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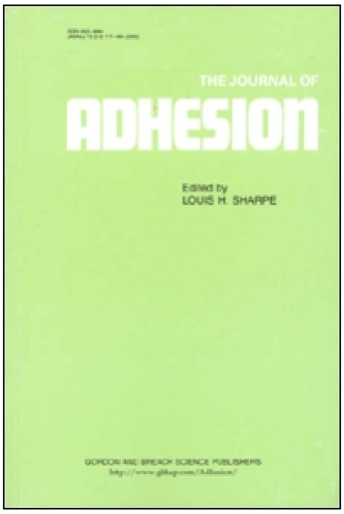

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Silicone Rubber Tack I: Relation to Network Structure

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The influence of the network structure on the poly(dimethyl siloxane) (PDMS) rubber is described. The telechelic polymers have crosslinking sites restricted to the ends of polymer chains only, giving well-defined networks. Rubber-rubber tack is related to the network structure, mostly to the amount of loose polymer chains not linked into the network, that can diffuse through the interface. The amount of mobile chains can be adjusted by varying crosslinker amount and functionality. By controlled variation of the degree of crosslinking of the telechelic silicone rubbers, various levels of tack are induced, which may be related to the network topology.

Keywords: Autohesion; PDMS; Rubber; Tack; Telechelic networks

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INTRODUCTION

Tack of materials is the ability to resist separation after bringing their surfaces into contact for a short time 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].

When the contact between two polymeric bodies is established, the bonding starts to take place. The diffusion theory of tack formation states that autohesive bonding takes place as a result of self-diffusion

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of polymer molecules across the polymer-polymer interface and subsequent entanglement of the migrated chain ends with their new neighbors. If the two contacted polymer layers are uncrosslinked, the interface will eventually disappear and the strength of the junction, the autohesive bond, will become identical to the cohesive strength in the bulk of the material. Historically, the first systematic studies on the subject were undertaken by the group of Voyutskii [2]. He postulated that, due to diffusion of segments of macromolecules, a sufficiently strong bond can be obtained, which results in a high adhesive strength. The problem of motion of individual chains in the polymer bulk has been investigated by many researchers. Rouse [3] and Zimm [4] derived models for the three-dimensional movement of chains dissolved in a solvent of low molecular weight. On the basis of these models deGennes developed a reptation theory of the movement of polymer chains in a one-dimensional manner within a strongly crosslinked polymer gel [5]. Finally, Wool applied de Gennes' model for the development of a theory of crack healing at a polymer-polymer interface [6,7] to predict the tack formation at the polymer-polymer interface.

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The synthesis of model poly(dimethyl siloxane) (PDMS) networks has been the subject of many previous studies [8,9]. In many cases, networks were prepared by crosslinking linear PDMS with γ radiation. Networks obtained in this way are statistical in nature and their structure is not well defined. Coupling end-linked chains, on the other hand, may lead to networks with well-defined topological structures. The reaction depends on the type of functional groups. Hydrosilane functions, $-$SiH, are known to react readily with vinyl and allyl double bonds in the presence of catalysts such as Karstedt's catalyst [10]: a 2% platinum divinyltetramethyl-disiloxane complex in xylene. The substrates can be PDMS fitted at the chain ends with vinyl groups or with silane groups. The former requires the use of a multifunctional silane as crosslinker, while the latter requires compounds with multiple vinyl or allyl bonds.

While it seems that exact stoichiometric amounts of end groups and crosslinking sites need to be combined, the networks obtained are never perfect, unfortunately. When crosslinking progresses and, *e.g.*, one end of a polymer chain is linked to the network, the mobility of the other end is seriously hampered, so that it has a problem finding a crosslinking site elsewhere. At the same time, the mobility is decreased by viscosity increase. Consequently, at stoichiometric amounts imperfect networks are still the result. As far as the defects are concerned, there can be pendent chains, and loops are formed to some extent [11]. Trapped chain entanglements yield additional physical crosslinks.

In addition to minimizing the amount of loose dangling ends and uncrosslinked polymer, the addition of more than stoichiometric amounts of crosslinker is a solution. However, the consequence is that all crosslinking sites on the crosslinker are not fully employed, so that the net functionality is lower than chemically possible and what is aimed at.

The problem can be looked at from the perspective of pressure-sensitive adhesives (PSA) technology, as pointed out in a recent review by Feldstein and Creton [12], based on the poly(N-vinyl pyrrolidone) (PVP)-poly(ethylene glycol) (PEG) PSAs. The phenomenon of tackiness can be considered to consist of three main stages: bonding, relaxation, and debonding. During the bonding phase, a good flow under compressive force is required to wet the substrate completely. During the second phase, elastic recovery of the deformation of polymer chains, as well as translational movements of polymer segments, reptation, are supposed to take place. For PVP-PEG adhesives the timescale of this process can range from 10 to 1000 seconds. The shorter times refer to restoration of polymer chain conformations; longer processes may be associated with entanglement of polymer chains.

In the debonding phase tack is mainly determined by high cohesive strength of the polymer at the interface. It was noticed by Feldstein and Creton that the work of adherence was maximal if the adhesive was able to relax for 500 seconds and longer. That suggests that for the highest adhesive strength the contact times should be comparable with the longer relaxation times.

Silicone rubber is widely used in belting for a variety of applications, where low tackiness is of crucial importance. The aim of the present study is to gain insight into mechanisms that influence poly(dimethyl siloxane) (PDMS) rubber tack. This includes a study of the influence of network structure, polymer molecular weight, and type of contact on PDMS tack and tack-time dependence.

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EXPERIMENTAL

Materials

Table 1 lists the vinyl-terminated poly(dimethylsiloxanes) that were used for the present study.

The structures of the tri and tetrafunctional silanes used as crosslinkers are shown in Figure 1. A multifunctional silane was also employed, provided by a proprietary source, of which the structure was not disclosed. The platinum-cyclovinylmethylsiloxane complex was used as cure reaction catalyst. All the above materials were

TABLE 1 Materials Characterization: Polymers

Material	Viscosity [Pa · s]	M_w [g/mole]	Average vinyl group content [mmole/kg]	Supplier
MQ 6	100	6 000	~400*)	ABCR
MQ 9	200	9 400	~230*)	ABCR
MQ 17	500	17 000	166	ABCR
MQ 28	1000	28 000	98	ABCR
MQ 50	5000	50 000	64	ABCR

*)the VGC (vinyl group content) varies depending on the batch of polymer used.

The polydispersity of all the polymers used was around 2. The fraction of cyclics is unknown.

obtained from ABCR (Karlsruhe, Germany) with the exception of the multifunctional silane. 1-ethynylcyclohexanol (99%) was used as a temporary reaction inhibitor, as obtained from Aldrich (Sigma-Aldrich, Zwijndrecht, The Netherlands). The solvents used were all of *pro analysi* quality.

Sample Preparations

For every batch of polymer, the exact amount of vinyl groups was determined using NMR measurements (Varian 300 MHz apparatus, Varian, Darmstadt, Germany) 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.

The samples were prepared using H/V ratios of 1.0, 1.2, 1.4, and 1.7, which means starting with the stoichiometric amount, up to 1.7

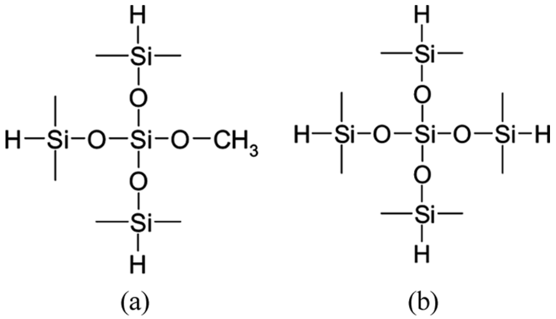

FIGURE 1 Chemical structures of (a) tri and (b) tetrafunctional silane crosslinkers.

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times excess of crosslinker. The curatives were mixed together with the polymer using a magnetic stirrer. During the preparation, it was important that the inhibitor was added to the reaction mixture before the catalyst. Without the presence of the inhibitor, the cure reaction proceeds quickly even at room temperature. While the amount of crosslinker varied depending on the vinyl group content (VGC) of the polymer used, the amounts of catalyst and inhibitor were kept constant at 10 and 50 ppm, respectively. The mixture was degassed and cured in a compression molding machine (WLP 1600/5 × 4/3 Wickert laboratory press, Wickert, Landau, Germany) 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 resulting 90 × 90 × 2 mm sheets were post-cured in an oven at 120°C for 48 hours.

Tack Measurements

Tack measurements were performed using a custom-made device based on the Tel-Tak principle [13]. Pieces of rubber 20 × 20 × 2 mm were used as test samples. Pairs of samples were pressed against orifice disks to generate a curved contact surface (Fig. 2). The curvatures were compressed under 2.5 N load for 10 minutes, and then separated with a speed of 4 mm/sec; the maximum separation force was recorded. For each sample, several tack measurements were done and the average was taken as the final result. The contact area was calculated from the radius of curvature. The measurements were always performed at room temperature. The measuring conditions

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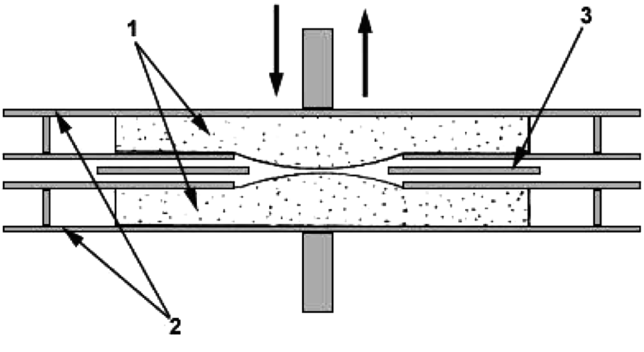

FIGURE 2 The principle of tack-testing device. (1) Rubber samples, (2) Clamps, (3) Separator.

were obviously non-equilibrium, where time effects are the subject of the second paper of this series [14].

Crosslink Density

Crosslink density measurements were made by swelling the rubber samples in toluene for 48 hours. Calculations were performed using the well-known Flory-Rehner equation [15]:

$$\nu = \frac{\chi \mathrm{v}_r^2 + \ln(1 - \mathrm{v}_r) + \mathrm{v}_r}{V_0(0.5\mathrm{v}_r - \mathrm{v}_r^{1/3})} \quad [\mathrm{mol/cm^3}], \tag{1}$$

where ν is the crosslink density, $\mathrm{v_r}$ is the equilibrium volume fraction of rubber in the swollen state, and $\mathrm{V_0}$ is the molar volume of the solvent. A polymer-solvent interaction parameter, χ, of 0.456 [16] was used for all calculations.

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Sol-Gel Analysis

Sol-gel analysis was performed by extracting the samples in toluene for 2 weeks. The samples were then dried until no further mass loss was observed, and then the total weight loss was calculated.

RESULTS

Trifunctional Crosslinker

Figure 3 shows the rubber-rubber tack and crosslink density dependence on hydrogen-to-vinyl (H/V) ratio for PDMS with different molecular weights crosslinked with the trifunctional silane. Note the different scales used for the various PDMS in order to accentuate the large differences in measured tack and, to a lesser extent, in crosslink densities, between the PDMS with varying molecular weights.

The trend observed in crosslink density is interesting. In all cases, the crosslink density increases at first with increasing amount of silane crosslinker. For the stoichiometric amounts of crosslinker (H/V = 1.0), the samples are still clearly undercrosslinked. The crosslink density of MQ 6 rises strongly with increasing H/V ratio between 1.2 and 1.4, reaching a maximum at H/V = 1.4. Then the crosslink density starts to decrease again. A similar trend is observed for MQ 9. The maximum is positioned at the H/V = 1.4 as well, but the crosslink density increase at lower H/V ratios is much smaller: the starting crosslink density at H/V = 1.0 is already quite high, although the overall maximal crosslink density is lower than is the case for MQ 6.

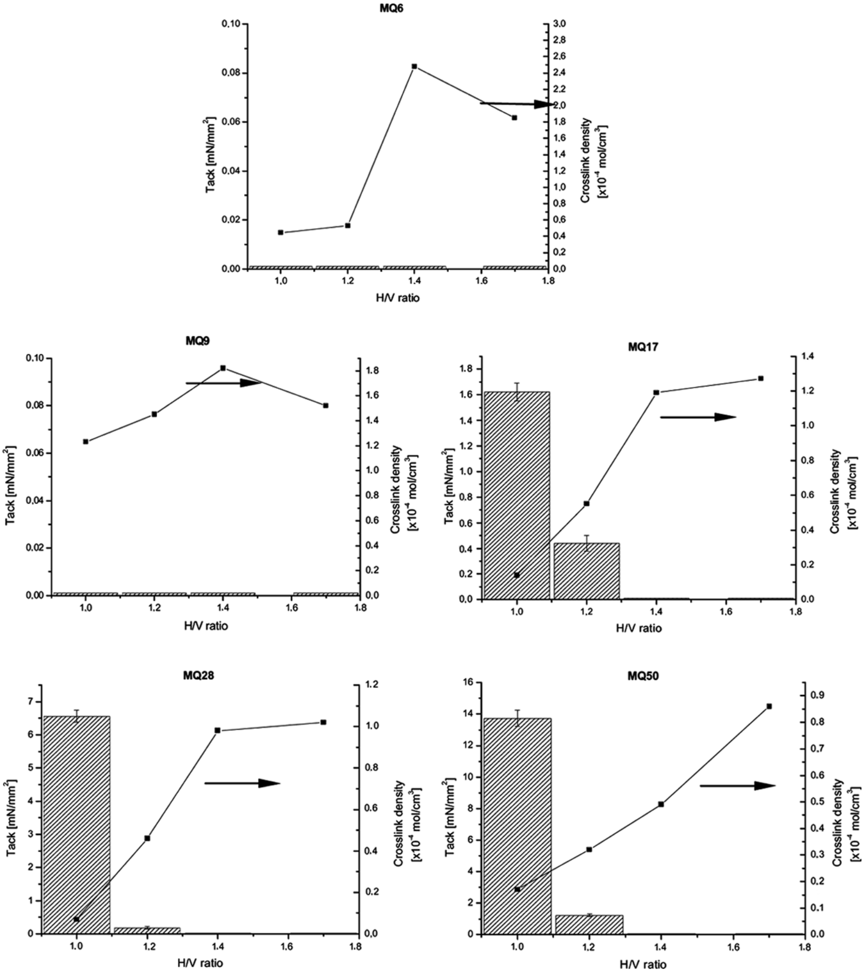

FIGURE 3 Tack and crosslink density of different molecular weight PDMS as a function of H/V ratio. Trifunctional crosslinker.

For both lowest molecular weight PDMS, MQ 6, and MQ 9, no detectable tack can be measured, no matter the crosslink density obtained.

The samples of MQ 17 crosslinked with H/V = 1.0 and 1.2 exhibit detectable values of rubber-rubber tack. Tack decreases with increasing crosslink density, finally falling below the detection level of the apparatus at H/V = 1.4. The absolute tack values are quite low, in the range of 1.6 mN/mm^2 for the lowest crosslinked sample. A small

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increase in crosslink density already causes the tack to drop about four-fold to 0.4 mN/mm^2. The crosslink density trend is somewhat similar to the lowest molecular weight polymer, but the crosslink density increases more linearly with increasing silane excess. It can be seen that at H/V = 1.7 the maximum in crosslink density has not yet been reached. The crosslink density is also much lower than that of MQ 9 and 6.

With molecular weight close to 30,000, MQ 28 starts to exhibit a substantial amount of tack at low crosslinking levels, much larger than the tack of MQ 17 at H/V ratio 1.0. The tackiness levels go down much more quickly, though, with an almost ten-fold decrease with change from H/V = 1.0 to 1.2. At higher crosslink densities rubber-rubber tack again becomes undetectable. The crosslink density trend is very similar to MQ 17: a linear increase at the start followed by the beginning of a maximum. The crosslink maximum or "saturation" point obviously has not been reached in the investigated H/V range.

The highest molecular weight polymer tested, MQ 50, exhibits the highest tack, approximately twice as high as MQ 28. Just as in the case of MQ 28, the rubber-rubber tack levels reduce very quickly with increase in crosslink density, becoming one order of magnitude lower at H/V = 1.2. More highly crosslinked MQ 50 samples do not exhibit any detectable tack, again similar to the other tested PDMS samples. The crosslink density trend of MQ 50 is strictly linear: crosslink density rises in proportion to the increase in silane excess. The plateau visible for lower molecular weight PDMS does not appear in the range tested.

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Tetrafunctional Crosslinker

Figure 4 shows the rubber-rubber tack and crosslink density dependence on the hydrogen-to-vinyl (H/V) ratio for different molecular weight PDMS, crosslinked with the tetrafunctional silane. Note that the same scale is used for the tack values of the various PDMS, but different scales for the crosslink densities.

It can be seen that for the tetrafunctional crosslinker the trend in tackiness change is similar to that for the trifunctional crosslinker. However, the overall values of recorded tack are significantly lower that those seen in Fig. 3. MQ 6 and 9 lack any detectable rubber-rubber tack. Tetrafunctional-crosslinked MQ 17 shows very low tackiness, almost two orders of magnitude lower than MQ 17 crosslinked with the trifunctional silane. The difference is even more pronounced with increased molecular weight: almost three orders of magnitude

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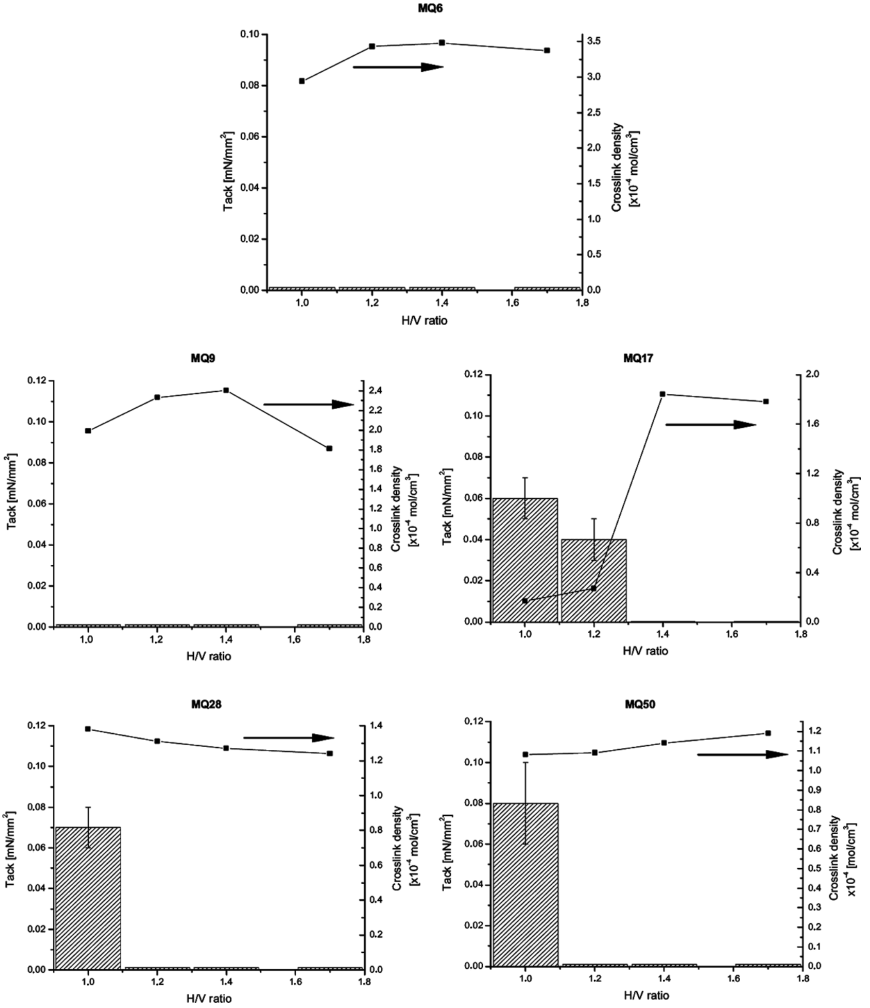

FIGURE 4 Tack and crosslink density of different molecular weight PDMS as a function of H/V ratio. Tetrafunctional crosslinker.

lower in the case of MQ 50. In addition, MQ 28 and 50 no longer exhibit any tack at H/V = 1.2.

The crosslink densities follow a slightly different trend as well; the absolute values are, in general, higher than those of the trifunctional-crosslinked samples at the same H/V ratios. MQ 6 exhibits only a slight increase between H/V ratios 1.0 and 1.2, and then at higher ratios the crosslink density stays more or less constant. MQ 9 shows a maximum at H/V = 1.4, while at H/V = 1.7 the crosslink density drops below the level of H/V = 1.0. The MQ 17 behavior differs from the lower molecular weight polymers: there is a large increase between H/V ratios 1.2 and 1.4, after which the crosslink density reaches a plateau. MQ 28 and 50 exhibit mutually similar behavior: the crosslink densities are almost constant, with a slight decreasing trend for MQ 28 and a slight increase for MQ 50 with increasing H/V ratio. The values of crosslink density of MQ 28 are higher than the values for MQ 50.

Multifunctional Crosslinker

Figure 5 shows the rubber-rubber tack and crosslink density dependence on H/V ratio for MQ 17 and 50, crosslinked with the multifunctional silane.

It can be seen that the increase in crosslinker functionality above four does not cause any further significant changes. MQ 17 and 50 show very similar behavior as in the case of the tetrafunctional crosslinker, only MQ 17 loses tackiness more quickly: there is no detectable tack left at H/V = 1.2.

The changes in rubber-rubber tack caused by the crosslinker functionality are further illustrated in Fig. 6.

The data have been taken for MQ 50 and H/V = 1.0. Using the trifunctional crosslinker gives samples high tackiness, which decreases drastically after increase of crosslinker functionality by one. Further increase in functionality does not cause further significant changes. The effect is basically the same for MQ 17 and 28, although the tack decrease is not as pronounced.

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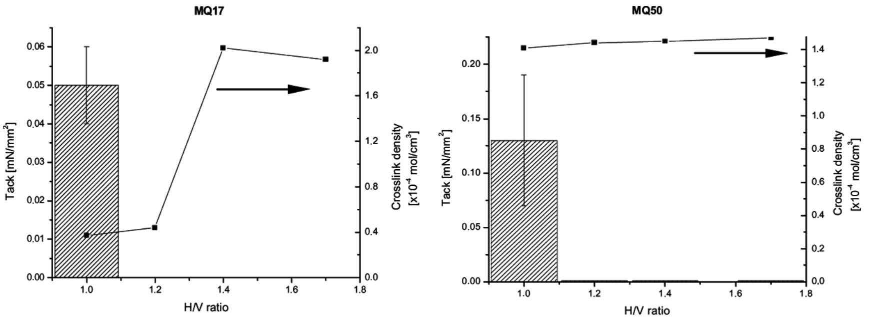

FIGURE 5 Tack and crosslink density of MQ 17 and 50 as a function of H/V ratio. Multifunctional crosslinker.

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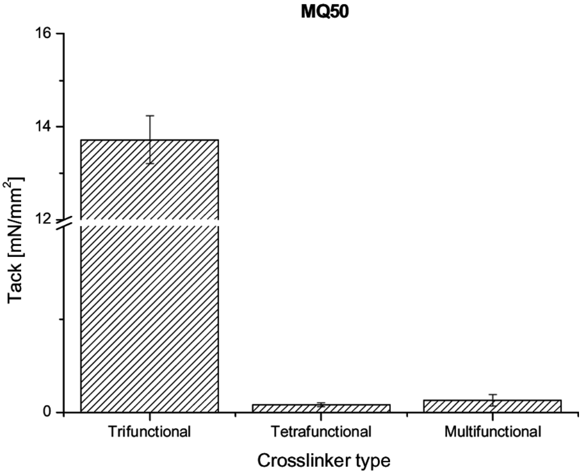

FIGURE 6 The effects of crosslinker functionality on rubber-rubber tack of MQ 50, H/V ratio 1.0.

Sol-Gel Analysis

Figure 7 shows the sol fractions of the crosslinked PDMS samples as a function of H/V ratio for both trifunctional and tetrafunctional crosslinker. In all cases the tetrafunctional crosslinker gives slightly, but significantly, lower sol fractions than the trifunctional one, indicating the better crosslinking ability of the tetrafunctional crosslinker.

The amounts of sol fraction in crosslinked samples correspond well with the trends in crosslink density. MQ 6 samples crosslinked with the trifunctional crosslinker exhibit high amounts of extractable fractions for H/V = 1.0 and 1.2, whereas the amounts drop significantly with higher H/V ratios. For the tetrafunctional crosslinker, the sol fraction stays more or less the same for every MQ 6 sample. MQ 9 exhibits a different behavior. The amounts of sol fraction are smaller than in any other samples, and the sample with H/V = 1.4 and trifunctional crosslinker shows a little higher extractable fraction. The tetrafunctionally crosslinked samples show a trend corresponding to that of crosslink density. A similar situation can be seen in the case of MQ 17: the extractable fractions follow the crosslink density trend closely. The amounts of extractable fraction are, in general, higher than the amounts of low molecular weight polymers, especially for H/V = 1.0.

The high molecular weight PDMS, MQ 28, and MQ 50, perform in a similar manner. Samples crosslinked with the trifunctional crosslinker and H/V = 1.0 have very high sol fraction, which decreases

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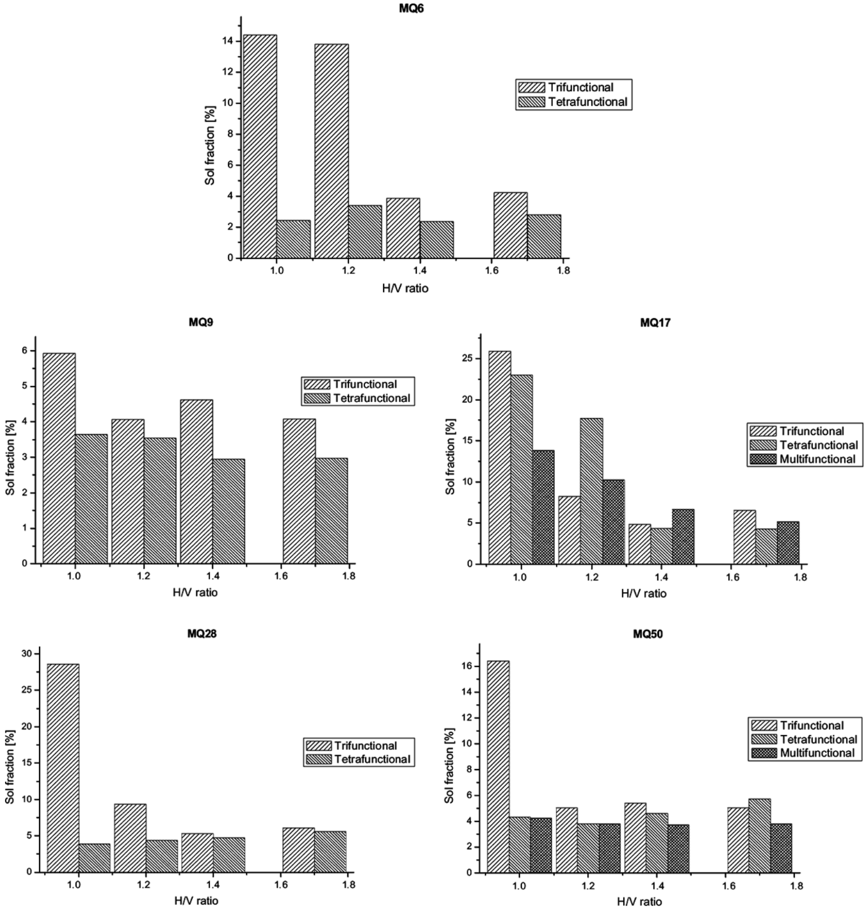

FIGURE 7 The sol fractions as a function of H/V ratio.

quickly with increase in crosslink density. Interestingly, the MQ 50 samples have a lower extractable fraction than the MQ 28 samples crosslinked at the same H/V ratio with trifunctional crosslinker. The changes disappear when crosslinker functionality is increased.

DISCUSSION

The Network Structure and Crosslink Density

The crosslink density-H/V ratio relationships show different trends, depending mostly on the molecular weight of the prepolymer and on the crosslinker type. First, with the densities of all PDMS samples being the same, the maximum attainable crosslink density for MQ 6 would have been eight times as high as for MQ 50, as determined by the ratio of their molecular weights. A correction needs to be made for the fact that, for MQ 6, eight times as much crosslinker needs to be added relative to MQ 50 to correspond to the same H/V ratio. However, this correction does not account for the fact that for MQ 6 in the case of either the tri- or the tetrafunctional crosslinker only approximately three times as high a maximum crosslink density is found. It is an indication of problems involved in obtaining a perfect telechelic network, particularly with the lower molecular weight PDMS.

Trifunctional crosslinker added in stoichiometric amounts, $H/V = 1.0$, to the telechelic PDMS results in low levels of crosslinking. The amount of crosslinker molecules per unit volume is too low for the polymer chain ends to find and attach themselves to the three-fold possible junctions, once the system solidifies. Increasing the crosslinker amount results in a higher probability of reaction occurring, thus the increase in crosslink density. However, this happens at the cost of crosslink junction functionality: from three to a lower value. Once the crosslinker excess reaches some threshold value, the crosslink density approaches a maximum (Fig. 3), and then starts to decrease again. There are most likely only two chain ends left to react with one silane crosslinker molecule in spite of its 3-functionality. But if only two chain ends of a prepolymer react with the crosslinker, then nothing else happens other than a chain extension and, thus, no network formation. So somewhere along the H/V ratio range an optimum exists, where the best possible network is obtained. However, unfortunately, not a perfect telechelic network. The more so, the lower the molecular weight of the prepolymer, because there are more crosslink sites competing with each other for crosslinkable chain ends. Therefore, the position of the maximum is dependent on the molecular weight of the prepolymer: where the maximum is reached at silane excess 1.4 for MQ 6 and MQ 9, MQ 17 and MQ 28 approach their plateau at 1.7. For the high molecular weight MQ 50 the “oversaturation” level is not reached within the measured range. The mobility of the long prepolymer chains and the availability of crosslink sites are too low, so that even a 1.7 times excess of crosslinker still causes a further increase in crosslink density. Interestingly, MQ 50 shows a slightly higher crosslink density at $H/V = 1.0$ than MQ 17. This is most likely the influence of the measurement method used. During determination of crosslink density by equilibrium swelling chain entanglements are

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also taken into account. MQ 50 with its long chains forms a loosely crosslinked network with a small amount of chemical, but lots of physical crosslinks, such as the entanglements.

Increase in crosslinker functionality from three to four does not create large behavioral changes in the case of the low molecular weight polymers, except that the crosslink density is, in general, higher as explained before. MQ 6 and MQ 9 show maxima in crosslink density *vs.* H/V ratio, but shifted to somewhat lower H/V ratio relative to the trifunctional crosslinker. Obviously, because of the increase in available crosslink sites per crosslinker molecule, the chance of simple chain extension by mere two-fold attachment is much lower. The high molecular weight polymers, MQ 28 and MQ 50, behave in a most conspicuously different manner than when crosslinked with the trifunctional silane. Both of the polymers show a saturation effect, crosslink density is high, and an increase in crosslinker excess causes only relatively small changes. This seems to be contradictory behavior, if we consider that the concentration of tetrafunctional silane molecules in the reaction mixture is actually smaller for the same H/V ratio than for the trifunctional ones. However, it confirms that the tetrafunctional crosslinker is much more effective compared with the trifunctional one by its reduced chance of chain extension. The actual maximum in crosslink density for MQ 28 and MQ 50 for the tetrafunctional crosslinker is therefore reached at H/V ratios close to 1.0. At higher H/V ratios a decrease of crosslink density should happen again (theoretically); however, the effect is so little that either a small increase or a small decrease may be found, depending on experimental variations. Samples crosslinked with tetrafunctional silane have a much lower extractable fraction than samples crosslinked with the trifunctional one, which supports this conclusion.

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A point of concern is that the surface crosslink density may be somewhat different from the bulk. The platinum cured systems are inhibited by the presence of oxygen, and the concentrations of crosslinker and inhibitor may enrich or deplete the surface, depending on the interface formed in the mold.

MQ 17 behaves a little bit differently, in particular in the case of the tetrafunctional crosslinker. We tend to relate this to either a somewhat less well defined molecular structure of the MQ 17 prepolymer (not extensively investigated) or experimental variations in preparing the compounds for the curing process.

The little difference in behavior after further increase in functionality of the crosslinker to the polyfunctional one is now an obvious matter. There are problems with reacting all, or even most, of the silane groups on the crosslinker, in addition to troubles with getting a relatively large number of polymer chain ends all into a small space next to the crosslinker molecule [17]. However, the large surplus of crosslinking sites on the crosslinker makes sure that practically all crosslinks have a functionality of at least three, and so contribute to network formation and not to chain extension.

Tack

There is a clear trend visible: the rubber-rubber tack decreases sharply with increase in crosslink density for most of the combinations investigated. This phenomenon has been observed for many types of polymers [18,19]: although crosslinking of a polymer melt may initially increase tack, further increase in crosslink density causes the opposite effect. Lower crosslink density results in larger amounts of unattached chains, pendent 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. Naturally, during the contact polymers may also exchange other interactions, like van der Waals forces or hydrogen bonding. However, 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 [20]. The contribution from these is negligible; thus, the tack increase for low crosslink densities is mainly due to the presence of pendent chains and increased chain mobility. In the telechelic networks, crosslink sites are situated at the ends of the polymer chains; thus, free chains and pendent (dangling) chains are the most common defects [21]. Taking this into consideration, the mechanism of tack formation can be explained on the basis of the de Gennes reptation model. Crosslinking creates topological constraints—a crosslinked polymer network can be considered as fixed obstacles, limiting the movement of chains. Secondly, increasing the amount of crosslinker increases the probability that the chain will get attached to more than one crosslinking site, thus, being effectively trapped and unable to cross the interface. This explains the fast tack decrease with increase in the H/V ratio, particularly for the tetrafunctional crosslinkers, where a much lower chance of chain extension exists, which otherwise still would have allowed reptation and crossing of the interface.

The samples of MQ 6 and 9 in Figs. 3 and 4 exhibit no detectable tack at all. It could be expected that very low molecular weight polymer would create many more pendent and unattached chains per unit of volume than higher molecular weight species. A different mechanism comes into play, though. In order to create a strong

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enough interface to result in measurable tack, polymer chains do not only have to cross the interface, but also entangle on the other side. Thus, the molecular weight (and length) of the pendent and loose chains should be at least equal to the critical molecular weight needed to form entanglements. The borderline for PDMS seems to be a molecular weight of around sixteen thousand [22,23]; MQ 6 and 9 are, thus, physically unable to form entanglements, which severely limits the possibility of creating interface strength. MQ 17 is just borderline, which may explain its somewhat erratic behavior.

The increase in molecular weight of the polymer results in large increase in tack values for the samples crosslinked with the trifunctional silane (Fig. 3). Again, the balance between the decreasing amount of possible bonds and consequent pendent and loose chains, because of increase in molecular weight, and increased ability of the chains to penetrate the interface and entangle, should be taken into account. Also, during separation the chains are extended before full release. The extensions and disentanglements cost more energy for the longer, higher molecular weight chains [24], also resulting in more energy dissipation.

From a perspective of PSAs, there are three points to be taken into account. During the bonding phase good flow is required. This is not the case: the tested PDMS is a crosslinked material compared with un-crosslinked PSAs and, as such, exhibits much worse flow behavior. In the relaxation phase the molecular mobility is important. Silicone elastomers are known for their high molecular mobility, because of a very large free volume, thus, accelerating the rearrangement processes to very short timescales. Viscoelastic effects, as seen in common PSAs, play a much less important role in this PDMS since it is already crosslinked. Finally, in the debonding phase, the tested polymer has a very high cohesive strength relative to the stresses needed for debonding, due to the crosslinking. The question remains, though, if it is enough to still cause a significant contribution from viscoelasticity in adhesive joint failure.

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CONCLUSIONS

For telechelic PDMS the trends in crosslink density are strongly affected by the molecular weight of the prepolymer and by the crosslinker functionality. High molecular weight prepolymers react strongly to changes in crosslinker functionality, whereas low molecular weight species only increase the overall crosslink density. On the other hand, low molecular weight PDMS strongly react to crosslinker excess, showing saturation effects on the crosslink density.

The network structure of telechelic polymer has a very substantial influence on rubber-rubber tack. The pendent and left-over loose chains created during the crosslinking reaction must be able to reptate through the interface and entangle on the other side to contribute to the overall strength. For the very low molecular weight rubbers, MQ 6 and MQ 9, where no tack is detected due to their inability to entangle at the other side of the interface, their molecular weight is substantially lower than the critical molecular weight between entanglements. When the possibility of entanglement increases, rubber-rubber tack increases significantly. Using crosslinkers with higher functionality and, hence, better ability to bind polymer chains leads to a large decrease in tack, as visible especially for the high molecular weight silicone rubber, MQ 50.

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