INFLUENCE OF THE NETWORK STRUCTURE OF SILICONE RUBBER ON TIME–DEPENDENT AUTOHESION AS MECHANISM FOR SELF-HEALING

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The influence of structure of polymer networks and molecular weight of the constituting polymers, on their tackiness and time-dependent autohesion as mechanism for crack repair has been studied. The polymer used was polydimethylsiloxane (PDMS), crosslinked with a trifunctional silane. The tack experiments were performed with a tack testing device, developed specially for this purpose, and the data were measured in terms of maximum tack force. The networks were characterized with swelling and mechanical properties. High molecular weight PDMS shows autohesion increasing with time in a form of a logarithmic curve. The autohesion curves of low-molecular weight PDMS show a maximum over a certain contact time, then the tack decreases to a plateau. The data indicate that the generally accepted ¼ power law increase between tack and time does not apply in this case. The exponent obtained is noticeably lower. The slopes of time–dependence curves obtained at different pulling speeds, however, behave according to theory, but the values are always lower than predicted. This sort of behavior can be attributed to the high polydispersity of the polymers used.

Keywords: rubber, PDMS, tack, autohesion, self-healing

1 Introduction

Tack of materials is the ability to resist separation, after bringing their surfaces for a short time into contact under pressure. Two types of tack can be defined: autohesive, when the materials in contact have the same chemical composition; and adhesive, when both materials have different compositions [1].

Adhesion of rubber is important in many industrial processes. Good adhesion is required for tire building and in adhesive labels and tapes: so called pressure-sensitive adhesives. The topic of polymer autohesion attracted lots of scientific attention in past years. Research in this area provides the insight into some practical aspects such as elastomer tack and crack healing.

However, the problem of contact development between two viscoelastic bodies is still subject to debate. In general, during the interface formation surface wetting occurs, followed by the interdiffusion of chain segments [2]. During the wetting process, initially, contact will only occur at the areas in which the asperities and craters of one surface meet those of the other due to a rough topography of samples.
Incomplete molecular contact limits the interfacial diffusion of polymer molecules. In order for the contact area to increase, the material must undergo viscous flow. Chain interdiffusion can only occur if there is enough contact area. According to DeGennes theory of reptation [3], polymer chains are confined to a “tube” having a shape similar to the random coil conformation of the chain. Due to the Brownian motion the chain migrates from the tube, allowing it to cross the interface, as shown in Figure 1.

![Figure 1: The interdiffusion process at the polymer-polymer interface with increasing time](image)

The strength of the interface develops in time, and the rate of adhesion development is a function of contact time, temperature and molecular weight of the polymer. For the adhesion time dependence a model was developed by Wool [4], based on the fact, that the average interpenetration depth $X$ of the interdiffusing polymer follows the relationship $X(t) \sim t^{1/4}$, where $t =$ time. A strain energy approach was used, in which the strain energy density per chain, $U_c$, behaves as:

$$U_c \sim \sigma^2 \cdot l$$  \hspace{1cm} (1)

where $\sigma$ is an uniaxial stress acting normal to the interface and $l$ is the length of the chains diffused across the interface. If the stored strain energy in the chain is used to pull it out across the interface, a fracture criterion can be written as:

$$U_c \geq U_p$$  \hspace{1cm} (2)

where $U_p$ is the energy to pull a chain out of its tube by a force $f$ and velocity $v$. The pullout force is given by $f = \mu \cdot l \cdot \frac{dl}{dt}$, where $\mu$ is the friction coefficient for the chain segment of length $l$. The friction coefficient is related to the monomer friction coefficient $\mu_0$ via, such that the force can be written as:

$$f = \mu_0 \cdot l \cdot \frac{dl}{dt}$$  \hspace{1cm} (3)
UP can be then derived from the integral of f·dl:

\[ U_p = \int f \cdot dl = \int_{l=0}^{l=1} \mu_0 \cdot l \cdot \left( \frac{dl}{dt} \right) \cdot dl \]

(4)

with solution:

\[ U_p = \frac{1}{2} \cdot \mu_0 \cdot \left( \frac{dl}{dt} \right) \cdot l^2 \]

(5)

or if:

\[ U_p = l^2 \]

(6)

From (1), (2) and (5) it now follows that:

\[ \sigma \sim l^{1/2} \]

(7)

And because, finally:

\[ \sigma \sim \chi \]

(8)

As it was already mentioned, \( \chi \sim t^{1/4} \), thus the fracture stress or tack should behave as:

\[ \sigma \sim t^{1/4} \]

(9)

This model was further developed by Prager and Tirrell [5], by assuming a chain–scission mechanism, while Wool postulated a chain pull–out mechanism [2, 6]. The behavior is observed for molecular weights with relaxation times \( t \leq t_\infty \), where \( t_\infty \) is the time needed for achieving full healing of the interface. For \( t \geq t_\infty \) \( \sigma \) behaves as:

\[ \sigma \sim M^{1/2} \]

(10)

Although mass transfer across the interface is not questioned, those adhering the wetting mechanism claim, that the same time dependencies can be obtained from the kinetics of surface wetting [7]. The material flows to fill the voids at the interface, and the bond strength development follows first order kinetics. Which of the mechanisms is the dominant factor still remains a matter of debate.

Silicone rubbers attract lots of interest due to their surface properties. The unique flexibility of siloxane chains causes the pendant side-groups to appear at the surface, thus causing a very low tackiness.
This makes silicone rubbers a perfect material for low tack applications. Furthermore, the versatility of crosslink chemistry of silicone rubbers also makes it a good choice for more fundamental studies on network structure as determining autohesion and corresponding self-healing.

2 Experimental

2.1 Materials

Table 1 lists the vinyl-terminated polydimethylsiloxanes that were used for the study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Viscosity</th>
<th>M_w [g/mole]</th>
<th>Vinyl group content [mmole/kg]</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>MQ 17</td>
<td>500</td>
<td>17 000</td>
<td>166</td>
<td>ABCR</td>
</tr>
<tr>
<td>MQ 28</td>
<td>1000</td>
<td>28 000</td>
<td>98</td>
<td>ABCR</td>
</tr>
<tr>
<td>MQ 50</td>
<td>5000</td>
<td>50 000</td>
<td>64</td>
<td>ABCR</td>
</tr>
</tbody>
</table>

As crosslinkers tris(dimethylsiloxyl)ethoxysilane (trifunctional), tetrakis(dimethylsiloxyl)silane (tetrafunctional) and a multifunctional silane were used. The platinum-cyclovinylnethylsiloxane complex was used as cure reaction catalyst. All the above materials were obtained from ABCR, Germany, with the exception of the multifunctional silane, which was provided by a proprietary source. 1-ethynylcyclohexanol (99%) was used as a temporary reaction inhibitor, obtained from Aldrich. Pyrazine (Aldrich, 99%) was used as an internal NMR standard without further purification. The solvents used were all of pro analysis quality.

2.2 Sample preparations

For every batch of polymer the exact amount of vinyl groups was determined using NMR measurements (Bruker 300 MHz apparatus) with pyrazine as an internal standard. The results of these measurements are included in Table 1. From those results and the molecular structure of the crosslinker, the hydrogen-to-vinyl ratio (H/V) was calculated.

For the MQ 17 and MQ 50 samples and the different crosslinker functionalities, testing samples were prepared using the H/V ratios: 1.0, 1.2, 1.4 and 1.7. The curatives were mixed together with the polymer using a magnetic stirrer, then the mixture was degassed and cured in a compression molding machine (WLP 1600/5x4/3 Wickert laboratory press) at 120°C for 30 min. Clean Teflon foil was placed between the cured mixture and the mold plates to avoid surface contamination and sticking of the material to the mold. The 90x90x2 mm sheets were post-cured in an oven at 120°C for 48 hours.

2.3 Crosslink density

All crosslink density measurements were made by swelling the rubber samples in toluene for 48 hours; calculations were made using the Flory-Rehner equation [8]:

\[
\chi = \frac{V_p V_m}{V_p + V_m} \frac{1}{RT} \ln \left( \frac{1}{1 - \theta} \right)
\]
\[ v = \frac{2v_r^2 + \ln(1 - v_r) + v_r}{V_0 (0.5v_r - v_r^{1/3})} \text{ [mol/cm}^3\text{]} \]  

where \( v \) is the crosslink density, \( v_r \) is the equilibrium volume fraction of rubber in the swollen state and \( V_0 \) is the molar volume of the solvent. The polymer-solvent interaction parameter \( \chi \) of 0.456 [9] was used for all calculations.

2.4 Mechanical testing

Shore A hardness was measured using a Zwick hardness meter according to the ISO R868 standard.

2.5 Tack measurements

Tack measurements were performed using a custom-made device based on the Tel-Tak principle [10]. Pieces of rubber 20x20x2 mm were used as test samples. Pairs of samples were pressed against orifice disks to generate a curved contact surface: Figure 2. The curvatures were compressed under 2.5N load for 10 minutes (unless mentioned otherwise), and then separated with a speed of 4 mm/sec; the maximum separation force was recorded. The contact area was calculated from the radius of curvature.

Figure 2: The principle of tack-testing device 1. Rubber samples. 2. Clamps 3. Separator

2.6 Self-healing measurements

Samples of MQ 17, 28 and 50 with hydrogen-to-vinyl ratio 1.0 were used for the measurements, and compressed under a load of 2.5 N. Times of compression were varied from 1 to 1000 minutes. For each time several tack measurements were collected and the average was taken as the final result.
3 Results

3.1 Tack as a function of molecular weight, crosslinker functionality and crosslink density

Figure 3 presents a sample separation curve after 10 minutes compression. A force less then zero means, that the samples are still under compression. At zero force separation starts, but the samples are still held together by the interfacial forces.

At the maximum force the contact between the two sample halves breaks. That value was taken for further calculations of rubber-rubber tackiness.

Figures 4 and 5 present the results of autohesion measurements for MQ 17 and MQ 50 vs. H/V ratio in correlation with crosslink density of the samples.
In both cases, the crosslink density increases with increasing amount of silane. For the stoichiometric amount of crosslinker, the sample is still clearly undercrosslinked and exhibits a high level of tack. The rubber autohesion decreases quickly with increasing crosslink density, finally falling below the detection level of the apparatus. Figures 5 shows the relation between rubber-rubber tackiness for the high molecular weight PDMS - MQ 50. It exhibits significantly higher levels of tack than its low molecular weight counterpart. The decreasing trend in tackiness is also more pronounced, a very high tack for H/V 1.0 decreases strongly after only a slight increase in crosslink density. The crosslink density increase is also shaped differently. For the low molecular weight PDMS it starts showing a saturation effect at the H/V = 1.4; the increase in crosslink density from 1.4 to 1.7 is much smaller than from 1.2 to 1.4. MQ 50 shows almost a linear increase of crosslink density with increase in crosslinker excess. High molecular weight PDMS somewhat surprisingly shows a similar crosslink density to the MQ 17 at H/V = 1.0, although due to the molecular weight difference it has less crosslink sites, thus should exhibit much less density of crosslinks. The difference starts to be visible at higher crosslinker excess.
Figure 6 shows how PDMS autohesion changes for MQ 50 with increase in crosslinker functionality for H/V ratio = 1.0. MQ 50 crosslinked with tetra and multifunctional silanes shows very low levels of tack. The level of tackiness decreases by orders of magnitude with increase of silane functionality from 3 to 4. Further increase in functionality does not cause significant changes anymore.

### 3.2 Tack as a function of contact pressure

Figure 7 shows how the tack depends on applied contact pressure. Particularly in the case of rubber–rubber contact, the tack shows a small dependence on the applied load.

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![Figure 7](image)

**Figure 7**: Tack-load dependence for MQ 50: (■): rubber – rubber contact; (●): rubber – chrome steel contact

The same type of experiment performed with a silicone rubber–chrome-plated steel contact shows, that the load dependence is somewhat increased. This is not surprising, because during the steel–rubber contact there is no possibility to form entanglements. Surprising is however, that the tackiness for the rubber-steel contact is higher for high loads, that for the rubber–rubber contact. The reason can be, that the formation of a well-wetted surface for the rubber-steel contact is easier, whereas it is slower for the rubber-rubber interface.

### 3.3 Self-healing measurements

Figure 8: Tack as a function of contact time for (a) MQ 17 and (b) MQ 50 for H/V = 1.0

Figure 8 shows the beginning of PDMS autohesion development for short contact times.
While the low molecular weight MQ 17 apparently shows a maximum in autohesion level for short contact time, the shape of the curve for the high molecular weight MQ 50 is more logarithmic of nature. For the low molecular weight PDMS maximum tack is reached quickly, and after that starts to decrease again. The situation is different in the case of the high molecular weight PDMS: the tack level rises slower, but within the considered timescale it cannot be determined if a saturation level is already reached: in fact the tack still rises after very long compression times, ranging till 1000 minutes. That does not necessarily mean that the ultimate interface strength was already reached after that period: further increase in rubber autohesion was observed for times higher by one order of magnitude, and the fracture stress achieved values independent of contact time [16].

Figure 9: Sample healing curves for MQ 28 at different pulling speeds, H/V = 1.0

Figure 9 shows how the healing of the PDMS – PDMS interface proceeds with time and increasing pulling speed. With the increase in pulling speed the tack force increases. Also the slope of the healing curves increases accordingly. There is one exception though; the healing curve for 2 mm/sec pulling speed shows a much higher slope than expected. This behavior is better visible in Figure 10, which shows the exponent values as a function of pulling speed:

Figure 10: Slopes of the healing curves of MQ 28 in relation to pulling speed; H/V = 1.0

The slopes rise monotonically with pulling speed, with the exception of the 2 mm/sec value. The slope and the forces measured are on the same level as 10 mm/sec pulling speed, which is a very unexpected behavior.
The situation is somewhat different in the case of high molecular weight PDMS, MQ 50.

The slopes of the healing curves rise monotonically with increasing pulling speed. The values of the slopes, however, are lower than those measured for the lower molecular weight PDMS MQ 28. Medium molecular weight PDMS reaches the exponent of 0.2 already at the speed of 12 mm/sec, while the high molecular weight polymer does not actually pass above an exponent of 0.18.

The behavior of the low molecular weight PDMS is very different. First of all, the healing curves show the presence of a maximum at short contact times, which is completely absent in the case of higher molecular weight polymers.
The presence of this maximum makes it very difficult to fit a curve – results are obtained with a very large error. The maximum is present on each healing curve for the speeds ranging from 4 to 10 mm/sec. Moreover, it shifts with increasing pulling speed to shorter contact times. The values of tackiness still increase with increasing speed, but the increase stops at 8 mm/sec. This is also a different behavior compared to higher molecular weight species.

4 Discussion

As anticipated, rubber autohesion increases with decreasing crosslink density for all combinations investigated. Lower crosslink density results in larger amounts of unattached chains, pendant network chains, as well as in a less constrained network. All these phenomena are known to promote tack by partial migration of polymer entities across the contact interface. During the contact, polymers can also exchange other interactions, like van der Waals forces or hydrogen bonding. It was already proven by others, that for PDMS-PDMS contact the forces are dispersive: van der Waals in nature, due to the presence of numerous methyl groups on the interface [12]. Thus the tack increase must mainly be due to the presence of pendant chains and to increase in chain mobility. An increase in molecular weight of the polymer results in a large increase in tack values for the samples crosslinked with the trifunctional silane: Figures 4 and 5. During separation the chains are extended before full release. The extensions and disentanglements cost more energy for the longer, higher molecular weight chains [13]. So, the increase in tack value can be explained by increased disentanglement energy and possibly a higher amount of entanglements formed by the large macromolecules.

An interesting phenomenon is the significant tack decrease by change from the trifunctional to tetrafunctional silane crosslinker. This is most pronounced for the high molecular weight PDMS: Figure 6. The big decrease in tack is combined with an increase in crosslinking density, which seems to be the main reason for this effect.

The tack-time dependence is more complicated. According to the reptation diffusion theory [2, 14] the tack stress should obey a time dependence $t^x$ with $0.25 < x < 0.5$, depending on whether a pull-out or a chain fracture mechanism prevails. This kind of behavior, however, was predicted for monodisperse polymers. The data for polydisperse elastomers obtained by other researchers show a slower increase of the stress with contact time [15, 16]. The values of $x$ lower than 0.25 can be explained by the polydispersity of the used material, which in the present case is around $\frac{M_w}{M_n} = 2$. The polydispersity is related only to the material before crosslinking – after the reaction $\frac{M_w}{M_n} = \infty$, because of the infinite molecular mass of the crosslinked polymer matrix related to the uncrosslinked, loose chains that cross the interface. The theory was developed primarily for the uncrosslinked polymers, and a very important question to ask is its application for the crosslinked species.

The healing behavior of the low molecular weight PDMS is complicated. The healing curves show well-pronounced maxima for short compression times, after which the tackiness levels down. However, after very long compression times, there is still an increase in tackiness level, showing that interpenetration and chain entanglements at least partially take place at the interface on the long term. Because of that sort of behavior the fitting of the curves to obtain the exponent value yields a large error. The maxima visible on Figure 12 shift to shorter contact times with increasing pulling speed.
This behavior is very similar to the viscoelastic phenomenon known as stress overshoot [11], where the shear stress passes through a maximum for large shear rates. Actually it is quite logical, if the timescale of the experiment is taken into account: where the surface chain interpenetration needs many hours to achieve an equilibrium value, pulling takes place in a time of seconds, thus the chains do not have time to orderly disentangle themselves [17]. It is interesting, that this sort of phenomenon does not appear during testing of the high molecular weight polymers, where one could expect it to be even more pronounced if the effect was based purely on viscoelastic dissipation. It should be noted however, that for the high molecular weight polymer the saturation level has not been reached for interpenetrating chains in the range of contact times applied.

The contact pressure data for MQ 50 show a pronounced dependence of measured tack on pressure applied. The diffusion is pressure-dependent only when large hydrostatic pressures are encountered [2]; for the normal tack experiment it is not important. However, the pressure dependence is taken as an indication that viscous flow is also a controlling process [7]. As can be seen in Figure 7, the pressure dependence of the tack for the rubber–rubber contact is less pronounced than for the rubber–steel contact. In the latter case there can be no interdiffusion, thus only surface wetting is possible. The molecular weights of MQ 50 and MQ 28 are high enough to form entanglements [18], contributing to the strength of the interface. MQ 17 is a borderline case, which may be the cause of the different behavior in Figure 8 from MQ 28 and MQ 50, both of which behave in a same manner. Still, distinguishing between surface wetting and chain interdiffusion as controlling processes remains very difficult. From the healing data it can be deduced, that wetting, the creation of the interface, is a short-time process, where the interdiffusion is a long timescale process.

5 Conclusions

There are several mechanisms involved in polymer autohesion. The reduction of chain mobility and decrease in amount of pendant chains with increasing crosslinker functionality seems to be the main reason for a drop in tackiness. The molecular weight effect is mostly the result of an increase in amount of entanglements of molecules and a higher energy needed to unravel the entangled chains. Crosslinker amount, functionality and molecular weight of the polymer have a large influence on the PDMS rubber-rubber tack. It decreases with increasing crosslink density and crosslinker functionality. The latter causes the most significant drop of tackiness. The healing of the PDMS-PDMS interface in time develops in the form of logarithmic curves, with a slope increasing monotonically with pulling speeds. The generally accepted and theoretically predicted \( \frac{1}{4} \) power law of tack vs. time does not apply, due to the high polydispersity of the polymers used. The healing curves of the low molecular weight PDMS exhibit an anomalous behavior, which origin has not been explained yet.

The pressure dependence data show that not only chain mobility and entanglements formation is responsible for the rubber-rubber tackiness. Surface wetting and viscous flow seem to play an important role too. The discrimination between all the influences is very difficult and needs further study.

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