Silicone Elastomers for Electronic Applications. I. Analyses of the Noncrosslinked Fractions

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ABSTRACT: In a study about silicone contamination on surfaces, crosslinked polydimethylsiloxanes have been examined focusing on the curing process and the noncrosslinked part in the bulk of the material. Curing was studied by following the development of gel as a function of curing time and temperature using Soxhlet extraction and differential scanning calorimetry (DSC) measurements. Gas chromatography–mass spectroscopy (GC-MS), size exclusion chromatography (SEC), and thermogravimetric analysis (TGA) analyses gave information about the composition and size of the noncrosslinked fraction. The experiments demonstrate that the curing kinetics are of Arrhenius type with a strong temperature dependence. Interestingly, we find that 5–20% of the material does not undergo crosslinking reactions, although only 0–1% of the total sample mass is volatile at ambient temperature and pressure. It is likely that the volatile components mainly give rise to problems when they are confined to closed compartments or when they are in direct contact with a cold surface so that condensation on the surface occurs. Most likely, surface contamination originates from the nonvolatile fraction of the noncrosslinked portion of the material. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2073–2081, 2003

Key words: silicones; silicone contamination; curing kinetics; crosslinking; differential scanning calorimetry

INTRODUCTION

Crosslinked polydimethylsiloxanes (PDMS) are highly flexible, nontoxic materials that have good insulating properties and excellent thermal and chemical stability. All this makes them interesting as protection in electronic components and products. Moreover, due to their inertness, they can be exposed to organic solvents and used at a wide range of temperatures. These materials are already to some extent used in the electronic industry, but a broader future use is desired. There are, however, some potential problems connected with the use of PDMS as low molecular weight (low MW) constituents can migrate out of the material and cause contamination of surfaces. In princial, adjacent surfaces run the largest risk of contamination, but even surfaces far away from the PDMS source may be affected. Silicones spread through the following mechanism. Uncrosslinked, low MW siloxane migrate by diffusion to the PDMS surface where the molecules either continue to spread slowly onto neighboring surfaces, a behavior that we refer to as "creep," or they are released by evaporation. Evaporated species can spread to environments far from the

source where they may cause problems in processes that are sensitive to PDMS contamination.

Silicone contamination is mainly a problem the electronic industry, because of potential problems that low MW siloxanes can cause. One such example is failure of electrical relays due to formation of SiO_2, a typical insulator. In this case, silicon dioxide is formed by a reaction that takes place at elevated temperatures between silicone and oxygen.[1] Furthermore, because of the low polarity of PDMS, adhesion problems can occur on the contaminated surface, which may affect conformal coating, paint and soldering. The potential problems have led to restrictions of the use of PDMS in electronic applications.

The silicone elastomers in this investigation are currently in commercial use. An important demand for silicone elastomers used for electronic applications is that they should not release corrosive components during or after curing. The materials studied undergo curing either through an addition or a condensation curing mechanism. The addition curing, i.e., a platinum catalyzed hydrosilylation reaction, produces no low MW by-product (Scheme 1). The condensation curing reaction takes place between methoxy silane end groups and produces only a noncorrosive low MW product, methanol (Scheme 2). Several more common silicone elastomers, used, e.g., in construction applications, are excluded from use in electronics since these systems contain acetoxy groups and form the corrosive product acetic acid upon curing.
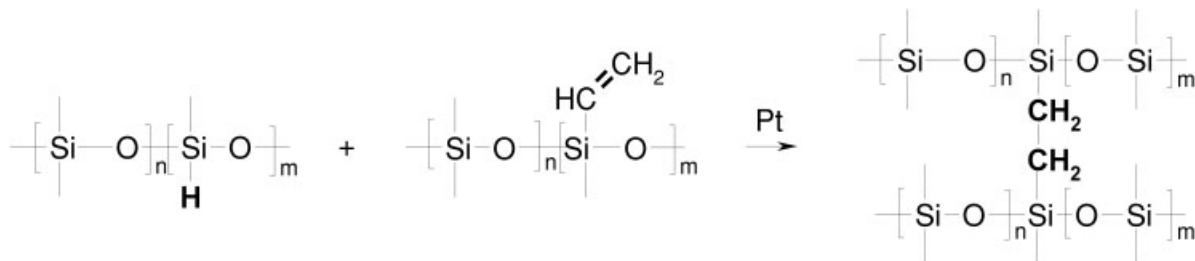
Scheme 1 Network formation in the addition cured system with a platinum complex as a catalyst.

The silicone elastomers were also chosen to cover a broad spectrum of product types and application areas—from systems with reasonably good mechanical properties after curing, such as silicone adhesives, to soft dielectric gels. Furthermore, several different curing conditions were studied, from curing at room temperature to oven curing. Both one- and two-component systems were used, both for the addition and the condensation curing systems.

Similar to all random crosslinking processes, it is mainly the low MW part of the molecular weight distribution of the starting PDMS that is expected to remain as free noncrosslinked material. The high flexibility of the siloxane main chain allows these low MW components to spread to the environment by migration to the surface and subsequent "creep" to and on neighboring surfaces, or by evaporation of volatile species. Earlier work in this field has mainly concerned species that are volatile at ambient temperature and pressure.[2–4] There are, e.g., several standardized testing methods to measure the amount of volatiles in silicone elastomers, developed in response to particu-

lar requirements from the space industry. In contrast, very few studies have been published concerning the nonvolatile and noncrosslinked part with somewhat higher MW, i.e., material that might cause contamination problems due to migration and creep.

It has not been our intention to develop new analytical techniques to determine the structure or the degree of curing of silicone elastomers. In general, all commonly used techniques for analysis of polymers and their low MW analogues can be used. In some instances, however, the special properties of PDMS, in particular its low polarity, call for special considerations, e.g., with respect to choice of solvents. Apart from an excellent book[5] giving a nice overview of the area as well as considerable details for certain techniques, there are not many published papers dealing with analysis of PDMS. In particular, publications on methods for following the curing process are lacking and the available information about the noncrosslinked part is also limited.

Our work has been part of a larger collaborative project concerning silicone contamination in the elec-
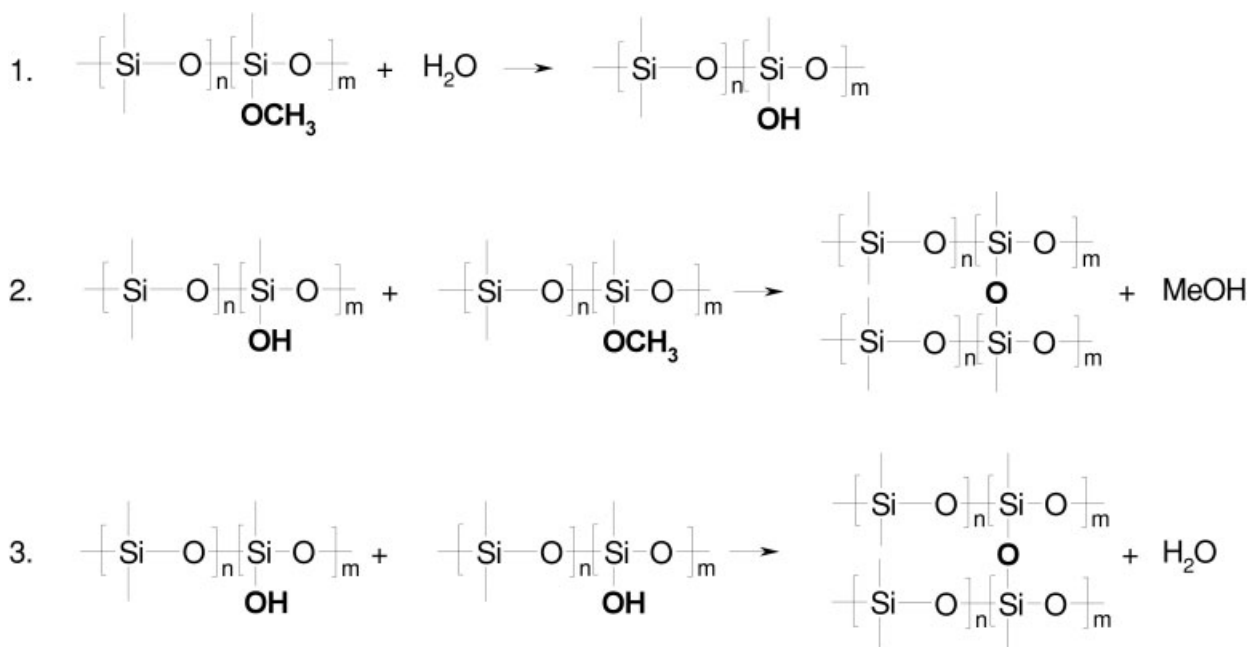
Scheme 2 Network formation in the condensation cured system.

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

Silicone	Type of curing	Fillers (wt %)	Curing temperature (°C)	Curing time (h)
A1	Add. 1 part	Quartz, 35%	100	3
		Surface-treated silica, 16%		
A2	Add. RT,[a] 2 parts	Surface-treated silica, 34%	25	24
A3	Add. RT, 2 parts	Quartz, 46%	25	8
A4	Add.2 parts	—	100	1
C1	Cond. RT, 1 part	$CaCO_3$, 46.5%	25	24
C2	Cond. RT, 1 part	Surface-treated silica, 22%	25	24
C3	Cond. RT, 2 parts	Diatomaceous earth, 21%	25	24
		$Al_2O_3 \cdot 3H_2O$, 7%		

[a] RT: room temperature.

tronic industry.[6] In the work presented in this paper we have investigated the noncrosslinked fraction of a number of commercial PDMS materials. The work has focused on two areas: the curing process and the extractable part of the cured PDMS. The crosslinking process was followed by DSC (differential scanning calorimetry) measurements and by measuring the gel content at different stages of the curing process. The extractable material, containing both volatile and nonvolatile species, was analyzed using size exclusion chromatography (SEC) and thermogravimetric analysis (TGA). The latter technique was used to obtain information about the amount of volatile species. The volatile fraction was also studied by gas chromatography–mass spectroscopy (GC-MS). The effect of contamination of low MW siloxane material on the function on relays, solderability, and adhesion as tested by some application-oriented methods will be presented in a forthcoming paper.[7]

EXPERIMENTAL

Materials

This work is based on the study of seven different commercial silicone elastomers provided by Dow Corning S.A, Seneffe, Belgium. The materials were chosen to constitute a representative selection of silicone elastomers used in the electronic industry. Table I lists the seven materials studied (A1–A4, and C1–C3) together with the curing conditions recommended by the supplier for the respective material. Apart from the fillers given in the table, these commercial silicones do contain small amounts of various additives. The two-parts silicones were mixed manually in a glass beaker.

In addition-cured PDMS, the crosslinking reaction is a hydrosilylation between a vinyl functionalized silicone and Si—H groups catalyzed by a platinum complex (Scheme 1). No by-products are formed when this curing takes place. The condensation curing reaction requires no catalyst (Scheme 2), and methanol is

the only by-product formed in all condensation curing materials included in this study. The water produced in step 3 is consumed in step 1, together with additional water, since there is a net consumption of water in the condensation reaction.

Differential scanning calorimetry

DSC measurements were performed to study the curing process. However, the DSC study had to be restricted to the addition curing systems since condensation curing systems need water to react (Scheme 2) and a controlled addition of water during the DSC run was impossible. All measurements were performed in a Perkin Elmer DSC 7. The typical sample weight was 10 mg.

Samples were analysed with temperature scans to measure the remaining heat of curing until complete curing was obtained. Prior to the run, bulk samples of A2 and C3 were allowed to cure for different times outside the DSC at 19°C. The temperature scans were run at a constant heating rate, 10°C/min, up to 150°C.

Isothermal measurements were performed to evaluate the temperature dependence of the curing and the curing kinetics of the investigated systems. Different temperatures, covering an interval of approximately 50°C, were applied and the heat flow was followed as a function of time. Three times were used to evaluate the kinetics; the time to start (t_{start}), the time to maximum cure rate (t_{max}), and the time to completion of the reaction (t_{end}).

Sample A4 shows a low gel content corresponding to a low amount of curing reactions. Indeed, the DSC equipment at hand was not sensitive enough to follow the crosslinking of A4 in a reliable way due to the low heat of curing involved.

Gel content

Two complementary techniques, SEC and Soxhlet extraction, were used to determine the gel content, i.e.,

the percentage of crosslinked material of the cured silicones. The basic principle is the same for the two methods: solvent penetrates and swells the crosslinked matrix, upon which the noncrosslinked material can diffuse out into the surrounding extraction medium. The extraction efficiency is increased by enhancing the swelling through the use of a good solvent for the polymer in question. For linear PDMS, alifatic hydrocarbons are considered to be the best solvents as their solution parameter is similar to that of PDMS itself, $\delta \approx 7.2$ (cal/cm^3)$^{1/2}$ and $\delta \approx 7.3$ (cal/cm^3)$^{1/2}$, respectively.[8]

We chose the solvent used in our SEC equipment, 1,2,4-tri-chloro benzene (TCB) at 135 °C, as extraction medium in the SEC method. TCB was chosen since it made possible the extraction of the noncrosslinked fraction, something that other SEC solvents did not accomplish in an acceptable way. The SEC samples were left to extract overnight, i.e., 16 h at 135°C. After the extraction, crosslinked material is filtered off yielding a smaller area of the SEC elution peak as compared to that obtained for a completely soluble sample. The amount of noncrosslinked material is then determined by comparing the areas obtained from a crosslinked material with the area obtained for a non-crosslinked and completely soluble reference sample (sample A4 before curing was used as reference).

For the Soxhlet extraction, two different solvents were used. Hexane was used initially, but it was later exchanged for pentane due to its toxicity. Pentane gave a constant amount of extract after a reasonable extraction time, 4 h compared to 2 h for hexane. Furthermore, pentane gave even faster evaporation after extraction than hexane. Here, the gel content is determined gravimetrically. About 0.3 g of the sample is placed in a preweighed 100-mesh stainless steel basket and is thereafter subjected to Soxhlet extraction in pentane for 4 h. The sample is oven dried at 50°C and weighed until the weight is constant, which took about 1.5 h.

The extraction method was also used to determine the increase of gel content as a function of curing time. This study was done with two room temperature curing systems, one curing through the addition mechanism (sample A2) and one through condensation curing (sample C3). The temperature was kept somewhat higher (35°C) than the recommended temperature (25°C) to speed up the measurements. The DSC study of the curing kinetics of sample A2 (see below) showed that the recommended 24 h to complete the curing at 25°C was equivalent to 8 h at the chosen temperature. The same time and temperature was used for sample C3 as the recommended curing conditions for this sample were the same as for sample A2. However, no kinetic studies of sample C3 could be performed by DSC since C3 is a condensation curing silicone that requires the addition of water (Scheme 2).

Size exclusion chromatography

SEC measurements were carried out in order to study changes in the MW of the extracts as a function of curing times. The partially cured materials were dissolved in TCB at 135°C over night at a concentration of ~2 mg/mL. After filtration the solutions were analyzed with a Waters 150 CV with TCB at 135°C as solvent. Three polystyrene–divinylbenzene columns were used for the separation and a refractive index detector was used to measure the concentration in the eluate. This was done with the extracts from sample C3 (cured with the condensation curing mechanism) and sample A2 (cured through the addition mechanism). The SEC instrument was calibrated with narrow polystyrene standards.

Gas chromatography–mass spectroscopy

To identify and measure the amount of volatile species in the fully cured silicone elastomers, a GC-MS, equipped with a thermal desorption accessory, was used. After curing at the conditions recommended by the supplier, 3.5 mg of each sample was taken from the interior of the material, as low molecular weight species would have been lost from the surface layer by evaporation. The sample was heated at 85°C for 30 min and the evaporated species were continuously collected in a cold trap ($-35°C$). The cold trap was thereafter electrically heated at rates exceeding 2000°C/min. to make sure that the entire collected product had desorbed. The desorbed products were then separated in a GC (50–250°C at 10°C/min) using a split injector so that 10% of the volatile species were analyzed. The column used was a capillary column (30 m long, 0.523 mm in diameter, 25 μm thick liquid phase consisting of 5% diphenyl/95% polydimethyl-siloxane).

Thermogravimetric analysis

An alternate way of measuring volatile species is by TGA. These measurements were performed on extracts from PDMS after different curing times and they thus complement both the GC-MS measurements and the determination of gel content as a function of curing time. As the extract is the total amount of non-crosslinked material, the aim of these measurements is to determine the proportion of volatile material.

Samples of A2 and A1 were cured for different times at 35°C and then extracted for 4 h by Soxhlet extraction using pentane. Half of the solvent volume was removed using a Rotavapour and the remaining solvent was then allowed to evaporate under ambient conditions until constant weight. A small part of the extract (2–5 mg) was analyzed in a Perkin Elmer TGA 7 at 70°C in synthetic air under atmospheric pressure,
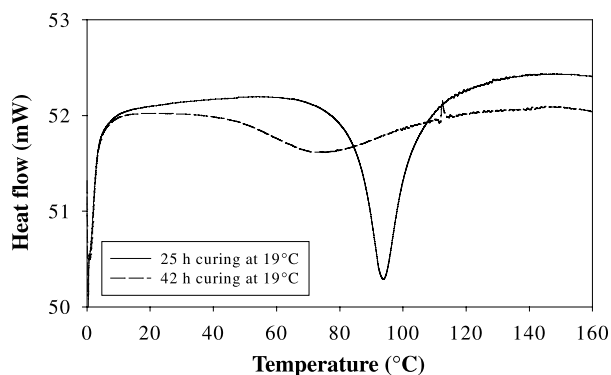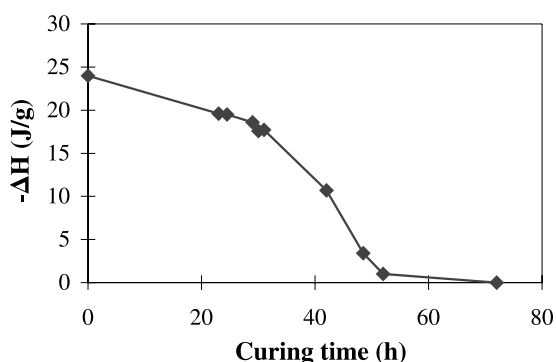
Figure 1 Temperature scans of sample A2 after 25 and 42 h of curing. The additional heat of curing is calculated to −19,989 J/g after 25 h and to −10,676 J/g after 42 h.

and the weight loss was determined. An increased temperature was chosen as it is the adopted procedure in standardised tests of volatile material.[9]
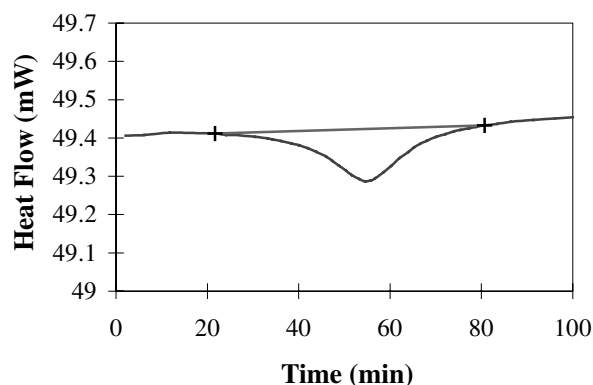
RESULTS AND DISCUSSION

Curing kinetics

DSC was used to study the curing process of the addition curing systems. Temperature scans and isothermal measurements were performed to measure the heat of cure, and to study the temperature dependence and the kinetics in more detail, respectively. Prior to the temperature scan experiments, bulk samples of A2 and A3 were allowed to cure for different time intervals at 19°C, i.e., somewhat lower than the recommended 25°C. Figure 1 shows the temperature scan, in which the area under the curve represents the additional heat of curing. The temperature scan at 0% cure, i.e., run directly after mixing, gives the maximum available heat of cure for the material in question. A comparison of the remaining heat of cure measured for the precured sample with the maximum heat of cure obtained for a noncured sample gives a measure of the degree of curing. Figure 2 shows the results obtained for sample A2. Note that the curing


Figure 3 Isothermal curing measurement with sample A2 at 55°C.

was not completed after 50 h at 19°C, although the recommendations state that this sample should be fully cured already after 24 h at 25°C. This indicates a strong temperature dependence for the curing reaction.

To examine the temperature dependence and the kinetics of the systems in more detail, isothermal measurements were performed at different temperatures. Three materials, A1, A2, and A3 were studied. Figure 3 shows the results for sample A2. Note that there is a certain induction time before any reactions leading to the release of any detectable heat of reaction takes place, and that this time is temperature dependent. The features of the temperature dependence of the curing reaction are represented by the parameters time-to-start (t_{start}), time-to-maximum cure rate (t_{peak}), and time-to-completion of the reaction (t_{end}). Assuming that the effective activation energy for the curing reaction follows an Arrhenius relation, and plotting the inverse of the three different times obtained from the DSC experiment as measures of the reaction rate, gave straight lines (Fig. 4). This shows that the addition curing for sample A2 indeed follows an Arrhenius expression within the investigated temperature range. Linearity is also observed for samples A1 and

Figure 2 Additional heat of curing vs curing time at 19°C for sample A2.
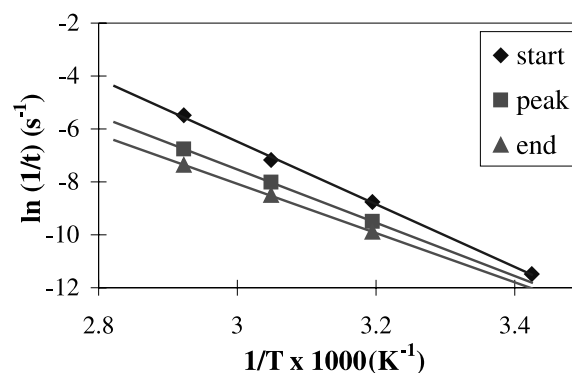
Figure 4 Arrhenius plot of sample A2 calculated from isothermal DSC measurements.
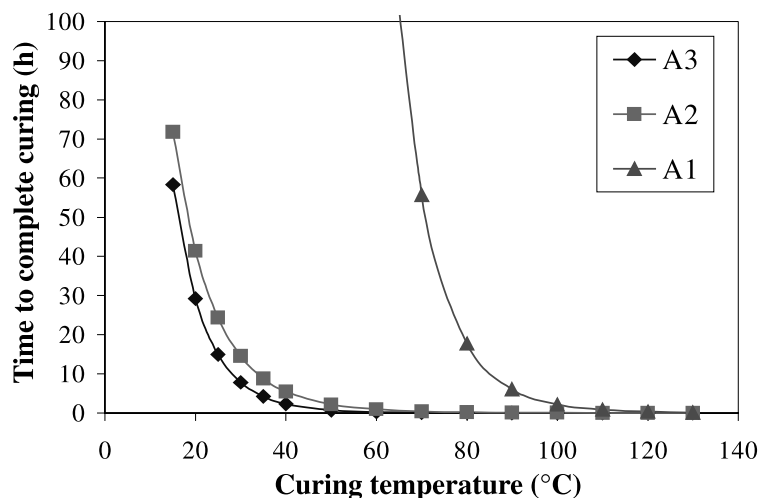
Figure 5 Temperature dependence of the curing time for samples A3, A2, and A1.

A3 even though the curing reactions are run at different temperatures. The three times used give similar temperature dependence, although t_{start} seems to be more strongly affected by the temperature compared to the other two (t_{peak}, t_{end}).

Figure 5 shows the time to complete curing as a function of curing temperature for samples A1–A3. The results show that the curing kinetics are strongly temperature dependent. For example, when the curing temperature for sample A2 is increased from 25 to 30°C, the crosslinking is completed after 14 h instead of 24 h as recommended by the manufacturer. Interestingly, the curing of sample A1 almost completely ceases at temperatures below 70°C. Such a strong temperature dependence might be critical for systems with curing temperatures similar to those at which they are to be used, since the actual curing temperature may vary substantially depending on the place and time (e.g., winter/summer). On the other hand, it opens the possibility to shorten the curing time, or to decrease the amount of noncrosslinked material by increasing the final degree of curing, by curing at a slightly elevated temperature.

Gel content

Table II shows the results from the determination of gel content. For all but one sample, the gel content varies between 80 and 95%, indicating that between 20 and 5% of the material does not participate in the network. This smaller fraction could, theoretically, leak out into the environment. It was not possible to obtain an accurate value of the gel content for the dielectric gel, sample A4, using either SEC or Soxhlet extraction, since this material swells to a very soft and weak gel, making the measurements very difficult. However, it is clear that the gel content for this sample is quite low, something that was expected considering the application area for dielectric gels. This also had consequences on the DSC measurements. Indeed, this material had to be excluded from most other analyses as well due to handling difficulties.

When comparing the gel content determined by the two methods, we note that the values obtained by the SEC technique are generally lower. The overall trends are, however, similar for the two methods. The larger amount of extract obtained by the SEC method is

TABLE II
Molecular Weight of the Extracts and Gel Content of the Analyzed Silicones After Curing at the Recommended Curing Times and Temperatures

Product	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	Gel content SEC (%)	Gel content extraction (%)
A4	7.8	18.3	<50	<50
C3	3.2	10.1	89.0	94.6
C1	4.6	9.4	76.8	84.5
A2	1.6	4.4	93.8	95.7
A1	1.4	4.2	91.7	96.5
A3	1.9	6.5	97.2	96.9
C2	9.5	19.1	92.6	91.7

probably explained by the more vigorous conditions used. The sample is dissolved at 135°C over night, which is the standard procedure used in our laboratory to ensure complete dissolution before running SEC. These conditions should be compared with the much lower temperature and shorter extraction time used for the pentane extractions: 36°C (boiling point of pentane) and 4 h. Another feasible explanation for the discrepancies in gel content is that in the SEC method, the amount of soluble material is determined by measuring the area of the elution peak and comparing it with that of a completely soluble material. We have used sample A4 in its noncured form as reference and assumed that there is a small difference in refractive index increment between this sample and the extract. However, as the MWs for some of the extracts are quite low (see below), this assumption might not be entirely valid.[10].

The SEC measurements reported in Table II also give the average MW of the soluble part of the samples. Based on gel content and MW of the extracts, the analyzed silicone elastomers can be divided into three separate groups. The first group contains samples A4, C1, and C3, i.e. those with a large extractable portion and a low gel content. As expected, the extracts of these samples have a relatively high MW. The materials with a higher gel content, i.e., samples A1–A3, all have extracts with a lower MW. This is what would be expected from a random crosslinking process as the probability for a polymer chain to be included in the network increases with increasing MW. The third group, including only sample C2, differs from the two others in that the MW of the soluble part is significantly higher than for the other samples, even though the gel content of this material is reasonably high. Sample C2 is the only so-called low-volatile PDMS, for which the low MW part of the starting material has been removed in a separate step in the manufacturing process, explaining how the cured material can be highly crosslinked and still have a soluble fraction with a high MW.

The gravimetric extraction method was also used to follow the development of gel as a function of curing time for one addition curing system, sample A2, and one condensation curing system, sample C3. The results obtained for sample A2 are shown in Figure 6. A slow initial curing rate is followed by a rapid increase in gel content after which the curing rate levels out. In the context of silicone contamination, it is interesting to note that the gel content continues to increase even after the recommended curing time (8 h at 35°C), i.e., after the curing is supposed to be completed. The increase might seem negligible, e.g., from 93 to 95% gel content when increasing the curing time from 8 to 28 h. However, this small increase in gel content corresponds to a decrease of approximately 30% in the amount of material that could potentially leak out to
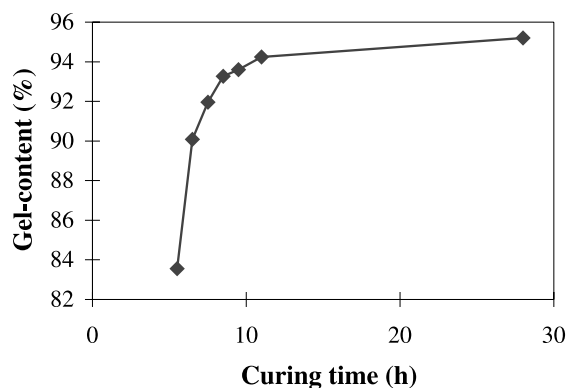
Figure 6 Gel content vs curing time for sample A2 at 35°C. Recommended curing time at 35°C is approximately 8 h.

the environment. For curing at room temperature this is not critical since such systems continue to crosslink even while the component is in use. For systems curing at higher temperatures, however, this might be of importance. In such cases, it is possible to minimise the noncrosslinked fraction by increasing the curing time. However, the improved properties must be balanced against the cost of curing for a longer time at the elevated temperature.

Identification of volatile species

To identify and determine the amount of volatile species that evaporate from completely cured silicone elastomers, a GC-MS equipment for thermal desorption measurements was used. This allows for a qualitative comparison of the amount of volatiles desorbed from the analyzed samples.

Table III shows that the detected species include both cyclic and linear oligosiloxanes containing 3–6 Si—O units, D4–D6 and L–L6, respectively. In addition to these compounds, the volatiles contain an undefined, branched siloxane containing 7 Si—O units. Furthermore, we found a number of higher homologues, both linear and cyclic, given in one entry in Table III. The tested samples can be divided into three separate groups. The first group contains samples that mainly give off cyclic siloxanes (A3, A4, C1, and C3). The second main group produces cyclic and linear siloxanes in almost equal amounts (samples A2 and A1, producing 60 and 40% linear siloxanes, respectively). Again, the low volatile PDMS sample C2 stands out by not releasing any volatile species.

The integrated areas of the chromatograms show that the silicone elastomers releasing the largest total amount of volatile material also contain mostly cyclic components, i.e., the samples in the first group above. Sample A3 contains slightly less volatile material than the others in the group, and this silicone elastomer also contains a smaller fraction of cyclic siloxanes. Clearly, the silicone elastomers containing a large

TABLE III
GC-MS Measurements Identifying the Linear (L) Species and the Cyclic (D) Species in the Volatiles from a Cured Sample[a]

Product	L3	L4′	L5	L6	7-Si[b]	>7 Si[c]	D4	D5	D6	Total
A2	2	17	28	7	6	18	2	3	4	87
A1		4	1	13	3	6	12	nd	3	42
A3			5	11	5	31	41	13	62	168
A4					45	25	42	86	75	273
C3					82	32	42	73	143	372
C1					44	7	25	90	110	276
C2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

[a] The numbers represent the integrated area in the mass spectrum.
[b] siloxane with 7 Si—O units, undefined structure.
[c] higher siloxanes, both linear and cyclic.

amount of cyclic species release more volatiles than the other materials.

Quantitative analysis of the volatile material was also performed.[6] The results show that only a minor fraction of the cured PDMS, 0.1–1%, had evaporated after 48 h at 85°C and ambient pressure.

Volatiles and curing time

The TGA runs give weight loss curves that indicate that the initial evaporation is fast and that the rate then decreases to reach a constant level. Taking into account possible weight loss during sample preparation, the amount of volatiles in an extract should be virtually the same as the amount of volatiles in the entire material. In Figure 7, the amount of volatiles that have evaporated from the extract of sample A2 are shown. The data points are somewhat scattered, but there is a clear indication that the *fraction* of volatile material of the extract increases with increasing curing time. This is a natural consequence as the probability to be connected to the network decreases with decreasing MW. Another way to express this is that the low MW fraction crosslinks more slowly. However, calculations on the *total amount* of volatiles show a decrease during the first 8 h of the curing—from ~1% after 6 h to ~0.45% after 8 h, and then it remains constant. It was
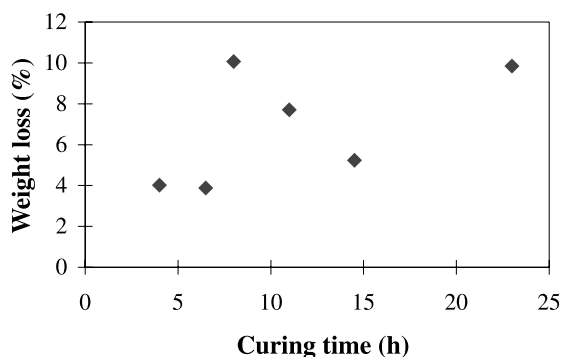

Figure 7 Amount of volatiles of the extract as a function of curing time for sample A2 studied with TGA at 35°C.

not possible to obtain any extract before 4 h of curing because of a too low degree of curing, which made an extraction impossible. It should be noted that 8 h is the recommended curing time for complete curing at the temperature used (35°C). This decrease may reflect the reaction of low MW material containing reactive groups. Another possibility is evaporation of the most volatile fraction during curing, as the system is not confined to a closed compartment. We have performed further GC-MS experiments using a head-space injection system.[6] In this study we detected oligosiloxanes containing groups that may react through the crosslinking mechanism, e.g., L3–L5 with a Si—H group. The decrease in amount of volatile material before 8h could reflect the inclusion of such material in the gel.

After 8 h, the amount of volatiles is constant throughout the rest of the curing. Consequently, this fraction will never participate in the network no matter how long the curing is allowed to take place. This agrees with our GC-MS measurements, which show that the major part of the volatiles consists of linear or cyclic oligomers of PDMS, i.e., material that does not contain groups that partake in the addition curing process. Therefore, to minimize deposition of volatile components on surrounding surfaces, the starting polymer should be modified to minimize the low MW tail of the molecular weight distribution. This can be done by the raw material producer, e.g., by trying to avoid the cyclic oligomers. Another alternative is to eliminate the lowest MW molecules of the raw material, something which is already done for the so-called low-volatile silicones such as sample C2.

CONCLUSION

Earlier work on the cause of silicone contamination has mostly concerned the volatile species of PDMS. In this study, the examined materials contained between only 0 and 1% volatiles. The GC-MS analyses showed that these volatiles consist mostly of cyclic siloxanes, D4–D6, and also some linear species, L3–L6. Further

work[7] on the volatile fraction has shown that the volatility of these species is very high. They should therefore not condense onto surfaces under normal conditions, and only cause problems when they are confined to closed compartments or when the surfaces are cold.

It is more likely that problems with surface contamination are caused by the nonvolatile fraction of the noncrosslinked part of the cured silicone elastomer, partly because this fraction is much larger than the volatile part, 5–20%. Incidentally, it is possible to reduce the noncrosslinked part by increasing the degree of curing beyond that reached at the recommended curing conditions. Kinetic studies of the curing process have indicated a relatively strong temperature dependence. Such knowledge can be applied in cases when it is important to reach the desired degree of curing at a specific time.

The ability of the nonvolatile fraction of the noncrosslinked part to spread is certainly dependent on a variety of factors, among them the size of the fraction and its average MW. Measurements showing how these factors affect the ability of the nonvolatile part to spread, together with some practical functional tests with electronic devices, will be presented in a future paper.

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