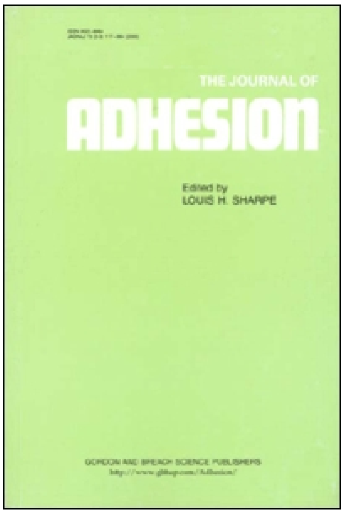

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Silicone Rubber Tack II: The Time-Dependent Autohesion for Symmetric Rubber-Rubber Contacts

M. Mikrut[a][b]; J. W. M. Noordermeer[a]; G. Verbeek[c]
[a] University of Twente, Faculty of Engineering Technology, Department of Elastomer Technology and Engineering, Enschede, The Netherlands [b] Dutch Polymer Institute Eindhoven, The Netherlands [c] Océ Technologies B. V. Venlo, The Netherlands

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Silicone Rubber Tack II: The Time-Dependent Autohesion for Symmetric Rubber–Rubber Contacts

M. Mikrut[1,2], J. W. M. Noordermeer[1], and G. Verbeek[3]
[1]University of Twente, Faculty of Engineering Technology, Department of Elastomer Technology and Engineering, Enschede, The Netherlands
[2]Dutch Polymer Institute Eindhoven, The Netherlands
[3]Océ Technologies B. V. Venlo, The Netherlands

The autohesion data are gathered for poly(dimethyl siloxane) (PDMS) with different molecular weights. The influence of molecular weight of the polymer is very pronounced. The data are interpreted on basis of the Wool-deGennes reptation theory; the application of first order kinetics of wetting is also tested. PDMS with a molecular weight only partially permitting the formation of entanglements exhibits a remarkably different and unusual behavior compared with the high molecular weight polymers. The latter develop tack in the form of logarithmic type curves, while the former show the presence of local maxima in the tack-time curves.

Keywords: Autohesion; Diffusion; PDMS; Rubber; Tack

INTRODUCTION

The problem of time dependence of polymer autohesion has attracted a lot of attention for many years. It addresses the strength of materials, which is connected to many practical engineering problems, such as polymer fusion and welding, rubber tack, etc. Research in this field brings fundamental insights into the physical processes of adhesive bond formation. Controversies, however, still exist when it comes to determining the controlling physical process. It is believed that there are two basic mechanisms responsible for the time dependence of

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Present address of Marek Mikrut is Ammenaal Beltech Manufacturing B. V. Macronictraat 15, 1700 AA Heerhugowaard, The Netherlands.

Address correspondence to J. W. M. Noordermeer, University of Twente, Faculty of Engineering Technology, Department of Elastomer Technology and Engineering, P.O. Box 217, 7500 AE Enschede, The Netherlands. E-mail: j.w.m.noordermeer@ctw.utwente.nl

polymer autohesion [1,2]: contact area formation through viscous flow and bond formation *via* chain penetration and entanglements across the interface.

Voyutskii appears to be the earliest person to work on this problem. He investigated the contact formation of the rubber-rubber interface and its influence on the joint strength [3]. With Lavrent'yev he constructed a model for the contact area-time dependence, with the following time relationship as a result:

$$\ln(1-\varphi)+\varphi=-Pt/\eta, \tag{1}$$

where ϕ is the fractional contact area, related to the development of tack in time as:$\varphi \sim tack(t)/tack(\infty)$, P is the applied pressure, and η is the viscosity of the polymer. The experiments of Voyutskii *et al.* showed that the contact area formation is not instantaneous; the interface strength developed further even after full contact was achieved. Thus, viscoelastic flow is a controlling factor during the early stages of contact.

Wool [4] used the reptation theory of deGennes [5] to depict the process of a polymer–polymer interface crack healing. Incomplete molecular contact limits the interfacial diffusion of polymer molecules. Thus, for simplicity, Wool assumed instantaneous wetting of the interface. According to the theory of reptation, 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. 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. On the basis on the relations summarizing the description of a linear polymer chain movement in an entangled melt, Wool developed a molecular description of the interface as a function of time, molecular weight of the polymer, contact pressure, and temperature. The most important theoretical predictions are summarized in Table 1.

Since the average penetration depth $\mathrm{X}(t) \sim t^{1/4} \sim \sigma$, this model regards the average monomer interpenetration depth as the controlling factor for σ, the macroscopic interfacial bonding strength. Still, it is important to note that not every chain crossing the interface will be able to support the bonding. Only those chains or chain segments are effective which, after crossing, are able to hook into entanglements, at least one on each side. This may be considered a modification of Wool's model described before, in the sense that a minimum molecular weight of the reptating polymer is required to be able to span the distance across the interface and to reach two effective entanglements, one at each side. Below a certain minimum molecular weight the load bearing bonding strength will not develop. Wool's theoretical model was a depiction of

TABLE 1 Summary of Scaling Laws for Wool's Theory of Crack Healing [4,6]

Molecular aspect	Symbol	Relation	Remarks
Number of chains	$n(t)$	$t^{1/4}M^{-5/4}$	$t \leq t_\infty$
Number of molecular bridges	$p(t)$	$t^{1/2}M^{-3/2}$	$t \leq t_\infty$
Average penetration depth	$X(t)$	$t^{1/4}M^{-1/4}$	$t \leq t_\infty$
Average bridge length	$l_p(t)$	$t^{1/4}M^{-1/4}$	$t \leq t_\infty$
Tack	$\sigma(t)$	$\begin{cases} t^{1/4}M^{-3/4} \\ M^{1/2} \end{cases}$	$t \leq t_\infty$ $t \geq t_\infty$
Strain energy at fracture	$U_c(t)$	$\begin{cases} t^{1/2}M^{-3/2} \\ M \end{cases}$	$t \leq t_\infty$ $t \geq t_\infty$
Time to reach equilibrium	t_∞	M^3	–

where t is time, and M is the molecular weight of the polymer.

an ideal case, where every chain is equally effective. A more general approach can be summarized in the following relation [7]:

$$\frac{\sigma(t)}{\sigma_\infty} = \frac{n(t, M_w, M_e)}{n(t_\infty, M_w, M_e)}, \tag{2}$$

where $n(t, M_w, M_e)$ is the number of effective crossings per unit area as a function of contact time t, weight average molecular weight, M_w, and molecular weight between entanglements, M_e. The denominator is the number of effective crossings per unit area of the interface after equilibrium conditions have been reached. The total number of effective crossings is still predicted to scale with $t^{1/4}$ and is considered to be the mechanism behind the time dependence of autohesive bonding.

The proponents of the surface wetting mechanism point out that the contact cannot develop instantaneously between two surfaces. On a microscale there will always be a rough topography, creating voids and disabling intimate molecular contact. Under pressure, material spreads with time, filling the voids *via* viscous flow. Increase in the apparent contact area causes the overall bonding strength to rise. The bond strength develops in time with first-order kinetics of wetting.

Skewis [8] calculated the rate of interpenetration of typical industrial elastomers from their diffusion coefficients, determined using radioactive-labeled polymers. He calculated that after one second of contact an elastomer chain interdiffuses around 45 Å—enough for substantial interpenetration. On the other hand, tack development can take up to days to reach the equilibrium state. This would lead to the point that, for common industrial elastomers with molecular weights around 200,000 to 300,000, the adhesive bond formation is surface contact limited.

Another strong argument for the contact-controlled bond formation is the fact that interpenetration should, in fact, be independent of contact pressure. Hamed [9], in his study, observed that in the case of NR and SBR tack was sensitive to the compression load applied, what also points to a contact-controlled mechanism. However, the diffusion process is not strictly fully independent of pressure, because of an influence of free volume [10], where the free volume depends on pressure. This dependency, however, is several orders of magnitude lower than the effect of the small loading pressure used in the present tack experiments on viscous flow. This effect is, thus, negligible.

The aim of the present study is to gain insight into mechanisms that influence poly(dimethyl siloxane) (PDMS) rubber tack. The present paper focuses on the effects of compression time and of separation speed on the tack developed over the interface of two contacted crosslinked silicone surfaces, based on starting polymers of different molecular weight.

EXPERIMENTAL

Materials

Table 2 lists the vinyl-terminated polydimethylsiloxanes that were used for the study.

As a crosslinker, trifunctional tris(dimethylsiloxy)ethoxysilane was used. The platinum-cyclovinylmethylsiloxane complex was used as a cure reaction catalyst. All the above materials were obtained from ABCR (Karlsruhe, Germany), with the exception of the multifunctional silane, which was provided by a proprietary source. 1-ethynylcyclohexanol (Aldrich, 99%, sigma-Aldrich, zwijndreclit, The Netherlands) was used as a temporary reaction inhibitor. Pyrazine (Aldrich, 99%) was used as an internal NMR standard without further purification. 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,

TABLE 2 Vinyl-Terminated Poly(dimethylsiloxane) Polymers

Material	Viscosity [Pa · s]	M_w [g/mole]	Vinyl group content [mmole/kg]	Supplier
MQ 17	500	17000	166	ABCR
MQ 28	1000	28000	98	ABCR
MQ 50	5000	50000	64	ABCR

Varian, Darmstadt, Germany) with pyrazine as an internal standard. The results of these measurements are included in Table 2. From those results and the molecular structure of the crosslinker, the hydrogen-to-vinyl ratio (H/V) was calculated.

The samples were then prepared using an H/V ratio of 1.0. The curatives were mixed together for 10 minutes 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 had to be varied according to the vinyl group contents of the polymers 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 press (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 90×90×2 mm sheets were post-cured in an oven at 120°C for 48 hours.

Tack Time-Dependence Measurements: Tack Measurements

Tack measurements were performed using a custom-made device based on the Tel-Tak principle [11]. 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. 1). The cured samples of MQ 17, 28, and 50 with hydrogen-to-vinyl ratio 1.0 were compressed under a load of 2.5 N. Times of compression were varied from 1 to 1000 minutes. For each compression time, several tack

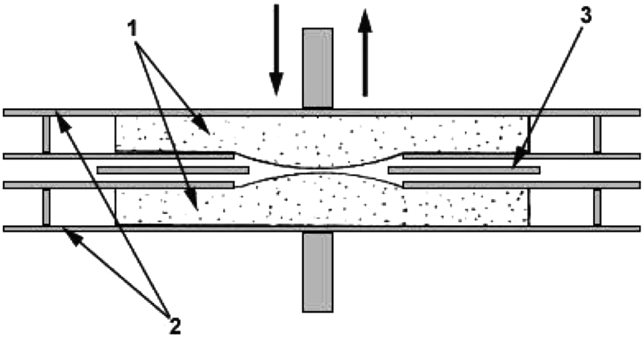

FIGURE 1 The principle of tack-testing device. 1) Rubber samples, 2) Clamps, 3) Separator.

measurements were collected and the average was taken as the final result. After each series of measurements, samples were exchanged, to provide a fresh, uncontaminated surface. The measurements were always performed at room temperature. The separation speed after the compression was varied from 0.25 to 15 mm/s.

RESULTS

Autohesion for Short Compression Times

Figure 2 shows the beginning of PDMS autohesion development for short compression times.

Notice the large difference in tack values between MQ 17 and the other two samples, MQ 28 and MQ 50. 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 in nature. The low molecular weight PDMS

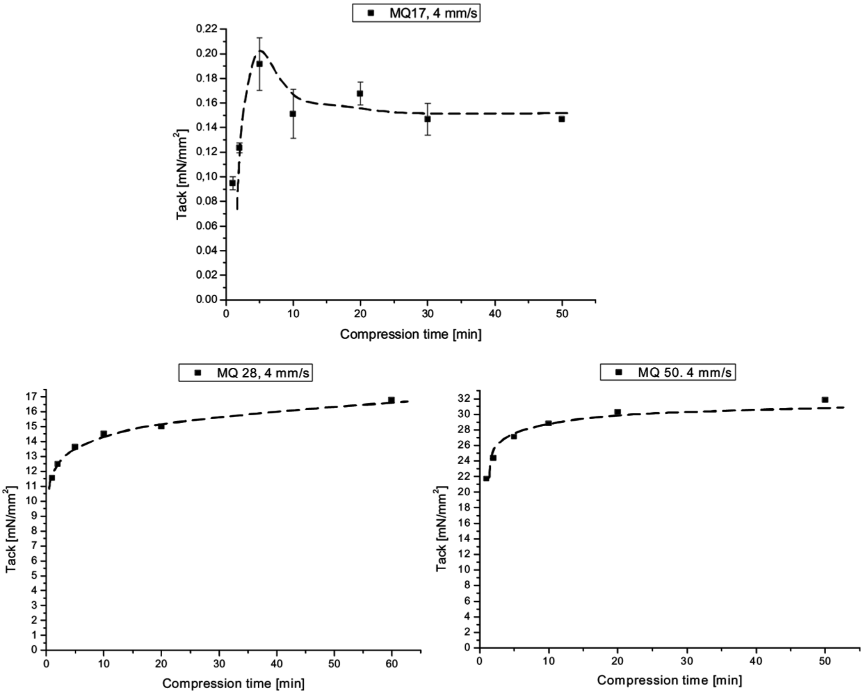

FIGURE 2 Tack as a function of compression time for MQ 17, MQ 28, and MQ 50, all cured with H/V = 1.0.

quickly reaches a peak in tack, and after that point tack decreases again to a plateau. The situation is different in the case of the high molecular weight PDMS: the tack level rises slower but steadily; within the timescale of the measurement it cannot be determined if a saturation level is already reached. In fact, the tack still rises after very long compression times, ranging over 1000 minutes (not shown). That means that the ultimate interface strength has not already been reached after that period: a further increase in rubber autohesion was observed by Stacer and Schreuder-Stacer for times longer than 10,000 minutes, when finally the fracture stress achieved values independent of contact time [1].

The Compression-Time-Dependent Autohesion of Intermediate and High Molecular Weight PDMS MQ 28 and MQ 50

In order to test if silicone rubbers behave according to deGennes/Wool's theory, another variable was introduced: testing speed. The theory predicts that the slopes of the tack-time curves should change with separation speed from $t^{1/4}$ to $t^{1/2}$, indicating the change in the chain unraveling mechanism. The pull-out mechanism is favored at low separation speeds, low molecular weights, and high testing temperatures. The chain fracture mechanism would be favored at high separation speeds and high molecular weight of tested polymers. Where the testing temperature remained constant, polymer molecular weight and separation speed could be varied.

Figure 3 shows an example of how the autohesion of the PDMS-PDMS interface of MQ 50 proceeds with compression time and increasing separation speed. With the increase in separation speed, the maximum forces of autohesion increase as well.

This behavior is better illustrated in Fig. 4, which shows how the slopes of the log tack *vs.* log time curves change with increase in separation speed. The slopes exhibit a local minimum at the speed of 4 mm/s, after which the exponent values rise monotonically with increase in separation speed. When the separation speed is decreased below 4 mm/sec, the exponent values also increase very fast. The situation is similar for the intermediate molecular weight PDMS, MQ 28 (Fig. 5).

The tack-time relationship for MQ 50 was measured over a somewhat broader range of separation speeds. Still, the behavior of both types of PDMS is similar: the minimum is located at the 4 mm/s s speed and the exponent values rise later practically linearly

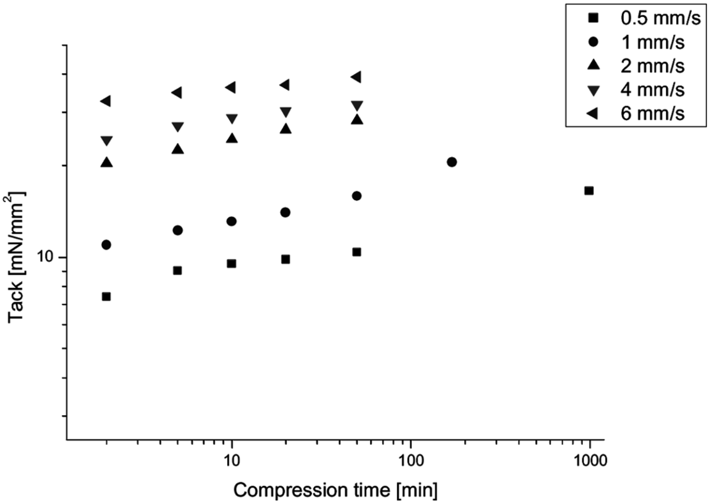

FIGURE 3 Autohesion curves for MQ 50 at different separation speeds.

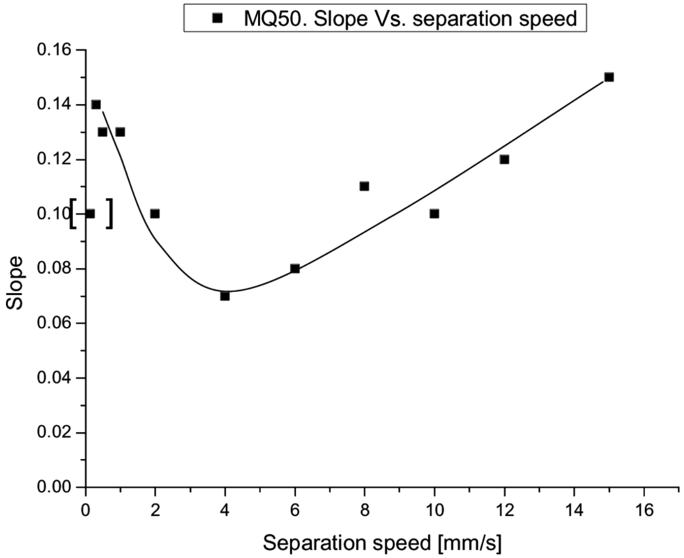

FIGURE 4 Slopes of the double logarithmic autohesion *vs*. compression time curves of MQ 50 in relation to separation speed. The line is intended to guide the eye.

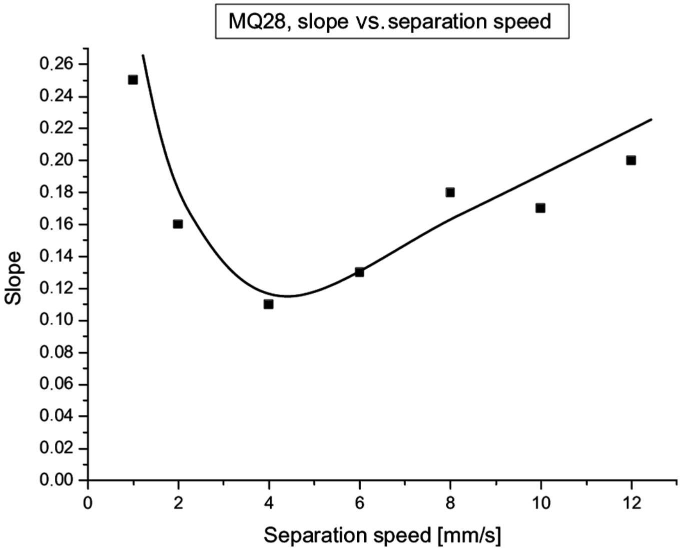

FIGURE 5 Slopes of the double logarithmic autohesion *vs*. compression time curves of MQ 28 in relation to separation speed. The line is intended to guide the eye.

with separation speed. When the speed is decreased below 4 mm/s the exponents rise very quickly. The slope values observed for MQ 28 are generally higher and closer to 0.25, as predicted by Wool, than for MQ 50.

The application of Vouytskii's equation for the autohesion data of MQ 28 and MQ 50 is shown in Fig. 6. With φ of Eq. (1) defined as $tack(t)/tack(\infty)$, plotting the $\ln(1-\varphi)+\varphi$ *versus* compression time should yield a straight line, if the contact formation obeys the first order kinetics of wetting. A limitation of the approach is that $tack(\infty)$ was never actually reached. The tack after the longest compression time employed was taken as the equilibrium value. For both MQ 28 and MQ 50, the plots do not give a straight line. This demonstrates that wetting is not the predominant process.

A closer look at the influence of separation speed on tack, after constant compression time, is given in Fig. 7 for MQ 50 and MQ 28. For simplicity of the picture, only the values of tack after 10 minutes of compression were taken for comparison. MQ 50 clearly exhibits a maximum in tack, which decreases with the increase in separation speed. The tack values for MQ 28 are, unfortunately, much more scattered.

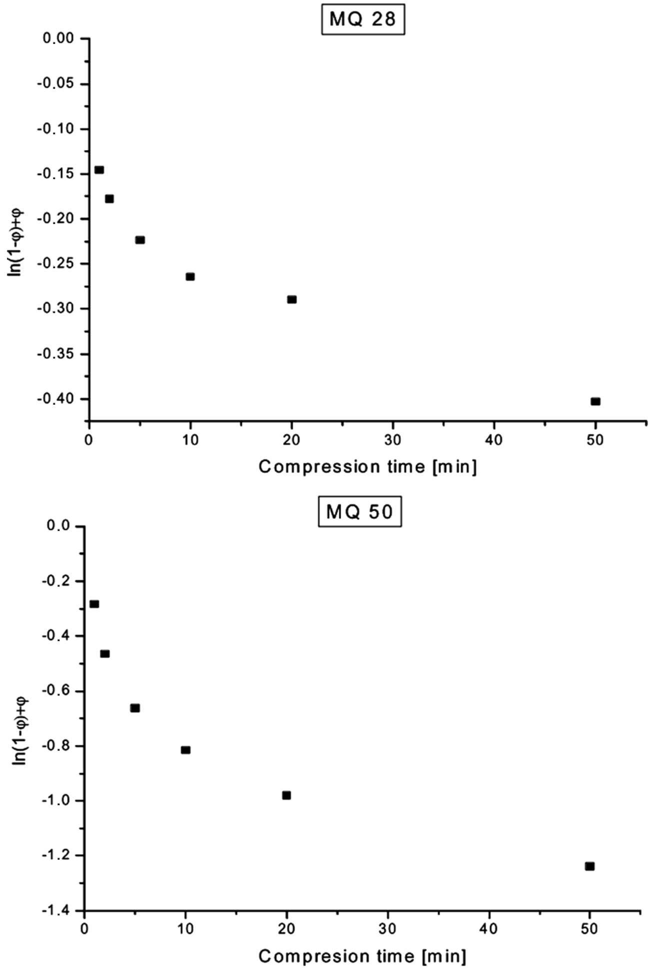

FIGURE 6 The application of the first order kinetics of wetting for autohesion data description for 4 mm/s separation speed.

The Compression-Time-Dependent Autohesive Behavior of Low Molecular Weight PDMS MQ 17

The behavior of the low molecular weight PDMS is very different (Fig. 8). First of all, the tack curves clearly show the presence of a maximum at short contact times: the tack rises quickly to its maximum value and then lowers down to a plateau. This sort of behavior is completely absent for the higher molecular weight polymers.

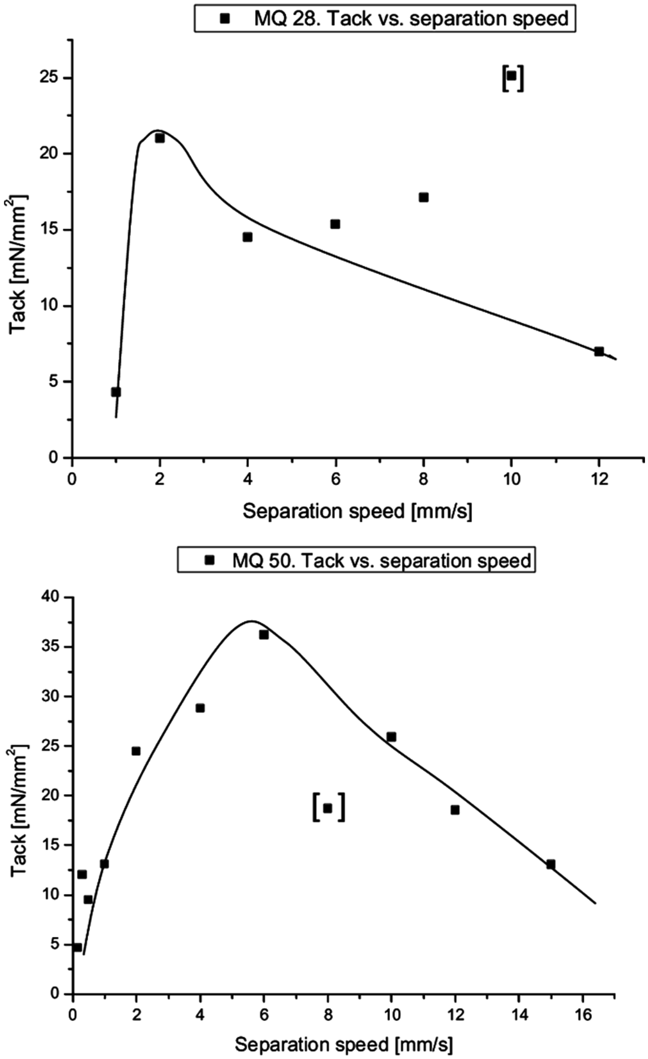

FIGURE 7 The tack as a function of separation speed for MQ 28 and MQ 50. The values after 10 minutes of compression were taken. The line is intended to guide the eye.

The presence of this maximum makes it very difficult to fit a curve—fitting results are obtained with a very large error. The maximum is present on each tack curve for separation speeds ranging from 4 to 10 mm/s. Moreover, it shifts with increasing separation speed to shorter contact times, vanishing completely at 12 mm/s. The absolute

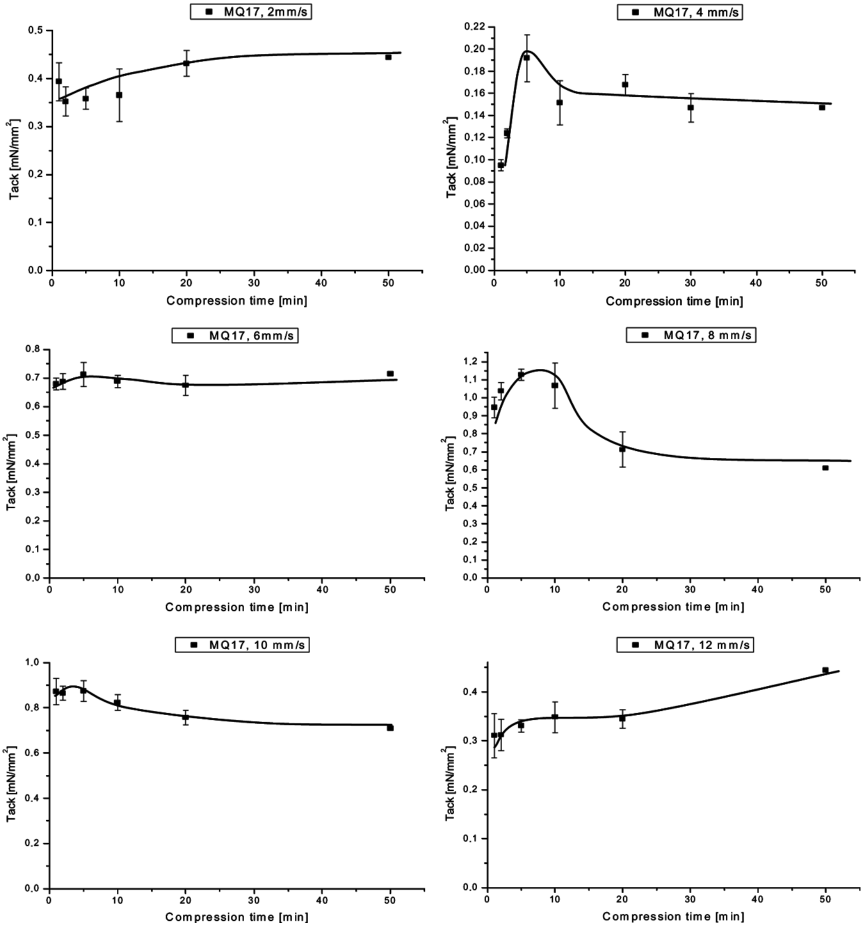

FIGURE 8 The beginning parts of the tack *vs*. compression time curves for MQ 17 at different separation speeds.

values of tack increase with increasing separation speed, but the increase stops at 8 mm/s.

It is important, however, to look at the tack curve for MQ17 at extended compression times. Even after the tack seems to have decreased to the plateau values after several minutes, after a long compression time, at 1000 minutes and more, a substantial increase in rubber-rubber tack can still be seen. Figure 9 shows two autohesion curves of MQ 17, for 4 and 10 mm/s separation speeds. The increase in the tack is very substantial for the low separation speed, and decreases when the separation speed increases.

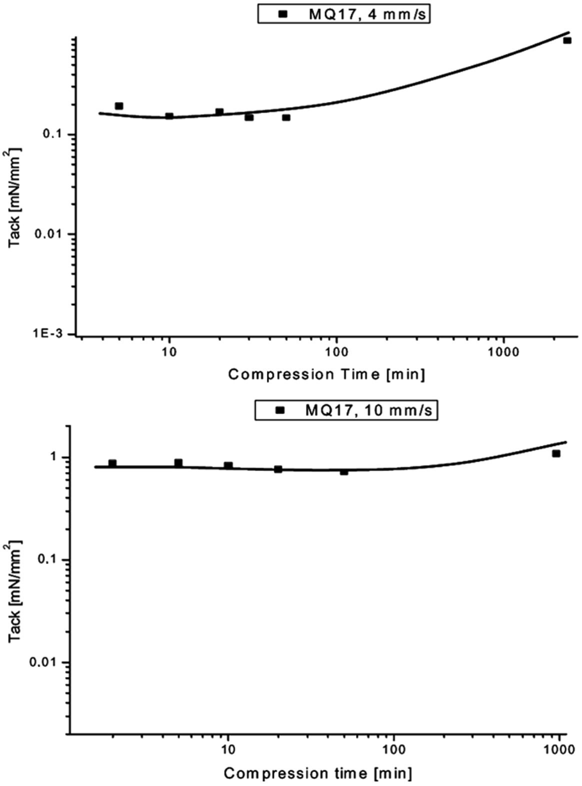

FIGURE 9 Tack curves for MQ 17, at 4 and 10 mm/s separation speed.

This trend is better visualized in Fig. 10, where the difference in tack values between the plateau, measured at 50 minutes of compression and at 1000 minutes compression time are shown as a function of separation speed. The difference in tack between 50 and 1000 minutes compression time decreases very quickly with increase in separation speed, being close to zero at 12 mm/s. If the tack is plotted as a function of a separation speed, see Fig. 11, it can be seen that there is roughly one broad maximum, spreading over the range of separation speeds. An exception is the 4 mm/s tack, which is anomalously low compared with the other results.

As was done for MQ 28 and MQ 50, the applicability of Voyutskii's model was tested. The results are plotted in Fig. 12. If an overshoot maximum is present in the autohesion data in Fig. 8, the Voyutskii's model does not seem to be applicable: the points are scattered. But when the overshoot maximum has disappeared with increase in

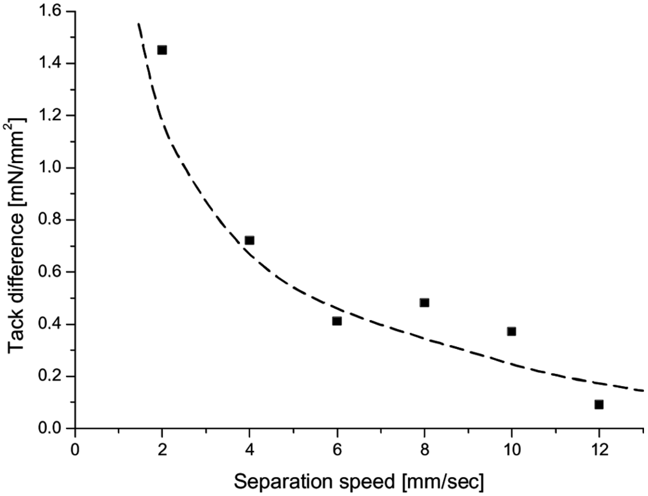

FIGURE 10 The difference between the 50 and 1000 min compression time tack as a function of separation speed for MQ 17.

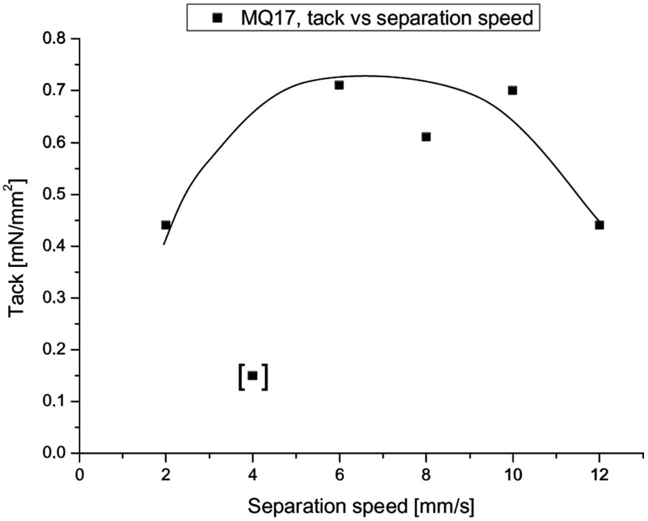

FIGURE 11 The tack as a function of separation speed for MQ 17. Tack at plateau (50 minutes of compression) was taken.

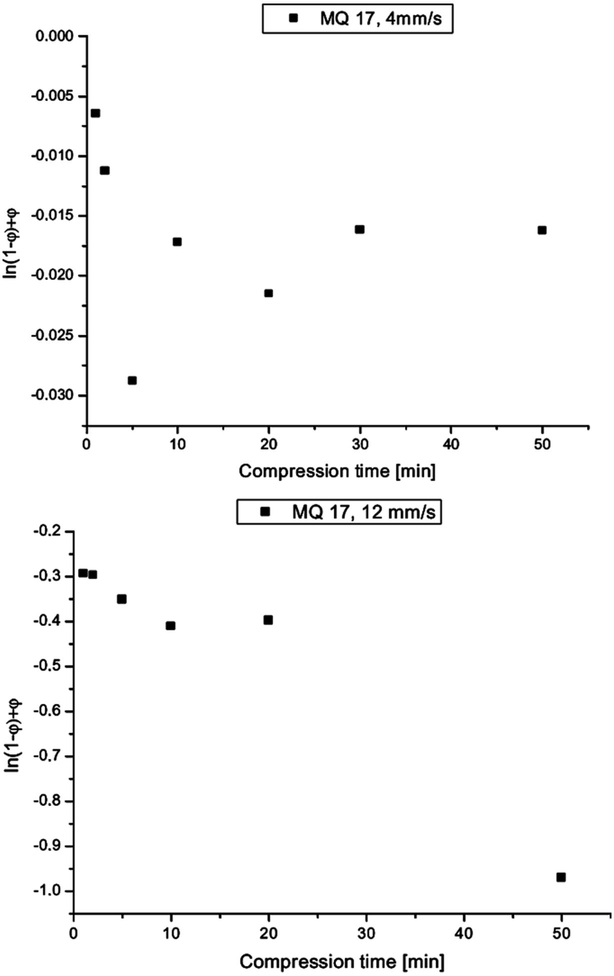

FIGURE 12 The application of the first order kinetics of wetting for autohesion data description of MQ 17 for 4 and 12 mm/s separation speed.

separation speed, the plot gives a linear relationship, as opposed to the fitting results for MQ 28 and 50.

DISCUSSION

The presented results demonstrate, just as others have seen with different systems [12], how difficult it is to accurately and reproducibly measure tack, to analyze the data on the basis of the few models available. The main reason is that the tack measurement encompasses two opposing, non-equilibrium effects:

- the development of tack or autohesion during compression time, with extra variables—compression load, temperature, and a major effect of molecular weight;
- cutting short the development of tack with time at the moment where separation is imposed is where the separation speed comes in as an extra parameter.

As to the first effect, Wool's model assumes that the separation resistance of the interface is dominated by molecules which diffuse through the interface. Basically, it is the strength required to pull the molecules from the "tube" created by the surrounding polymers and back from the interface. The longer the molecules are, the deeper the interpenetration may be, and the stronger the separation resistance. From this model there is a relationship predicted for the time needed for achieving equilibrium, t_∞. This time scales with the third power of the molecular mass of the polymer (Table 1).

With the molecular weights of the two extremes MQ 17 and MQ 50 differing by a factor of 2.9, the time span required for MQ 50 to reach a similar state of equilibrium compared with MQ 17 is already 25 times as large! In other words, if we assume that equilibrium has been reached in the experiments with MQ 17 after compression time of approximately 50 minutes (Fig. 7), then for MQ 50 a time span of 20 hours or more would have been required, which is an impractical experimental condition within the scope of this research. Therefore, it is reasonable to assume that the tack values measured for MQ 17 more closely resemble an equilibrium situation, while those for MQ 28, and far more for MQ 50, are tack values when equilibrium molecular interpenetration has not yet been reached.

High Molecular Weight PDMS: MQ 28 and MQ 50

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 (Table 1). How well this describes the autohesion data can be seen from Figs. 3 and 5. Although the time dependence of autohesion manifests itself in the form of double logarithmic-type curves, the exponent values are lower than the theory predicts. It is important to note, however, that the exponents were predicted for monodisperse polymers. The data for polydisperse elastomers obtained by other researchers show a slower increase of the stress with contact time

[1,13]. Values of x lower than 0.25 can be explained by the polydispersity of the initially used polymer, which in the present case is around $\frac{\overline{M_w}}{\overline{M_n}} = 2$. This polydispersity is related only to the material before crosslinking; after the crosslinking $\frac{\overline{M_w}}{\overline{M_n}} = \infty$, because of the infinite molecular mass of the crosslinked polymer matrix related to the uncrosslinked polymer and left over pendant chains that cross the interface. Wool's model was developed primarily for uncrosslinked polymers. A very important question to ask is how far it still applies for the partially crosslinked species.

The other model, known to describe the tack time development, was based on first order kinetics of wetting. If the contact formation is flow-controlled, the plots in Fig. 6 should have yielded a straight line. This is not the case, which strongly suggests that the viscous flow is not the controlling process even during the early stages of contact. These results, however, should be taken with caution: in order to calculate properly the fractional fracture stress the value of tack at equilibrium ($\varphi(\infty)$) was required. It was already mentioned that during the time scale of the experiment equilibrium was not yet reached.

The interesting behavior observed during the separation speed experiments (Figs. 7 and 11) is that a maximum in tack is observed over the range of separation speeds. These results are similar to those obtained by Gent and Petrich [14]. They measured the force-separation rate dependence for butadiene-styrene random copolymer and found a very similar pattern, as shown in Fig. 13. There are two transitions visible, one at low and one at high peeling rate. The maximum of the transition observed for MQ 50 and perhaps for MQ 28 falls in the area of 0.1 cm/s separation speed (Fig. 7), or -1 on the scale seen in Fig. 13. The authors attributed the sudden change in strength at low separation rates to an alteration of the bulk viscoelastic behavior of the sample during pulling. At a certain speed the rate of deformation is so high that the material is not capable of liquid-like flow any more and starts to exhibit rubber-like behavior. It should be noted, again, that the experiments of Gent and Petrich were performed on uncrosslinked polymer. The crosslinked rubber is very unlikely to exhibit a liquid-like behavior. However, silicone elastomers are known for their extraordinary chain mobility, due to the very low glass transition temperature of below -100°C compared with other rubbery polymers. The results of separation rate experiments for PDMS suggest that there may be a second transition region at higher separation speeds than have been measured.

The scattering of the MQ 28 data in Fig. 7 is a result of an artefact from the sample preparation stage. The liquid, uncrosslinked PDMS prepolymer always contains some amount of an uncrosslinkable

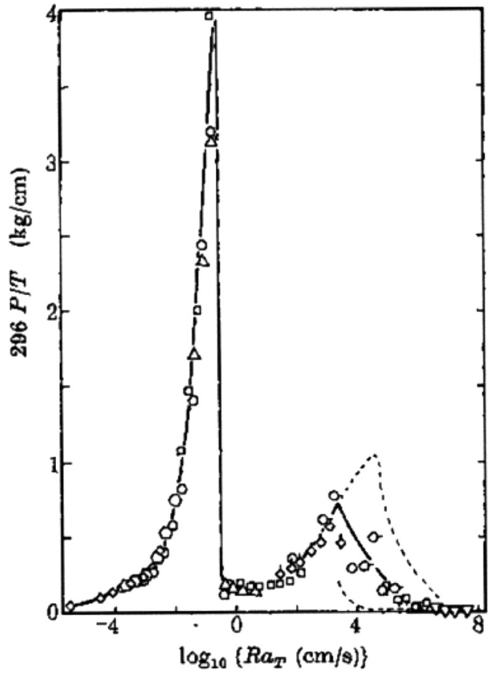

FIGURE 13 Master curve relation for peel force against rate of peeling for butadiene-styrene random copolymer, reduced to 23°C [14].

fraction: silicone oil. This is the remains of the polymerization process, where the amount of oil varies from batch to batch. Samples of MQ 50 were all prepared from a single, large batch of material, while the samples of MQ 28 were prepared from different batches. During the testing stage, the oil can diffuse towards the interface, forming a thin liquid layer interrupting the interface formation process. As a result, the absolute tack values for MQ 28 differ, while for MQ 50 they form a consistent picture—this is a problem often encountered in elastomer technology. Note that the interface strengthening process is not affected by this phenomenon; the slopes of tack-time dependence curves are unchanged.

DeGennes extended the presence of a maximum from the uncrosslinked to the loosely crosslinked systems with large amounts of entangled free chains and dangling ends [15]. In this view, the increase in force indicates a transition from "soft rubber", with the network dominated by few crosslinks, to "hard rubber", with the network dominated by "frozen" entanglements. Figure 14 shows a schematic visualization of the fracture profile. If the crack propagation

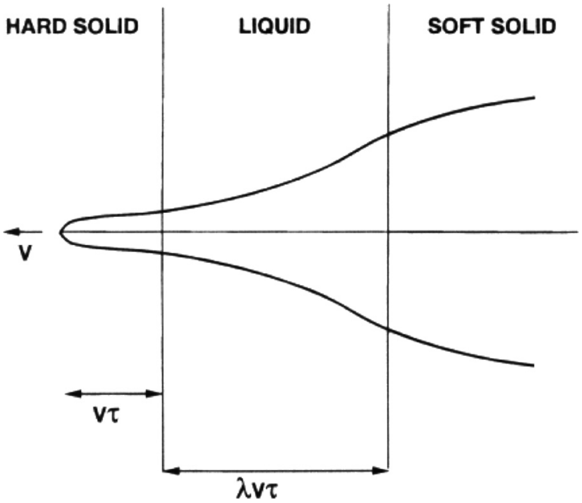

FIGURE 14 The crack tip profile [15]. V is the separation speed, τ relaxation time, and λ is the low to high frequency modulus ratio.

velocity is high enough, the entanglements do not have time to relax and retract. The relaxation time of the polymer chains, therefore, plays a crucial role here.

Low Molecular Weight PDMS: MQ17

The tack behavior of the low molecular weight PDMS is more complicated. The tack curves show well-pronounced maxima for short compression times, after which the tackiness decreases to a plateau. However, after very long compression times, there is still an increase in tack level, showing that interpenetration and chain entanglements at least partially take place at the interface over the long term. Because of that sort of behavior, the fitting of the curves of log tack *vs*. log time to obtain the exponent value is virtually impossible: it yields a large error. The maxima visible in Fig. 8 shift to shorter contact times with increasing pulling speed. This behavior is very similar to the viscoelastic phenomenon known as stress overshoot [16], where the shear stress *vs*. time 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 disentangle themselves in an orderly way [17]. It is interesting that this sort of phenomenon did 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 may or will not have been reached at all for interpenetrating chains in the range of contact times applied.

MQ 17 still shows a tack increase after very long compression times. Surprisingly, the relative increase depends heavily on separation speed (Fig. 10). The explanation of this phenomenon may be related to the minimum molecular weight between the entanglements. Depending on the specific author, M_e of PDMS can be as low as 8,100 g/mol, based on retardation spectrum measurements [10], but the most often used value is 12,300 g/mol [18]. The molecular weights of MQ 50 and MQ 28 are high enough to form entanglements, contributing to the strength of the interface. MQ 17 is a borderline case. According to some sources, PDMS with a molecular mass around 16,000 can be regarded as practically non-entangled [19,20]. Even if the molecular mass of MQ 17 is high enough for the chains to still entangle, they cannot bear the stress well enough. If the interface is separated quickly, the polymer chains unravel very easily; hence, their contribution to the joint strength diminishes. This can be the explanation for the different tack-separation speed behavior for MQ 17 (Fig. 11) where, instead of the abrupt transition as in a case of high molecular weight PDMS (Fig. 7), one broad maximum over a whole range of separation speeds can be observed. The very low tack values for the 4 mm/s separation speed are, again, the result of the sample preparation process, mentioned before.

Fitting the first order kinetics to the autohesion data of MQ 17 encounters the same problem as fitting the power curve. Where the maximum is present, fitting yields a large scatter. It is striking, however, that when the maximum is gone, the graph takes the form of a straight line. This would suggest that the interface forming process for low molecular weight rubber MQ 17 is mostly wetting controlled. This correlates well with the critical entanglement molecular weight hypothesis.

The possibility to analyze the data from the perspective of pressure sensitive adhesives was discussed in the other paper of this series [21].

CONCLUSIONS

Wool's theoretical model for the diffusion-driven interface formation seems to have somewhat limited application for the PDMS telechelic network. The autohesion curves of high molecular weight PDMS show a double logarithmic tack-time-dependence, but the generally accepted $t^{1/4}$ power law does not apply. This is possibly due to the high polydispersity of the polymers used, but more probably because the theory was developed for uncrosslinked polymer melts.

The autohesion curves of the low molecular weight PDMS exhibit an anomalous behavior, most probably due to the polymer chains being at the edge of minimum molecular weight needed for entanglements. The tack-time development quickly reaches equilibrium, but the molecular weight is too low to follow Wool's model. Fitting another model, *i.e.*, Voyutskii's, shows that the interface forming can be described in this way, when the maximum is not present, at least for the lowest molecular weight PDMS.

For MQ 28 and MQ 50 the interpenetration process is not quite in equilibrium yet, in spite of the fact that the molecular weight is high enough for Wool's model to apply. The tack-separation speed relationships exhibit sharp transitions for high molecular weight PDMS, MQ 50, and broad for the low molecular weight material. These are the signs of a viscoelastic response of the material, where the separation speed exceeds the retardation abilities of polymer chains. The intermediate molecular weight PDMS exhibits different behavior, due to the way samples have been prepared.

The question whether the contact development for a silicone rubber-rubber interface is primarily diffusion, or viscous flow, controlled, can still not be unequivocally concluded from the experiments shown. Most probably both mechanisms play a more or less equal role.

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