

Kinetic investigation of the addition curing vulcanization

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ABSTRACT

The network formation reaction of addition-curing systems with modifier is studied by means of rheology and compared to theoretical predictions. The different reaction steps are altered by addition of inert oil to change the viscosity of the reaction medium and thereby the mobility of the reacting molecules.

INTRODUCTION

There exists a large variety of studies on the kinetics of polymeric networks. The addition-curing system of endlinked polydimethylsiloxane (PDMS) is a very well-studied system due to a very limited degree of unfavorable side reactions which among other properties makes PDMS a model network¹. For an extensive review on end-linked systems, see Hild². A recent work by Scherble *et.al.*³ measures the silicone network formation by means of in-situ mid-infrared spectroscopy. Thereby they have a direct measure of the conversion as function of time but they need a model to translate their data into elasticity measures. In addition to experimental data, there exists a wide range of simulations⁴ which in general are based on 3- or 4-functional crosslinkers (low functionality crosslinkers, in the following denoted LFCs). However, in most commercial applications high-functional crosslinkers (HFCs) are applied. The initial kinetics of LFCs and HFCs is similar but the crosslinking systems with HFCs experience a sequence of reactions where the network

(or branched structures) is already formed and thus the mobility of the polymers is extremely small and relatively restricted. The network structures will (in contrast to the reptating polymers in the melt) move by a 'breathing' motion where the dangling arms are withdrawn by an 'activated' process⁵.

Networks which are not highly crosslinked e.g. by means of radiation will always consist of a fraction of unreacted material and material, which is not connected to the network. This fraction is traditionally denoted the sol. Polydispersity effects play a large role in the dynamics of polymer melts and the effects are even stronger for networks and the sol fraction.

In this work we have decided to focus on the situation where there is a large excess of PDMS and furthermore there is added inert oil of different molecular weights, i.e. the resulting networks are extremely soft and show very long relaxation times. The resulting systems will be only slightly past the gelation point and therefore needs to be regarded as a ternary system consisting of network, low- and high-molecular weight solvent, respectively⁶. The silicone oil will enhance the molecular motions of the developing network substructures via dynamic dilution effects^{5, 7}.

EXPERIMENTAL

Very soft silicone networks were prepared from an addition-curing reaction

of vinyl-terminated polydimethylsiloxane (PDMS), high-functional hydridemethylsiloxane (HMS), and end-linked difunctional HMS, which acted as a chain extender, also known in technical terms as modifier. The networks were diluted with different silicone oils. The applied silicones were: PDMS (Polymer VS 10.000), HMS (Crosslinker 120), modifier (Modifier 705), catalyst (Catalyst 510), which were all sponsored by Hanse Chemie, AG. The silicone oils were both obtained from Dow Corning 200(R) series (1.000, 12.500, and 30.000 cPs, respectively).

The reaction mixtures were prepared such that mixture A contained PDMS and catalyst. Mixture B contained PDMS, HMS, and modifier. The amounts of reactants in the two mixes are given in table 1. Both mixtures were mixed by hand for ten minutes. 2.00(\pm 0.01) g mix A was weighed in a small plastic beaker and the required amount of oil was added and mixed thoroughly before 2.00(\pm 0.01) g of mix B was added. The stopwatch was started when mix B was completely transferred and the mixing was started. The mixture was mixed for 1 minute by hand before the reaction mixture was transferred to the rheometer. Air bubbles were removed, and the rheometer was rapidly heated to 40°C, and the experiment was started after 1 minute of equilibration. The exact time from start of mixing to the start of experiment was noted down.

Linear rheology was performed by use of a controlled-strain rheometer (AR2000, TA Instr.). The applied geometry was 10 mm parallel plates. The strain was 4%. It was ensured that the applied strain was within the linear regime by performing strain sweeps. The rheometer was set to measure the storage and loss modulus of the mixture at 1.00 rad·s⁻¹ at 40°C with a sampling frequency of 0.5 s⁻¹ for 30 minutes after the temperature equilibration.

Mixture	A	B	η / [cPs]	$[i]$ / [$\frac{mmol}{g}$]
PDMS	19.93	14.0	10.000	0.05
HMS	-	0.28	500	1.1
MOD	-	5.72	500	0.16
CAT	0.07	-	500	0.14*

Table 1. The amount of components for a 40 g network basis. The two mixtures A and B are mixed 1:1. The viscosity η and the concentration of reactive groups $[i]$ are data supplied from Hanse Chemie AG. *The catalyst is diluted to 5000 ppm Pt content in 500cPs PDMS.

All the curing profiles were adjusted to take into account the small, but nevertheless significant, variations in mixing and equilibration times.

THEORY

The recursive method for calculating crosslink density beyond the gelation point developed by Miller and Macosko⁸ (MM theory) is usually applied to LFCs but it can also be applied to HFCs.

The reaction scheme for the system is that a reaction site of PDMS (denoted B in the following to follow the nomenclature of MM) can either react with a reaction site of HMS (denoted A) or a reaction site of the modifier (denoted C). The development of the network can be followed by e.g. the extent of reaction of B sites, i.e. the relative consumption of vinyle groups:

$$p_B = \frac{[B]_0 - [B]}{[B]_0} \quad (1)$$

where $[B]$ is the concentration of B reaction sites, and the subscript 0 denotes initial conditions. The extent of reaction of B is closely related to the extents of reaction of A and C sites via the stoichiometries $r_1 = ([A]_0 + [C]_0)/[B]_0$ and

$r_2 = [C]_0/([A]_0 + [C]_0)$. Since we assume same reactivity of all hydride reaction sites, i.e. A and C reaction sites, we get $p_A = p_C$ and $p_B = r_1 p_A$.

The methodology is: Let the polymerization proceed to a given extent of reaction. Pick an A group at random. Let F_A^{out} be the event that looking out from the A chain leads to a finite chain, i.e. either an unreacted A site or a dangling arm. We can then calculate the probability by applying the law of total probability:

$$P(F_A^{out}) = P(F_A^{out}|Q)P(Q) + P(F_A^{out}|\tilde{Q})P(\tilde{Q}) \quad (2)$$

where Q is an event and \tilde{Q} its complement.

In general we have the relation between the probability looking outwards and inwards from a polymer chain:

$$P(F_A^{in}) = P(F_A^{out})^{f-1} \quad (3)$$

where f is the functionality of the polymer, which means that for difunctional polymers $P(F_i^{out}) = P(F_i^{in})$.

In figure 1, some possible network structures are shown. The numbers at different reaction sites refer to specific combinations and the arrows indicate the in the text mentioned directions. Looking at **1** and **2** in the figure, we derive via equation 2:

$$P(F_A^{out}) = P(F_A^{out}|+r)P(+r) + P(F_A^{out}|-r)P(-r) = P(F_B^{in})p_A + 1(1 - p_A) \quad (4)$$

where '+r' means 'A reacts' and '-r' means 'A does not react'.

The same procedure is followed for the modifier (C), where looking at **9** and **10** in the figure leads us to:

$$P(F_C^{out}) = p_C P(F_B^{in}) + (1 - p_C) \quad (5)$$

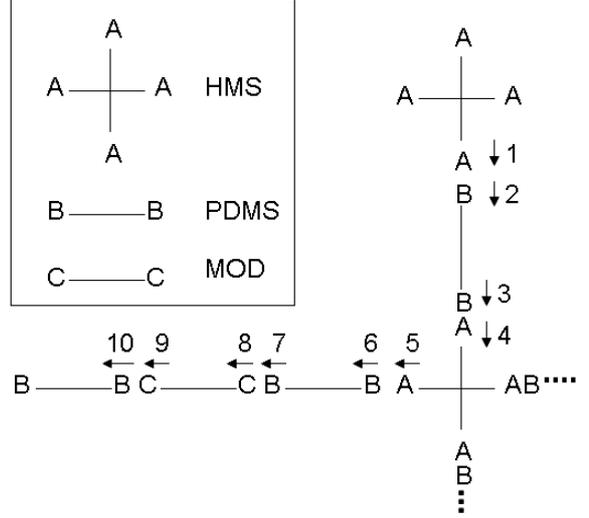


Figure 1. Illustration of the different combinations occurring in a network with modifier present. The numbers are referred to in the main text.

For the PDMS (B) we look at **3**, **4**, **7**, and **8** and obtain:

$$P(F_B^{out}) = r_2 p_B P(F_C^{in}) + (1 - r_2) p_B P(F_A^{in}) + (1 - p_B) \quad (6)$$

Equation 6 holds only since we assume the same reactivity of A and C reaction sites such that the probability for B to react with one of them is proportional to the relative amount.

Finally, equations 3-6 are solved numerically to obtain $P(F_A^{out})$ as a function of (p_A), which then can be related to rheological measures. The gel point with respect to extent of reaction of the crosslinker can also be determined from the model:

$$p_{A,g} = p_A (P(F_A^{in}) \rightarrow 1_+) \quad (7)$$

The concentration of elastically active crosslinkers $[X]$ is calculated from the concentration of crosslinkers, which are connected to the infinite network via at least three B chains:

$$[X] = [X]_0 \sum_{m=3}^f P(X_m) \quad (8)$$

where $[X]_0 = [A]_0/f$ and

$$P(X_m) = \binom{f}{m} [P(F_A^{out})]^{f-m} \cdot [1 - P(F_A^{out})]^m \quad (9)$$

where $\binom{f}{m}$ is the binomial coefficient. Since HFCs tend to act as a series of three-functional crosslinkers rather than as a single f -functional crosslinker except in the case of very low molecular crosslinkers^{8, 9}, we can write the concentration of chemical crosslinks as:

$$\nu_c = \sum_{m=3}^f \frac{m-2}{2} P(X_m) [X]_0 \quad (10)$$

The elastic modulus will according to the affine model develop as:

$$G = \nu_c RT \quad (11)$$

where ν_c depends on the extent of reaction via $P(F_A^{out})$. We do not include contributions from trapped entanglements in this model as the contribution from trapped entanglements to the modulus is vanishing in networks with excess of PDMS due to the fact that entanglements are binary events. The probability of an elastically active PDMS chain scales with $(1 - P(F_B^{out}))^2$, which means that the probability of a trapped entanglement (two elastically active chains entangling) scales with $(1 - P(F_B^{out}))^4$.

We normalize the elastic modulus by $G[P(F_A^{out})|p_A = 0.95]$ such that we have a normalized modulus $G_{n,t} = G/G[P(F_A^{out})|p_A = 0.95]$ ranging from 0 to 1 as function of the extent of reaction of the deficit component (the crosslinker or the modifier in our case). The choice of $p_A = 0.95$ rather than $p_A = 1$ is due to the general trend that the extent of reaction of the silicone addition reaction never tends to approach 1 but rather 0.93-0.97¹⁰.

Finally, we can derive the rate constant of the elasticity development k , which depends on the extent of reaction, from

the measured normalized storage modulus $G'_{n,e}(t) = G'(t)/G'(t \rightarrow \infty)$ via:

$$k(p_A) = k(p_A | G'_{n,e} = G_{n,t}) = \frac{1}{(t | G'_{n,e} = G_{n,t})} \quad (12)$$

It is important to notice that k is not a rate constant for a specific reaction as such but rather an overall rate constant, a so-called apparent reaction rate. This seems reasonable since there will be a huge number of individual rate constants involved in the network reaction where the polymers develop from linear molecules via slightly branched molecules to hyperbranched structures before becoming part of the infinite network.

RESULTS AND DISCUSSION

The functionality of the applied crosslinker is calculated from data from the supplier to $f = 21$. The two stoichiometries are calculated to $r_1 = 0.70$ and $r_2 = 0.75$. In words this means that there for every 10 vinyl reaction sites are only 7 hydride reaction sites, and that 3 of 4 of these hydride reaction sites are from the modifier. This also means that there are $3 \cdot 21/2 \sim 32$ as many modifier molecules as crosslinker molecules.

In figure 2 the measured normalized storage modulus as function of reaction time for networks with different amounts of viscous silicone oil (12,500 cPs) is shown. It is clear that the oil content influences the development of elasticity in a nontrivial way. Therefore it is very interesting to develop a simple method to investigate the overall reaction rate of elastically active material as function of the extent of reaction. This method may seem more complex than IR measurements but IR does not reveal anything about the structural formation, only about the consumption of hydride groups. However, combined in one experiment these two methods would be

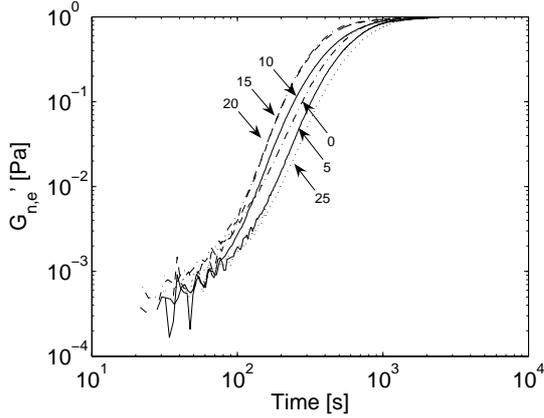


Figure 2. The normalized storage modulus as function of reaction time for networks with different amounts (given in percent) of 12,500 cPs silicone oil.

even stronger because with IR measurements one would know the exact extent of reaction as function of time, which is unknown for the rheological method, where the determination of the extent of reaction is based on theoretical considerations.

Before applying the developed theory to derive reaction kinetics from the measurements, some predictions of the model are clarified. In figure 3 it is shown how the probabilities $P(F_B^{in}) = P(F_B^{out})$, $P(F_A^{in})$, and $P(F_A^{out}) = P(F_C^{out}) = P(F_C^{in})$ develop as a function of the extent of reaction for our investigated system with $r_1 = 0.70$ and $r_2 = 0.75$. The predicted development of elasticity in the network is also shown in the figure. It is obvious that even though the gel point is reached at $p_A = 0.4$, the elasticity develops slowly only until $p_A \simeq 0.6$, where the increase in elasticity becomes stronger due to the fast decrease in $P(F_A^{out})$. The gel point, which is determined from equation 7, is $p_{A,g} = 0.4$. This means that in average 8 reaction sites of the crosslinker need to react before the crosslinker becomes attached to an infinite structure. It is a clear evidence of the very loose structure

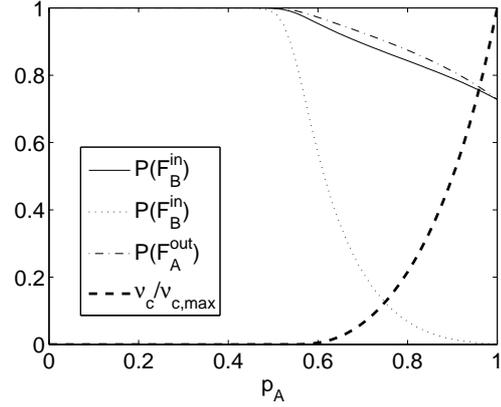


Figure 3. The theoretical prediction of three different probabilities and the normalized crosslink density as function of extent of reaction.

of the network. Another measure that can be derived from the figure is that $P(F_B^{out})[p_A = 0.95] = 0.7$, which means that at the end of reaction there are 35% of the vinyl reaction sites that are connected to the infinite network structure. This means that -if we neglect the molecular weights of HMS and modifier - that the actual weight fraction of the network is $1 - 2(1 - p_B)p_B P(F_B^{out}) - p_B^2 = 0.26$, and that the weight fraction of unreacted PDMS is $(1 - p_B)^2 = (1 - r_1 p_A)^2 = 0.1$, so the systems are indeed ternary with at least 10% linear molecules (which can be regarded as solvent after the reaction), 64% long linear molecules, and 26% actual network. There are no branched molecules in the sol fraction since all the crosslinkers are connected to the network. If the stoichiometry r_1 is decreased just slightly, $P(F_A^{out}[p_A = 1]) < 1$ and therefore hyperbranched structures will exist in the sol fraction. It can also be discussed if the 3% incompleteness of the reaction leads to the existence of hyperbranched structures in the sol fraction, but we will not come into the discussion here. We just conclude that the system is strongly swelled by the

two types of solvent, and solvent can easily be forced out of the system by applying a force to the network.

In figure 4 the model prediction of the extent of reaction as function of time is shown. The model can only predict the properties properly for $p_A \geq 0.55$. We have not included elasticity of the prepolymers so we can not predict the early measured data, which on the other hand has fluctuations of the same size as their absolute value, so it seems a reasonable model limitation. The data is fitted to a series of differential equations of the form

$$\frac{dp_A}{dt} = \frac{k_i}{t} \quad (13)$$

with smooth turn-overs from one behavior to the other i.e. the individual apparent reaction rates are inversely proportional to time. The different regimes are indicated in the figure. We have chosen to fit the data to this form since it fits the data fairly well without too many parameters. The form is not a traditional form for reaction kinetics, but e.g. traditional first or second order kinetics can not be expected since there are large changes in viscosity (of both reacting species but also of the reaction medium) and there will be steric hindrance effects due to the high functionality of the crosslinker.

In figure 5 the determined apparent reaction constants as function of the weight fraction of 12,500 cPs silicone oil are shown. The apparent rate constant for the diffusion controlled reaction k_2 can be seen to increase rapidly when the amount of inert oil is increased. This is in good agreement with the dynamic dilution effect. The effect should be even stronger for the 'breathing' motion but it is very hard to determine the exact value of the rate constant since the experiments need to run for infinite time to ensure correct comparison between theory and experiments.

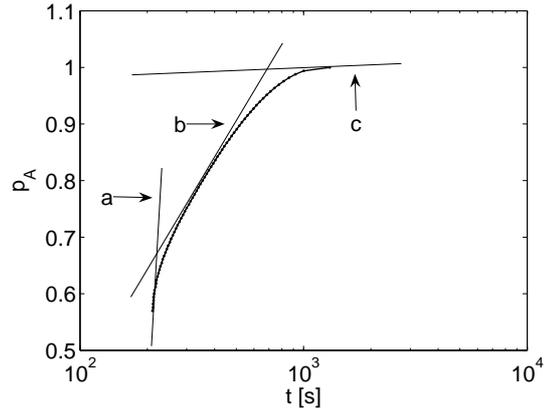


Figure 4. Illustration of the different regimes in the network reaction. (a) The very fast collision rate controlled reaction, which can not be determined by this methodology. (b) The diffusion controlled reaction. (c) The slow reaction controlled by 'breathing' motion of the entangled polymers where steric hindrance for the high-functionality crosslinker is thought also to play a role.

Therefore we focus on the determination of k_2 which is the regime where the network almost fully develop from being a complex system of network, hyperbranched and linear structures to a system consisting of network and linear structures. The value of the apparent rate constant for the system without any oil is 0.6, which can be expressed as an absolute value when multiplied by the initial concentration of hydrides, i.e. $k'_2 = k_2[H]_0 = 4.5\text{mmol/L}$, when it is assumed that the all densities are equal to the density of silicone oil ($\rho = 0.97\text{g/cm}^3$).

A comparison of the apparent reaction rates for the networks with three different silicone oils is shown in figure 6. There is not a big difference between the networks with the two high-viscosity oils (12,500 and 30,000 cPs), but this can be explained by the fact that both oils have molecular weights far above the molecular entan-

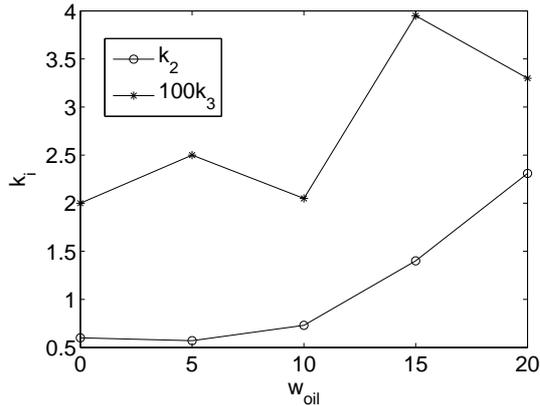


Figure 5. The apparent reaction rates of the network formation reaction as function of the weight fraction of inert 12,500 cPs silicone oil.

gument weights. The networks with the low-molecular weight oil (1000 cPs) shows faster reaction kinetics than the the others but here the viscosity of the reaction medium for the same extent of reaction will be significant lower, and the concentration of entanglements will be lower since the low-molecular oil dilutes the entanglements.

There are as discussed previously limitations of the model, since our analysis depends on the assumption of spatial homogeneity (continuously stirred reaction). This is of course an assumption as there is no stirring in the rheometer. Experimental uncertainty is also introduced by the catalyst concentration. The catalyst is assumed not to influence the reaction rate as such since we keep the catalyst concentration constant (within 1-2%) throughout the experiments such that the concentration dependency will be implicit in the rate constant, but the effect of small variations in the catalyst concentration has not been investigated. Furthermore the model does not include the possibility of loops and other network imperfections. However, the MM theory has been further developed to

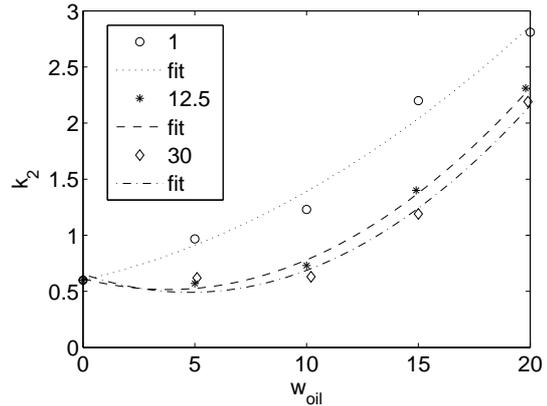


Figure 6. The apparent reaction rates k_2 of the diffusion controlled regime as function of the weight fraction of inert silicone oil for the three different oils (the viscosities in units of 10^3 cPs are given). The dotted lines are just guidelines.

take this into account¹¹ as well as polydispersity effects¹².

CONCLUSIONS

This method to determine apparent rate constants is based on the recursive method of Miller and Macosko to predict post-gel properties. The developed method can predict apparent rate constants for the diffusion-controlled regime of the addition curing network reaction.

The model shows via experimental data how inert silicone oil influences the apparent reaction time involved in the regime, where the reaction sample has started to develop a three-dimensional infinite network structure, via dynamic dilution effects influencing the reptation of linear and branched molecules. It is shown how increasing the amount of oil also increases the apparent reaction rates. The rates are also influenced by the molecular weight of the inert oil but when the molecular weight is far above the entanglements threshold, the effect seems to vanish. Low-molecular weight of the silicone oil results in faster ki-

netics since dynamic dilution effects cause faster motion of the entangled polymers. The presence of low-molecular weight oil furthermore decreases the concentration of entanglements which also increases the molecular motions in the reaction mixture.

The model fails to predict the apparent rate constants of the initial, fast collision rate controlled regime. The apparent rate constant for the very slow 'breathing' controlled regime, where steric hindrance also is thought to play a role, requires extremely long data sampling of the network formation reaction in order to give sufficient precision so the developed method is not really suitable, but can however be applied if long data sampling is not a problem.

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