

The Influence of Loose and Semianchored Siloxane Polymer Chains on the Tack of Crosslinked Silicone Rubber

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ABSTRACT: The influence of addition of nonreactive silicone oil or semianchored silicone polymer on crosslinked poly(dimethylsiloxane) (PDMS) rubber–rubber adhesion was studied. The additives can be considered either a tackifier, or connector molecules, able to cross the interface and entangle. In both cases, it influences the tack of the elastomers. An additional variable is the molecular weight of the additive, which affects the reptation of the polymer chains. Polymer–polymer demixing, which is the result of thermodynamic incompatibility of mixed polymers is another factor that influences tack. It causes the free chains to appear at the surface forming a layer of oil, which

actually destroys the tack of the PDMS samples. The resulting tack phenomena as a function of oil, respectively semianchored silicone polymer chains, are very much dependent on the transient nature of the polymer reptation: in many cases the polymers need very long time periods to obtain equilibrium in interphase crossing, or oil sweats out of the crosslinked polymers, forming a liquid layer between the two phases resulting in a low tack value, due to hydrodynamic wetting alone. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1357–1364, 2009

Key words: rubber; PDMS; tack; adhesion; diffusion

INTRODUCTION

The interdiffusion and entanglements of polymer chains are the most important factors responsible for polymer adhesion.^{1,2} Reptating polymer chains may cross the interface and entangle on the other side, thus contributing to the overall interface strength. In this article the possible role of free, nonattached silicone polymers and of silicone polymer purposely linked to the network on one side only (semianchored) on adhesion of crosslinked similar silicone rubber will be highlighted.

Polymer–polymer miscibility

For most polymers it is thermodynamically unfavorable to form homogenous mixtures with each other.³ The necessary requirement for miscibility is:

$$\Delta G = \Delta H - T\Delta S < 0 \quad (1)$$

where ΔG , ΔH , and ΔS are the Gibbs free energy, enthalpy and entropy of mixing, respectively. The

contribution of the entropy change for polymers is generally small due to their large molecular weights. On the other hand, the enthalpy change in general is positive for most nonpolar polymers; thus the necessary Gibbs energy change is hardly ever negative. The miscibility can be improved by introducing strong interactions between the mixed polymers, which results in a negative specific heat of mixing.

The problem of polymer compatibility on chains interpenetration, and as a result adhesion, was already early investigated by Voyutskii et al.^{4,5} The adhesion strength of incompatible polymers decreased with the increase in difference in solubility parameters. The polymers were still capable of mutual interdiffusion.

Free chain diffusion in poly(dimethylsiloxane)

Because of the common chain structure, poly(dimethylsiloxane) (PDMS) polymer chains can easily penetrate into a crosslinked PDMS matrix. The characterization of the diffusion of different molecular weight PDMS loose chains (oils) into a siloxane matrix led to the following observations:

- The chain penetration is heavily influenced by the network mesh size (crosslink density) and

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the length of penetrating chains. It is obvious, that the longer the polymer chain, the longer it takes to "crawl" between the obstacles;⁶ the penetration depth is lower as well.

- The diffusivity of linear PDMS oil is approximately independent of molecular mass for polymers with molecular weight below the PDMS critical M_e needed to form entanglements.⁷

Silicone oil, because of the very low surface energy of the siloxane liquid, tends to phase separate and diffuse from the bulk to the surface. Depending on the application, this can be a very beneficial or an unwanted phenomenon!

Influence of oil additives on adhesion of elastomers

Depending on the point of view, an oil additive can be considered as a tackifier or as connector molecules. In both cases it promotes adhesion. A tackifier loosens up the entanglement network and so increases the compliance.⁸ An excess of additive should be avoided in order not to weaken the rubber. This feature is a function of the molecular weight of the tackifier: if the molecular weight is too high it will act as an incompatible solid, stiffening and strengthening the elastomer but preventing wetting.⁹ On the other hand, if it is too low, the tackifier may act as a plasticizer, which to a certain extent promotes tack. In addition, tackifiers with bad compatibility with the elastomer or used in large amounts can migrate to the surface, thereby lowering tack.¹⁰ Thus, the effect of tackifier addition to a rubber can influence tack either from the side of surface energetics, or by an influence on the bulk viscoelastic properties. The latter is especially important during the bonding stage of a compression test: reduction in modulus (increase in compliance) is reflected in easier viscous flow. That may enable better contact formation in the early stages of the test, and hence increase the rate with which intimate molecular contact is achieved. The influence of a tackifier on the debonding stage is difficult to estimate, since it depends heavily on the type of contact. It was already mentioned, however, that tackifier addition affects the bulk properties, and thus affects energy dissipation processes.¹¹

The effect on surface energy of a tested system is associated with the possibility of migration of the tackifier to the surface of the sample. The effects can vary a lot, because the migrating additive can promote wetting, and thus increase tack, but can also form a layer between the contacting surfaces, effectively lowering tack. Separating the surface energy influence from the bulk effects during tack testing is a very difficult task. The general perception is that a

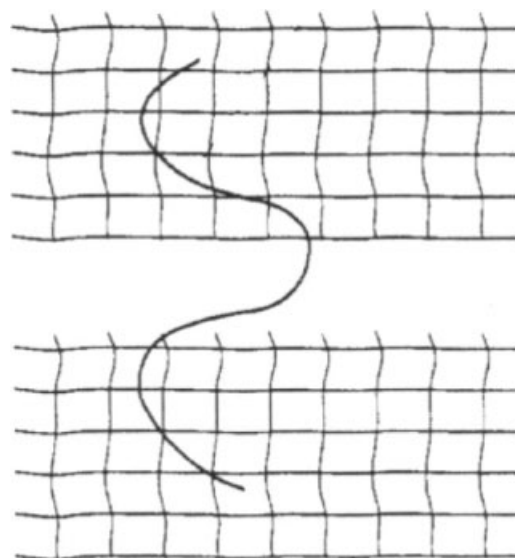


Figure 1 The connector molecule between two identical rubber blocks¹³.

large effect on tack can be expected if the tackifier causes appreciable changes in surface energy. Small changes do not affect the wetting stage, and the change in thermodynamic work of adhesion is too small to influence the debonding force.

The influence of the amount of added tackifier on tack seems to follow a similar trend, not depending on the elastomer and tackifier type: first, tack increases with increasing concentration of tackifier, but after reaching a certain threshold level it starts to go down. Curves of this kind were first noted by Wetzel,¹² who interpreted them in terms of a two-phase character of a rubber-tackifier system and the presence of the maximum was attributed to a phase inversion. However, this does not explain similar behaviors noticed in the case of single-phase systems. The effect is there correlated with the influence of the tackifier on the debonding process¹¹.

Mobile chains between two rubber blocks

The problem of mobile polymer chains connecting two identical rubber blocks and forming a loose bridge has been theoretically investigated by Brochard-Wyart et al.¹³ The single loose bridge is shown in Figure 1.

Theoretical analysis of such "many stitch" systems shows, that the influence of connector molecules on adhesion or fracture energy can be given:

$$G_f \sim \phi N_p^{1/2} \gamma \quad (2)$$

with ϕ being the volume fraction of connector polymer chains, N_p their degree of polymerization and γ surface tension of a melt of connector molecules. This equation applies only to the regime of very low

TABLE I
Materials Characterization: Polymers

Material	Viscosity (Pa s)	M_w (g/mole)	Average VGC (mmol/kg)	Supplier
MQ 6	100	6000	~ 400 ^a	ABCR
MQ 9	200	9400	~ 230 ^a	ABCR
MQ 17	500	17,000	166	ABCR
MQ 28	1000	28,000	98	ABCR
MQ 50	5000	50,000	64	ABCR
MQ 63	10,000	63,000	25	ABCR

^a The VGC varies depending on the batch of polymer used.

separation speeds, where viscoelastic relaxation near a separation front is not important.

EXPERIMENTAL

Materials

The PDMS rubbers used for the study are listed in Table I. Monovinyl-terminated PDMS, MQ 63, with molecular weight of 63,000 g/mol and average vinyl group content (VGC) of 25 mmol/kg was used as an additive. A trifunctional silane, tri(dimethylsiloxy)-methoxysilane, was used as crosslinker. A platinum-cyclovinylnmethylsiloxane complex was used as cure reaction catalyst. Ethyldimethylhydrosilane (monofunctional) was used as end-capping agent. All the above materials were obtained from ABCR, Germany. 1-ethynylcyclohexanol (99%) was used as a temporary reaction inhibitor, as obtained from Aldrich. The solvents used were all of LR/AR grade.

Preparations of unreactive chains

The reaction is schematically shown in Figure 2. Unreactive siloxane polymer chains with different molecular weights were synthesized through a hydrosilylation reaction of the MQ rubbers with monofunctional silane. A 5% excess over a stoichiometric amount of silane was added to a flask containing vinyl-terminated PDMS polymer. Then 10 ppm of catalyst was added and the reaction mixture was heated to 120°C and allowed to react, while constantly stirred. The extent of hydrosilylation reac-

tion was checked periodically using NMR and IR. The disappearance of NMR vinyl peaks (δ 5.6 – 6.2 ppm) was used as an indication of full polymer conversion. The IR silane peak at around 2160 cm^{-1} was used to check if there was still silane present. If so, the mixture was stirred further, until the leftover silane groups were oxidized, so that they could not interfere with the subsequent crosslinking reaction anymore.

Loose chains samples preparation

For every batch of polymer the exact amount of vinyl groups was determined using NMR measurements (Varian 300 MHz apparatus) with pyrazine as an internal standard. The results of these measurements are included in Table I. From those results and the molecular structure of the crosslinker, the hydrogen-to-vinyl ratio (H/V) was calculated. Preliminary experiments had shown, that MQ17 crosslinked with H/V ratio 1.7 does not exhibit any detectable tack. Thus crosslinked samples were based on MQ17 with H/V ratio of 1.7 as a matrix. This composition ensures that the PDMS matrix does not have any detectable tack by itself, and thus does not interfere with measurements. Before the curatives, unreactive loose chains were added to the prepolymer in amounts ranging from 5 to 120 wt %. It was impossible to make samples with higher quantities of loose chains, because these samples did not cure anymore. Then the curatives were mixed together with the polymer and unreactive chains 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 proceeded quickly even at room temperature. While the amount of crosslinker varied depending on the VGC of the polymer used, the amounts of catalyst and inhibitor were kept constant: 10 and 50 ppm, respectively. The mixture was degassed and cured in a compression molding machine Wickert laboratory press (1600/5 \times 4/3) 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 \times 90 \times 2 mm sheets were post-cured in an oven at 120°C for 48 h.

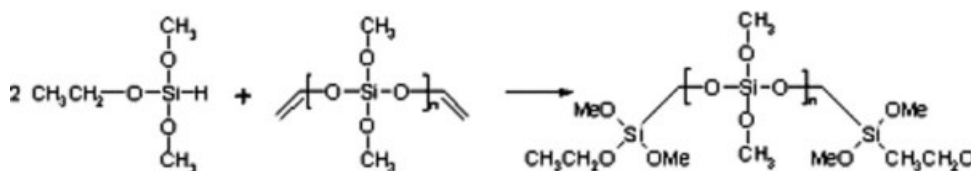


Figure 2 The schematic of the chain blocking reaction.

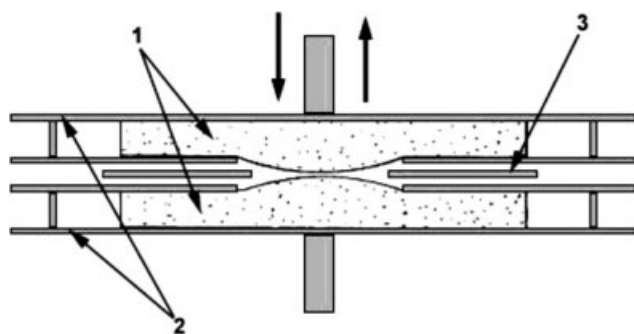


Figure 3 The principle of tack-testing device. (1) Rubber samples (2) Clamps (3) Separator.

Preparation of samples with monofunctional chains

Samples with embedded monofunctional chains were prepared in a similar way as samples with embedded unreactive loose chains. The amount of crosslinker was adjusted based on the amount of monofunctional prepolymer added, so the H/V ratio was always kept constant at 1.7.

Tack measurements

Tack measurements were performed using a custom-made device based on the Tel-Tak principle.¹⁴ 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: Figure 3. The curvatures were compressed under 2.5 N load for 10 min, and then separated with a speed of 4 mm/s; 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 a temperature of around 20°C.

Crosslink density

Crosslink density measurements were made by swelling the rubber samples in toluene for 48 h; calculations were performed using the well-known Flory-Rehner equation:¹⁵

$$v = \frac{\chi v_r^2 + \ln(1 - v_r) + v_r}{V_0(0.5v_r - v_r^{1/3})} \text{ (mol/cm}^2\text{)}, \quad (3)$$

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. A polymer-solvent interaction parameter χ of 0.456¹⁶ was used for all calculations.

DSC measurements

DSC measurements were performed using a Perkin-Elmer DSC 7 machine with Pyris version 8.0 soft-

ware. Samples weighing about 10 mg were put into aluminum pans, cooled rapidly to -170°C from room temperature and then heated at $10^\circ\text{C}/\text{min}$.

RESULTS

The influence of loose PDMS chains on tack

Figure 4 shows how the amount of blocked, unreactive chains derived from MQ17 influences the tack and crosslink density of silicone rubber samples. These chains cannot react with the crosslinker and remain loosely embedded in the otherwise crosslinked matrix of MQ17.

A small addition of blocked loose chains does not have any influence on the MQ17 tack. When the amount of loose silicone molecules or oil reaches 7.5 wt %, the rubber starts to show some detectable tack, however still very low. If the amount of silicone oil in the samples is further increased, the tack disappears again. When the amount of loose chains reaches 100 phr, i.e. 50 wt % of the sample, the rubber-rubber tack rises again, with values higher than previously measured. Above 55 wt % of silicone oil added, the tack starts to decrease again. It is important to note, that samples having more than 50 wt % of silicone oil were already gel-like, and the addition of more than 60 wt % of oil resulted in complete inability of the samples to crosslink.

The first detectable tack appears in a region, where the crosslink density of the samples is stable and does not change with the increasing amount of oil additive. It starts to decrease only after the amount of loose siloxane chains exceeds 15 wt %. The decrease is very pronounced at the beginning, and then crosslink density lowers down slower. Crosslink density of the highest oil-containing

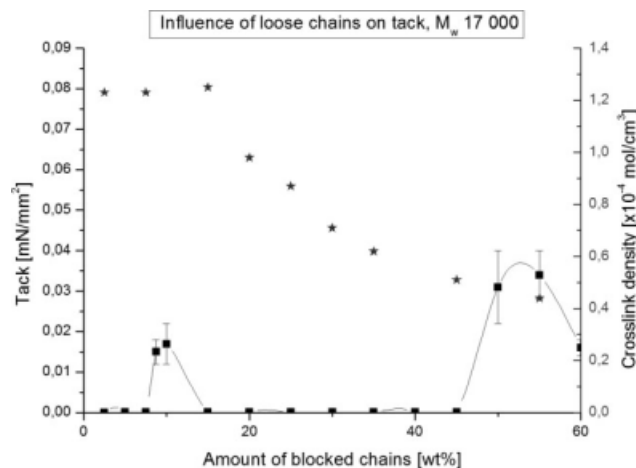


Figure 4 The influence of the amount of loose chains on the PDMS rubber tack. M_w of loose chains: 17,000 g/mol. The line is intended to guide the eye.

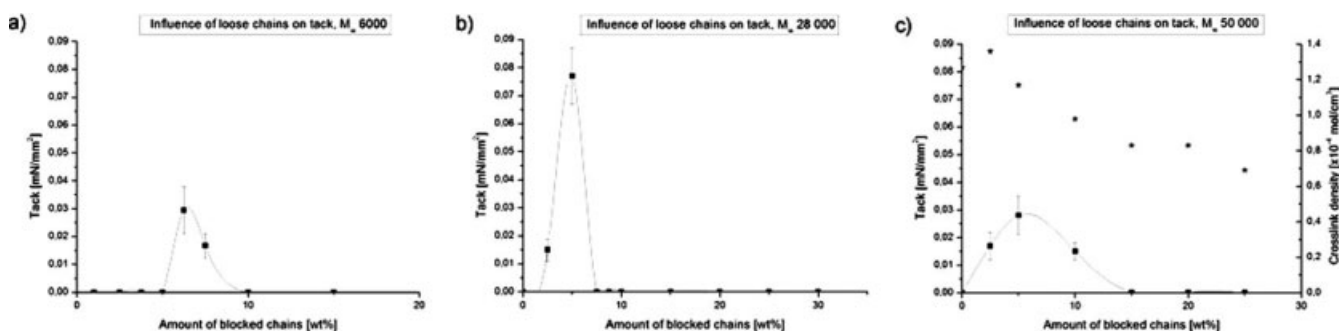


Figure 5 The influence of the amount of loose chains and their molecular weight on the PDMS rubber tack. The lines are intended to guide the eye.

sample was impossible to measure, because the sample almost dissolved during swelling.

Figure 5 shows the influence of the molecular weight of the loose chains and their amount on the tack of a network based on MQ17. As can be seen, the addition of very low molecular weight loose PDMS chains MQ6, also promotes tack, at a similar level as MQ17-based loose chains, which was shown previously in Figure 4. However, the tack increase happens at a higher amount of additive than is in case for MQ17-based loose chains. Besides that, the picture is similar: the tack rises at a certain amount of loose silicone oil added and later goes down to zero again. The addition of blocked loose MQ28-based chains results in much higher absolute levels of tack achieved, as well as in a shift to smaller amounts of oil needed to achieve that tack. After that, like in the two previous cases, tack lowers down to zero after a certain amount of oil is embedded in the samples. It is interesting, that the tack after addition of blocked MQ50-based chains is much lower than after addition of MQ28-based chains. The maximum also spans a broader range of additive amounts.

Crosslink density measurements were also performed for the samples with addition of MQ50-based blocked chains. The trend is the same as in the case of MQ17-based chains: the crosslink density initially stays constant, but this period is much smaller than in the case of MQ17-based loose chains addition. Actually, there is a small increase in crosslink density after some MQ50-based loose chains were added, but most probably this is a reflection of an increased amount of physical entanglements. The increased tack region already coincides with the area of decrease in overall crosslink density of the tested samples.

The influence of semianchored PDMS chains on tack

Figure 6 shows the influence of the addition of semi-anchored, monofunctional PDMS chains of M_w

63,000 on tack of MQ17 samples. The tack of samples with some amount of monofunctional PDMS chains added behaves in a different way than the tack of samples with loose PDMS chains. In the range measured, the tack rises slowly but steadily with the addition of monofunctional chains, and seems to reach a plateau after 15 wt % are added. The values of tack are very low, lower than the tack of samples with MQ6 chains added, however still detectable.

The influence of loose PDMS chains on tack as a function of molecular weight

The influence of addition of loose chains of various molecular weights is better visible in Figure 7, where the amount of loose chains was recalculated from wt % to mmol, on basis of the initial average vinyl-group content of the blocked chains.

The shorter the chains are, the more is needed to induce tack. For $M_w = 6\ 000$ tack starts to appear at

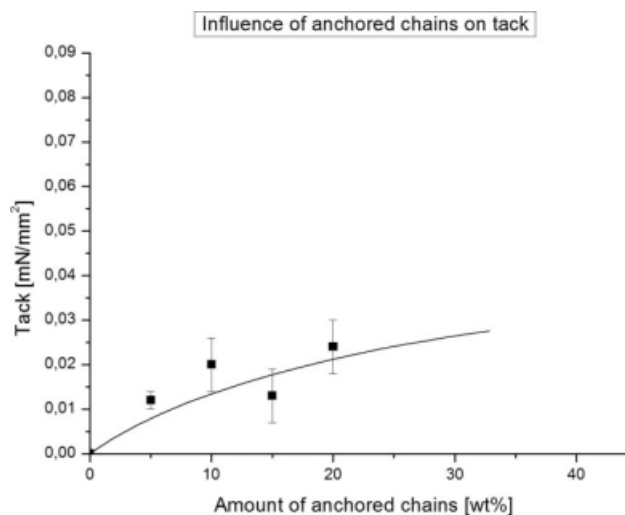


Figure 6 The influence of the amount of semianchored chains of M_w of 63,000 on the PDMS rubber tack. The line is intended to guide the eye.

around 2.5 mmols addition. This point shifts to 1.3 mmols for the molecular weight of 17,000, 0.7 for 28,000 and 0.4 for 50,000 molecular weight. The semianchored, monofunctional chains addition works slightly different: the tack shows up at 0.25 mmols of chains added and then rises slowly with the amount of monofunctional chains in the sample.

Figure 7 also clearly shows the quantitative differences in tack caused by the addition of different molecular weights of the blocked chains. The effect of MQ6 and MQ17 is similar, even slightly larger for MQ6. MQ28 addition causes a relatively large tack increase, and the tack caused by the addition of MQ50 is again small, on the level of MQ6.

Glass transition temperature

On the DSC curves of samples with blocked chains two glass transition temperatures are commonly present, at around -150°C and -120°C . The first one corresponds to the glass transition temperature of a siloxane prepolymer, the second one then should be the glass transition of the cured PDMS matrix.¹⁷ The dependence of the transitions on the amount of blocked MQ17 chains in the polymer matrix is shown in Table II. The dash indicates the spectra, where the presence of a T_g could not be unequivocally detected.

The lower T_g does not depend on the amount of blocked chains added in the samples, but the higher T_g shifts suddenly upon the addition of loose chains from -90°C for the fully crosslinked MQ17 sample without any additive, to -112°C for only 5 wt % of blocked chains added, and further to -120°C for 10 wt % of unreactive chains. Further increase in the amount of additive did not cause a substantial T_g shift.

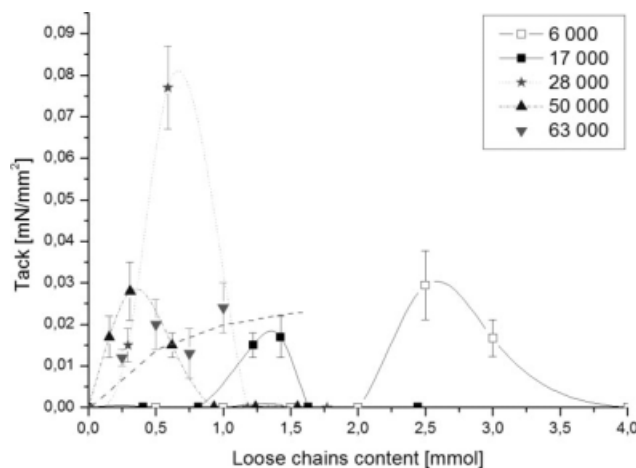


Figure 7 The tack as a function of amount of blocked loose chains – an overview. The lines are intended to guide the eye.

TABLE II
Glass Transition Temperatures for the Samples With MQ17-Based Blocked Chains Added

Amount of blocked MQ17 chains [wt%]	T_{g1}	T_{g2}
0	None	-90
5	-148	-112
10	-148	-120
15	-142	–
25	-148	-120
30	-150	-120
35	-148	-122
40	-145	-122
45	-145	-120
50	–	-120

DISCUSSION

The addition of free, not crosslinkable chains to a crosslinked PDMS matrix does influence the tack of the crosslinked polymer. Figure 4 shows, that this influence can be divided into two regions: the tack rises, disappears and rises again. The second tack maximum appears at more than 40 wt % addition; at this point the noncrosslinkable siloxane oil addition has substantially loosened the polymer network already. It should be noted, that the preparation of samples resembles the preparation of polymer gels, with the unreactive chains acting as a solvent. The tack increase after a large addition of loose chains results in a large decrease in crosslink density, thus decrease in the sample's modulus. The resulting tack is a combined effect of viscoelastic flow and a heavily diluted network.

The first maximum in tack is far more interesting. The addition of uncrosslinked siloxane chains can work in two ways: one is already mentioned as diluting the crosslinked network, what is usually combined with a decrease in segmental friction⁸, so that the chains can much easier penetrate and entangle. This is the general effect of a tackifier. The second mechanism is an increased amount of free chains, which can diffuse through the interface and entangle on the other side, thus increase tack.

The important factor to take into account is the critical molecular weight of PDMS, above which it can only form entanglements. The borderline for PDMS seems to be a molecular weight of around 16,000.¹⁸ Thus MQ6 should be completely unable to form entanglements and MQ17 is a borderline case. It can be seen in Figures 4 and 5 that both of them still promote tack, when added in small amounts to the crosslinked PDMS samples. Since none or just very few entanglements can be formed, this should be an effect of network loosening.

With the increase of molecular weight of the uncrosslinked chains the tack first increases for MQ28 and then decreases again for MQ50: see

Figure 7. This may seem contradictory at first glance, but there are several aspects to take into account. First of all, the MQ28 polymer is the first one from the series tested that can form entanglements. This explains the almost threefold increase in tack. Following the same reasoning, addition of MQ50 chains should increase the tack even more. However, their molecular weights differ by a factor of 1.8 in comparison with MQ28. If it is assumed, that a chain reptation is the factor responsible for the tack increase, then MQ50 chains would need $5.8\times$ longer time to achieve a similar level of interpenetration, since the reptation time scales with the third power of molecular mass of the polymer.¹⁹ Thus, on the timescale of the experiment, the MQ50 chains may not have had sufficient time to reptate and entangle to their full extent.

The addition of monofunctional semianchored PDMS chains also promotes tack. Still, the situation here is slightly different from the case of free, uncrosslinked chains. Monofunctional chains are anchored to the polymer matrix at least on one side; the interdiffusion or reptation will therefore be seriously hampered, which is visible in Figure 6. The tack detected is very low, lower than the MQ17 addition effect. However, even an addition of a small amount of anchored chains gives a detectable tack as a result, which rises with increasing quantity of the additive. The molecular weight of the monofunctional PDMS can be partially responsible for this effect; the monofunctional chains have a M_w of 63,000, even larger than for MQ50.

The effect is better visible in Figure 7, where the amounts of additives were recalculated to milimols of chains, on the basis of the average vinyl group content of the blocked and monofunctional polymer. The amount of MQ6 chains needed to induce tack is far larger than the amount of MQ17 chains. This may actually explain the higher tack after MQ6 addition: the possible network dilution is larger. With the increase in molecular weight of the additive, the tack maximum shifts towards lower amounts of blocked polymer chains. Starting from the MQ17, PDMS chains are able to entangle; the longer the chain, the more entanglement formation is possible. Figure 7 illustrates the difference between semianchored chains and loose chains as well. Addition of loose chains causes a sharp increase, and then decrease in tack, whereas tack created by semianchored chains rises slowly.

The question remains, why there is a sudden tack decrease after the addition of loose chains. If we consider the mixing of two polymers, as it was described in the introduction, we may see that the enthalpy of mixing, ΔH , will be most probably close or equal to zero: both polymers are essentially the same PDMS. The change in entropy, however, can

be large and negative. The loose chains are restricted in their mobility after being embedded in the crosslinked matrix. Thus, the overall change in Gibb's free energy of mixing will be positive – the system will tend to demix and PDMS uncrosslinked chains will diffuse to the surface of the samples. This phenomenon can be even promoted by the testing procedure, where samples stay under compression for a certain period of time. PDMS oil will then gather on the surface forming a layer of liquid with a very low surface tension. As a result, the tack disappears when more uncrosslinked chains are added. Anchored chains, due to the fact that they are crosslinked to the matrix on one side, cannot demix. They may only be able to partially migrate to the surface.

The DSC data confirm the fact, that the systems containing uncrosslinked PDMS chains embedded in the crosslinked PDMS matrix are immiscible. If they were fully miscible, the presence of only one T_g should be expected. On most of the curves two glass transition temperatures are present, a proof of phase separation.²⁰

It should be noted, that the tack of systems with free, uncrosslinked chains purposefully added to a crosslinked matrix is a complicated phenomenon. The polymer–polymer demixing, and as a result oil gathering on the surface of samples, is an unavoidable factor which is in addition hard to quantify. The molecular weight–tack dependence of these chains deserves therefore far more in-depth study to fully understand their influence on tack formation.

CONCLUSIONS

The addition of uncrosslinked and mobile siloxane chains to a crosslinked PDMS matrix influences rubber–rubber tack to a small extent. The increase is quite small and visible only for minor quantities of the additive. Further addition of uncrosslinked chains results in a tack reduction. The tack is influenced by the molecular weight of the loose chains – the higher, the less material is needed to induce tack. This dependence is more complicated: increase in molecular weight causes first a tack increase, then a decrease again. This effect is most probably caused by the timescale needed for the chains to reptate and entangle.

The tack disappearance at large amounts of mobile chains added is caused by migration of the PDMS oil to the samples' surface and the formation of a liquid layer. Because of this layer, two sides of the interface cannot come into direct, molecular contact, and further interface strengthening is then restricted. This problem does not exist if the chains are somehow attached to the matrix. The addition of monofunctional, semianchored PDMS polymer that

can be vulcanized into the network does not seem to cause such a layer formation.

References

1. Wool, R. P.; Lee, L. H., Ed. *Fundamentals of Adhesion*; Plenum Press: New York, 1991.
2. Prager, S.; Tirrell, M. *J Chem Phys* 1981, 75, 5194.
3. Kammer, H. W. *Acta Polym* 1983, 34, 112.
4. Voyutskii, S. S. *Autohesion and Adhesion of High Polymers*, Wiley: New York, 1963.
5. Kamenskii, A. N.; Fodiman, N. M.; Voyutskii, S. S. *Vysokomol Soyed* 1969, 11, 394.
6. Mazan, J.; Leclerc, B.; Galandrin, N.; Couarraze, G. *Eur Polym J* 1995, 8, 803.
7. Gedde, U. W.; Hellebuyck, A.; Hedenqvist, M. *Polym Eng Sci* 1996, 36, 2077.
8. Kraus, G.; Rollmann, K. W.; Gray, R. A. *J Adhes* 1979, 10, 221.
9. Gent, A. N.; Hamed, G. R. *Elastomer Technology – Special Topics*; ACS Rubber Division: Akron Ohio, 2003.
10. Hamed, G. R.; Roberts, G. D. *J Adhes* 1994, 47, 95.
11. Aubray, D. W. *Rubb Chem Technol* 1988, 61, 448.
12. Wetzel, F. H. *Rubber Age* 1957, 82, 291.
13. Brochart-Wyard, F.; De Gennes, P. G.; Léger, L.; Marciano, Y.; Raphael, E. *J Phys Chem* 1994, 98, 9405.
14. Beatty, J. R. *Rubber Chem Technol* 1040, 1969, 42.
15. Flory, P. J. *J Chem Phys* 1943, 521, 11.
16. Hild, G. *Prog Polym Sci* 1998, 23, 1019.
17. Urayama, K.; Yokoyama, K.; Kohjiya, S. *Polymer* 2000, 41, 3273.
18. Orrah, D. J.; Semlyen, J. A. *Polymer* 1988, 29, 1452.
19. Wool, R. P. *Rubber Chem Technol* 1984, 57, 307.
20. Lorentz, G.; Blanc, D.; Odoni, L. In *Proceedings of RAPRA Silicone Elastomers*, Frankfurt, Germany, 19–20 September 2006.