Silicone Elastomers for Electronic Applications. II. Effects of Noncrosslinked Materials

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ABSTRACT: We performed applied functional tests to examine how the noncrosslinked fraction of a cured silicone elastomer affected the performance of electrical devices and the solderability and adhesion on gold-plated printed circuit boards. To obtain information about the spreading tendencies of commercial silicone elastomers, and to complement the function tests, we conducted so-called creep tests to examine the migration and spreading of the noncrosslinked fraction. The electrical tests, performed with both reference oligomers and cured commercial poly(dimethyl siloxane)s, showed that failure occurred even at very low silicone contamination levels. The solderability and adhesion, however, were not affected by the presence of poly(dimethyl siloxane)s, especially not the reference solutions, which consisted mainly of volatile siloxanes. The creep tests, performed on commercial silicone elastomers, indicated that the noncrosslinked, nonvolatile part had to be taken into account in a discussion of silicone contamination. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3780–3789, 2003

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INTRODUCTION

Crosslinked poly(dimethyl siloxane) (PDMS) is a material that exhibits several favorable properties that make it an interesting choice for the protection of electronic components. It is only slightly affected by heat and most solvents, and it has good insulating properties and highly flexible main chains. There is, however, a major problem connected with its use: its tends to cause silicone contamination.[1] This means that low-molecular-weight components of PDMS can migrate out of the material and contaminate surrounding surfaces. This is fatal in situations in which these components form SiO_2 and cause failure in electrical contacts or when they have an adverse effect on adhesion.[2] Because of this problem, many companies have restricted their use of PDMS, even though the material in many cases has unique advantages.

Upon the crosslinking of PDMS, as in all random crosslinking processes, it is mainly the low-molecular-weight part of the starting material that is expected to remain as free (i.e., noncrosslinked) material. Because of the high flexibility and low surface tension of PDMS, this low-molecular-weight fraction will tend to spread to the environment by migration to the PDMS surface[3] and subsequent creep on neighboring surfaces, or by the evaporation of any volatile fraction. Silicone contamination by volatile siloxanes has been studied, most often with respect to open contacts. However, most studies are performed either in an atmosphere of only one volatile siloxane or when unspecified silicone oils are used as the contaminating source.[4–10]

Our work is part of a larger cooperative project concerning silicone contamination in the electronic industry.[11] In a previous study,[1] a number of commercial silicone elastomers were investigated with respect to their noncrosslinked fraction. That work focused on monitoring the curing process and analyzing the extractable part of the cured PDMS. It was concluded that the extractable part constituted 5–20 wt % of the total material and that only 0–1 wt % of the total material was volatiles. The manufacturer can reduce the volatile fraction through a special extraction process, whereas we demonstrated how to reduce the nonvolatile fraction by increasing the curing time.

There are several applied techniques aimed at studying different aspects of silicone contamination. However, most of these very specifically focus on examining the effect of PDMS on open contacts. Very little has been done to quantitatively study the effect of PDMS on other devices. Furthermore, only a few attempts have been made to establish the upper concentration limit at which PDMS is not harmful. In this work, the possibility of establishing such limits has been studied along with how and where the handling of PDMS is most likely to cause major problems. The focus of previous work has been on the volatile mate-

TABLE I
General Characteristics and Recommended Curing Conditions of the Silicones Used in This Study

Silicone	Type of curing	Curing temperature (°C)	Curing time (h)	Extractables (%)	Volatiles (%)
A1	Addition, 1 part	100	3	3.5	0.30
A2	Addition, RT, 2 parts	25	24	4.3	0.16
A3	Addition, RT, 2 parts	25	8	3.1	0.45
A4	Addition, 2 parts	100	1	>50	0.39
C1	Condensation, RT, 1	25	24	15.5	0.74
C2	Condensation, RT, 1	25	24	8.3	0.27
C3	Condensation, RT, 2	25	24	5.4	0.68

[a] Ref. 11.

rial in PDMS, which in fact represents only a very small part of the noncrosslinked fraction. The only kind of test that has been performed on the nonvolatile part is an adhesion test, which is very specific and gives only limited information. These previous studies have clearly shown that PDMS has a very negative effect on adhesion and that the adhesion problems must be caused by PDMS that is not airborne but instead remains on the surface. This makes the creeping of PDMS an interesting phenomenon, and we have tried to establish a more general correlation between the amount and type of the noncrosslinked material and the creeping tendencies of PDMS.

This work is focused on how migrating PDMS affects the functions of electrical devices and how solderability and adhesion are influenced by PDMS exposure. To complement these applied function tests, we performed spreading tests to determine how much of the nonvolatile, noncrosslinked part could contaminate the surroundings by migrating to the surface of the silicone elastomer from which it then spread. These tests are called *creep tests*, and the migration and spreading of PDMS is called *creep*. The molecular weight of the noncrosslinked fraction was also determined, and the results are, together with information on the gel content for each cured silicone elastomer, compared with the results from the creep experiments.

The spreading tests, the molecular weight determination, and the gel content measurements were all performed at Chalmers University of Technology, and the applied functional tests were performed at the Swedish Institute of Production Engineering Research.

EXPERIMENTAL

Materials

Seven different commercial silicones, provided by Dow Corning (Senette, Belgium), were used. As in the previous study,[1] they were chosen to represent a relevant selection of silicone elastomers used in the electronic industry. They were divided into four different

categories with respect to their curing methods and temperatures (see Table I).

The two crosslinking reactions were a platinum-catalyzed addition reaction between vinyl-functionalized PDMS and Si—H groups and a condensation-cured system in which no catalyst was needed (Scheme 1). An important advantage of the addition-cured system was that no byproducts were formed in the curing process. The only low-molecular-weight byproduct formed in the condensation reaction was methanol for all the materials included in this study.

The functional tests were largely performed on reference mixtures of low-molecular-weight siloxanes. We used three cyclic compounds (D4, D5, and D6, with cyclic structures containing 4, 5, or 6 Si atoms, respectively) and three linear compounds (L6, L7, and L8, with linear chains containing 6, 7, or 8 Si atoms, respectively). These siloxanes were chosen to mimic low-molecular-weight siloxanes that evaporated from samples A4 and A2.

Electrical resistance in open contacts

The effects of PDMS on open relays and contacts were examined with two methods. Method 1 included a closed compartment in which a siloxane-containing atmosphere built up. In method 2, a closed compartment was simulated in which the open contacts were exposed to a siloxane atmosphere for a long time under such conditions that the condensation of siloxanes on the contact occurred. A stable and controllable siloxane atmosphere, as well as controlled condensation of siloxanes on surfaces, was created with a contamination chamber (Fig. 1), which was designed and carefully evaluated for this purpose.[11] In addition to a stable siloxane atmosphere, the condensation process required a cold surface on which the siloxanes could condense.

Method 1

An equimolar mixture of the cyclic siloxanes D4, D5, and D6 in hexane was used to create a siloxane-con-
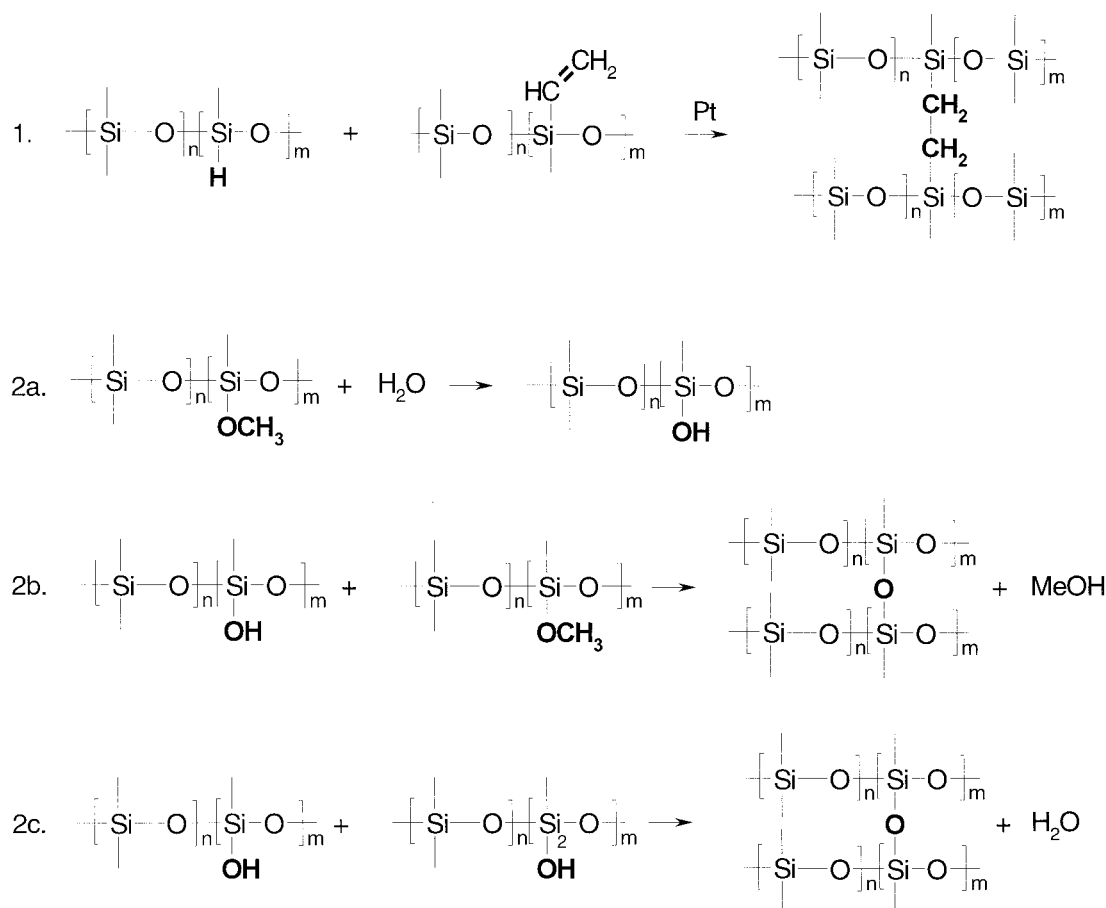
Scheme 1 Crosslinking reactions for PDMS: (1) the addition-curing system and (2) the condensation-curing system.

taining atmosphere. The mixture (500 μL) was injected into the chamber, after which the chamber was closed and the pressure was increased to 0.5 bar above atmospheric pressure with helium. The temperature in the chamber was set to 45°C, which was between the maximum operating temperature of the relay and the temperature needed to obtain a uniform siloxane at-

mosphere in the chamber. The measurements started after 20 min.

Method 1 was also used to study the contamination effect of two commercial silicone elastomers, samples A4 and A2. Here, 3.4 and 3.0 g of A2 and A4, respectively, were placed in the chamber, and the effect of the evaporating siloxanes was analyzed.
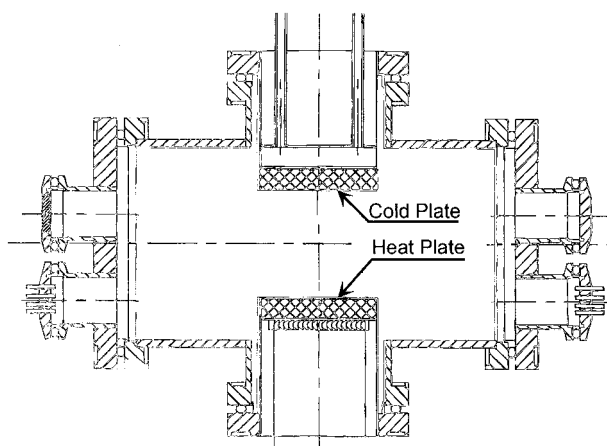
Method 2

An equimolar mixture of cyclic and linear siloxanes D6, L6, L7, and L8 was used as a reference solution. D4 and D5 could not be used because earlier tests had shown that they were extremely volatile and, therefore, not likely to condense. A constant volume (500 μL) of the solution was injected into the chamber, and the pressure was kept at 0.6 bar. The temperature in the chamber was raised to 120°C, and the contact was allowed to cool to room temperature (RT) so that siloxane condensation could occur.

After 2 h, the heater was turned off, the siloxane-containing atmosphere was evacuated, the pressure was increased to atmospheric pressure, and the chamber was opened to let in air. The chamber was then

Figure 1 Contamination chamber.

cooled to RT, and the resistance measurements were started.

In both test methods, the contact was placed in the contamination chamber without any prior cleaning. The contacts were Fujitsu FBR211B subminiature relays with silver–palladium overlaid with gold as a contact material. The switching power in the contacts was 6.0 W, and the voltage was 26.9 V in both tests. The cycle time was 10 s, and this means that the contacts were closed 5 s and open 5 s. The resistance was measured every 20th cycle. The resistance increased as silicon dioxide, a typical insulator, was formed in a reaction between PDMS and oxygen stimulated by the electric discharge occurring on the contact. The contact was classified as a failure when the resistance exceeded 1 Ω.

Solder-paste spread test

In this test, the solderability on a gold-plated printed circuit board (PCB) was evaluated by the measurement of the diameter of a solder dot and the time required to melt the solder. An increased dot diameter or melting time indicated a negative influence on the adhesion. Two solder spread tests were performed. The first one examined the influence of the solderability on a surface covered with a reference solution. The second one examined the solderability on a real surface covered with a commercial silicone elastomer. The solder paste was a fine line paste (2000, RMA390DH3 62/36/2). The reported melting times and dot diameters are averages.

Solderability test 1

Test pads (11.6 cm^2) were treated with a reference siloxane solution containing equimolar amounts of D6, L6, L7, and L8 in hexane. Five different solution volumes were used: 1.5, 3, 15, 31, and 306 μg/cm^2. The siloxane solutions were applied to the PCB pads, which were then allowed to dry in a fume hood for 5 min. Thereafter, the solder paste was stencil-printed on the treated test pads. Three solder-paste dots, each with a diameter of 6.7 mm and a thickness of 0.3 mm, were printed on each test pad.

After the solder-paste application, each PCB test pad was placed on a 200°C hot plate. The time from the placement of the test pad on the hot plate to the beginning of the melting of the solder was measured for different amounts of siloxane. The test board was removed 1 min after all the solder paste had melted, and the diameters of the solder spots were measured after cooling.

Solderability test 2

The solderability on a PCB pad covered with sample A2 was tested. The whole test pad was covered with the sample, which was cured at 65°C for 4 h and left at RT for 24 h. The silicone elastomer was stripped off, and the test pad was washed in acetone in an ultrasonic bath for 10 min and thereafter rinsed with isopropyl alcohol to remove contamination sources other than siloxane. A solder-paste dot with a diameter of 2 mm was stencil-printed on the test pad, and the spreading on treated test pads was compared to the spreading on nontreated pads.

Adhesion tests

To examine the influence of PDMS on adhesion, we treated a gold-plated PCB with 3–6 μL of the two aforementioned reference siloxane mixtures containing D4, D5, and D6 and D6, L6, L7, and L8 in n-hexane, respectively. The siloxane-treated surface was allowed to dry for 3 min to allow the hexane evaporate, and then it was brought into contact with another test pad covered with a standard epoxy adhesive. Two types of epoxy were used: one heat-curing epoxy, cured at 120°C for 3 h, and one two-component epoxy, cured at RT for 24 h. The adhesion was tested by a lap shear test. The lap shear tester was a Dage BT 22 with a shear rate of 0.35 mm/s. To ensure the same thickness of the adhesive joint, a 0.2-mm stainless steel plate was placed between the test pads. Epoxy (1 mg) was used for each joint. The two test pads were brought together, and a weight was applied to ensure a fixed distance between them. The RT-curing epoxy was only tested with L7 siloxane because of the limited amount of reference siloxanes. The values in the figures are averages based on 10 experiments.

Creep experiments

The creep experiments were tests of migration and spreading onto neighboring surfaces. They were performed to examine the ability of the noncrosslinked, nonvolatile part of the cured PDMS to migrate and contaminate surrounding areas. All seven commercial silicone elastomers provided by Dow Corning (Table I) were used in the experiment. One end of the gold-plated PCB test pads was completely covered with the uncured PDMS samples. PDMS was then cured on the test pads according to specifications. For the removal of any released volatile material, the test pads were placed in a closed fume hood with air circulation. At certain time intervals, the contact angle of water on the gold-plated PCB was measured to determine whether PDMS had spread on the gold-plated PCB. The contact angles were all measured only a few millimeters from the PDMS edge. The measured contact angles were compared to the contact angles for water on gold and on a continuous PDMS layer, that is, approximately 40 and 110°, respectively.
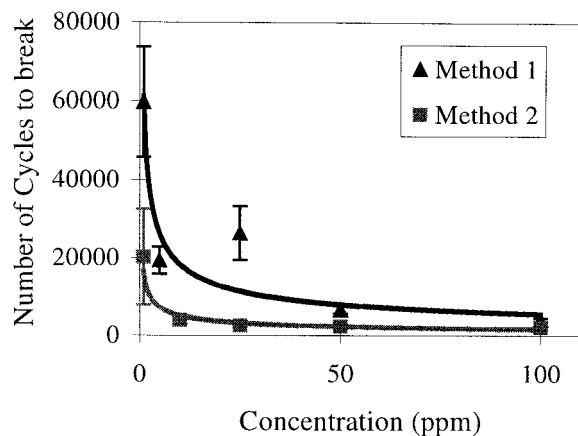
Figure 2 Number of cycles to failure for different siloxane concentrations, with two different deposition methods.

Size exclusion chromatography (SEC) measurements

The molecular weight distribution (MWD) was measured on noncrosslinked extracts from cured PDMS samples. The extracts were obtained from a fully cured sample with Soxhlet equipment after extraction with pentane for 4 h. This procedure has been shown to dissolve uncured PDMS.[1] The first half of the solvent volume was removed with a rotavapour, and the second was allowed to evaporate at ambient temperature and pressure to a constant weight. The PDMS extracts were then collected as viscous fluids. This extraction method also gave the gel content of each PDMS sample as the difference in the sample masses before and after extraction.

The SEC analyses were performed with a Waters 150 CV at 30°C. The instrument was equipped with a column combination giving good separation in the low-molecular-weight region. The extracts were dissolved in distilled tetrahydrofuran (THF) over night at a concentration of approximately 2 mg/mL and then injected into the column system and fractionated according to the sizes of the polymers. A refractive-index detector, placed in series with the columns, was used to measure the concentration in the eluate. THF was used as the eluent at a flow rate of 1.0 mL/min. The calibration was performed with narrow-molecular-weight polystyrene standards.

RESULTS AND DISCUSSION

Electrical resistance in open contacts

Figure 2 shows the number of cycles to failure at different concentrations of siloxanes in the reaction chamber. It is obvious that the contact resistance increases rapidly, even at very low siloxane concentrations. In the background test, which was performed at less than 0.5 ppm siloxanes, as determined by gas

chromatography/mass spectrometry (GC–MS), only one of five contacts failed even after 80,000 cycles, at which point the test was interrupted. When the siloxane mixtures were injected into the chamber at a concentration of 1 ppm, the number of cycles to failure decreased to 60,000 for method 1 (stable atmosphere) and to 20,000 for method 2 (forced condensation). For method 1, the number of cycles to failure continued to decrease dramatically when the concentration was increased from 1 to 5 ppm, from 60,000 to 19,000. At 100 ppm, the number was only 4000.

The number of cycles to failure obtained by method 2 was lower for all concentrations, and at 100 ppm, contact failure occurred after only 2000 cycles. The observed difference between the two test methods is reasonable, as the amount of siloxane on the contact is considerably larger upon condensation. This may be due to the fact that it is the siloxane film that causes the failure of the contact. When a certain film thickness is reached, increasing the thickness does not further affect the function of the contact. Unfortunately, it is difficult to estimate the actual amount of siloxane on the contact surface. During the experiment, equilibrium is established between the condensed siloxanes and the vapor, and it is difficult to estimate how much stays on the surface after the chamber has been evacuated. Furthermore, it is unlikely that the surface coverage is uniform, as the relays are not as cold as the cold metal plate.

Two commercial silicone elastomers, samples A4 and A2, were also tested with method 1. The gas chromatograms for each sample were recorded at the end of the experiments, giving concentrations of about 8 ppm D4, 5 ppm D5, and 1.5 ppm D6 for sample A4. The concentrations were calculated by the comparison of the areas in the gas chromatogram of sample A4 with those of an equimolar mixture of D4, D5, and D6 at a total concentration of 5 ppm (Fig. 3). The average lifetime of the contacts was approximately 6100 cycles when sample A4 was used as the contamination source. The amount of low-molecular-weight siloxanes evaporating from sample A2 was considerably smaller than that from sample A4, and the evaporating species were not the same. This was also verified in GC–MS tests, which showed that the major volatile components from sample A2 were linear, mostly L4 and L5. The average lifetime for the contacts contaminated with sample A2 was somewhat longer than for those contaminated with A4, approximately 7400 cycles.

The results from the commercial silicone elastomers are in line with the values obtained with the reference solutions, but in both cases, the average contact lifetimes for the commercial silicone elastomers are somewhat lower than expected from the gas chromatograms. For sample A4, this could be explained by the GC–MS results presented in an earlier publication.[1] In
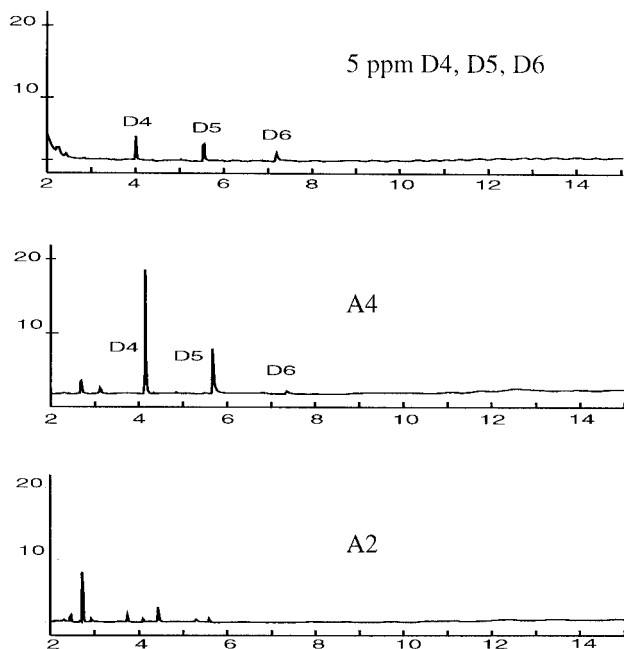
Figure 3 Gas chromatogram from a 5 ppm mixture of D4, D5, and D6 compared to gas chromatograms from samples A4 and A2.

this article, GC–MS measurements show that sample A4 contains some siloxanes with seven or more silicon atoms. It is possible that some of these siloxanes condense on the contact surface and, therefore, cause a severe reduction in the number of cycles to failure. The results obtained with method 2 also clearly demonstrate that even a very small amount of higher molecular weight siloxanes, present on the surface, is sufficient to reduce the lifetime of the contact. For sample A2, a similar explanation is probable. Even if the gas chromatography (GC) chromatogram from this experiment shows a very low amount of volatile species in comparison with sample A4, it is still clear from the aforementioned GC–MS test that sample A2 contains more linear species that do not evaporate that easily.[11]

The aforementioned experiments clearly show that the concentration of PDMS in a closed compartment must be kept very low. There is a drastic decrease in the number of cycles to failure already when the concentration of siloxane vapor is 1 ppm. As the detection limit of the employed GC test is 0.5 ppm, it is difficult to determine an absolute allowed maximum level of silicone contamination for open contacts. The maximum level is also dependent on the testing conditions, where the contacts are used, and the reliability demands. In an article by Tamai,[7] a limiting siloxane concentration of 10 ppm was established, below which no effect on the contact reliability was found. However, these experiments used a different testing setup and different testing parameters, and a direct compar-

ison is difficult to make. Furthermore, our experiments show that contamination involving the condensation of siloxanes on the contacts is more detrimental to the function of the contacts than a contaminating atmosphere of siloxanes in which no condensation occurs. In most cases, a zero limit is desirable, but when PDMS is present in the surrounding atmosphere, this can only be achieved with sealed contacts.

Solderability

PDMS affects the surfaces of materials. The low surface energy and low polarity of PDMS, together with the low adhesive strength between PDMS and the surfaces of many other materials, are both factors that create adhesion problems. Adhesion problems may affect important industrial procedures, such as the solderability of surfaces contaminated with PDMS. We have investigated how different types and amounts of PDMS influence the solderability. The solderability can be examined with different methods. One way is to study the spreading of the solder by the measurement of the contact angle of the solder paste on the surface. Another is to analyze the solderability with a solder-paste dot test. The latter method is used here, and so the solderability is evaluated by the measurement of the diameter of the solder dot and the melting time of the solder.

When the mixture of D6, L6, L7, and L8 was used to contaminate the surface, a dramatic increase in the melting time was observed with an increasing amount (Fig. 4). On a clean test pad, the solder paste melted after 11 s, whereas the melting time was twice as long even at siloxane concentrations as low as 3 $\mu g/cm^2$. The melting time increased to approximately 36 s for 30 $\mu g/cm^2$, after which a steady level was reached. Figure 5 shows the results from test 2, in which sample A2 was used to contaminate the surface. This contamination also caused an increase in the melting time,
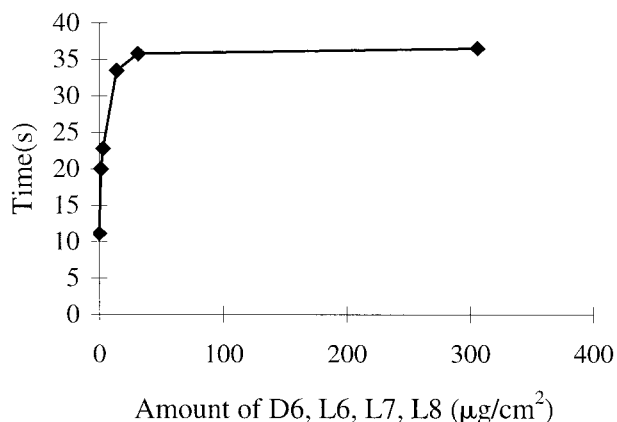

Figure 4 Melting time for the solder paste for different concentrations of siloxane.
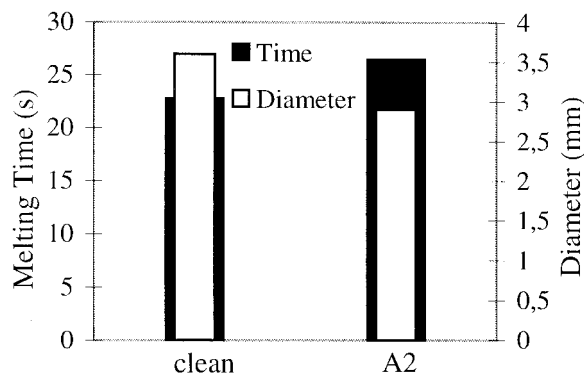
Figure 5 Diameter of the solder dot and the solder-paste melting time for a surface previously covered with sample A2 compared with results for a clean surface.

though not too dramatic an increase: from 22 s for a clean surface to 26 s for the most contaminated surface.

Figure 6 shows the influence of the siloxane mixture on the diameter of the solder dot. No evident change in the diameter can be seen, except for a small reduction for the lowest amounts, that is, below 30 μg/cm^2. Apart from that, the amount of siloxane had no influence on the spread of the solder. In contrast, the diameter of the solder dot on the test pad contaminated with sample A2 was reduced to approximately 80% in comparison with that on a clean surface (see Fig. 5). This was also clearly detected with the microscope.

Siloxanes indeed have some effect on the solderability, although quite small, but increasing the concentrations of siloxanes beyond 30 μg/cm^2 does not affect the soldering any further. This may be explained as follows. When the solder-paste dots are put down on the contaminated surface, only a certain amount, that is, a certain thickness, of siloxane stays under the solder dot. The rest of the siloxane is pushed away
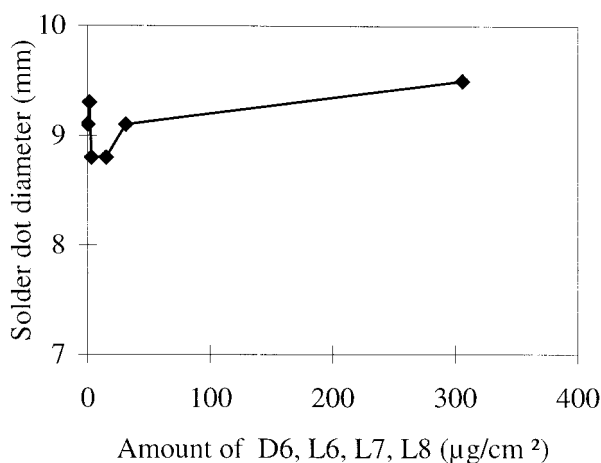

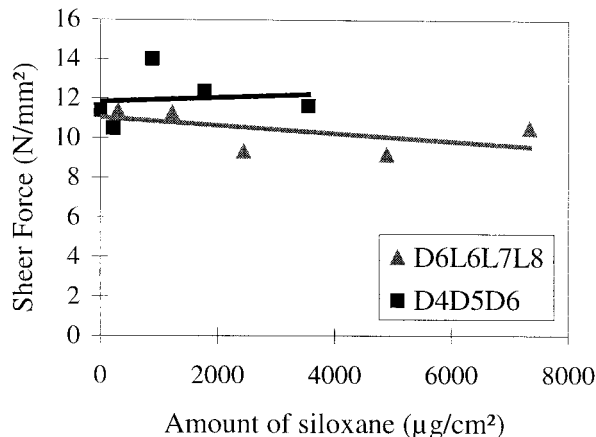**Figure 6** Diameter of the solder dot at various siloxane concentrations.

Figure 7 Results from the adhesion test with the heat-curing globe-top joint.

from the solder dot and, therefore, does not interfere any further with the soldering, especially as this siloxane most likely evaporates as soon as the test pad is placed on the hot plate.

Adhesion of adhesives

The adhesion test is somewhat connected to the aforementioned soldering test, as they both examine how PDMS affects the surface of a material. In this experiment, the focus is on adhesion problems that can occur in the electronic industries. Two different epoxy adhesives have been used: one heat-curing globe-top material and one RT-curing epoxy system.

The experiment with the heat-curing globe-top joint showed only a small reduction in the adhesion strength, even at concentrations of PDMS as high as 7500 μg/cm^2 (Fig. 7). However, a small reduction in the adhesion was observed when the high-molecular-weight siloxane mixture was used. This small effect on the adhesion has at least two explanations. First, the siloxanes may evaporate. This is probably the case for the mixture of D4, D5, and D6, which are all very volatile siloxanes. Second, the siloxanes may dissolve in the globe top; this is more feasible for large and linear siloxanes.

The results from the RT-curing epoxy system agree with the previous discussion. Here, only L7 was used to contaminate the surface, and Figure 8 shows that the decrease in shear force was more pronounced at higher concentrations. However, it is clear that the amounts needed to affect the shear strength are quite high, and such high amounts are unlikely to occur in a normal production environment. For example; at 100 μg/cm^2, the siloxane film created on the surface will be as thick as 1 μm. One possible situation in which such a case could occur is when uncured PDMS is
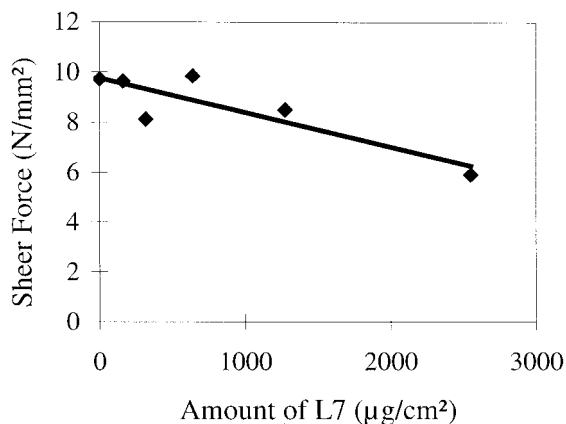
Figure 8 Results from the adhesion test with the RT-curing epoxy adhesive on a test board contaminated with an L7 siloxane.

applied to a PCB because PDMS creeps considerably before curing.

Creep experiments

The aforementioned function tests all describe contamination caused by the volatile fraction of PDMS. Earlier experiments in this series of studies have shown that only a minor part of the cured silicone elastomer is volatile. Because the nonvolatile part is the major part of the noncrosslinked material, tests have been performed to examine the creeping tendencies of PDMS, with the contact angle of a water droplet used as the test parameter. The results from these measurements, taken after 7, 17, and 33 weeks, are shown in Table II.

For all silicone elastomers, surface contamination leads to an increased water contact angle in comparison with that on a clean surface because of the hydrophobicity of PDMS. However, the droplets begin to spread after a certain time, and this leads to decreased contact angles. The contact angles obtained after 7 weeks did not give any clear information about the migration and spreading tendencies. For some silicone elastomers, which showed no increase in the contact angle, 7 weeks was simply too short a time to obtain a reliable value because the droplet collapsed back to 40° after only a short time. However, the measurements indicated creep for three silicone elastomers, samples C3, C1, and A4. In these cases, the time to collapse of the water droplet was more extended, but after 1–2 min (somewhat faster for A4), even these droplets had collapsed. This behavior can be explained by the PDMS layer not being continuous, but rather existing as small islands on the gold-printed surface, especially because the amount of outleaking PDMS is still very small. When the water droplet is applied on the surface, the PDMS islands are pushed

aside by the water. This is likely to happen, as the water/gold affinity is higher than both the PDMS/gold and PDMS/water affinity.

The measurements performed after 17 weeks confirmed the creep tendencies detected after 7 weeks. The contact angles of samples C1, C3, and A4 continued to increase, to approximately 80° for C1 and C3 and to 60° for A4. The contact angle for the droplet on a surface contaminated with sample A4 decreased relatively rapidly after application, and the droplet had completely collapsed after 1 min. The contact angles for samples C3 and C1 also decreased with time, but at a much lower rate. Even after 5 min, both contact angles were well above 40° (65 and 70°, respectively). An increased contact angle was also detected for sample A1. The water droplet was not stable, however, and had collapsed to 45° after 5 min; this indicated that a uniform PDMS layer had not yet developed.

The third measurement was performed after 33 weeks. At this time, samples C3 and C1 showed a contact angle of 90° with almost no tendency to collapse. Sample A4 also showed a contact angle of around 90°, but in this case, the angle decreased somewhat over time and reached 70° after 3 min. Indeed, on sample A4, a PDMS surface layer was clearly visible at least 20 mm from the edge of the cured silicone elastomer, showing that spreading had occurred. Even 30 mm from the edge, the contact angle was 50°. In contrast, a high contact angle of 84° was initially measured for sample A1, but the water droplet collapsed after 5 min. The situation was similar for samples A2 and A3, with increased contact angles but rapidly collapsing droplets. Sample C2, a so-called low-volatile silicone, showed a small but detectable increase in the contact angle to about 50°.

In summary, the creep experiments clearly showed that sample A4 was most prone to creep. Even if this sample did not give rise to the highest contact angle in the shortest times, it was the only sample for which the outleaked PDMS layer was eventually visible to the naked eye. Samples C3 and C1 showed a similar pronounced creep behavior, with a detectable creep

TABLE II
Contact-Angle Measurements in Water after 7, 17, and 33 Weeks of Curing

Silicone	Contact angle (°)		
	7 weeks	17 weeks	33 weeks
A1	44	70	84
A2	45	39	49
A3	44	45	70
C3	70	83	90
C1	55	83	90
A4	50	60	87
C2	40	40	50

already after 7 weeks. For sample A1, the creep was not evident in the beginning, but the sample showed a clear tendency toward creeping after 17 weeks. The next three samples, A2, A3, and C2, exhibited small creep tendencies, a tendency that was almost negligible for the low-volatile silicone, C2.

SEC measurements

The creep experiments shows that the creep tendency is very sample-dependent. However, the ability of low-molecular-weight PDMS to migrate through the material and leak out to the surroundings should be mostly influenced by the amount and MWD of the noncrosslinked PDMS.

For simplicity, the creep of a noncrosslinked material, that is, its migration through the crosslinked matrix and spreading on and contamination of surrounding surfaces, can be considered a two-step process. The rates of these two processes should depend strongly on the molecular weight of the noncrosslinked material. The migration is a diffusion process, the rate of which is generally inversely proportional to the molecular weight. In this case, we study the diffusion of a polymer molecule through a matrix composed of the same kind of polymer. The self-diffusion constant has been shown to be inversely proportional to n^2, where n is the number of repeating units in the chain.[12]

Upon migration, the noncrosslinked material reaches the surface of the silicone elastomer and then spreads onto surrounding surfaces; this process is energetically favorable because of the low surface energy of PDMS. The viscosity (η) of the migrating species will counteract this, and the spreading decreases with increasing η of the migrating PDMS. η is directly proportional to the molecular weight (M) at values of M below the critical molecular weight for entanglements (M_c). For PDMS, M_c is relatively high (29,000).[13] Above M_c, η increases dramatically with M; that is, $\eta \propto M^{3.4}$.

From the previous discussion, it is evident that the molecular weight can be translated into the mobility of the polymer chains. The mobility is most pronounced in the lower molecular weight region, when the molecular weight is less than 5000, whereas we can expect the mobility to be lower already at a molecular weight of approximately 10,000. A molecular weight greater than 29,000 should give rise to a practically insignificant mobility of the polymer chains.

The results from the SEC runs can be found in Figure 9, along with the amount of the noncrosslinked material for each sample. It is not only the molecular weight of the noncrosslinked material that is important; the amount of the noncrosslinked material ultimately determines the amount that theoretically can leak from the cured sample.

To facilitate a comparison between the SEC results and the creep experiments, we discuss the two extreme cases first. Sample C2, the low-volatility silicone, contained a very small fraction with a molecular weight of less than 5000 and correspondingly showed a very small creep tendency. The other extreme was sample A4. SEC showed that A4 contained only a small fraction with a low molecular weight. However, the percentage of noncrosslinked material was very high, around 50%, which, together with a loose network structure, was responsible for considerable creep.

Among the remaining silicone elastomers, it is possible to make a direct comparison between samples A1, A2, A3, and C3, as they had approximately the same gel content and similar MWDs. Samples C3 and A1 seemed to have the highest amounts of noncrosslinked material, with molecular weights of less than 1000, according to the SEC measurements. Indeed, sample C3 contained the largest amount of noncrosslinked material of all four silicone elastomers. From the creep experiments, it is also clear that these two samples were relatively prone to creep. Samples A2 and A3 had very similar MWDs; sample A3 perhaps had a somewhat larger fraction of the lowest molecular weight material. However, sample A3 had a low total amount of the noncrosslinked material, and the creep experiments showed that these two samples exhibited only minor creeping.

Sample C1 is more difficult to fit into this discussion. It showed the same creep behavior as sample C3 but contained a considerably smaller fraction of the lowest molecular weight PDMS, as shown by the extract. The creep behavior of C1 can probably be explained in the same way that of sample A4; because of its lower gel content (84.5% vs 94.6% for sample C3), C1 contained a relatively high total amount of noncrosslinked material.

From the creep tests, some general conclusions can be drawn: (1) with a gel content higher than 90% and almost no material with a molecular weight of less than 10,000, we can expect a silicone elastomer with a small or very small creep tendency, and (2) with a gel content lower than 85%, there is a distinct risk of having a silicone elastomer that exhibits more or less severe creeping.

CONCLUSIONS

Clearly, the presence of PDMS in a gas phase gives rise to contact problems, even at very low concentrations. If PDMS is to be used in a closed system, it is extremely important to use the right grade. Our results suggest using a low-volatility silicone such as sample C2.

The adhesion and solderability tests, performed to examine how a siloxane layer might affect a surface,
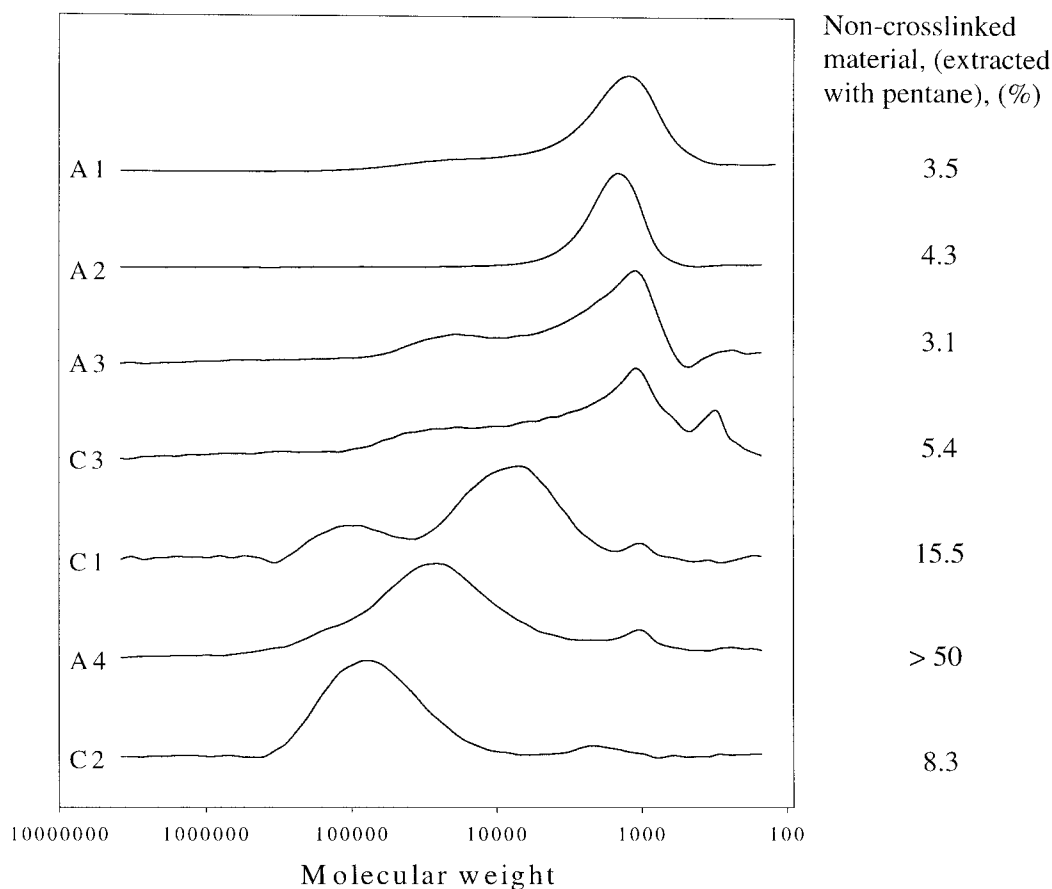
Figure 9 SEC measurements with THF along with the amount of noncrosslinked material obtained from each silicone sample.

showed no major detectable effects. However, adhesion problems may develop in other situations, primarily with water-based systems, for which the adhesion to a PDMS surface is known to be extremely poor.

Creep might be avoided with a PDMS sample of a high gel content (a low amount of noncrosslinked material) and a noncrosslinked fraction with a high molecular weight.

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