

Characterization of Polymer Networks by Swelling

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ABSTRACT

The linear dynamic response of cross-linked PDMS samples with different stoichiometries, as well as the sol and network fractions, was investigated. It was found that all the networks showed similar properties after removal of the sol indicating only small deviations in the network structure upon changing the stoichiometric imbalance.

INTRODUCTION

Crosslinking of polymers to form networks changes the properties of the polymer radically. During the process of crosslinking the material changes from being a large number of individual and finite molecules into in theory one large infinite molecule. This abrupt change is denoted the gel point and has been investigated to a large extent for networks of different types and with different stoichiometries.^{1,2} The stoichiometry of the network, r , is defined as:

$$r = \frac{[\text{hydride}]}{[\text{vinyl}]} = \frac{f[\text{HMS}]}{2[\text{PDMS}]} \quad (1)$$

where f is the functionality of the crosslinker, $[\text{crosslinker}]$ is the concentration of the crosslinker and $[\text{PDMS}]$ is the concentration of poly(dimethyl siloxane) (PDMS). The stoichiometry expresses the relationship between the active functional

groups. In the ideal case for $r < 1$ there are more vinyl functionalities than hydride functionalities and some PDMS-chains will not be part of the crosslinking process, for $r \geq 1$ the opposite situation is present and all PDMS molecules should be linked to a crosslinking molecule. Another important definition is that of the critical stoichiometric imbalance r_c :

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

f is the functionality of the used crosslinker. Stoichiometries below r_c will not result in the formation of networks.

An ideal network is an “infinite” polymer - a system containing only one great molecule, where all coupling points are connected to the networks. However, practice shows that crosslinking of finite polymers to form a network gives a system with at least two phases; the network fraction and the sol fraction. The sol fraction for networks with excess of linear PDMS polymer consists mainly of unreacted PDMS molecules and star molecules.

Larger structures within the sol fraction also exist but the probability of finding such structures decreases with increasing stoichiometry. The network fraction consists of elastically active network chains, i.e. PDMS chains connected in both ends to the

network and reacted with an active crosslinker. Furthermore dangling chains and substructures exist, all connected to the network by a single chain.³

In the work presented here a series of networks of PDMS polymers were investigated for changes in rheological properties caused by removal of the sol from the network.

The viscoelastic properties were measured in small amplitude oscillatory shear (SAOS) experiments, and the measured storage and loss moduli were analysed. In the cases where the two components have formed gels they will behave as viscoelastic solids. This means that a plateau is reached for the storage modulus, G' , in the low frequency regime, and it will often be orders of magnitudes higher than the loss modulus, G'' . At higher frequencies G' and G'' will be of the same order of magnitude, however the plateau regime will increase as the crosslink density increases, hence as r increases. For ideal gels, G'' is following a power law behaviour over the whole frequency range and is thus proportional to the applied frequency, ω .³⁻⁶ One way to analyse G' and G'' is to use the gel equation proposed by Winter and Chambon:^{1,2}

$$G(t) = St^{-n} \quad (3)$$

The relation between G' and G'' is very simple and can be derived from Eq. 3:⁴

$$G' = \frac{G''}{\tan\left(\frac{n\pi}{2}\right)} \quad (4)$$

Eq. 3 is a simple model for the relaxation modulus of a critical gel versus time. By critical gel is meant a sample at the gel point where the viscosity is infinite while the equilibrium modulus is zero. S , in Eq. 3, is a measure for the gel stiffness with respect to the number of entanglements of the precursor chains, while n is a relaxation exponent, and it is thus the slope of G'' in a

double logarithmic plot. Winter and Chambon^{1,2} made a thorough investigation of the size of n at the gel point, and they found that for a stoichiometric balanced gel ($r = 1$), n was equal to 0.5, and that G' and G'' would be congruent over the entire frequency range, $0 < \omega < \infty$. For stoichiometric imbalanced gels ($r \neq 1$) n would increase and lie in the range $0.5 < n < 1$. Hild³ found a similar result for $r < 1$, while for $r > 1$, n was found to be equal to 0.5 at the gel point. A more general indication of the size of n , can be found in Eq. 4, which predicts that if $n > 0.5$ then $G'' > G'$, while $G'' < G'$ if $n < 0.5$. It is important to notice that this analysis has been performed on gels at the gel point. In this study some samples are beyond the gel point. When analyzing data beyond the gel point, it is necessary to modify the gel equation, such that it accounts for the plateau obtained for G' . This was done by Jensen et al.⁴ They analyzed imbalanced stoichiometric polypropylene oxide networks, $r < 1$, cured to complete reaction, by adding an additional term to Eq. 3:

$$G(t) = St^{-n} + G_0H(t) \quad (5)$$

$H(t)$ is the Heaviside step function, while G_0 is the equilibrium modulus or plateau modulus obtained for G' at low frequencies. The study by Jensen et. al.⁴ showed that even for gel beyond the gel point n can change significantly. n would be high (> 0.5) for very soft gels, while for $r \rightarrow 1$, n could drop to about 0.35. Hence n is a measure for the softness of the gel. A similar analysis of n will be made in this study with imbalanced PDMS networks, which are also cured to complete reaction.

EXPERIMENTAL

Sample Preparation

A series of networks of PDMS, see Fig. 1, were prepared by endlinking of divinyl terminated PDMS with the trifunctional crosslinker, phenyltris(dimethyl-silyloxy)si-

lane, Fig. 2. A platinum-cyclovinylmethylsiloxane complex was used as catalyst. The chemicals were provided by Gelest, Inc, and were used as received. The molecular weight of the PDMS was determined by NMR to be 24600 g/mol.

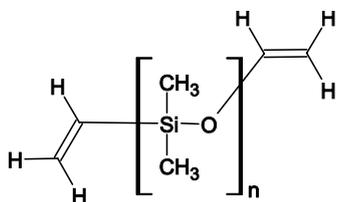


Figure 1. The repeating unit and the vinyl end groups of the used poly(dimethylsiloxane).

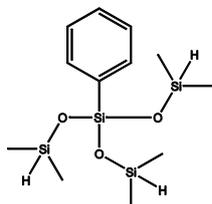


Figure 2. The trifunctional crosslinker phenyltris(dimethylsilyloxy)silane.

The networks were made in simple weight based ratios from two ready-made mixtures of PDMS and crosslinker (Mixture A) and PDMS and catalyst (Mixture B) respectively, see Table 1. The A and B mixtures were made beforehand by mixing the components and stirring until complete mixing was obtained.

Table 1. Quantities of the components in the applied mixtures A and B.

Mix	PDMS/ g	Catalyst/ g	Crosslinker /g
A	50	-	0.66
B	50	0.035	-

The networks were made by mixing predetermined amounts of mixture A and B thoroughly and left to cure for 12 hours. Mixture A and B were combined in five different ratios resulting in five initial networks with different stoichiometries. The

investigated stoichiometries were $r = 0.71$, $r = 0.75$, $r = 0.85$, $r = 0.95$ and $r = 1.07$. In Table 2 an overview of the relative amounts used as well as the amount of collected sol fraction and the relative weight loss can be found.

Swelling of Networks

The initial networks were swelled in heptane for 48 hours. After the 48 hours the networks were separated from the heptane solution. The heptane was removed by evaporation over 48 hours under atmospheric conditions. The procedure resulted in two samples which were analysed; the network fraction and the corresponding sol fraction.

Linear Viscoelasticity Measurements

The samples were investigated with linear rheology. The measurements were made with a TA 2000 Rheometer from TA Instruments set to a controlled strain mode. The applied strain was 2%, which was ensured to be in the linear regime. The measurements were done with parallel plate geometry of 20 mm in the frequency range from 0.01 Hz to 100 Hz and at temperatures between 0 and 200 °C.

The data were shifted using the time-temperature superposition principle (TTS).

RESULTS AND DISCUSSION

The PDMS networks with low stoichiometries were liquid-like and very soft, both before and after swelling. The initial networks with higher stoichiometries were soft, but rubbery, like winegums, and slightly greasy to the touch before swelling. After swelling the network fractions were still rubbery but they were not greasy anymore.

In Fig. 3 the relative weight loss is shown as a function of the stoichiometry. It is obvious that an ideal network with no sol fraction and thus no weight loss at $r \approx 1$ is not obtained. It rather seems that for values of r around 1 we obtain a constant value of 5% weight loss, which gives a clear indication of inactive species within the

Table 2. Stoichiometry, weight percentages (weight-%), mass of collected sol fraction and the weight loss after swelling in percent.

r	Weight-% PDMS	Weight-% Crosslinker	Weight-% Catalyst	Mass of collected sol fraction/g	% weight loss after swelling
0.71	99	0.65	0.035	0.65	58
0.75	99	0.68	0.035	0.10	6.8
0.85	99	0.78	0.038	0.15	8.0
0.95	99	0.87	0.023	0.14	6.3
1.07	99	0.98	0.017	0.44	8.2

pre-polymer and imperfections in the formed network. Furthermore for values of approaching 0.7 it seems that there is a large variation in the weight loss indicating that we are close to the gel point. This is a rather high value of r_c compared to traditional gel theories such as the Flory-Stockmayer theory which predicts the gel point for a trifunctional crosslinker to occur at a value of r_c around 0.5 according to Eq. 2. The problem with the high value of the stoichiometric imbalance at the apparent gel point may be due to steric hindrance of the crosslinker.

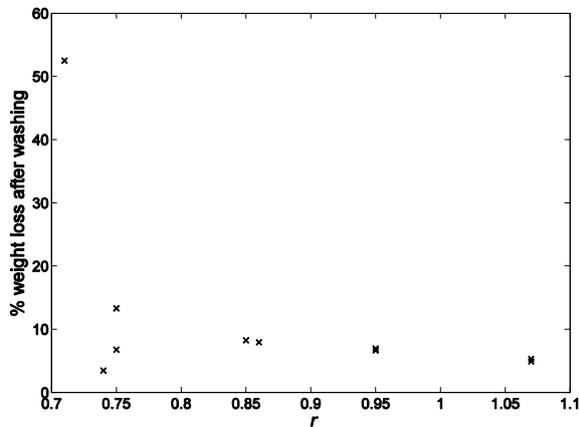


Figure 3. The relative amount of the sol fraction as function of the stoichiometric imbalance. For some values of r more than one measuring point is included since several samples were investigated.

In order to clarify if steric hindrance was a kinetic problem we investigated the curing profiles obtained in the rheometer at a constant frequency of 1 Hz where we fol-

lowed the structural development of the networks for several hours. Post-curing processes could not be detected within 5 hours after a constant level, and we therefore conclude that our procedure ensured complete reaction.

It is expected that the network fraction will have a higher value of the stoichiometry compared to the initial network since we are mainly looking into crosslinker deficient networks. Similarly the sol fraction will have a lower stoichiometry.

In Figs. 4-6 the dynamics for the initial network, the networks fraction and the sol fraction are shown. The values shown are averages of 2-3 measurements.

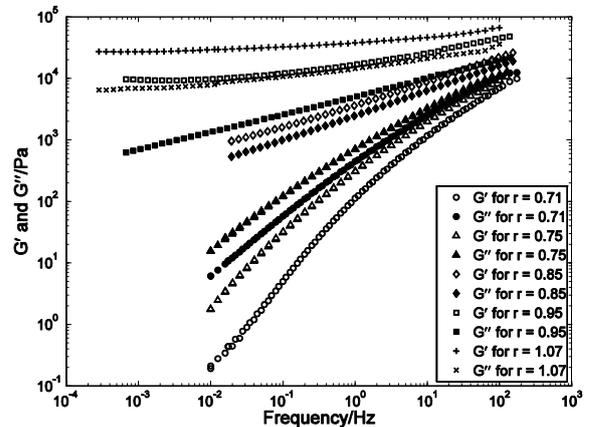


Figure 4. The dynamics for the initial networks. The stoichiometric imbalance is given in the figure. The higher the stoichiometric imbalance the more elastic the network.

Fig. 4 shows the dynamics for the initial networks. It is observed that the samples with r

= 1.07 and $r = 0.95$ and partly $r = 0.85$ act as viscoelastic solids indicated by the plateau seen for G' at low frequencies and that $G' > G''$. The networks with $r = 0.71$ and $r = 0.75$ behave as viscous materials with no indication of network properties since $G'' > G'$ in the entire frequency range and no plateau is observed.

In Fig. 5 the dynamics of the network fractions are seen. All the samples with $r \geq 0.85$ show viscoelastic properties. The sample with $r = 0.75$ which before removal of sol fraction showed only viscous response now shows a clear indication of network properties since $G' > G''$ and a plateau is indicated at low frequencies. It is interesting that removal of the mainly viscous sol fraction gives this result. It is expected that the presence of the viscous sol fraction smears out the elastic response from the network fraction and thus upon removal of the sol fraction the network characteristics are obvious. The sample with $r = 0.71$ almost has $G' = G''$ in the entire frequency range proving that a network fraction close to the gel point is formed. If $G' = G''$ the network at the gel point.¹

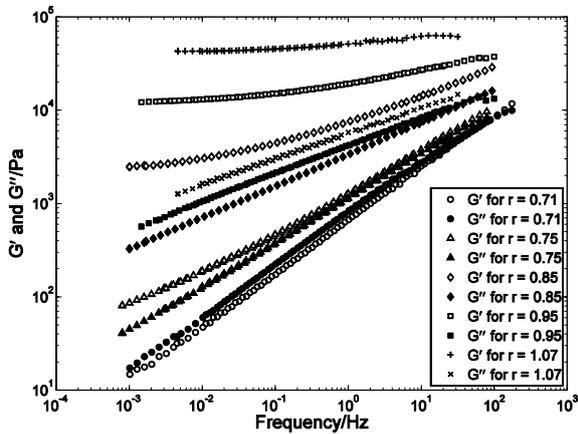


Figure 5. The dynamics of the network fractions. The stoichiometric imbalance of the according initial network is given in the figure. The tendency towards more elastic networks with higher stoichiometric imbalances is also seen here.

Fig. 6 shows the dynamics of the sol fractions. The sol fractions for $r = 0.71$ and $r = 0.75$ are viscous, but for $r = 0.95$ and $r = 0.85$ a tendency towards elastic properties is indicated by a plateau. For the samples with the higher stoichiometries the sol fraction shows elastic properties because the presence of large amounts of crosslinkers will give rise to formation of crosslinks in the sol.

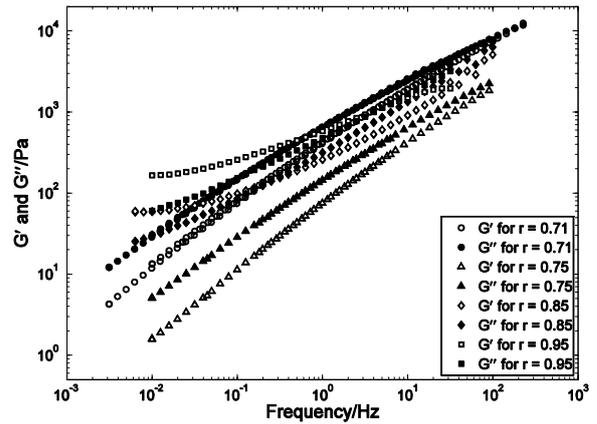


Figure 6. The dynamics of the sol fractions. The stoichiometric imbalance of the according initial network is given in the figure.

Upon the washing procedure one should obtain a practical purely elastic network (i.e. $G' \gg G''$) for the almost ideal networks where the fraction of pendant chains should be limited. The sol fraction should consist of a small fraction of inert PDMS molecule which according to the manufacturer should be less than 1%, unreacted PDMS chains and molecular structures without any chemical or physical attachment to the network. The physical attachment happens via inter-chain entanglements and is therefore not a result of the structural development of the network which can be described by applying a simple stochastic model.

So in the network fraction we would expect to see dynamics caused by the elastically active network and the dangling chains and substructures. In the sol fraction we

would expect to see linear polymers, stars, and structures with higher seniorities. The relative sizes of the structures are expected to be a result of the initial stoichiometry.

The loss tangent, $\tan \delta = G''/G'$ for the sample with $r = 0.75$ is shown in Fig. 7. For the initial network $\tan \delta$ is higher than 1 at the measured frequencies but it can be seen that the loss tangent approaches 1 at high

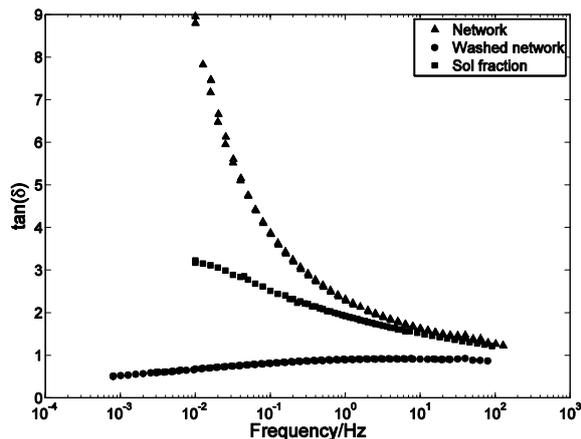


Figure 7. The loss tangent, $\tan \delta = G''/G'$, for the network fractions of the network with the stoichiometric ratio of $r = 0.75$.

frequencies. The dynamics of the sol fraction are not significantly different from the initial networks at the measured frequencies as expected since the initial network shows limited elasticity only. The network fraction has a loss tangent close to or slightly lower than one in the whole frequency range. In order to get measures of the softness and stiffness parameters the slopes of the curves have been determined with a power law fit in the frequency regime from 0.01 Hz to app. 100 Hz. In Table 3 the slopes of the curves (n) for the samples can be found. The data shows that n decrease when r increase and thus show that the softness decrease when the stoichiometry increase. The networks get harder when r increase. In Fig. 8 the residuals of the elastic modulus is shown by plotting $\delta G'(\omega)$ as a function of the frequency, ω . $\delta G'(\omega)$ is determined as:

$$\delta G'(\omega) = G'(\omega) - [G'_{net}\varphi_{net} + G'_{sol}\varphi_{sol}] \quad (6)$$

φ_{net} and φ_{sol} are the relative amounts of the network and sol fraction respectively. Thereby one can evaluate if the two phases contribute to the elastic modulus in a linear way by use of a linear mixing rule. If $\delta G'(\omega) = 0$ the mixing rule applies. This is the situation for the networks with $r = 0.71$ and $r = 0.75$ for $\omega < 1$ Hz approximately. For the networks with $r = 0.85$ and $r = 0.95$ $\delta G'(\omega)$ is equal to 0 only when $\omega \approx 1$ Hz. This clearly indicates that dynamic dilution plays a significant role within the networks and thereby a simple linear mixing rule will not apply in general. However, for the softest networks the sol and the network fractions are so similar that the simple rule applies. If one wants to take into account the concept of dynamic dilution, the inclusion of a volume fraction dependent time superposition is necessary.⁷

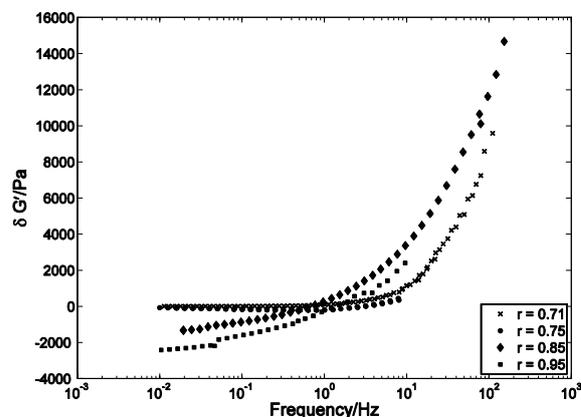


Figure 8. $\delta G'$ as a function of the frequency for the $r = 0.71, 0.75, 0.85$ and 0.95 networks.

Table 3. Slopes of G' and G'' for the network, the washed network and the sol fraction. The slopes are determined as a power law fit of the measurements in the low frequency regime, $\omega \leq 1$ Hz.

r	Network		Washed Network		Sol fraction	
	Slope of G'	Slope of G''	Slope of G'	Slope of G''	Slope of G'	Slope of G''
0.71	1.1	0.80	0.57	0.54	0.69	0.60
0.75	0.91	0.71	0.45	0.48	0.79	0.68
0.85	0.37	0.40	0.25	0.34	0.48	0.59
0.95	0.17	0.30	0.12	0.29	0.34	0.50
1.07	0.083	0.15	0.053	0.27	-	-

The plateau moduli, see Fig. 9, for the networks showed that they were very soft compared to traditional silicone networks which are prepared with crosslinkers of higher functionality than three.⁸ The moduli of these are in the order of 10^2 - 10^4 Pa, see Fig. 9. This is easily explained by the properties of the trifunctional crosslinker which requires that all the reaction sites on the crosslinker have reacted and that all the polymers are reacted with the infinite network in both ends in order to be elastically active. If only two chains are connected to the crosslinker, the crosslinker will in fact only act as a chain extender and therefore not act as a crosslinking point. This will lead to a rapid decrease in the resulting modulus.

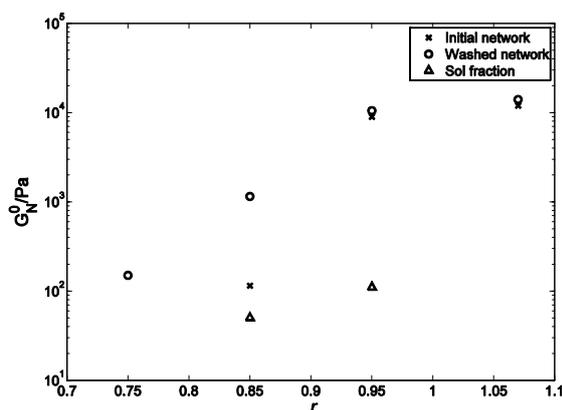


Figure 9. G_N^0 as a function of r for the initial network, the washed network and the sol fraction. For some values of networks, washed networks and sol fractions it was not possible to identify the presence of a plateau and thus G_N^0 .

CONCLUSION

A number of PDMS samples with different stoichiometries was investigated. The initial networks were swelled in order to separate the network and sol fractions. It was possible to divide a sample which initially showed no signs of network properties into two fractions – the sol and the network – and get a viscoelastic response indicating a network from the network fraction. This point towards that it is possible for the viscous sol fraction to completely smear out the elastic response from a network fraction.

A linear mixing rule for G' proved to apply for the networks with low stoichiometries ($r = 0.75$, $r = 0.85$). For the networks with higher stoichiometries it was observed that the linear correlation failed thus indicating that dynamic dilution plays a significant role.

Investigation of the values for n proved that n decrease when r increase – hence the softness goes down when the stoichiometry is increased towards stoichiometrical balanced networks. This was expected since harder networks are formed when the stoichiometry is raised.

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