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SPECTROSCOPIC CHARACTERIZATION OF LOW MOLECULAR WEIGHT FLUIDS FROM SILICONE ELASTOMERS

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ABSTRACT

The migration of low molecular weight (LMW) silicone fluid from the bulk to the surface of polydimethylsiloxane (PDMS) elastomers results in hydrophobic recovery after thermal or UV damage. The identification and analysis of these silicone fluids is an important step in understanding the process which ultimately affects the service lifetime of the elastomer and may provide one approach to assessing residual service lifetime in applications such as high voltage insulation. LMW silicone fluids were extracted from the bulk of four different silicone elastomers used as the weather sheds on high voltage insulators and differences were observed both in the total amount of fluid and the amounts obtained on successive extractions. MALDI-MS analysis of the extracted fluids showed significant differences in the proportions of cyclic and linear species. The extracted fluids were also analyzed by FTIR and Raman spectroscopy to determine trimethyl silyl end-group concentration using a calibrated series of PDMS standards containing known proportions of linear and cyclic species. Comparison of FTIR and Raman analysis with the

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MALDI-MS showed a major limitation in vibrational spectroscopic analysis of cyclic/linear content occurred when the linear species terminated in dimethylhydroxyl rather than trimethyl silyl groups.

Key Words: Polydimethylsiloxane; Low molecular weight silicones; Matrix-assisted laser mass spectrometry; MALDI, FTIR

INTRODUCTION

Polydimethylsiloxane (PDMS) has long been used in the manufacture of elastomers for demanding applications. One such recent application has seen this material used as weather sheds on high voltage power insulators in place of ceramic or glass. The strength, durability, and hydrophobic nature of the resulting elastomer are desirable properties for such applications. Hydrophobicity is an important property as it enables the insulator to resist the formation of a continuous film of conductive moisture. Although the surfaces of the insulator weather sheds are initially hydrophobic in nature, UV exposure, electrical discharge (dry band arcing or corona) and the deposition of pollution on the surface can greatly reduce hydrophobicity and subsequently compromise the insulator's performance by promoting leakage currents. Silicone rubber elastomers, however, have a unique ability to regenerate surface hydrophobicity after a period of recovery. The mechanism of this recovery has been widely attributed to the migration of low molecular weight (LMW) silicone fluid from the bulk of the elastomer to cover the damaged or polluted surface and restore the hydrophobicity of the insulator surface.^[1-3]

Preliminary studies conducted by this group utilized MALDI-MS and GC/MS to examine the LMW fluid sampled from the surface of several commercially produced high temperature vulcanized (HTV) silicone elastomers from high voltage (HV) insulators.^[1] This work revealed that the surface material contained low molecular weight PDMS with both linear and cyclic chemical structures illustrated in Fig. 1. Linear PDMS is synthesized by the catalytic ring-opening polymerization of low molar mass cyclic siloxanes and the resulting equilibria ensure that cyclic oligomers are also produced.

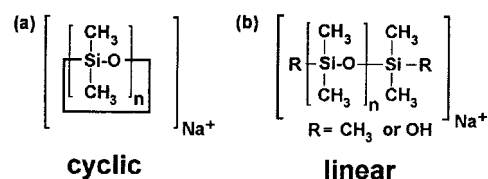


Figure 1. General chemical structures of a) linear and b) cyclic poly(dimethylsiloxane) species previously observed in low molecular weight fluid obtained from the surface of silicone rubber elastomers.

The residual concentration of cyclic species after commercial polymerization is expected to be around 10% but much higher concentrations of cyclic species were found on the surface of silicone elastomers.^[1] To further examine the chemical basis of the hydrophobicity recovery process, a series of tests were devised with the aim of characterizing the LMW material in the bulk of the elastomer that migrates to the surface. A range of commercially produced HTV silicone elastomers used as weather sheds on high voltage insulators was studied in order to determine the composition of the extractable materials and the effect of exhaustive extraction on this composition.

Among the techniques used for characterizing the LMW material present in HTV silicone elastomers, matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS)^[1] and vibrational spectroscopy^[2,3] are among the most sensitive and chemically informative. At the molar masses encountered with these materials, MALDI-MS analyses allow accurate determination of the mass and hence the chemical structure of each oligomer present in the polymeric mixture. This allows discrimination of linear and cyclic oligomers but is limited in determining molar mass in polydisperse polymers where fractionation by size exclusion chromatography is required prior to analysis.^[4] FTIR is generally a simpler and more robust technique and, although limited to identification of chemical groups rather than complete molecular structures, may enable molar mass to be determined by analysis of end-groups.^[5] In principle, the relative amounts of cyclic and linear oligomers can be determined by FTIR. Raman spectroscopy is a complementary technique and, depending on composition, may also enable endgroup analysis. Overall, the ease of use of vibrational spectroscopy and the ability to obtain good spectra from very small samples (sub-milligram) would make it very useful in routine condition monitoring of silicone elastomers. In this paper we compare the results of FTIR, Raman and MALDI-MS methods to determine the nature and concentration of the LMW silicones in vulcanised PDMS elastomers and assess the feasibility of the techniques for in-service monitoring.

EXPERIMENTAL

MALDI-MS

MALDI spectra were acquired using a TofSpec E (Micromass, Wythenshawe, UK) spectrometer, equipped with a nitrogen laser operating at 337 nm, producing a maximum energy of 180 μJ , delivered to the sample in 4 ns pulses. Pressure in the instrument was maintained at approximately 10^{-7} mbar. The instrument has a path length of 1.4 m in linear mode and approximately double this in reflectron mode. For samples prepared without

the addition of matrix, ionization was achieved at maximum laser intensity. Time of flight mass analysis was performed in reflectron mode. Ions were accelerated with a potential of 20 kV and detected by an annular multi-channel plate reflectron detector.

MALDI analyses were performed on 10 mg cm^{-3} chloroform solutions of the silicone elastomers. The matrix used for these experiments was 4-hydroxybenzylidenemalononitrile, prepared as a 0.1 M solution in acetone. A 0.05 M NaI salt solution (90% acetone/10% water) was used to enhance cation attachment during ionization. These solutions were mixed in a ratio of 10:1 (matrix to salt solution). For each analysis $1 \mu\text{L}$ of this solution was deposited on a stainless steel target plate and allowed to dry at room temperature followed by deposition of $0.5 \mu\text{L}$ of the sample solution. When dry, these preparations were analyzed in reflectron mode using threshold laser power and 20 kV acceleration potential. All spectra were acquired in positive ion mode.

MALDI mass spectra were generated by summing the spectra of 450 laser shots and the resulting spectra were smoothed and baseline subtracted. These spectra were obtained and processed using MassLynx software (Micromass, Altrincham UK) and all other calculations were achieved using Poly32 software (Sierra Analytics, Modesto, USA). Average molecular weights and the relative proportions of different silicone species were calculated from polymer mass spectra using relative peak heights as a measure of relative abundance for each oligomer.^[6,7] The relative proportions of linear and cyclic species were estimated by dividing the sum total of all linear peaks by the sum total of all cyclic peaks.

FTIR

Transmission spectra were run between KBr disks on a Perkin Elmer series 1000 FTIR at 2 cm^{-1} resolution. Spectra were also obtained by Fourier transform infra red emission spectroscopy (FTIES) using a modified BioRad FTS7 FTIR spectrometer described previously.^[8] Normally one drop of the silicone in chloroform solution was placed on the hotplate at 120°C in the emission bench in a nitrogen atmosphere, the solvent flashed off and emission spectra collected over 64 scans at 4 cm^{-1} resolution. In order to keep within the linear range of the instrument it was necessary to ensure only a very thin film ($<10 \mu\text{m}$) of silicone was on the hotplate. After correction for the emissivity of the platinum stub and the spectrometer, the ratio of the corrected spectrum to that of a black body emitter was obtained. The spectral band areas and peak heights were subsequently determined using Grams32 software (Galactic). FTIES spectra were further manipulated using Fourier self deconvolution (FSD) centred on the bands between 750 and 900 cm^{-1} .

Raman Spectroscopy

Spectra of mixtures of cyclic and linear PDMS were also obtained from a Renishaw System 1000 microprobe Raman spectrometer. The band at 644 cm^{-1} (representing the terminal tri-methyl group) was ratioed to that at 710 cm^{-1} which represents total silicone.

Materials

PDMS 200, a silicone oil having a viscosity of 50 cSt, was obtained from Aldrich and used as received. Analysis of this material by MALDI-MS (as described in 3.1 above) showed that it contained almost exclusively linear PDMS chains. The low molecular weight siloxanes, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane and decamethyl-cyclopentasiloxane were also obtained from Aldrich and were used as received. Their properties are given in Table 1. The refractive index of PDMS 200 was checked by a Abbe refractometer and found to be as quoted by Aldrich.

Four different HTV silicone elastomers (A, B, C, and D) were used to provide LMW silicone for this study. These materials were in the form of weather sheds on high voltage insulators and came from four different manufacturers. Their filler content (mainly hydrated alumina) was determined by thermogravimetric analysis (TGA) from 30 to 900°C at 10° min^{-1} in nitrogen using a Setaram 92 TGDTA instrument.

Material extracted from the bulk of a silicone elastomer (D) was chosen as a cyclic standard following analysis by both MALDI and FTIR. It was shown to contain almost exclusively cyclic PDMS. Mixtures of this and the linear material (PDMS 200) were prepared in chloroform to give a set of standards with 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100% cyclic content.

Table 1. Purity, Properties, and Source of Silicones Used (Source: Aldrich)

Sample	% Purity	Density	Refractive Index	bp $^\circ\text{C}$
Hexamethyldisiloxane	98	0.764	1.378	101
Octamethyltrisiloxane	98	0.820	1.384	153
Decamethyltetrasiloxane	97	0.854	1.389	194
Dodecamethylpentasiloxane	97	0.875	1.391	230
Decamethylcyclopentasiloxane	97	0.958	1.396	ns
PDMS200 (linear) 50cSt	ns	0.960	1.403	ns

ns = not stated.

Extraction of LMW Fluids

LMW fluids were extracted from the four different silicone rubber elastomers as follows. Approximately 10 g of the bulk material from each elastomer was prepared by first removing a 1 mm layer of surface material. The remaining "bulk" material was then sliced into thin sections (approximately $0.1 \times 5 \times 20$ mm), weighed and then extracted with AR grade chloroform for 6 h using a soxhlet extraction apparatus. At the end of the extraction process, most of the solvent was removed in a rotary evaporator and the extract and remaining solvent transferred to a small vial. The remaining chloroform was allowed to evaporate at room temperature. The refractive index of the extracted oil was determined at ambient temperature. The dried elastomer was further extracted every two days for a maximum of three extractions (depending on the yield for the second extraction). The elastomer was then allowed to stand for three months before the final extraction was performed. After each extraction, the remaining, solvent-free elastomer was reweighed and the loss due to the extraction was calculated.

Estimation of Crosslink Density

Several rectangular sections of each elastomer (A, B, C, D) were carefully measured and weighed and then were placed in chloroform. The solvent caused swelling of the elastomer and after 24 h, the specimens were re-measured and the volume change calculated. Samples of the rubbers were also subjected to thermogravimetric analysis (TGA) to determine the inorganic content. A Setaram TGA 92-16.18 was used with the sample being heated at $10^\circ \text{ min}^{-1}$ from 30 to 900°C . The swelling results were then normalized to 100% polymer using the estimates of polymer content from the TGA analysis. Polymer content was assumed equal to the weight loss by TGA.

RESULTS AND DISCUSSION

Solvent Extraction of Elastomers

The mass of the material remaining after chloroform extraction of the four different types of elastomers was compared to that prior to extraction and the change in mass determined. The same material was extracted a second time and if the weight loss was again significant a third extraction was performed. The extracted elastomer was then allowed to stand for three months at room temperature, after which a final extraction was performed. Table 2 shows the weight of material extracted from each elastomer expressed as a percentage of the original weight. The extracts were oily clear liquids. The refractive index of the extracts were measured at 28°C and are given in Table 2. The volume change due to swelling of the elastomers in chloroform

Table 2. Characterization of Silicone Elastomers (A, B, C, D)—% Wt Loss After Successive Chloroform Extractions and After TGA, % Volume Change on Swelling in Chloroform and Refractive Index of Oil from the First Extraction

	1st Extract (%)	% of Total 1st Extract	2nd Extract (%)	3rd Extract (%)	3rd/4th Extract* (%)	Total Extracted (%)	TGA % Loss	Swelling % Change Elastomer	RI# 1st Extract
A	2.41	90.3	0.17		0.09	2.67	48.0	500	1.406
B	2.04	93.2	0.08		0.07	2.19	45.0	509	1.408
C	1.81	79.7	0.27	0.08	0.11	2.27	47.5	585	1.405
D	1.58	93.5	0.04		0.07	1.69	43.6	521	1.421

*3 months after previous extraction; # Refractive Index.

was corrected for the percent in the rubber and the results are also given in Table 2.

The extract from elastomer D which is known to contain 100% cyclic material, has the lowest percentage of extractible material. This may be significant as it may reflect threading of some cyclic oligomers above a critical size.^[9] Elastomer C produced slightly less material on extraction, but it was retained in the elastomer to a higher degree than the other samples. It also has the largest increase in volume upon swelling indicating the lowest cross-link density which from Table 2 is (highest to lowest) $A > B > D > C$. The total level of extractible material (highest to lowest) is $A > C > B > D$. It can be seen that there is no relation between swelling and the ease of removal of LMW silicones or the amount removed.

MALDI-MS Results

Analysis of the Standards

MALDI-MS spectra of the linear silicone oil (PDMS 200) and the cyclic material extracted from elastomer D are shown in Fig. 2. Each of these spectra are characterized by a single distribution of ions with spacings of m/z 74 which corresponds to the mass of the polydimethylsiloxane (PDMS) repeating unit. The masses of the individual peaks in the spectrum of the oil (Fig. 2(a)) correspond to linear structures with chain lengths that vary from 13 to 45 repeating units. For example, the expanded peak at m/z 1369, shown in Fig. 2(b), corresponds exactly to the mass of a linear chain of 17 repeating units plus a sodium cation (attached during analysis). At these relatively low masses, isotopic resolution is achieved producing a series of peaks for each ion due to the relative abundances of each isotope of the constituent elements. Therefore, the monoisotopic mass of the molecule is equal to the lowest mass peak of the series of peaks which constitutes the peak.

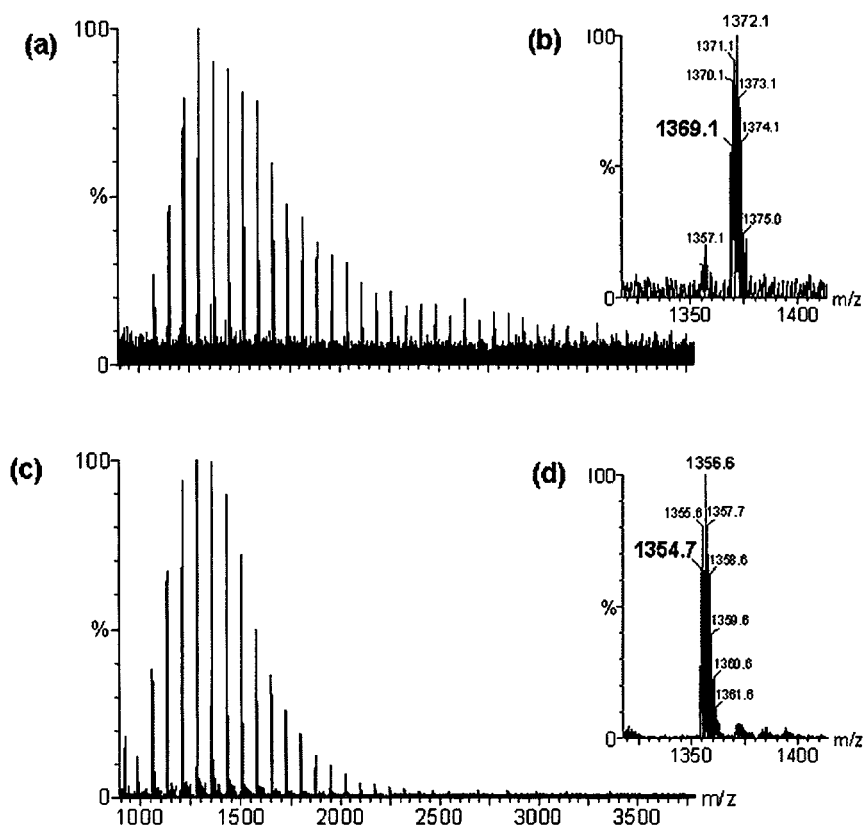


Figure 2. MALDI mass spectra of linear and cyclic standards: (a) silicone oil (PDMS 200) with expanded region (b) showing the m/z 1369 peak and (c) extract from elastomer D with expanded region (d) showing the m/z 1353 peak.

Examination of the individual peaks in the MALDI mass spectrum of the extract from Sample D (Fig. 2(c)) shows that the polymeric species in the main distribution correspond to cyclic oligomers varying from 14 to 32 repeating units in size. This can be seen by examining the expanded peak at m/z 1355, shown in Fig. 2(d), which corresponds exactly to the mass of a cyclic molecule of 18 repeating units (plus one sodium cation). The MALDI-MS analyses of these materials showed that the silicone oil contained predominantly linear silicone species and the Sample D, predominantly cyclic species.

Analysis of the LMW Fluids from Silicone Elastomers

LMW fluid obtained from the elastomers by soxhlet extraction were analyzed by MALDI-MS and compared to the standards in order to determine their cyclic content and results are summarized in Fig. 3. From these

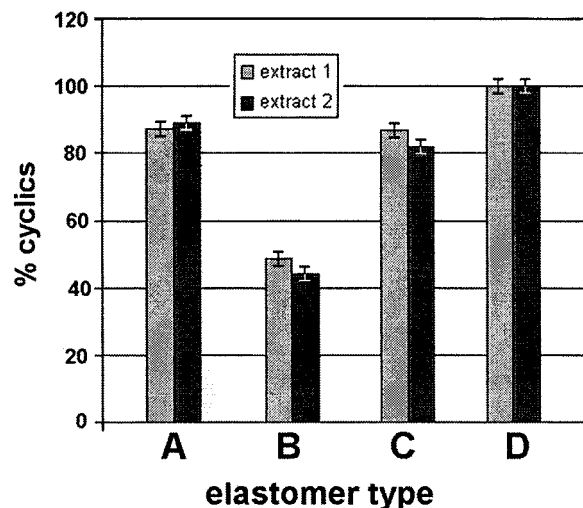


Figure 3. Cyclic content of extracts obtained from silicone elastomers, expressed as a percentage of all silicone species identified from their MALDI mass spectra.

results, it was observed that the material from elastomer D has the highest cyclic content – no linear species were observed in either the first or second extraction of this elastomer. Elastomers A and C gave very similar results of 87.7% and 87.2% cyclics, respectively for the first extraction and 89.2% and 81.8% cyclics for the second extraction. A third extraction performed on elastomer C showed a decrease to 76.3% in the cyclic content. This elastomer type showed the slowest rate of extraction of LMW fluid. The most unusual result, however, was obtained for elastomer B, which gave the lowest level of cyclics (49.1% cyclics first extraction and 43.9% cyclics second extraction).

MALDI mass spectra of the fluids obtained from the first extractions of elastomers B and C are compared in Fig. 4(a) and (c), respectively. The far greater proportion of cyclic species in elastomer C is immediately apparent. Examination of the expanded region of the spectrum from insulator B shown in Fig. 4(b), however, reveals that the peak for the linear species at m/z 1373.4 is 4 mass units higher than the corresponding methyl terminated linear species observed at m/z 1369 in the expanded region of the MALDI mass spectrum of linear standard (Fig. 2(b)). All of the linear peaks observed in all MALDI mass spectra of sample B extracts were found to be consistent with the mass calculated for hydroxy terminated species, the general structure of which is illustrated in Fig. 1(b) where **R** represents hydroxyl groups.

Molecular weight calculations were also performed using the polymeric distributions observed in the MALDI mass spectra of the material extracted from the insulators. Results of these calculations are shown in Fig. 5. Little variation is observed between insulator type and subsequent extractions, that

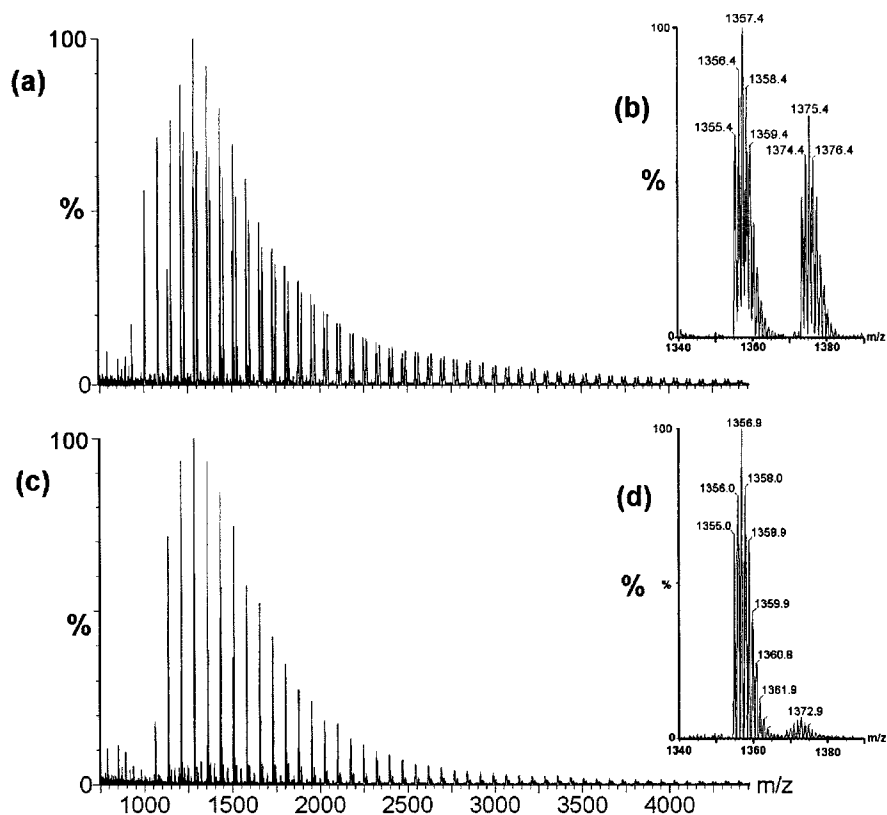


Figure 4. MALDI mass spectra of the residues obtained from the first extractions of elastomers B (a) and C (c). Expanded regions of these spectra are shown in (b) and (d), respectively.

is, all results fall within the range of m/z 1721 to 1978, a variation that is somewhat greater than the reproducibility (± 75) of the technique. The low variation in M_n values may indicate that this distribution represents the entire mobile fraction contained in the insulators and that molecules of higher mass cannot be extracted because of entanglement or threading. It may also indicate that all of the molecules within this mass range have similar extraction efficiencies as little variation was observed in subsequent extractions. Another factor, which must be considered in the interpretation of these results, is the phenomenon of mass discrimination. Problems in obtaining accurate average molecular weights for polymers with polydispersities greater than 1.2 is frequently reported^[4] and this is believed due to the preferential ionization of low mass species. Therefore, the persistent presence of low mass species could conceivably be masking the appearance of some higher mass species in subsequent extractions. Correlation of these results with well established methods of average molecular weight determination must therefore be performed to validate these results.

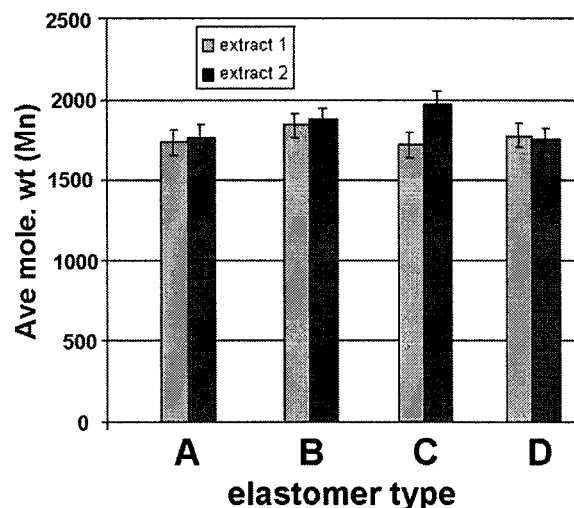


Figure 5. Average molecular weights (M_n) calculated using the polymeric distributions observed in the MALDI mass spectra of the material extracted from the elastomers.

FTIR Results

Assignment of End-Group Vibrations from FTIR Transmission Spectra of Siloxanes

In his treatise on silicone materials, Noll^[10] presents infra red spectra of both long chain and very short chain PDMS materials. The bands between 1020 and 1100 cm^{-1} were assigned to Si-O-Si bending (open chain) with the narrow range between 1050 and 1090 cm^{-1} showing a maximum in cyclic polysiloxanes. Of more use was the assignment of the absorption of the dimethyl (in-chain) group $[-(\text{Me})_2\text{Si-O-}]$ between 790 and 830 cm^{-1} compared with the trimethyl end-groups $[(\text{Me})_3\text{Si-O-}]$ at 840 and 750 cm^{-1} . The band at 1260 cm^{-1} appears of limited value for this analysis as it represents mono, di and tri methyl groups. The spectra presented by Noll showed some change in band absorption maxima for both the -Si-O-Si- and silicon-methyl bands as the number of siloxane units increased from two (the simplest siloxane) to 10 siloxane units but no change once the number of units rose above this number. In this study we have applied Fourier self deconvolution (FSD) to the spectra of some very short chain siloxanes to quantify these changes. The ability to distinguish between terminal and in-chain methyl groups is very important to this study as it may provide discrimination between linear and cyclic species.

Transmission FTIR spectra of the simplest siloxanes available (two to five siloxane units) were run as well as a cyclic compound with five siloxane units. In addition, spectra were also obtained of the linear and cyclic silicone oils. FSD was performed on all the spectra and peak areas in the region from

Table 3. Peak Area Ratios of the Si(Me)₃ and Si(Me)₂ Bands Following FSD of FTIR Spectra Collected at 2 cm⁻¹ as Compared to Total Band Area Between 920 and 730 cm⁻¹ (Small Bands at 860 and 880 cm⁻¹ Constitute the Remaining Area)

Sample	% Area 753	% 841	% Area 820	% Area 795	Comment
Hexamethyldisiloxane	15.1	55.1	24.8	0	100% end group methyl
Octamethyltrisiloxane	9.0	43.1	24.6	14.3	75% end group methyl
Decamethyltetrasiloxane	7.4	34.6	17.9	29.2	60% end group methyl
Dodecamethylpentasiloxane	5.7	30.4	12.6	40.5	50% end group methyl
Decamethylcyclopentasiloxane	0	0	46.6	47.1	0% end groups
Linear	0.75	4.6	15.2	71.0	small % end group methyl
Cyclic	0	0.05	15.5	81.0	~0% end groups

Linear = PDMS 200, Cyclic = Sample D

730 to 920 cm⁻¹ were calculated. Individual band areas were then ratioed to the total band area from 770 to 920 cm⁻¹. The peak area results are given in Table 3 below and shown diagrammatically in Fig. 6.

It may be seen from Fig. 6 that there is a decrease in intensity of the bands at 841 and 753 cm⁻¹ with increased chain length, consistent with these bands arising from the terminal methyl groups [(Me)₃Si-O-]. In contrast, the simultaneous increase in intensity of the band at 795 cm⁻¹ indicates that it is

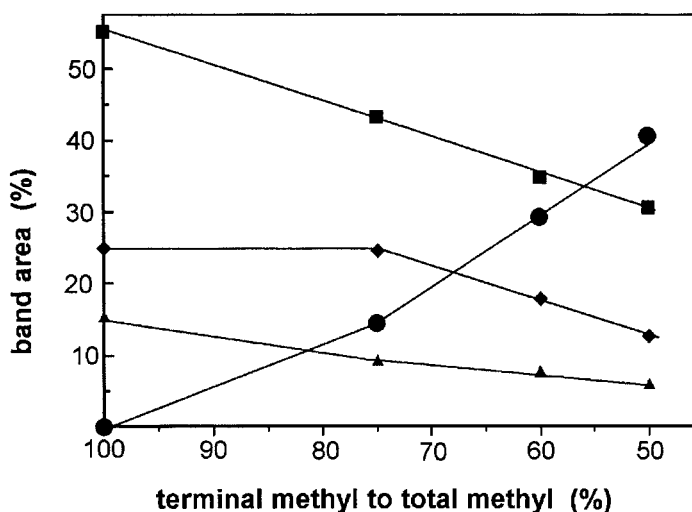


Figure 6. Change in band areas in the region 730 to 920 cm⁻¹ with increasing chain length from 2 to 5 siloxane units. The X axis numbers refer % terminal to total methyl groups. Band areas determined by FSD. (■ = 841 cm⁻¹ - linear, ● = 800 cm⁻¹ - cyclic, ◆ = 753 cm⁻¹ - linear, ▲ = 820 cm⁻¹ - combination).

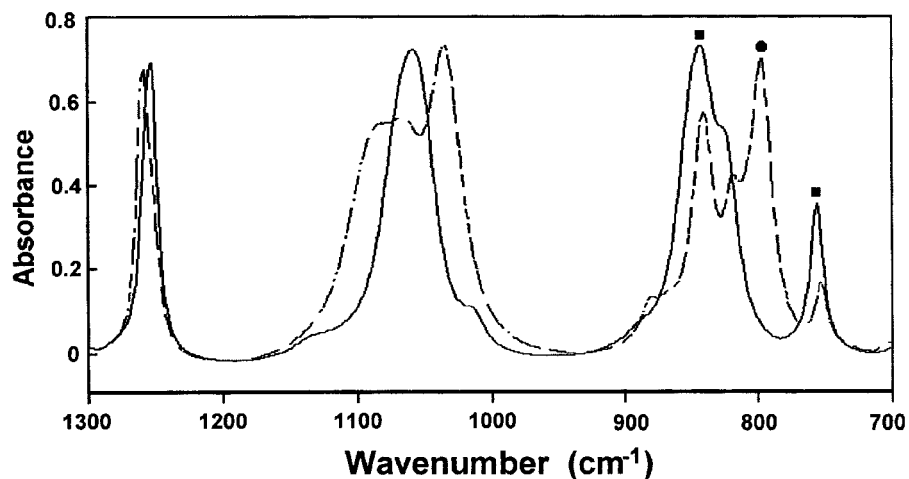


Figure 7. Comparison of spectra between hexamethyldisiloxane (solid line) and dodecamethylpentasiloxane (dashed line) showing changes in the -Si-O-Si- band in the region between 1000 and 1100 cm^{-1} and changes in $\text{Si}(\text{Me})_x$ band between 750 and 900 cm^{-1} . The ■ indicates bands attributed to terminal tri-methyl $\text{Si}(\text{Me})_3$ while ● indicates the band attributed to in-chain methyl $\text{Si}(\text{Me})_2$.

associated with in-chain methyl groups $[-(\text{Me})_2 \text{Si-O-}]$ as this is confirmed in Fig. 7, where it is seen to be absent in the spectrum of the disiloxane. The absence of a band at 841 cm^{-1} in the deconvoluted spectrum of the 5-unit cyclic siloxane (Table 3) confirms this. The two spectra given in Fig. 7 show the significant changes in both the Si-O-Si vibration frequencies (1000–1100 cm^{-1}) as the chain length is increased from 2 to 5 units as well as changes in the region from 770 to 900 cm^{-1} as the influence of end groups decreases. The band at 820 cm^{-1} may be due to vibrational coupling of the Si-C and $-\text{CH}_3$ group^[11] as it is present in all samples.

Comparison of Linear and Cyclic PDMS

The set of 11 standard mixtures of linear and cyclic siloxanes were analysed by FTIES at 120°C in triplicate. Fourier self-deconvolution (FSD) of the region between 925–725 cm^{-1} show distinct peaks at 795, 820, 841, and 860 cm^{-1} as for the small siloxanes discussed above. Figure 8 shows the enhancement of the band at 841 cm^{-1} after FSD which is attributed to the presence of trimethyl silyl end groups found only in linear siloxanes. The absence of this band was consistent with cyclic species. The area of this peak (841 cm^{-1}) was ratioed to the area of the whole band between 780 and 900 cm^{-1} and plotted against known cyclic content. The plot, Fig. 9, gave a very good correlation ($r=0.997$). In order to check the validity of this analysis, several standards were also examined by Raman spectroscopy. The

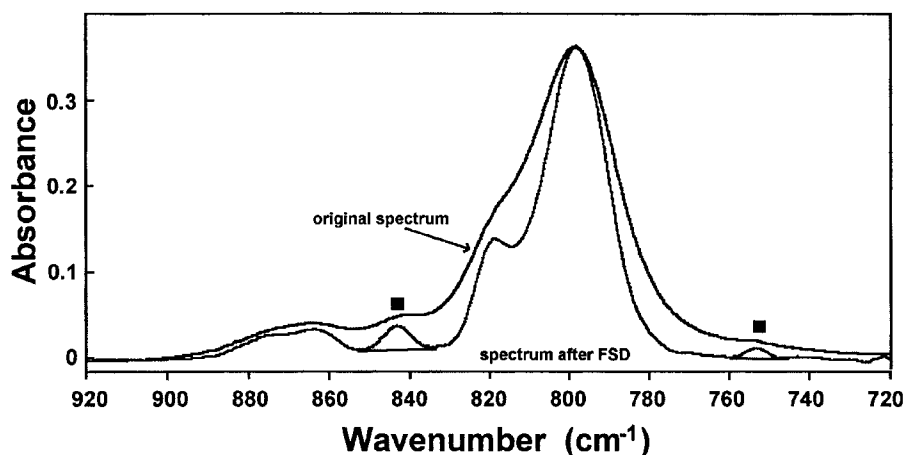


Figure 8. Selected spectral region of 0% cyclic (100% linear) LMW silicone showing the original spectrum and that after Fourier self deconvolution. Bands attributed to the terminal methyl are marked with a ■.

terminal trimethyl group has a band at 644 cm^{-1} in the Raman and Fig. 10 shows a selected region of the spectrum for the 5 standards having the lowest linear concentration. Because of the low level of linear material, the band at 644 cm^{-1} was small but when the peak area ratios were plotted, there was excellent correlation of linear content with band area (Fig. 11).

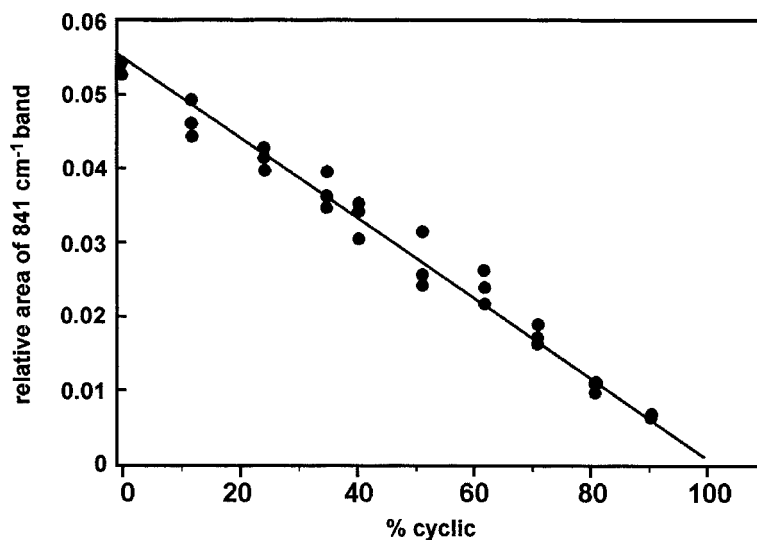


Figure 9. Calibration Set: Relative areas of the band at 841 cm^{-1} as a function of the level of cyclic silicones in the sample. (from FTIR spectra run at 120°C).

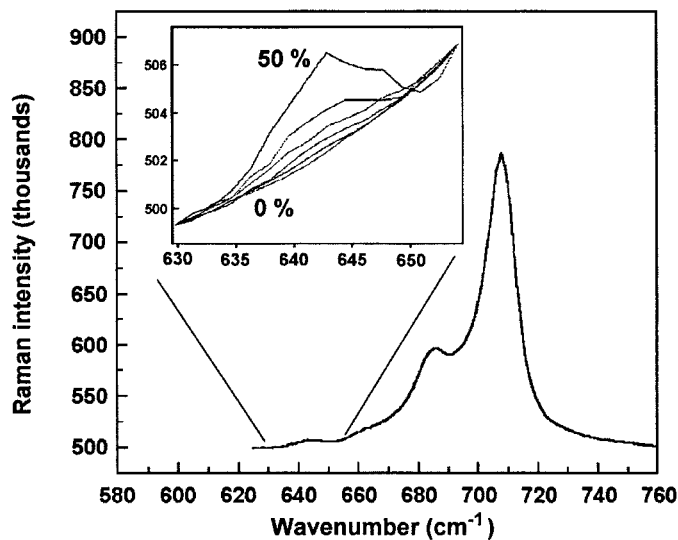


Figure 10. Raman spectra for 5 calibration standards with low levels of linear material; *inset* expanded region showing terminal trimethyl group for calibration standards from 0 to 50% linear material.

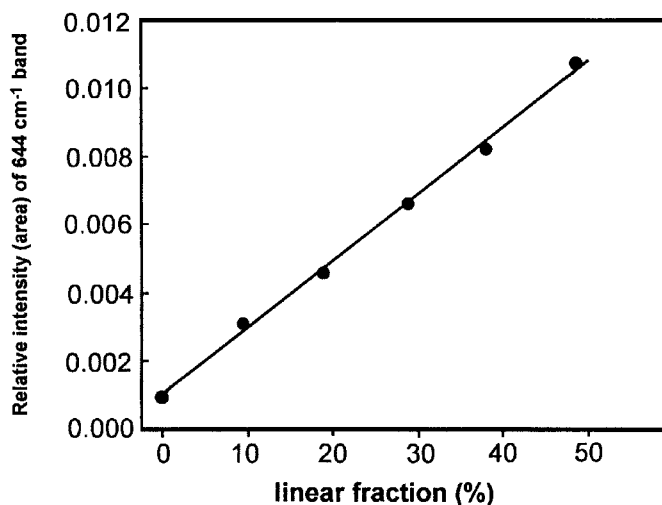


Figure 11. Calibration plot for the Raman data shown in Fig. 10.

Evaluation of Cyclic Content of Elastomers by FT-IES

The material previously obtained from the bulk of the elastomeric insulator material by soxhlet extraction was analyzed by FTIR emission (FT-IES). Several spectra were collected for each sample of insulator. After performing FSD on the spectra, the area ratios were calculated and % cyclics

Table 4. Level of Cyclic Silicones in the First Extraction of Elastomers as Determined from the FTIR Calibration Curve and MALDI-MS Analysis Showing the Poor Correlation Between the Methods.

Elastomer	% Cyclic Silicone by FTIR $\pm 5\%$	% Cyclic Silicone by MALDI-MS $\pm 1\%$
A	79%	88%
B	79%	49%
C	70%	87%
D	(100%)	100%

calculated from the slope and intercept determined by linear regression of the line in Fig. 9.

The cyclic content of LMW material from elastomers A and C were also calculated from the regression line in Fig. 9. The results of these calculations are given in Table 4. They showed lower values for the cyclic content than that calculated by MALDI. It would appear that the FTIR technique may underestimate the level of cyclics present when compared to the MALDI-MS results. Alternatively, MALDI may overestimate the cyclic content due to incomplete ionization of all oligomers, a problem with polydisperse samples^[4] and/or because of end-group differences.^[12]

Samples from elastomer B were determined by FTIR to contain approximately 79% cyclic material whereas MALDI-MS indicated approximately equal amounts of linear and cyclic material. This result may be reconciled when the end groups observed in extracts from elastomer B are compared with those from other elastomers. The MALDI-MS showed the terminal group observed from linear LMW extracts from elastomer B were dimethylhydroxyl silyl rather than the trimethyl silyl.^[1] This results in a major error since the basis set assumes that the terminal groups on each linear PDMS molecule are trimethyl silyl and the analysis involves measuring the area of the band at 841 cm^{-1} assigned to this group. The absence of this band in the series of samples from elastomer B confounds the analysis.

CONCLUSION

Low molecular weight fluids were obtained from the bulk of four different silicone rubber elastomers by a series of extractions with chloroform. Differences were observed both in the total amount of fluid and the amounts obtained on successive extractions. This evaluation of FTIR sought to distinguish between linear and cyclic low molecular weight siloxanes, a process that can be achieved by MALDI-MS, by discrimination between terminal methyl groups and in-chain methyl groups.

Studies with siloxanes up to 5 units long showed that it was easy to pick this difference from the raw spectra. Terminal methyl groups give a strong absorbance at 841 cm^{-1} , whereas in-chain methyl absorb at $795\text{--}800\text{ cm}^{-1}$. Some changes in the relative separation of the O-Si-O- vibrations (1080 to 1090 cm^{-1} and 1020 and 1013 cm^{-1}) were also observed but their application to siloxanes with more than 5 repeat units may be difficult. MALDI-MS analysis of the extracted fluids showed significant differences in the proportions of cyclic and linear species. One elastomer sample was found to contain cyclic species only, two contained between 11 and 24% linear (all extracts) and one sample (B) contained more than 50% linear species. The latter linear species differed significantly in structure compared to those found in the extracts of the two insulators showing smaller proportions of linear species. Average molecular weight calculations performed using the MALDI mass spectra displayed little difference in any of the extracted material, however, these results require further confirmation via the use of size exclusion chromatography. The extracted fluids were also analysed by FTIR, which had previously been calibrated using a series of PDMS standards containing known proportions of linear and cyclic species. FTIR was found to underestimate the level of cyclic species in the sample in two cases. In the case of sample B totally anomalous results were obtained due to the differences in the end-groups of the linear species in this sample. Because of weak overlapping bands, it was necessary to deconvolute the spectra using FSD. In this way it was possible to quantify the level of the terminal methyl groups. The standard solutions produced a linear relationship with satisfactory correlation coefficients with changing concentration of cyclic siloxanes. Raman spectroscopy confirmed this result.

These results illustrate that the FTIES/FSD technique has shown merit for the determination of cyclic PDMS content in LMW fluids obtained from the polydimethylsiloxane elastomers but only when a clear basis set is established for the species diffusing from that class of insulator. Significant errors may occur when there are different end groups or long chain polysiloxane molecules. However, the ability of FTIR to analyse tiny samples of silicone gives it a significant advantage over MALDI-MS. One particular limitation to MALDI-MS is that polydisperse samples must be fractionated (eg., by size exclusion chromatography) if accurate molar mass is to be obtained. Thus, a much larger sample would be required to accurately determine linear/cyclic ratios.

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