2. Characterization of Silicones

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Most analytical methods commonly used for organic materials also apply to silicones. Extensive reviews have been published about the different analytical techniques that are applicable for detecting and characterizing silicones [1]. The focus here will be on methods as they relate to typical application problems; some of these are commonly used methods. Others, such as elemental analysis and thermal analysis, are described in more detail.

Common Methods Applied to the Analysis of Silicones
Infrared spectroscopy and, in particular, Fourier transform infrared spectroscopy (FTIR), is widely available and the easiest technique for detecting the presence of silicones and obtaining information about their structure. Silicones have strong absorption bands in the mid-infrared spectrum range, at 1260, 1100-1000 and 770 cm^{-1}, meaning that levels as low as 1% can be detected. This method differentiates polydimethylsiloxane, trimethylsilyloxy groups, and copolymer-type materials. Quantification is possible using one of the strong silicone absorption peak signals. Corresponding height or area can then be correlated to a known standard and actual level calculated using Beer-Lambert's law.

Other infrared-based techniques like FTIR/ATR or FTIR/DRIFT are specifically used to detect silicones adsorbed on a substrate (see Figure 1). However, in many cases, the layer of silicone on the top of the sample surface is so thin that only the fingerprint of the bulk of the sample is seen. Better samples can be prepared through extraction using a good solvent: hexane (most alkanes are suitable), methylisobutylketone, toluene for siloxane or tetrahydrofuran for more polar copolymers like silicone polyethers. However, extraction recovery yields can be significantly lowered if the siloxane strongly bonds to the substrate. This issue is often encountered with amino-functional siloxanes.
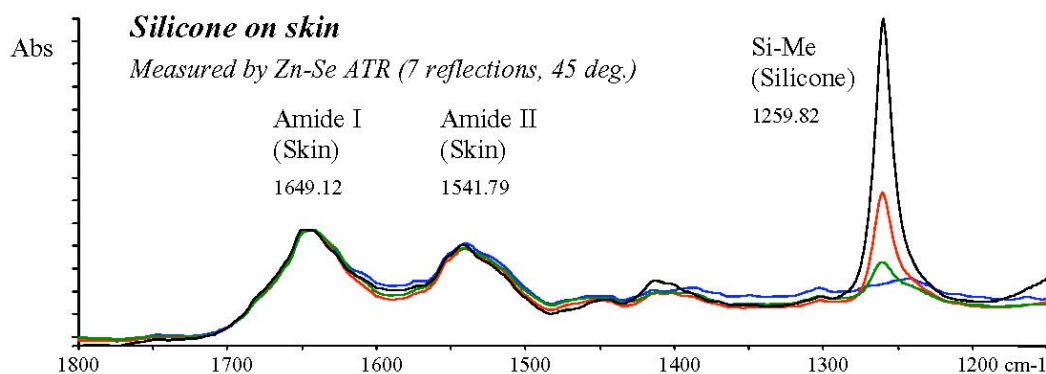

Figure 1. *FTIR/ATR (attenuated total reflection) analysis of a silicone polymer applied on human skin (the amide skin peaks can be used as internal standards).*

Gas chromatography coupled with mass spectroscopy detection (GC-MS) is another method used to detect silicones in a formulation, looking for the presence of siloxane cyclic oligomers, as such low molecular weight species are always associated with silicone polymers. The neat sample can be heated at a specific temperature (up to 250 °C) in a headspace bottle and the generated volatiles injected. An alternative is to dissolve the sample,

if feasible, and inject the solution.

The most flexible injection mode is the use of a pyrolyser coupled to the GC-MS. This allows collecting and identifying volatiles within any selected temperature range. Yet CG-MS does not allow precise quantification.

A precise quantification of those volatile cyclics is routinely done by coupling gas chromatography with flame ionization detection (GC-FID).

In addition to GC, other techniques can be used to identify and/or quantify the lowest molecular weight species present in silicone polymers; for example, gel permeation chromatography (GPC) or supercritical fluid chromatography (SFC) (see Figure 2).
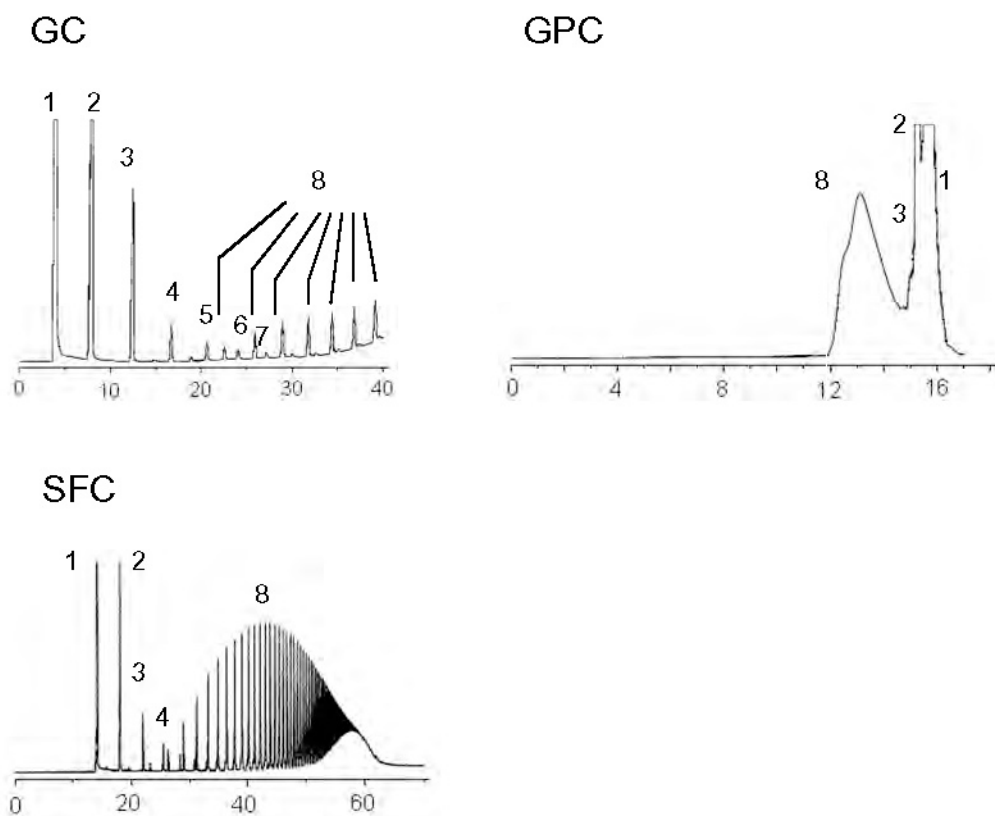

Figure 2. *Comparison between different chromatographic techniques with a trimethylsilyloxy terminated polydimethylsiloxane before stripping. Peak 1 to 12 = cyclics (m = 4 to 10) and peak 8 = polymer.*

Gel permeation chromatography (GPC) (also called size exclusion chromatography or SEC) using a refractive index detector allows one to obtain molecular weight averages and distribution information. Calibration is done with polystyrene standards, and Mark-Houwink constants are used to correlate results between the standards and siloxanes' molecular weight. Adding a laser angle scattering detector provides information on the three-dimensional structure of the polymer in solution.

In addition to infrared methods, nuclear magnetic resonance spectroscopy (NMR) can be used to obtain polymer structural details ^{1}H and ^{13}C NMR bring information about the type of

organic substituents on the silicone backbone such as methyl, vinyl, phenyl or polyester groups, and identify the degree of substitution in these polymers. ^{1}H NMR is also a technique used to measure the relative content of the SiH groups (proton chemical shift at 4.7 ppm) versus dimethylsilyloxy species (proton chemical shift close to 0 ppm). However, in some cases (e.g., as after a hydrosilylation reaction), the residual SiH levels are too low to allow for quantification. Here gas chromatography coupled with a thermal conductivity detector (GC-TCD) is a more appropriate method. This method works in an indirect way, analyzing the hydrogen generated when the sample is hydrolyzed in presence of a strong base as a catalyst.

Application Specific Methods for the Analysis of Silicones
In addition to the methods described above, some more specific techniques are used to detect the presence of silicones as formulation ingredients or contaminants or to study their high/low temperature behavior.

Atomic absorption spectroscopy (AAS) allows quantification of the silicone element in a given formulation. This approach is widely used to quantify the silicone content in materials made of, treated with or contaminated by silicones.

If the formulation is known not to contain any other silicone element source than silicones, the presence of silicones can be easily detected by X-ray fluorescence (XRF), as the method does not require any particular sample preparation. XRF is capable of measuring silicone contents if standards can be prepared in the same matrix as the formulation.

Surface tension measurement is another easy way to detect surface contamination by siloxanes, through comparison with a virgin reference. Contact angles of both suspected and clean surfaces are measured with a set of suitable liquids. Silicone contamination will be indicated by large contact angles resulting from a significant decrease in surface energy.

X-ray photoelectron spectroscopy (XPS) or time of flight-secondary ion mass spectrometry (TOF-SIMS) are more sophisticated techniques that can also be applied to detect and characterize silicones within the 10-50 Å depth layers from the surface of materials.

The average structure of silicone polymers is accessible through ^{29}Si NMR thanks to the [29]Si isotope nuclear spin (I = 1/2) and its relative abundance (4.7%). However, the relative sensitivity of ^{29}Si NMR is low versus ^{1}H NMR (7.8×10^{-3} times lower), which implies long accumulation times for any measurements. Peak assignments are eased by large chemical shift differences and the use of decoupling (see Table 1). Yet silicone chain ends cannot always easily be detected by ^{29}Si NMR, especially in high molecular weight siloxane polymers.

For structural purposes, a complementary technique to ^{29}Si NMR has been developed by depolymerizing the siloxane backbone in the presence of an excess of an appropriate endblocker using a strong base or acid as catalyst. The recovered volatile oligomers are then quantified by GC-FID. This approach has proven applicable to quantifying traces of silicones on substrates like wool, paper or hair [2].

Table 1: Typical ^{29}Si NMR Chemical Shifts

Unit Structure	Unit Type	Chemical Shift
$Me_3SiO_{1/2}$	M	+ 7 ppm
$Me_2SiO_{2/2}$	D	- 22 ppm
$MeSiO_{3/2}$	T	- 66 ppm
$SiO_{4/2}$	Q	- 110 ppm
$HOMe_2SiO_{1/2}$	M^{OH}	- 10 ppm

The performance of silicones versus organic polymers at high or low temperatures is verified when using thermal analysis methods such as thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC), whether under air or inert atmosphere. In the latter conditions, the onset of polymer depolymerisation to cyclic species is usually found at temperatures higher than 350 ºC. However, traces of base or acid are sufficient to significantly decrease the temperature at which decomposition starts to occur by catalyzing the re-equilibration of the polymer into low molecular weight volatile species. TGA is the most appropriate technique for measuring the onset of weight loss (temperature ramp mode) or the amount of weight loss at a fixed temperature (isotherm mode).

It is recommended to run TGA under inert atmosphere as the presence of oxygen will allow, at temperature higher than 300 ºC, the partial oxidation of the silicone chain groups into silica and the formation through methyl substituents oxidation into species like carbon monoxide, carbon dioxide, formaldehyde, hydrogen and water. However, unlike GC-MS techniques, TGA does not give information about the nature of the species volatilized (see Figure 3).

On the other hand, DSC is particularly appropriate for analyzing the behavior of silicones at low temperatures. Due to the flexibility of the polysiloxane backbone, glass transition typically occurs below -120 ºC, a remarkably low temperature if compared to other polymers. This is why polydimethylsiloxanes remain fluid and silicone elastomers remain flexible at low temperatures. Nevertheless, crystallization can be made to occur, at least for a fraction of the polymer, on slow cooling below -40 ºC. The cooling rate should be low enough to allow chains to form crystalline structures. Silicone polymers can also be supercooled to a glassy state without crystallization under fast cooling or quench. In this case, on reheating, a cold crystallization exotherm is observed followed by the usual endotherm(s) around -50 ºC (several "melting points" can be observed as multiple crystallization/melting events occur in the sample in the same temperature range) (see Figure 4).
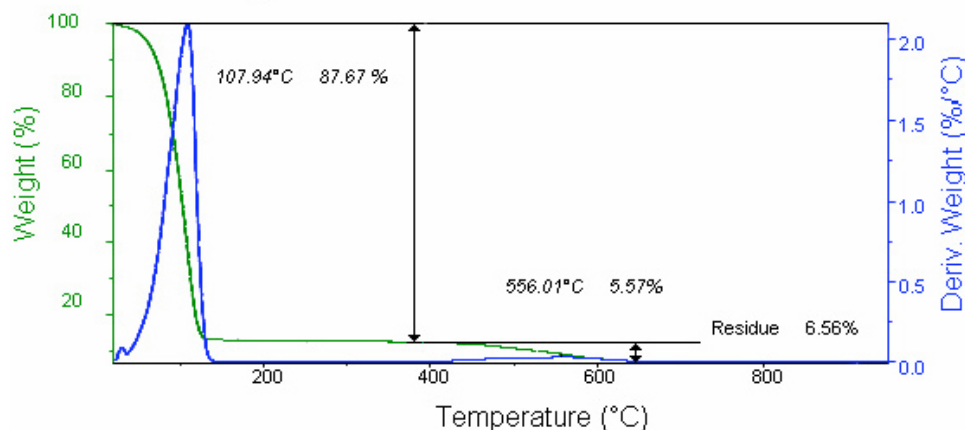
Figure 3. *TGA analysis under dry nitrogen of a blend of silicone volatile species and silicone elastomer (weight loss curve in green, first derivative curve in blue); precise content in volatile species (weight loss up to 150 ºC) and in elastomer (second weight loss step between 400-700 ºC and residue in 950 ºC).*
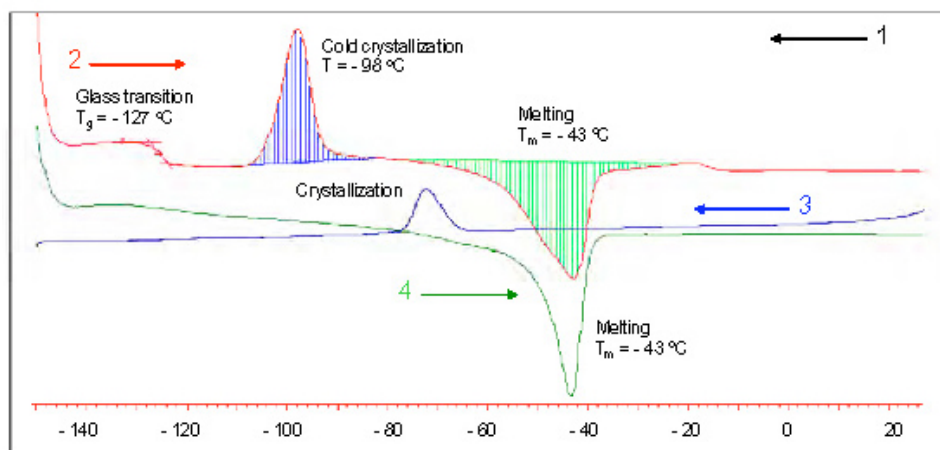

Figure 4. *Typical low temperature DSC analysis of a silicone elastomer: the sample is super-cooled at -150 ºC (1 - black / no curve), then heated from -150 ºC to 25 ºC (2 - red curve). The following are detected: glass transition (T_g) at -127 ºC, cold crystallization at -98 ºC and melting (T_m) at -43 ºC. Afterwards, the sample is cooled down at a low cooling rate and reheated. A crystallization exothermal peak is observed during the cooling step (3- blue curve) and only a single melting endothermic peak during the second heating step (4 - green curve).*

DSC is also a powerful technique for studying exothermic reactions such as the hydrosilylation reaction, which is associated with a strong exotherm. Dynamic or isotherm modes allow characterization of the cross-linking and optimization of formulations based on the temperature corresponding to the onset of cure of to the maximum cure rate (see Figure 5).
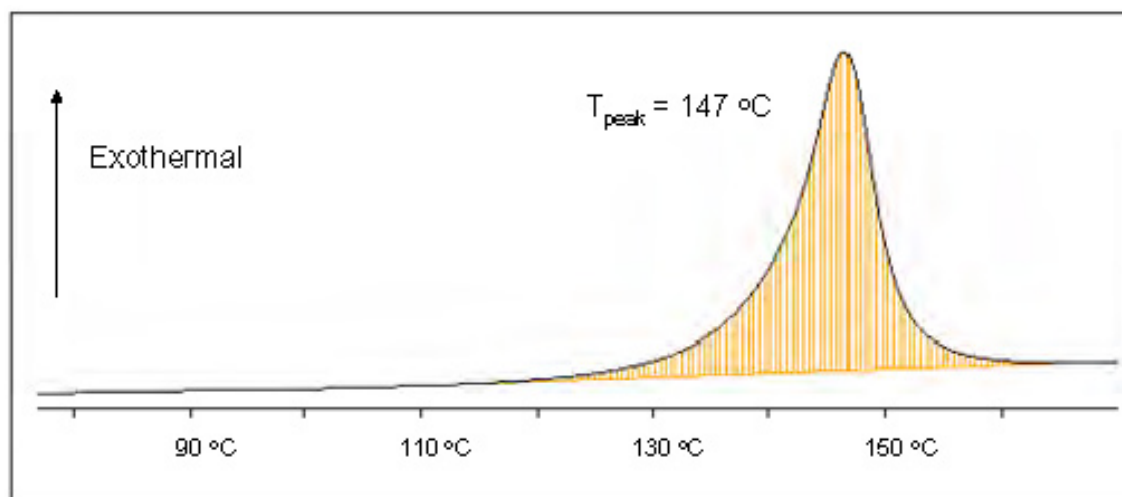
Figure 5. *Differential scanning calorimetry of the reaction between silicone polymers with SiVi groups and polymers with SiH groups in presence of a platinum catalyst.*

References

[1] Smith, A. L. *The Analytical Chemistry of Silicones,* John Wiley & Sons, Inc.: New York, 1991.

[2] Smith, A. L. *The Analytical Chemistry of Silicones,* John Wiley & Sons, Inc.: New York, 1991; 210-211.