IR SPECTROSCOPIC METHOD FOR DETERMINATION OF SILICONE CROSS-LINKING

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1. Introduction

Release liners based on silicone chemistry (PDMS) with polyolefin substrates are a very important product in the pressure sensitive market. The main tasks of release liner are to provide protection of the adhesive layer during storage and transportation, along with a residue-free removal of the liner without damaging the adhesive layer. Furthermore the silicone layer must not affect the adhesive properties of the tape. To ensure this, the silicone must be even and consistently applied to the substrate and completely cross-linked, allowing no migration from the silicone into the adhesive layer. Silicone release liners are considered as fully cured, when the benchmark of 5 % extractables is undercut. For certain market segments it is desirable to achieve the best curing possible whereas other applications will not be affected by some silicone migration.

An IR spectroscopic method for determining the silicone cross-linking is presented, which represents a quick and easy alternative to conventional extraction measurements. In comparison with time-consuming and waste producing extraction measurements, IR spectroscopic results can be achieved within minutes with well-known equipment. With this method it is also possible to measure the amount of residual hydride groups after the curing, which can lead to adhesive interaction and affect the release force. Furthermore, IR spectroscopy provides the potential to not only measure the curing rate, but also the application weight of the silicone layer.

2. Thermal Silicone Release Liner

Release liner are siliconized films which protect an adhesive layer and can be removed without damaging and changing the adhesive properties. Considering the costumers requirement, the properties of the release coating like application weight, release force and elasticity can be adjusted. For different areas of application silicones are classified in three groups with specific properties: solvent free, solvent based and emulsion systems. In addition it is distinguished between thermal- and UV-cured silicone systems. In the PSM marked thermal silicone systems are most commonly used because of a brought variety of adjustable release forces and their good release properties against the used adhesives. [1]

The thermal cross-linking reaction or curing of PDMS takes place via hydrosilylation reaction:

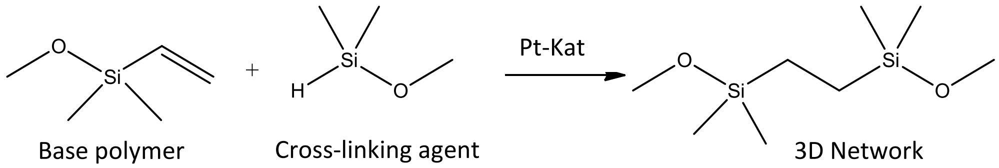


Figure 1. Platinum catalyzed hydrosilylation of polydimethylsiloxane.

In the platinum catalyzed addition reaction the unsaturated carbon-carbon bond of vinylsiloxane and a silane group cross-link to a PDMS network. Hydrosilylation reactions are promoted by soluble platinum catalysts like Karstedt's catalyst, a Pt(0)-siloxane complex.

Thermal curing silicone systems consist of up to five components: a base polymer, a cross-linking agent, a catalyst, an inhibitor and optionally release force regulators or other additives. In addition curing systems vinyl functionalized silicone polymers represent the basis of the silicone system. Chain length, structure and the number of reactive groups decisively determine the properties of the resulting network and thereby the release selection and the release force profile. Mono-functional structures result in a network with loose ends, which is elastic and flexible, has good anchorage and a low friction coefficient. Linear and branched base-polymers build a narrow network, leading to a reduced dependence of release force on peel speed and thereby result in a flat release force profile. [1]

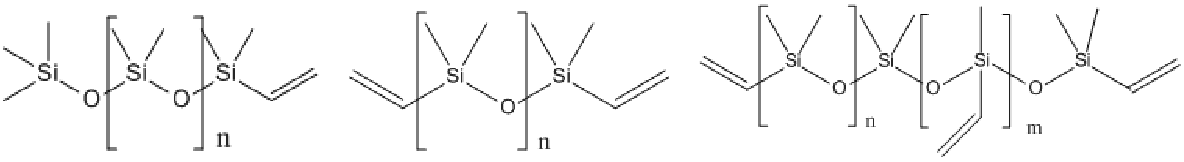
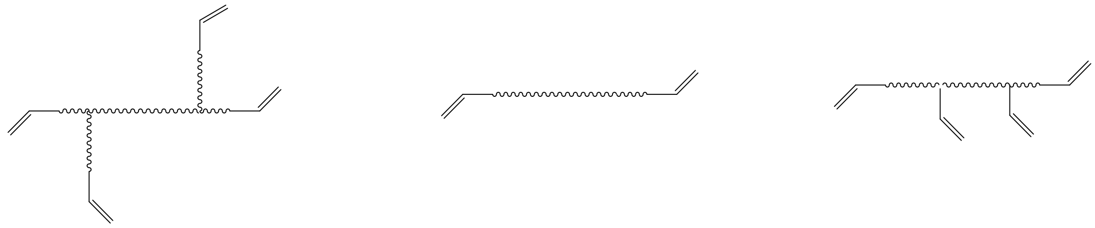


Figure 2. Mono-functional, linear, pendant.

On the one hand the curing speed increases with the decrease in viscosity and on the other hand with the mobility and number of the vinyl groups of the base polymer.

Curing speed

Branched > Linear > Pendant



Low viscosity > High viscosity

Silicone hydride-containing silicone polymers are used as cross-linkers. Type and amount of cross-linking agents have a major influence on the reaction speed of the system, the anchorage of the coating to the substrate and the interaction with the adhesive. It is distinguished between branched cross-linkers, which are sterically flexible and thus cure faster, but have only few Si-H groups for anchorage and linear polyhydrogenmethylsiloxane with various numbers of continuous Si-H groups, which cure slowly but with very good anchorage. [1]

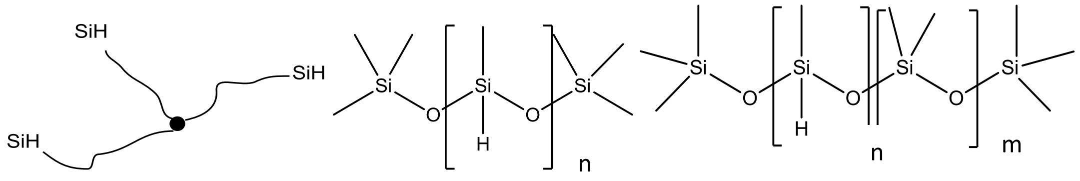


Figure 3. Branched cross-linker: fast curing, but critical anchorage; continuous Si-H-groups: good anchorage, relatively slow curing; continuous Si-H-groups with loose ends: fast curing, needs less catalyst.

The ratio of cross-linking agent to base polymer is characterized by the Si-H/Vinyl ratio. The formulation of addition cross-linking systems usually contains an excess of cross-linker. Firstly, sufficient Si-H groups for the cross-linking reaction and the anchorage on the substrate must be present, secondly an increase in Si-H/Vinyl ratio results in faster curing.

Common ratios lie between 1.2 to 2.5. Excessive hydride may lead to stability problems in the adhesive layer, as some adhesives react sensitive on Si-H residues in release liners. [2]

For the acceleration of the reaction speed a platinum catalyst is used. The curing rate is most easiest regulated by the catalyst proportion. Due to the high platinum price, 100 ppm catalyst contented is regarded as a benchmark in the release liner industry. Certain additives which are contained in film surfaces can affect the application process and inhibit the platinum catalyst in addition curing systems. Therefore the smallest amounts are sufficient. The catalyst poisons include organic compounds, amides or phosphides. [1][2]

In order to increase the pot life of the silicone system and to allow a smooth processing of the silicone an inhibitor is used. The inhibitor coordinates better to the platinum then the divinyltetramethyldisiloxane, but not as strong as a catalyst poison. The deactivation of the inhibitor is normally achieved through application of heat. Very volatile inhibitors provide very fast curing systems but also short pot life. [1]

Release force regulators, silicone resins in vinyl silicone polymer, determine the individual release force level. In the production of adhesive tapes and transfer films release force regulators are of great importance. By building special silicone resins in the chemical structure of the coating system, they decrease the flexibility of the silicone chains and thereby increase the release force level. [1]

Other components of the silicone system can include adhesion promoters, thinners and anti-misting agents.[1]

3. Determination of Silicone Cross-Linking

The measurement of the silicone curing is a very important indicator for the production of release liners as it affects production parameters, like oven temperature and track speed, as well as product properties. The most common method for the determination of the silicone curing in the silicone coating industry is the so-called extraction measurement. The benchmark for cured silicones is determined at 5 % extractables, due to the purity of the silicone systems and measurement uncertainties. Depending on the application of the release liner the silicone system with the appropriate maximum curing rate has to be chosen.

3.1 Extraction Measurement

The extraction measurement, used in the silicone coating industry, mostly consists of a combination of XRF measurement and atomic absorption spectroscopy (AAS). The coating thickness of the silicone is determined by XRF measurements and the extractable amount of silicone, so the uncured portion, is measured by AAS. With the ratio of the two results the degree of silicone curing can be determined.

For the extraction measurement pieces of siliconized film with a defined size were placed in a headspace vial and filled with isobotylmetylketone (MIBK). The vials were gas-tight sealed to prevent evaporation of the volatile MIBK. So the non cross-linked silicone can dissolve completely, the samples were left for at least 24 h and mixed shortly before the AAS measurement. By a repeat determination of the sample the homogeneity of the sample was classified and the measurement error was minimized.

3.2 IR Spectroscopy

Although the focus of IR spectroscopy lies on the qualitative analysis and on the structural determination of unknown molecules, a quantitative determination of two or more components using IR spectroscopy is also possible. For silicones different measuring techniques are commonly used like transmission through a liquid cell for liquid silicones or solutions or through thin pieces of silicone elastomer. [3]

A simple procedure for obtaining an IR spectrum of the silicone coating of an release liner is the reflection technique, attenuated total reflectance (ATR). A thin slice of the sample was cut to closely match the crystal area on the horizontal ATR accessory from Spectra-Tech with a ZnSe crystal. The sample was slightly pressed onto the crystal surface and the IR spectrum was recorded on a Thermo Nicolete Nexus 470 FTIR spectrometer by Thermo Fischer Scientific Inc. with a resolution of 4 cm^{-1} and 62 scans.

3.3 Quantitative IR Spectroscopy

The correlation between the experimentally detectable quantity, the amount of absorbed electromagnetic radiation and the substance concentration is described by the Lambert-Beer's law.

$$A = \varepsilon c d \qquad (1)$$

Since the layer thickness of the silicone coating is not constant, relative absorption specification may be used. In this connection the absorption is expressed as the ratio with the absorption of a constant band. Mathematically this corresponds to a division of the respective approaches of Lampert-Beer's law:

$$\frac{A_{\text{Si-H}}}{A_{\text{k}}} = \frac{\varepsilon_{\text{Si-H}} c_{\text{Si-H}} d}{\varepsilon_{\text{k}} c_{\text{k}} d} \qquad (2)$$

whereby $\varepsilon_{\text{Si-H}}$ and ε_{k} are material constants, c_{k} is a constant concentration and $c_{\text{Si-H}}$ is to be determined. The layer thickness d is canceled.

When the concentration of the Si-H in the cross-link reactant is not known and no calibration line can be created, the turnover degree is specified:

$$X_{\text{Si-H}} = \frac{\frac{A_{\text{Si-H,0}}}{A_{\text{k,0}}} - \frac{A_{\text{Si-H}}}{A_{\text{k}}}}{\frac{A_{\text{Si-H,0}}}{A_{\text{k,0}}}} \qquad (3)$$

The turnover degree is the proportion of converted amount of Si-H ($\frac{A_{\text{Si-H}}}{A_{\text{k}}}$) based on the beginning amount ($\frac{A_{\text{Si-H,0}}}{A_{\text{k,0}}}$). For each measurement the uncured silicone is measured once.

3.4 Measuring Method

The fundamental principal for the use of IR spectroscopy for the examination of the reaction progress of the hydrosilylation reaction, lies in the possibility to measure the reduction of the Si-H bond or vinyl bond. As the vinyl stretching at 1600 cm^{-1} and 3070 cm^{-1} has a lower extinction coefficient and is present in lower concentrations, the change of Si-H absorption at 2168 cm^{-1} is measured.

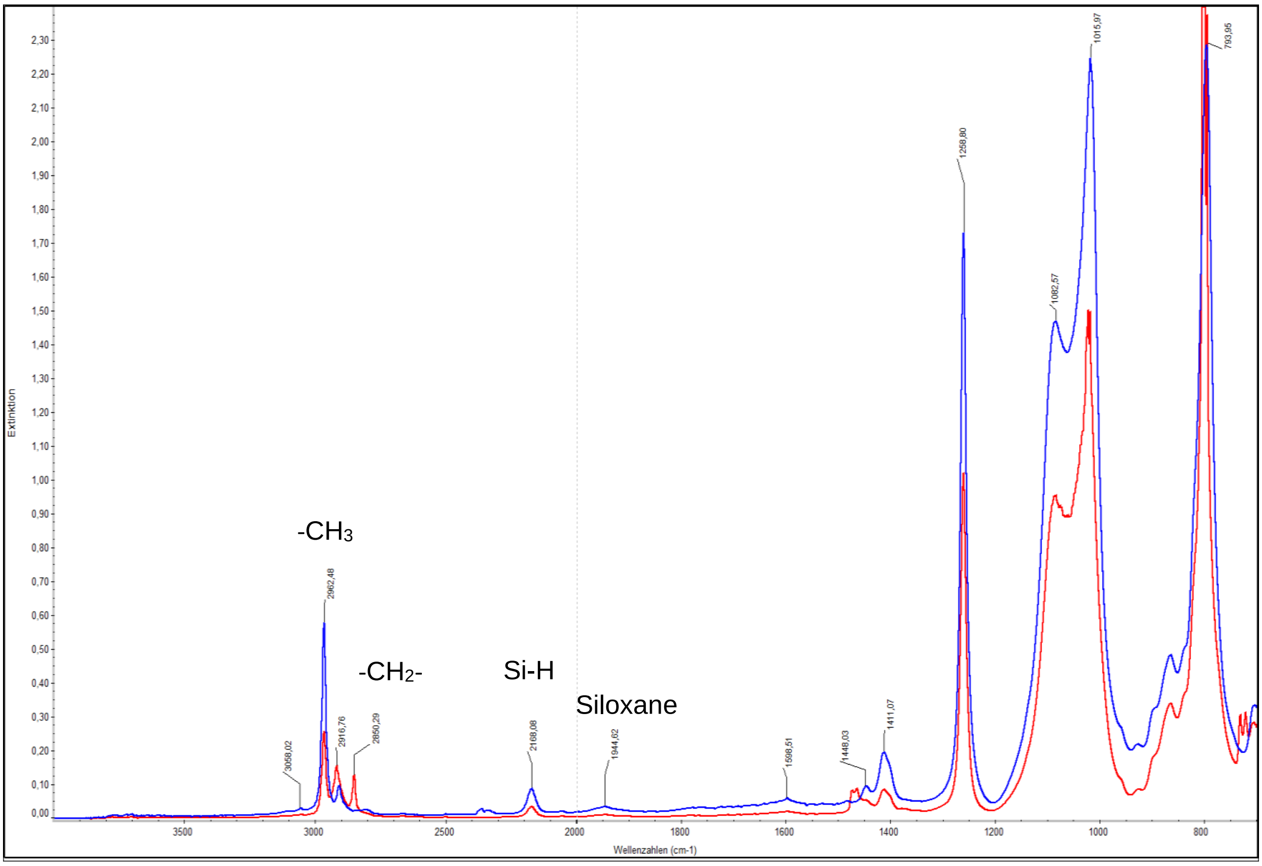


Figure 4. Blue: FTIR spectrum of Silicone without catalyst on aluminum film; red: FTIR spectrum without catalyst on LDPE film.

For an internal standard the asymmetrical or the symmetrical stretching of the Si-CH_3 band at 2962 cm^{-1} or 2913 cm^{-1} can be used, as the Si-CH_3 band is available in the same concentration in the base polymer as well as in the cross-linking polymer. In Figure 4 the spectrum of the silicone on LDPE can be seen with the symmetrical stretching and the deformation stretching of the -CH_2 bond at 2847 cm^{-1} and at 1462 cm^{-1}. It is therefore likely that these bands affect the next lying -CH_3 bands. Another option for the internal standard, the siloxane stretching vibration at 1945 cm^{-1} is provided by Karlsson [4]. However, this band shows only low absorption and can therefore lead to larger standard deviations. The shoulder at 1013 cm^{-1} and the band at 796 cm^{-1} representing the Si-O-Si stretching vibration and the corresponding deformation vibration of the open-chain polysiloxane, cannot be used as a ratio band since the absorption lies over 1,2 and thus no longer follows Lambert-Beer's law.

Table 1. Assignment of the IR bands of the spectra of silicone 1 without catalyst on LDPE and aluminum foil.

Wave number / cm^{-1}	Vibration	Structure
3070	ν_{as} (CC)	-CH=CH_2
2962	$\nu_{as}(CH_3)$	-CH_3
2913	$\nu_s(CH_3)$	-CH_3 [5]
2847	$\nu_s(CH_2)$	-CH_2-
2160	ν_s([O2]Si-H)	O_2Si-H
1945	$\nu_s(SiO_2)$	-Si-O-Si- [4], [6]
1604	ν_{as} (CC)	-CH=CH-
1462	$\delta_{as}(CH_2)$	-CH_2-
1412	$\delta_s(CH_3)$	-CH_3
1258	δ(SiC)	Si-C
1079	$\nu_{as}(SiO_2)$	-Si-O-Si-
1013	$\nu_{as}(SiO_2)$	-Si-O-Si-

796	δ(SiO_2)	-Si-O-Si-

In order to automate the analysis a macro with the program macros/basic was created. The measured transmission spectrum is transferred in absorption and a baseline correction is performed. The closest peaks for Si-H at 2160 cm^{-1},CH_3 at 2961 cm^{-1} and for siloxane at 1945 cm^{-1} are being searched and the straight base line is applied to the points from Table 2. After calculating the relative absorption, the output of the results is carried out in a text file.

Table 2. Parameter for the determination of the peak height with the program Macros/Basic.

Compound	Peak search / cm^{-1}	Base line start / cm^{-1}	Base line end / cm^{-1}
Si-H	2160	2270	2100
CH_3	2961	3400	2700
Siloxan	1945	2020	1850

Figure 5 and Figure 6 show two series of measurements of two silicones 1 and 2 on LDPE substrates at 110 °C and retention times from 5 s to 60 s in a convection dryer, which were created with the IR spectrometer and the extraction measurement. The recording of the IR spectrum was carried out directly after the thermal treatment in the convection dryer. Meanwhile, the samples were taken for extraction measurement. Furthermore, four measurements were performed after 24 h. The series of measurements show a very similar course with both silicones, IR measurement showing a steeper increase at low curing degrees. The plateau of maximum curing is achieved at 35 s in both measurements. The maximum curing of silicone 1 lies at 97 % in the extraction measurement and at 0.7 at the Si-H turnover degree. The results after 24 h show that these values are not significantly increasing.

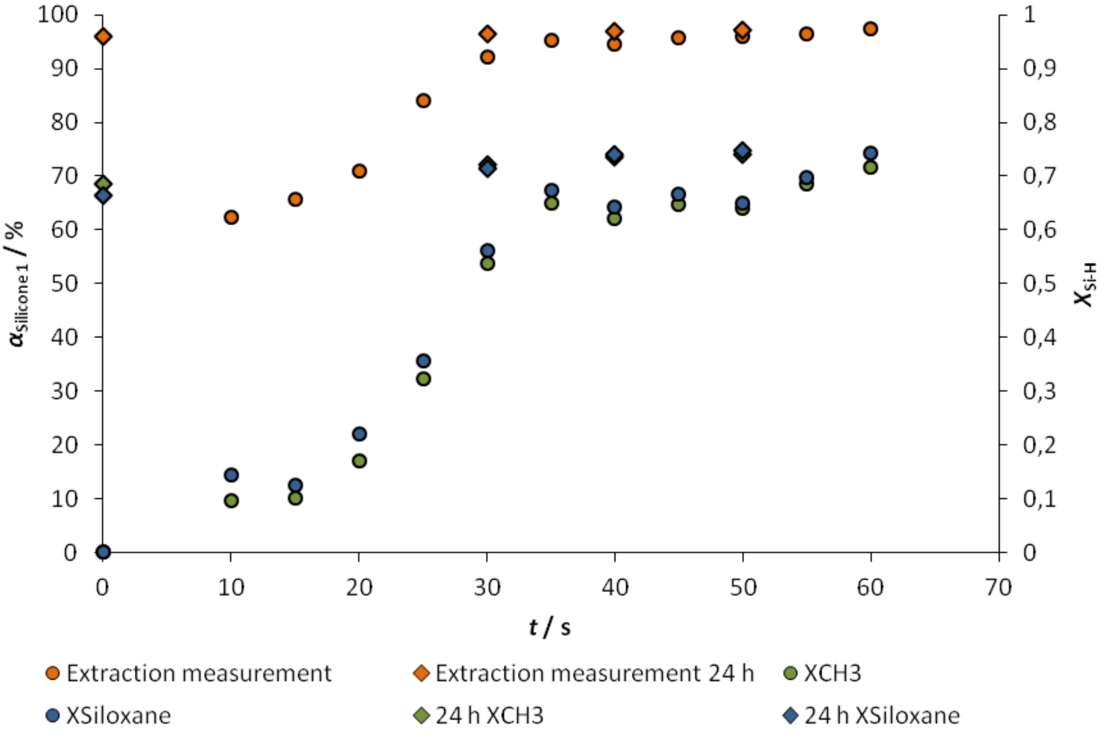


Figure 5. IR spectroscopic measurement and extraction measurement of silicone 1 on LDPE, cured in a convection dryer at 110 °C with different retention times.

Silicone 2 has a maximum curing degree of 90 % and a Si-H turnover degree of almost 0.8.

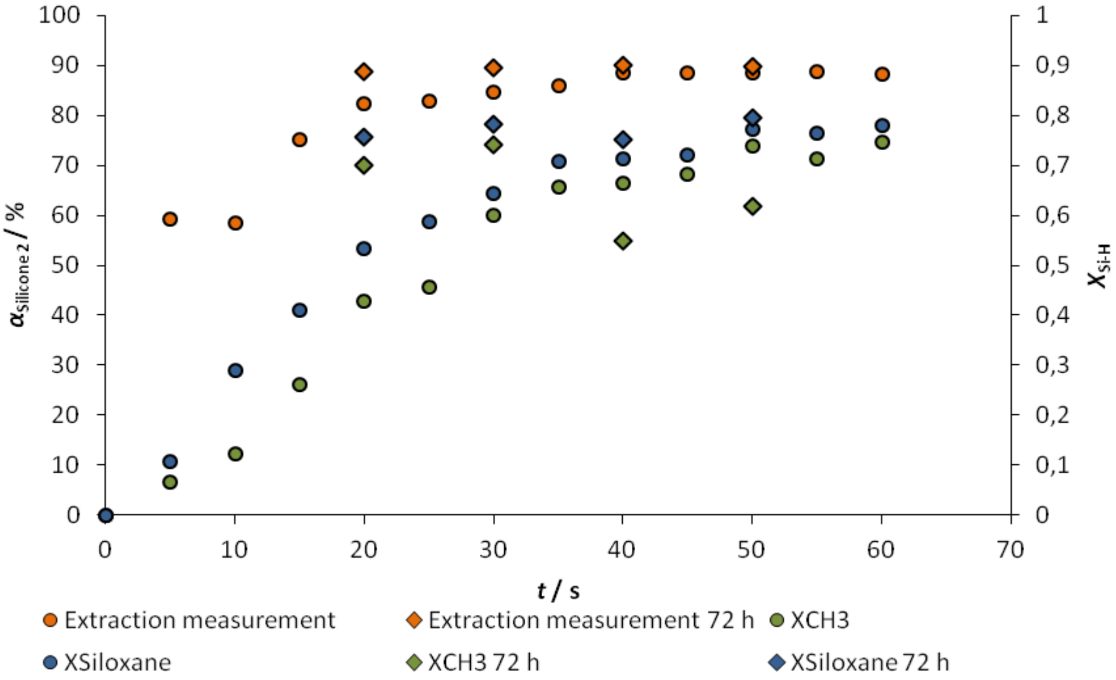


Figure 6. IR spectroscopic measurement and extraction measurement of silicone 2 on LDPE, cured in a convection dryer at 110 °C with different retention times.

The plot of the turnover degree, determined via IR spectroscopy against the curing degree, calculated on the extraction measurements, is shown in Figure 7 and Figure 8. The coefficient of determination of the trend line for silicone 1 is 0.965 for the CH_3 band and 0.986 for the siloxane band. For silicone 2 a value of 0,908 for the CH_3 band and 0,921 for the siloxane band were calculated. So there is a good comparability of the both measurement methods for both silicones on LDPE, where there is little difference between the two bands, CH_3 and siloxane.

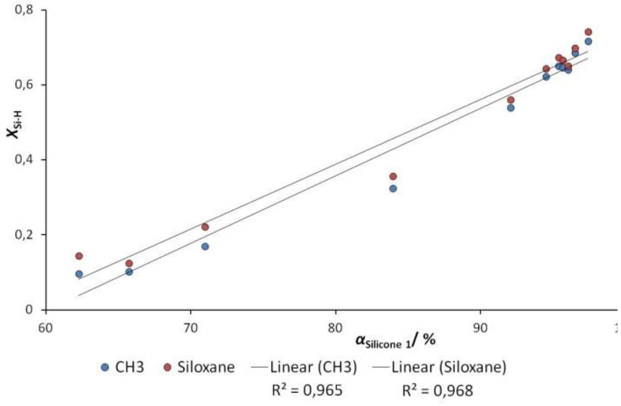


Figure 7. Parity diagram of Si-H turnover degree by IR spectrometer against curing degree by extraction measurement of silicone 1 on LDPE

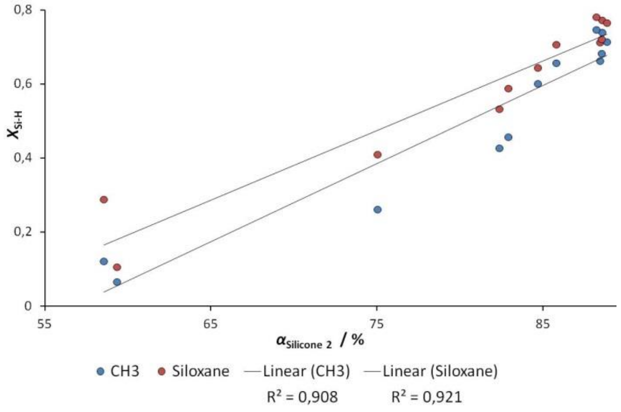


Figure 8. Parity diagram of Si-H turnover degree by IR spectrometer against curing degree by extraction measurement of silicone 2 on LDPE

Table 3 shows the arithmetic average and the standard deviation of the absorption ratio $A_{Si\text{-}H}/A_{CH3}$ and $A_{Si\text{-}H}/A_{Siloxane}$ of five IR measurements of the uncured silicone 1 on LDPE and aluminum film. The catalyst was not added in order to rule out a reaction during the measurements and to set a constant amount of Si-H. Due to the liquid state of the silicone and a similar contact pressure in the measurements it can be assumed that the layer thickness for all the measurements is comparable and therefore also the influence of the CH_3 band of the substrate to the measuring result. This can also be seen in the standard deviations. For LDPE the standard deviation is 2 % with CH_3 and for aluminum film it is 3 %. The standard deviation of the adsorption ratio of siloxane is 3 % to 4 %, slightly above CH_3, since the band is clearly smaller and deviations have a greater impact.

Table 3. Arithmetic average and standard deviation in percent of the absorption ratios of the Si-H band to the CH_3 band and to the siloxane band of five IR measurements of uncured silicone 1 without catalyst on LDPE and aluminum film.

		$\bar{x}$	σ / %
LDPE	$A_{\text{Si-H}}/A_{\text{CH3}}$	0.133	2
	$A_{\text{Si-H}}/A_{\text{Siloxane}}$	5.12	4
Aluminum film	$A_{\text{Si-H}}/A_{\text{CH3}}$	0.138	3
	$A_{\text{Si-H}}/A_{\text{Siloxane}}$	4.59	3

With fully cured silicone 1 (~97 %) the standard deviation is significantly higher, as can be seen in Table 4. This is due to the fact that firstly at high curing degree the Si-H band is very small and secondly the concentration of Si-H can be inhomogeneously distributed on a DIN A4 sample. The influence of the LDPE on the standard deviation is now clearer with 14 % for LDPE to 11 % in the measurements with aluminum film, as the silicone coating comprises an inhomogeneous layer thickness. The standard deviation of the siloxane ratio is located at 6 % in the measurements with LDPE and at 13 % with aluminum film.

Table 4. Arithmetic average and standard deviation in percent of the absorption ratios of the Si-H band to the CH_3 band and to the siloxane band of five IR measurements of silicone 1, cured for 48 h, on LDPE and aluminum film.

		$\bar{x}$	σ / %
LDPE	$A_{\text{Si-H}}/A_{\text{CH3}}$	0.0378	14
	$A_{\text{Si-H}}/A_{\text{Siloxane}}$	1.17	6
Aluminum film	$A_{\text{Si-H}}/A_{\text{CH3}}$	0.0387	11
	$A_{\text{Si-H}}/A_{\text{Siloxane}}$	0.89	13

4 Results

The adsorption ratio of the CH_3-band as well as the siloxane band show a good comparability with the extraction measurements on LDPE. So both bands can be used as an internal standard. The results to date demonstrate that the developed IR spectroscopic method provides a simple, cost effective and quick method for determining the degree of conversion and is therefore a good alternative to the extraction measurement. However, in order to install the IR measurement in a production environment a lot more experience with different silicone systems and substrates is needed.

5 Literature

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