Spontaneous Adhesion of Silicone Rubber

A. N. GENT and P. VONDRÁČEK,* *Institute of Polymer Science,*
The University of Akron, Akron, Ohio 44325

Synopsis

Lightly crosslinked silicone rubber has been found to bond spontaneously to polar substrates and to itself. The strength of adhesion increases linearly with time, eventually reaching the fracture strength of the rubber. The process is accelerated by raising the temperature (activation energy $\simeq 60$ kJ/g · mol), by the presence of moisture, and by ammonia vapor. It is tentatively attributed to hydrolytic decomposition of the polymer leading to the formation of reactive groups which interlink with surface groups, probably hydroxyls, on polar substrates, or with each other in the case of self-adhesion.

INTRODUCTION

Silicone rubber has a relatively low surface energy, about 25 mJ/m^2.[1] In consequence, it is generally found to adhere only weakly to itself and to other substrates when it is crosslinked to prevent liquidlike flow.[2,3] For example, the intrinsic strength of adhesion between crosslinked silicone rubber and Plexiglas is reported to be only about 300 mJ/m^2,[4] and between two identical sheets of silicone rubber it is only about 100 mJ/m^2.[5] We have therefore been surprised to find that relatively strong adhesion develops between lightly crosslinked silicone rubber and quartz or glass substrates or between two identical sheets of silicone rubber, when they are held in contact for several days. Some experimental observations of this phenomenon are reported here, and a tentative explanation is advanced in terms of chemical reactions at and near the interface.

EXPERIMENTAL

Materials and Sample Preparation

Two silicone polymers were used in the experiments, a high-molecular-weight sample of polydimethylsiloxane, denoted PDMS (SE-30, General Electric Co.) with a weight-average molecular weight ($\overline{M}_w$ of about 1.3×10^6 g/g·mol, and a similar material, denoted PMVS (SE-33, General Electric Co.) with similar molecular weight ($\overline{M}_w = 8.6 \times 10^5$ g/g·mole) but containing a small amount of methylvinylsiloxane units to give better and more uniform crosslinking with a free-radical crosslinking reagent.

Crosslinking was effected in both cases by incorporating small amounts of dicumyl peroxide (Di-Cup R, Hercules Chemical Co.) and then heating the mixtures in a closed mold for 2 h at 150°C to form thin sheets, 0.5–2 mm thick.

* On leave from the Department of Polymers, Institute of Chemical Technology, 16628 Prague 6, Czechoslovakia.

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The sheets were molded in contact with smooth Teflon-coated aluminum foil and given a post-vulcanization heat treatment of 16 h at 150°C in an air oven. The protective foil was then removed, and strips cut from the sheets were lightly pressed in contact with the desired substrate. In some instances the strips were extracted by immersing them in toluene for 48 h and then drying them *in vacuo* at 70°C before use.

Quartz and Pyrex glass plates were used as substrates after cleaning them first in a chromic acid–sulfuric acid glass cleaning solution (Chromerge, Monostat, New York) for 48 h followed by rinsing them and then repeatedly washing them with freshly distilled boiling water for 24 h. They were then dried and stored in a dessicator before use. The results obtained with quartz and Pyrex plates were virtually indistinguishable, as described later.

Measurement of the Work G_a of Detachment

Samples were peeled apart at 180° after storage under various conditions for various periods of time. The silicone rubber layer was generally backed by a thin layer of finely woven cotton cloth to prevent it from stretching under the action of the peel force. Peeling was carried out at 25°C at a rate of about 100 μm/s. These conditions are not sufficiently gentle to eliminate viscoelastic contributions to the work of separation altogether, and the results therefore do not correspond to threshold strengths of adhesion. Some measurements were carried out under threshold conditions, i.e., at 110°C and at a peel rate of about 1 μm/s [6] for comparison with the intrinsic strength of the crosslinked elastomer. The work G_a of detachment per unit area of interface was calculated from the time average of the peel force P per unit width of the detaching layer:

$$G_a = 2P.$$

Some measurements of self-adhesion were carried out under threshold conditions, with samples swollen with a low-molecular-weight silicone oil. Values of the work G_a of detachment were multiplied by λ_s^2 for these samples, where λ_s is the linear swelling ratio, to take into account the reduced number of network strands crossing the interface.[7] Measurements of the cohesive fracture energy G_c were also carried out under threshold conditions using split-strip test pieces.[6]

Some samples were exposed to ammonia atmospheres before determining the strength of adhesion. They were placed in a closed container with an open beaker of NH_4OH and were thus exposed to vapors of both water and ammonia. Similar results were obtained with samples exposed only to dry gaseous ammonia. After these vapor treatments, the samples were stored *in vacuo* for about 10 h to remove water and ammonia before measuring the strength of adhesion.

RESULTS AND DISCUSSION

As shown in Figures 1, 2, and 3, the work of detaching a lightly crosslinked silicone rubber sheet from a Pyrex glass substrate was found to increase continuously with the time t of contact, approximately in proportion to t. The rate k of increase depended strongly upon the storage temperature. At 135°C the detachment energy increased in a period of 30 h from an initial value of about
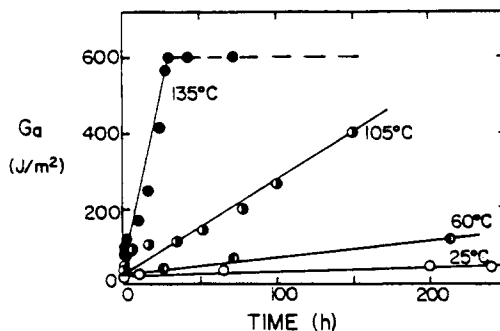
Fig. 1. Development of adhesion with time of contact between a lightly crosslinked layer of PDMS and a Pyrex surface.

25 J/m² to about 600 J/m². The bond to Pyrex glass was then so strong that the rubber layer broke apart rather than detaching. At 25°C, on the other hand, the rate of increase of adhesion strength was relatively slow, and, by extrapolation, it would have taken about 5000 h for the bond strength to reach the cohesive strength of the silicone rubber layer.

Values of the rate k of increase of detachment energy with time of contact are given in Table I for various storage temperatures. They were obtained from Figures 1–3, and yield values of activation energy of about 58 kJ/g·mole (Fig. 4)
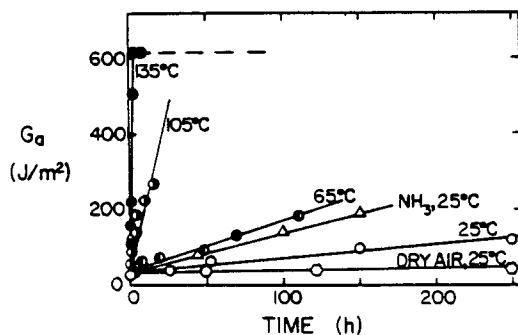

Fig. 2. Development of adhesion with time of contact between a toluene-extracted layer of lightly crosslinked PDMS and a Pyrex surface.
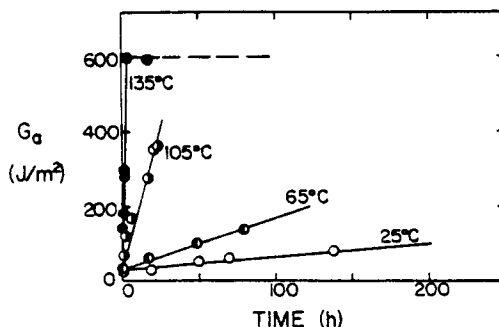

Fig. 3. Development of adhesion with time of contact between a toluene-extracted layer of lightly crosslinked PDMS and a quartz surface.

TABLE I
Rates of Increase k (J/m²·h) in Work of Detachment from Various Substrates[a]

Storage temp (°C)	System			A on A (self-adhesion)
	A on Pyrex	B on Pyrex	B on quartz	
25 (dry air)	—	0.05	—	0.22
25	0.12	0.38	0.34	0.61
25 (NH₃)	—	1.05	—	1.35
65	0.43	1.35	1.35	—
105	2.45	15.5	16.0	—
135	19.0	185	165	40

for both extracted and unextracted samples. However, the extracted material was found to develop adhesion to glass and quartz substrates considerably faster than the unextracted rubber. It is thought that low-molecular-weight species are present at the surface of unextracted samples and delay the proposed bonding reaction (discussed later) between silicone rubber and glass or quartz. Such low-molecular-weight material may gradually diffuse away from the interface as chemical bonding proceeds. Roberts and Othmann have suggested that low-molecular-weight material at the surface is responsible for other time-dependent adhesion phenomena in silicone rubber.[8]

It is noteworthy that similar bonding was also observed with ferrochrome plates[9] and in self-adhesion between two silicone rubber layers (Fig. 5). Moreover, the presence of moisture appears to catalyze the reaction. These features suggest that hydrolytic processes within the silicon rubber result in the formation of reactive groups capable of interlinking with surface groups (most probably
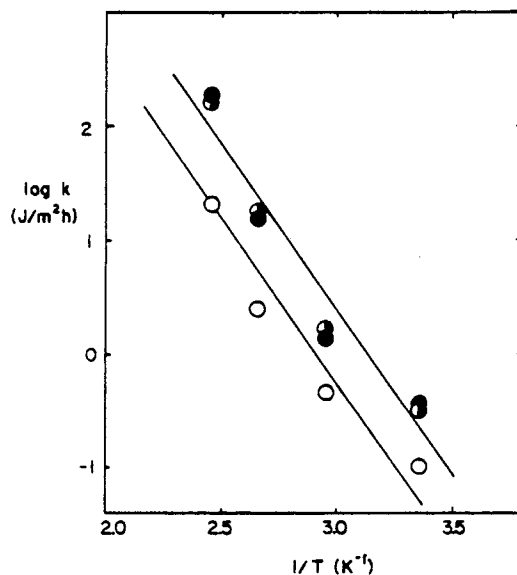

Fig. 4. Rates k (J/m²·h) of development of adhesion plotted against the reciprocal of the storage temperature T. Values of k were obtained from the linear relations shown in Figures 1–3. Unextracted PDMS in contact with Pyrex (O); extracted PDMS in contact with Pyrex (●); with quartz (◑).
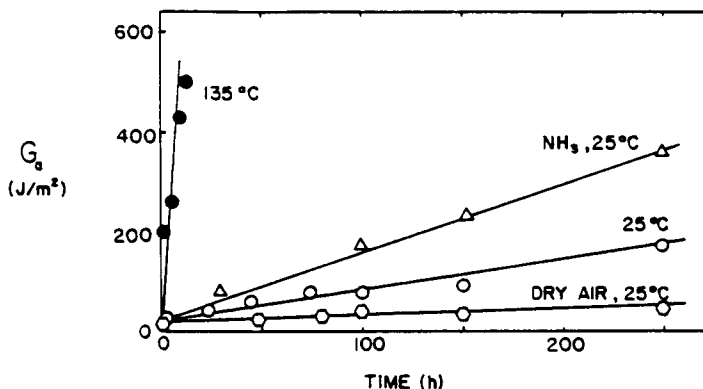
Fig. 5. Development of adhesion with time of contact between two thin layers of lightly crosslinked PDMS.

hydroxyls) on polar surfaces, e.g., glass, quartz, and metal, or with each other across an interface in the case of self-adhesion. This proposed mechanism of bonding is supported by the catalytic action of ammonia vapor in promoting adhesion. Ammonia is known to sever hydrogen bonds, and, if these are assumed to be responsible for the enhanced strength of adhesion, then ammonia vapor should weaken the bond. Instead, it accelerates bonding, probably by promoting a hydrolysis reaction.

Silicone polymers may contain OH groups that are formed during the polymerization process or subsequently by hydrolysis. These groups could well be responsible for the development of adhesion to other OH-containing surfaces. In an attempt to test this hypothesis, the PDMS material was treated with hexamethyldisilazane, which readily reacts with silanol groups,[10] and then crosslinked with dicumyl peroxide as before. The modified polymer was found to develop adhesion to a Pyrex surface much more slowly than before, at a rate of only 7 J/m²·h at 135°C, compared to a previous rate of 19 J/m²·h. Because the modified polymer attained a somewhat lower level of crosslinking than the unmodified one, this lower rate of development of adhesion is even more significant. It strongly supports the hypothesis that OH groups in silicone rubber are responsible for the interlinking reaction with polar substrates or with itself.

Other physical changes occur in silicone rubber during prolonged storage. They also indicate that molecular scission and bond formation take place under relatively mild conditions. For example, the molecular weight of uncrosslinked polymers tends to decrease, and the soluble fraction of crosslinked materials tends to increase. Moreover, crosslinked samples held in the strained state show continued stress relaxation over long periods of time. These observations are reported elsewhere.[11] Together with the present studies of the spontaneous development of adhesion during storage, they strongly suggest that molecular rearrangements take place fairly readily in silicone rubber.

In order to minimize viscoelastic contributions to the observed work of detachment, some measurements were carried out at much lower rates of peeling, about 1 μm/s, and at a temperature of 110°C. In some cases of self-adhesion and for determining the fracture energy (tear energy) of the crosslinked material

itself, measurements were also made using test pieces swollen with an equal volume of a low-molecular-weight silicone oil. Values of the fracture energy for these swollen samples were found to agree closely with those obtained for unswollen samples when a geometrical correlation factor of λ_s^2 was employed to take into account the reduced number of network chains crossing the fracture plane, where λ_s denotes the linear swelling ratio, about 1.25. This agreement confirms that threshold conditions had indeed been established and that viscoelastic contributions to the work of detachment were insignificant.[12]

The results obtained under threshold conditions are given in Table II. They lie generally between the low values, about 1 J/m² or less, characteristic of non-bonded elastomeric layers adhering to themselves or to rigid substrates,[12] and the much higher values, 30–100 J/m², characteristic of the threshold tear strength of crosslinked elastomers.[6] Indeed, the magnitudes of the detachment energies under threshold conditions of detachment (Table II) provided unambiguous evidence for increasing chemical bonding at the interface with increasing time of contact and with temperature, up to a level characteristic of the degree of crosslinking of the PDMS network itself.

Measurements of the work of detachment were usually carried out at ambient temperature (25°C) and at a convenient rate of peeling (about 100 μm/s). Under these conditions, the values obtained were about 10 times greater than under threshold conditions, probably because of dissipative processes within the elastomer layer. More highly crosslinked materials are, of course, less dissipative, and it was found that the level of adhesion decreased sharply as the degree of crosslinking of the silicone rubber was increased. Moreover, the further development of adhesion with time took place much more slowly at any temperature. Some representative results are given in Table III. Values of the average molecular weight M_c between crosslinks were calculated from equilibrium swelling ratios in toluene, using the Flory–Rehner equation.[13] As M_c decreased, the development of adhesion was much less pronounced. Apparently, the inferred bonding reaction at an interface is greatly impeded by crosslinking of the silicone rubber layer.

TABLE II
Threshold Values of Work of Detachment G_a for PDMS Crosslinked with 2% Dicumyl Peroxide

Substrate	Storage conditions[a]		G_a (J/m²)
	Time (h)	Temp (°C)	
PDMS (self-adhesion)	0.1	25	1.1
	220	25[b]	7.6[c]
	1	135	21
	500	25	37
PDMS (tear energy)	—	—	42.5[c]
Quartz	0.1	25	1.6
Quartz	240	25	13
Pyrex	6500	25	21.5

[a] All samples were heated for about 1 h at 110°C during the measurement of G_a.
[b] Exposed to ammonia during storage.
[c] Similar values were obtained for both unswollen and swollen samples.

TABLE III
Effect of Degree of Crosslinking upon Adhesion of Silicone Rubber

Elastomer	Dicumyl peroxide (%)	Equilibrium volume fraction v_2 in toluene	M_c calculated from v_2[13]	Storage time (h) at 25°C	G_a (J/m^2)
PMVS	0.025	0.112	22,000	1	10
	0.025	0.112	22,000	650	530
	0.025	0.112	22,000	96 (in NH$_3$)	1100
PDMS	2.0	0.131	15,000	1	3
	2.0	0.131	15,000	650	70
	2.0	0.131	15,000	96 (in NH$_3$)	145
PMVS	0.5	0.219	4,000	1	1
	0.5	0.219	4,000	650	3
	0.5	0.219	4,000	96 (in NH$_3$)	25

CONCLUSIONS

Lightly crosslinked layers of silicone rubber have been shown to develop strong adhesion to polar substrates and to each other. The strength of adhesion increases linearly with time of contact, and the process takes place more rapidly at higher temperatures. It appears to be catalyzed by moisture and by ammonia vapor. Eventually, the bond strength becomes comparable to the tear strength of the elastomer itself, and it retains this relative magnitude even under threshold conditions, i.e., when detachment takes place at low rates of peeling and at high temperatures. All of these observations suggest that chemical interlinking occurs between silicone rubber and various substrates under relatively mild conditions. It is suggested that the process involves hydrolytic decomposition of silicone rubber. Hydroxyl groups formed in this way are inferred to react readily with each other, or with surface hydroxyl groups on polar substrates, leading to strong adhesion. This phenomenon indicates, once again, that minor structural changes in polymeric materials can result in major changes in their adhesive behavior.

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