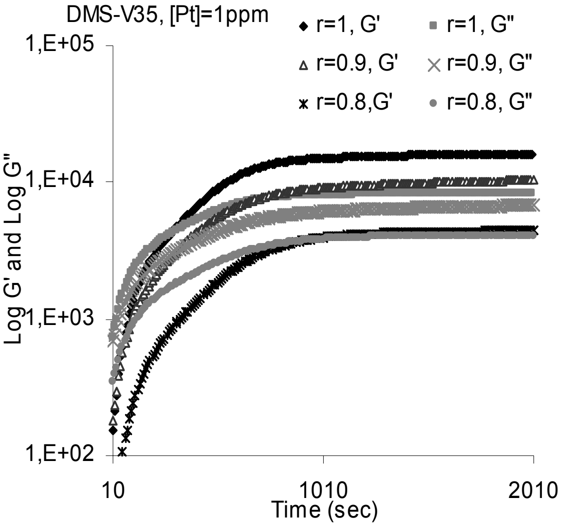


Figure 5. Curing profiles of DMS-V35, [Pt] = 1 ppm.

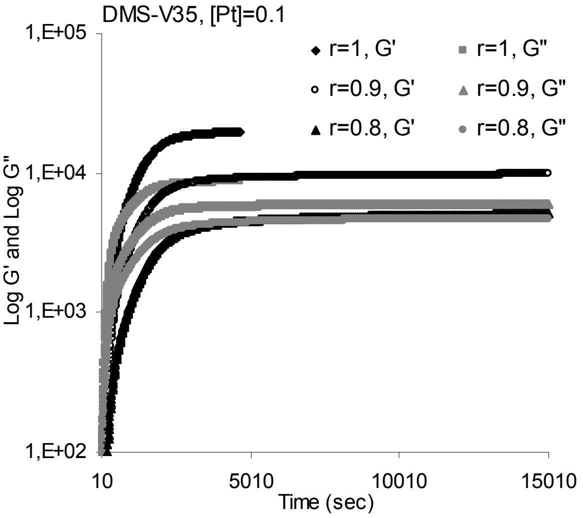


Figure 6. Curing profiles of DMS-V35, [Pt] = 0.1 ppm.

Analyzing the G' and G" values (Table. 3) for every synthesized sample, it is evident that the samples based on the polymer characterized by long molecular chains form networks with good elastic properties. In this case it is necessary to use [Pt] = 0.1 in order to have sufficient time to mould the sample. For the shorter polymer the formed networks are less elastic because of the relatively short distance between crosslinks.

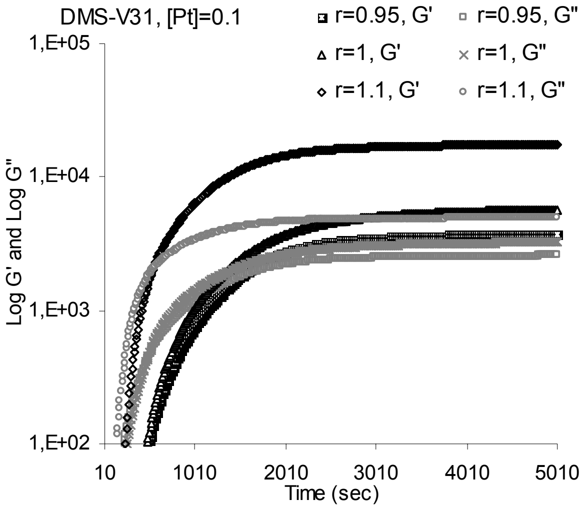


Figure 7. Curing profiles of DMS-V31, [Pt] = 0.1 ppm.

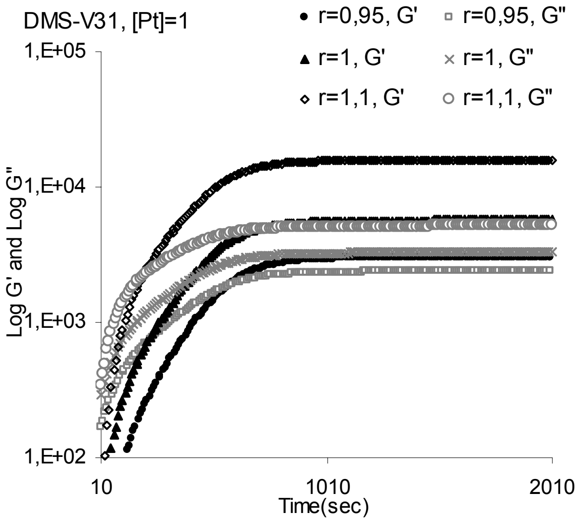


Figure 8. Curing profiles of DMS-V31, [Pt] = 1ppm.

Using a filament stretching rheometer (FSR) surrounded by a thermostatic chamber and equipped with a micrometric laser it is intended to perform large amplitude oscillatory elongation (LAOE) on polymeric PDMS based networks.

Table 3. The G’ values of the synthesized PDMS networks.

	r values	G’ (Pa)
Polymer DMS-V35	0.8	5000
	0.9	9600
	1	19730
	r values	G’ (Pa)
Polymer DMS-V31	0.95	4000
	1	5680
	1.1	17360

Usually, the extensional measurements of polymer network are typically performed using rectangular film or ‘dog-bone’ shaped samples, which are not very well defined. The new sample fixture proposed for the LAOE measurements is designed as an add-on to the FSR (Fig.9).

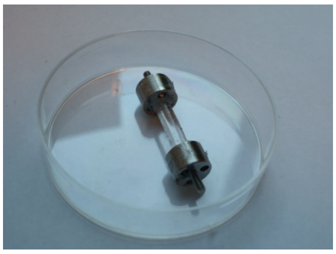


Figure 9. 3D dumbbell shaped PDMS sample.

Using the tested synthesis parameters (DMS-V31, r = 0.95, [Pt] = 0.1 ppm) it is possible to synthesize and to mould a symmetrical circular shaped PDMS samples suitable to FSR in 10 minutes (Fig. 9).

The first LAOE experiments are performed on a PDMS network applying a Hencky strain (ε) of 0.7 with a frequency (ω) of $0.02s^{-1}$. One cycle of the measurement is presented in Fig. 10.

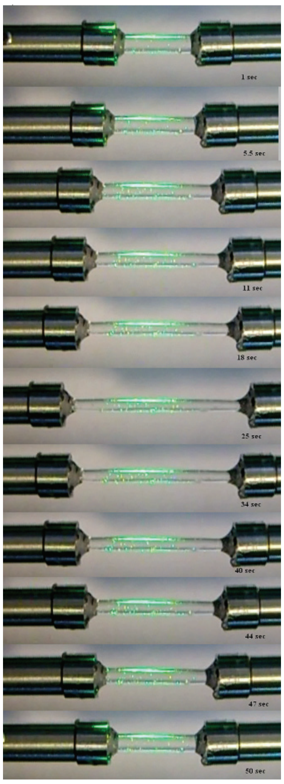


Figure 10. LAOE experiment ($\varepsilon = 0.7$ and $\omega = 0.02s^{-1}$) applied on the PDMS cylindrically shaped network.

CONCLUSIONS

In order to test a new FSR fixture PDMS based networks shaped as 3D dumbbell samples are synthesized through a hydrosililation reaction using a 3-functional crosslinker. The synthesis parameters are varied in order to obtain soft networks within an appropriate curing time and the experiments are carefully designed in order to preserve the samples shape integrity.

Curing profiles are achieved from a time sweep procedure at 25°C and the curing time value is picked as the crossover point between G' and G" evolution curves with time. The obtained t_{cure} and G' values for every network are analyzed and finally symmetrical circular shaped PDMS samples suitable to FSR are moulded.

Finally, LAOE measurements are successfully applied on PDMS networks.

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