Network Structure and Properties of Platinum-Catalyzed Addition Cure Release Coatings

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SYNOPSIS

Silicone-release coatings are used by the pressure-sensitive adhesive industry for labeling applications. Typical release coatings are prepared by the platinum-catalyzed addition reaction of a silicone hydride fluid with a silicone vinyl polymer. Methodology has been developed to determine the network structure of cured release coatings, which involves degradation of the network with trifluoromethane sulfonic acid in excess hexamethyldisiloxane. Gas chromatography–mass spectrometry (GC–MS) and gas chromatography (GC) were employed to identify and quantify residual functionality and cross-links. Residual hydride functionality was also determined by attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR). The observation of network structure by solid-state ^{29}Si-NMR using cross polarization (CP) and magic angle spinning (MAS) is also discussed. The networks underwent a postcure as evidenced by a decrease in residual hydride functionality and an increase in silane content and/or cross-links. © 1993 John Wiley & Sons, Inc.
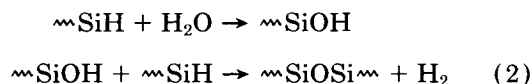
INTRODUCTION

Release coatings are generally prepared by reaction of silicon hydride fluids (SiH) with silicone vinyl fluids [Si(Vi)] using platinum catalysts according to eq. (1).[1,2a-g]:

$$R_3SiH + R_3'Si(Vi) \rightarrow R_3SiCH_2CH_2SiR_3' \quad (1)$$

The hydride-containing polymer usually contains several SiH groups per molecule, whereas the Si(Vi) polymer may contain only terminal vinyl groups or both terminal and on-chain vinyl groups. In addition to the platinum catalyst, the formulation also contains a catalyst inhibitor that stabilizes the formulation against premature gellation but allows the formulation to cure at elevated temperatures. To enhance cure speed or to lower the temperature necessary for cure, an excess of SiH is generally used. A typical network structure for a release coating prepared from SiH fluid and Si(Vi) polymer containing both chain and terminal vinyl groups is shown in Figure 1.

It is possible that residual functionality may undergo subsequent or postcure reactions that may change the physical properties of the network. Types of postcuring reactions include reaction of residual SiH groups with Si(Vi) groups, resulting in an increase in cross-link density or, alternatively, the reaction shown in eq. (2) in which a SiH group is hydrolyzed and can then condense with another SiH group. The reaction has been studied using silicone gels by Quan[3]:

$$\sim\!\!\sim\!SiH + H_2O \rightarrow \sim\!\!\sim\!SiOH$$

$$\sim\!\!\sim\!SiOH + \sim\!\!\sim\!SiH \rightarrow \sim\!\!\sim\!SiOSi\!\sim\!\!\sim + H_2 \quad (2)$$

A particular issue with these coatings is their tendency to weld or "lockup" when laminated against an acrylic adhesive. It has been speculated that lockup is caused by reaction of residual SiH with acrylics. It is therefore of interest to determine the types and amounts of the residual functionality and to determine the effect of aging on the residual functionality.

In a previous report[4] we described preliminary results on development of methodology to determine the network structure of thermally and photolytically cured release coatings. In this report, we de-
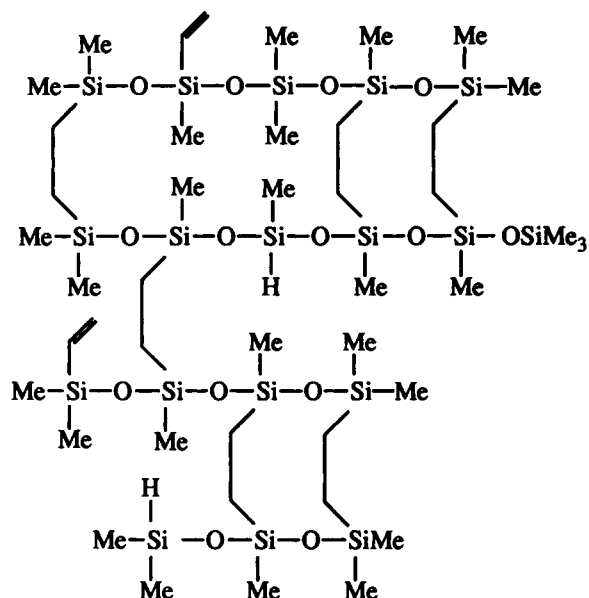
Figure 1 Network structure of cured silicone-release coatings.

scribe the methodology for thermally cured samples and compare several different coating compositions before and after aging. In addition, we have studied these networks using attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR) and ^{29}Si cross polarization magic angle spinning (CPMAS)-NMR. Lastly, we speculate on the effect of residual hydride and vinyl functionality on the tendency for laminates to exhibit acrylic weld or lockup. Silicone nomenclature is described in Table I.[5]

EXPERIMENTAL

Sample Preparation

Samples I and II were prepared by combining 96 parts of a vinyl stopped fluid containing about 3% vinyl gum blended to a viscosity of 400 cps and 4 parts of a silicone hydride fluid containing about 40 silicone hydride units per chain, 75 ppm Pt and 0.5% inhibitor. Samples III and IV were prepared in the same manner except a silicone polymer containing both on-chain and terminal vinyl groups of a viscosity of 340 cps was used. Vinyl polymers and hydride polymers were obtained from GE Silicones and are also available from Hüls America. The formulations were coated onto Super Calendared Kraft paper (SCK) using a differential offset gravure roll and cured using three oven zones of 8 ft each at 200 ft/min. The zone temperatures were 215, 262, and

293°F for Sample I, 200, 250, and 250°F for Sample II, 250, 350, and 350°F for Sample III, and 200, 250, and 250°F for Sample IV. Completeness of cure was determined by absence of rub-off and smear and no loss in tack when a piece of tape that had contacted the silicone surface was doubled back against itself. Samples I and III satisfied these criteria. Samples II and IV showed slight smear. Coat weights were determined using a Princeton Gamma Tech Silicon Chemical Analyzer and were found to be between 0.48 and 0.50 lb/ream.

For release testing, samples were cut to 12 × 10 in. and coated with a pressure-sensitive acrylic adhesive (Monsanto Gelva 263). The sample was passed through a pan containing adhesive, then pulled through two rollers resulting in a 3 mil adhesive thickness. Samples were air-dried for 10 min and dried for 8 min at 70°C in a forced-air area. A 13 × 12 in. sheet of Super Calendared Kraft laminate was rolled out upon the adhesive and the composite passed through two rollers at 90 psi to remove any bubbles remaining between the laminate and adhesive. Testing was performed on a Release and

Table I Silicone Nomenclature

$M = (CH_3)_3SiO_{1/2}$

$M^H = (CH_3)_2Si(H)O_{1/2}$

$M^{Vi} = (CH_3)_2SiO_{1/2}$

$D = (CH_3)_2SiO_{2/2}$

$D^H = (CH_3)Si(H)O_{2/2}$

$D^{Vi} = (CH_3)SiO_{2/2}$

$T = CH_3SiO_{3/2}$

$MDM = (CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_3$

$MD^HM = (CH_3)_3SiOSi(H)(CH_3)OSi(CH_3)_3$

Adhesion Tester purchased from Testing Machines, Inc. Specimens of 2 in. wide and 9 in. long were tested at 300 in. min at 180° peel angle. Delamination force is measured in g/2 in. Specimens were tested at 1, 3, and 4 weeks after lamination.

FTIR Instrumentation

Infrared spectra were taken on a Nicolet 7199 FTIR. In each case, 256 scans were accumulated before the interferogram was transformed. The data were collected at 1 wave number resolution. Spectra were plotted without smoothing or base-line corrections. A few of the spectra show the CO_2 peak between 2300 and 2400 wave numbers. This peak arises from slight differences in instrument purge and is not related to the sample. Since slight differences in penetration depth can occur as a function of surface contact, spectral intensities for each time series were adjusted to yield a constant height for the CH peak at 2850 wave numbers. Therefore, the height of the SiH peak at 2150 wave numbers, as read from the plots, has been normalized for path length within each time series.

ATR Sample Preparation

Samples were examined using the ATR technique with a KRS-5 crystal. Samples were cut into strips, approximately $\frac{1}{2} \times 1\frac{3}{4}$ in. Two strips, one on either side of the crystal, were mounted with the cured coating against the crystal. The clamp was tightened against the surface with 15 in.-pounds of pressure. As shown in the figure below, light is directed into the crystal at one end and exits at the other. In between, it bounces back and forth. Each time the light bounces, some of the radiation extends beyond the crystal face and examines the material contacting the surface. In this manner, spectra are obtained of a thin section along the front surface of the sample. The thickness examined is from 1 to 15 microns depending on the crystal material, angle of incidence, and refractive index of the sample. All sample spectra were ratioed against a background spectrum obtained with just the crystal:
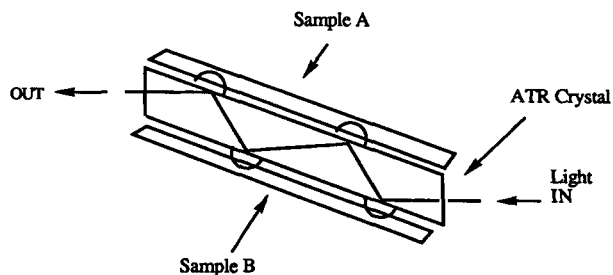
Degradation Procedure

Approximately 0.2 g of polymer was scraped from the paper and placed in 30 mL hexamethyldisiloxane, and 0.3 mL trifluoromethane sulfonic acid was added. The solution was stirred for 2 days, after which time the acid was quenched with 2 g MgO. The reaction was monitored by gas chromatography (GC) using a Shimadzu GC9A equipped with a 6 ft SE-30 column and flame-ionization detector.

GC–MS Analysis

Degraded coatings were analyzed by GC–MS with a JEOL SX-102 double-focusing mass spectrometer that was set to a mass resolution of 1000. For mass spectra obtained from 70 eV electron impact ionization, m/z 25–800 was scanned at the rate of 1 spectrum per second. For mass spectra obtained from 200 eV chemical ionization (220°C) with isobutane as the reagent gas, m/z 125–800 was scanned at 1 spectrum per second. GC was performed by programming the temperature of the J & W Scientific DB-5 GC column (30 m long with an i.d. of 0.32 mm, coated to a thickness of 0.25 μm) from 10°C (HOLD 1 min.) to 250°C at 10°C/min.

NMR Instrumentation

Solution ^{29}Si-NMR spectra were obtained at 59.6 MHz on a Varian XL-300 NMR spectrometer. A small amount of $Cr(acac)_3$ was added to each solution to shorten ^{29}Si T_1 and facilitate obtaining the spectra. Gated decoupling was also used to suppress any residual nuclear Overhauser enhancement (NOE). Typical spectral parameters included a 16 kHz spectral width, pulse width corresponding to a 45° flip angle, 32K data points, and a 5 s recycle delay to ensure that quantitative data were obtained. Chemical shifts are referenced to internal tetramethylsilane.

^{29}Si-CPMAS spectra were also obtained at 59.6 MHz on a GE GN-300 wide-bore spectrometer equipped with auxiliary high-power amplifiers and a Chemagnetics solid-state probe for magic angle spinning (MAS). The spectra were recorded with a 20 kHz spectral width, cross polarization (CP) contact time of 5 ms, relaxation delay of 5 s, and 4K time domain data points. Chemical shifts were measured relative to an external standard, dodecamethylcyclohexasilane ($^\delta$Si = −42.5 ppm), and are reported in ppm relative to tetramethylsilane.
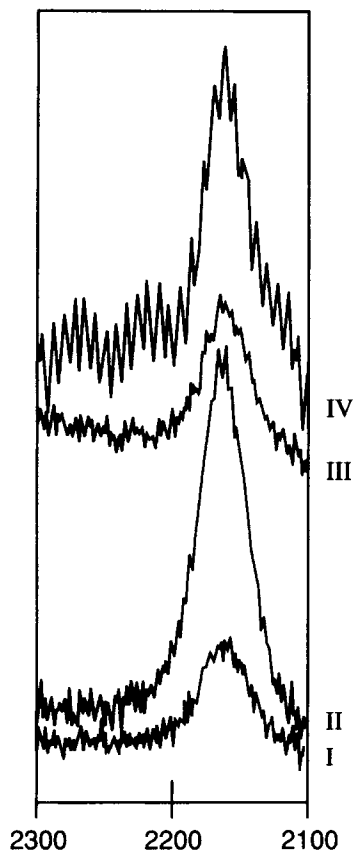
RESULTS AND DISCUSSION

Four samples of thermally cured silicone-release coatings were prepared on a pilot coater. The four samples are described in Table II. Analysis of the samples by ATR–FTIR showed residual hydride functionality (2100–2000 cm^{-1}) in all cases, but a larger amount was present in the less well cured samples. The SiH region of four normalized spectra 1 day after preparation is shown in Figure 2.

FTIR analyses over a period of several weeks showed a continual decrease in the residual hydride functionality, as shown in Figure 3. The data were normalized to both the initial SiH peak and the CH peak at 2850 cm^{-1}, as explained in the Experimental section. The observed trends are indicative of a postcure reaction. However, ATR–FTIR provided no information about the mechanism of the postcure reaction. In addition, neither Raman nor infrared spectroscopy was useful in determining the amount of residual vinyl functionality.

Solution ^{29}Si-NMR spectroscopy of the uncured formulation of Sample I is shown in Figure 4. The peaks have been assigned as follows: The resonance at 10 ppm is due to a small amount of trimethylsiloxy groups (M), the peak at -4.1 ppm is due to dimethylvinyl siloxy groups (M^{Vi}), the peaks between -19 and -22 ppm are assigned to dimethylsiloxy groups (D), the peak at -34.7 ppm is due to methylhydrogen siloxy groups (D^H), and the peak at -35.7 ppm is due to a small amount of methylvinyl siloxy groups (D^{Vi}). The solution ^{29}Si-NMR spectrum (Fig. 5) of Sample I after cure, run as a swollen polymer in CDCl$_3$, is essentially featureless except for a resonance assignable to D groups at -22 ppm and small, broad resonances centered at 7.7 and -36.5 ppm, which suggest the presence of M groups and residual D^H groups, respectively.

**Figure 2** ATR–FTIR spectra of release coating samples immediately after preparation.

The ^{29}Si-CPMAS spectrum (Fig. 6) of solid Sample I provided more definitive information than did the solution spectrum. The CP technique relies on polarization transfer from protons to nearby silicon nuclei through dipolar interactions. Under the ex-

Table II Silicone-Release Coating Samples

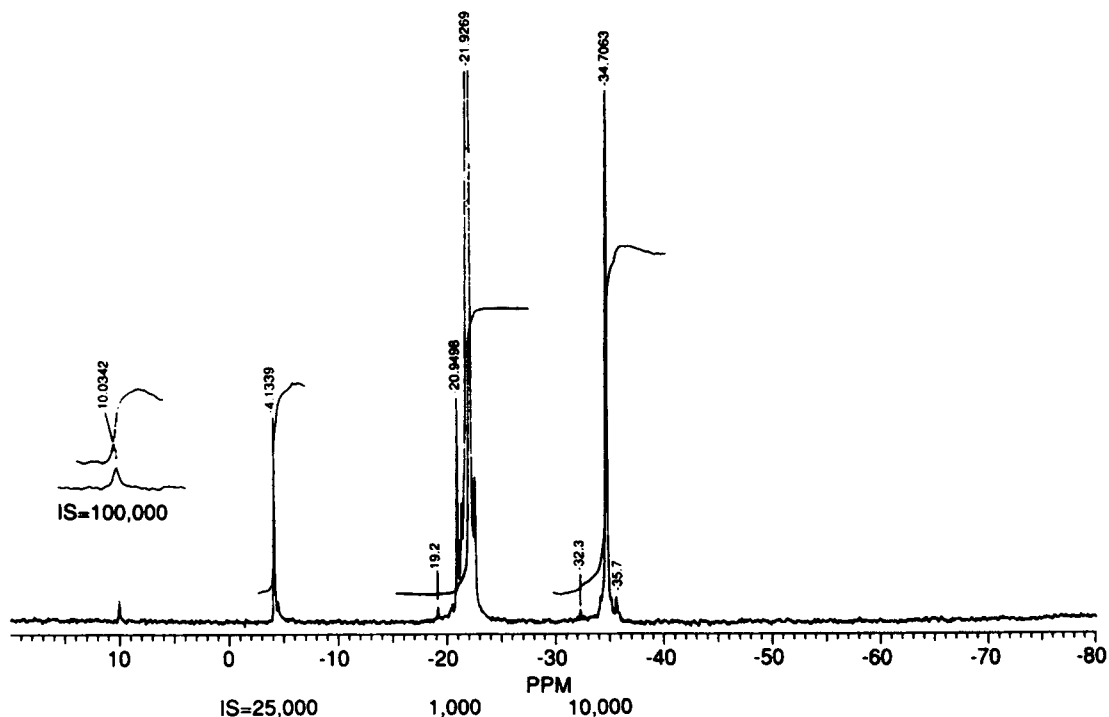| Sample	Composition	Cure State
I	M^{Vi}D$_x$M^{Vi} + 1% MD^{Vi}gum M^{H}D$_x^H$M	Well cured
II	M^{Vi}D$_x$M^{Vi} + 1% MD^{Vi}gum M^{H}D$_x^H$M	Undercured
III	M^{Vi}D$_x^{Vi}$D$_y$M^{Vi} M^{H}D$_x^H$M	Well cured
IV	M^{Vi}D$_x^{Vi}$D$_y$M^{Vi} M^{H}D$_x^H$M	Undercured
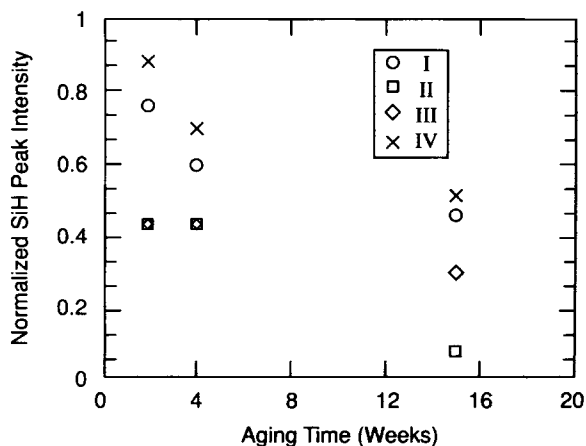
Figure 3 SiH intensity as a function of time.

Figure 4   Solution ^{29}Si-NMR spectrum of uncured Sample I.

perimental conditions employed to obtain the spectrum in Fig. 6 (5 ms CP contact time), the signal intensities of the residual D^H units and those arising from silicon atoms at or near rigid cross-link sites

are enhanced relative to the signal arising from the exceptionally mobile D units (the molecular motion diminishes dipolar coupling). The peak at 8 ppm in this spectrum includes resonances from both normal
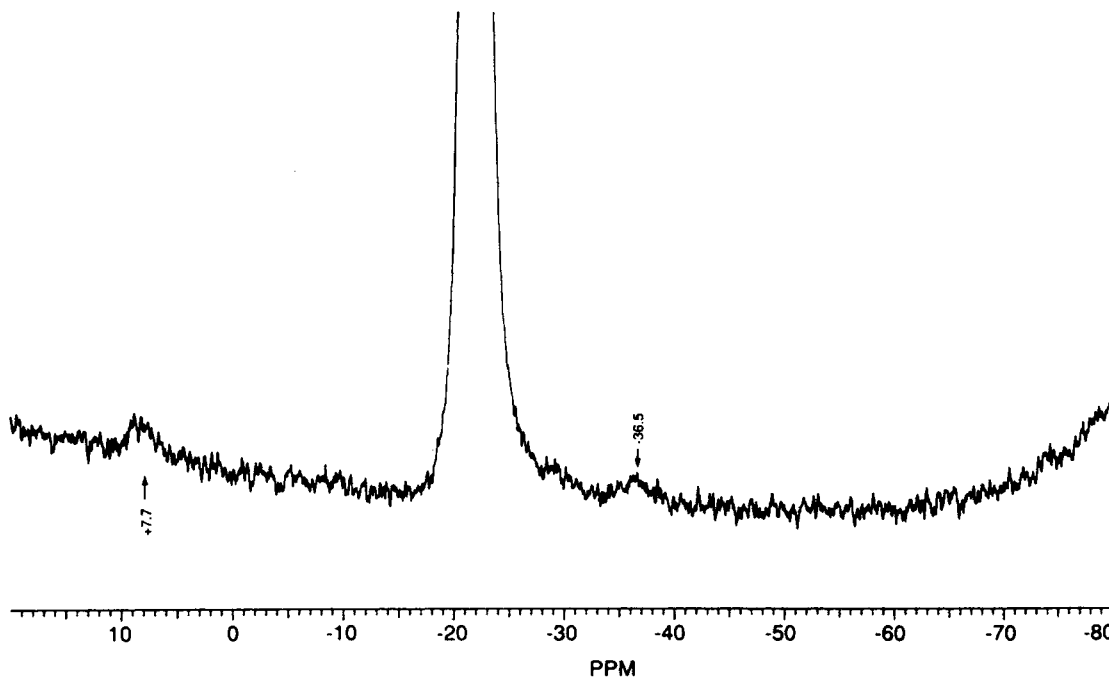

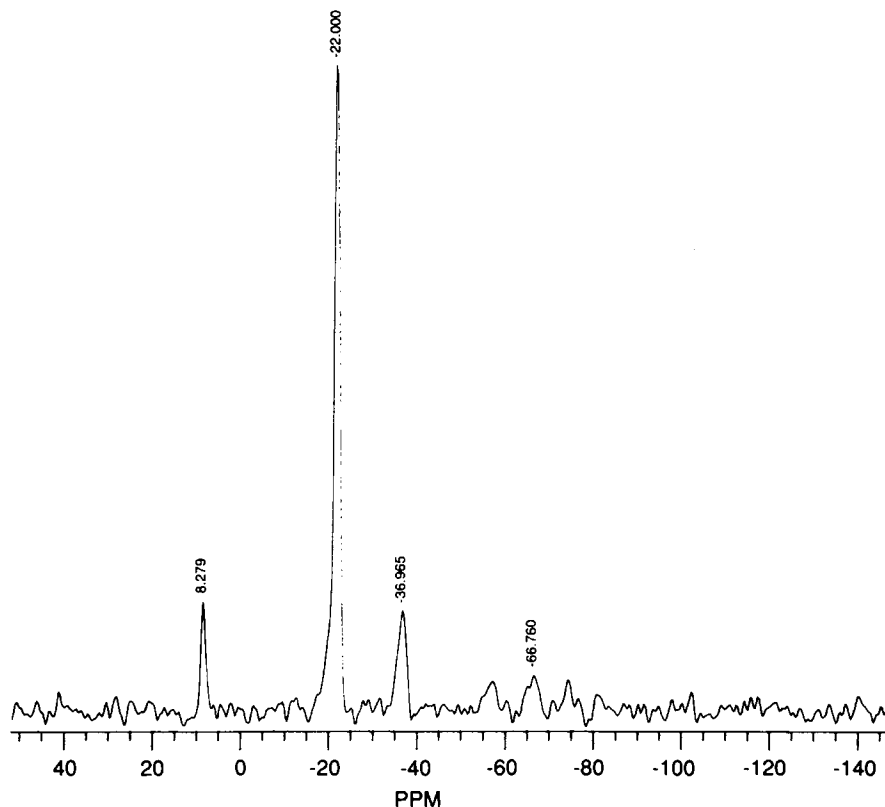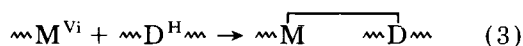**Figure 5**   Solution ^{29}Si-NMR spectrum of cured Sample I.

Figure 6   Solid-state ^{29}Si-CPMAS-NMR spectrum of cured Sample I.

M groups (trimethylsiloxy units) and cross-link sites (M') in which the M^{Vi} has reacted with D^H of another chain to form a disilylethane bridge [eq. (3)]:

$$\sim\!M^{Vi} + \sim\!D^H\!\sim \rightarrow \sim\!\overline{M \qquad \sim\!D}\!\sim \qquad (3)$$

The solution ^{29}Si-NMR spectrum of uncured Sample III is shown in Figure 7. The spectrum is similar to that obtained for Sample I with the exception that Sample III contains a greater amount of D^{Vi} groups. The solution spectrum of the cured swollen sample in this case does show, in addition to a trace of residual M^{Vi} at -4.3 ppm, a peak at -35.9 ppm, but it is not obvious whether this is due solely to excess silicon hydride or if both D^H and D^{Vi} contribute to the signal (Fig. 8). This peak is clearly enhanced relative to the D peak in the ^{29}Si CPMAS spectrum of Sample III shown in Figure 9. As expected, the peak arising from M and M' (at 8 ppm) is smaller than for Sample I, since in this sample, a significant number of the cross-link sites arise from reaction of D^{Vi} groups with D^H groups instead of M^{Vi} with D^H:

$$\sim\!D^H\!\sim + \sim\!D^{Vi}\!\sim \rightarrow \sim\!\overline{D\!\sim \qquad \sim\!D}\!\sim \qquad (4)$$
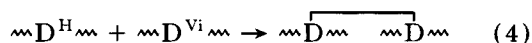
In samples of both I and III, after aging for several months, no residual hydride or vinyl functionalities were detected. Unfortunately, neither spectroscopic technique could provide information on the exact nature and quantification of cross-links or the amount of vinyl functionality remaining in the system. We therefore decided to degrade the networks with trifluoromethane sulfonic acid in excess hexamethyldisiloxane according to the method of Buese[6] and identify the products using GC–MS. Using this methodology, every difunctional silicon group is capped with two trimethylsiloxy groups and each monofunctional group becomes coordinated to one trimethylsiloxy group [eq. (5)]:

$$M^R D_x^R D_y M^R + MM \xrightarrow{H^+}$$

$$2MM^R, x MD^R M, y MDM + MM \qquad (5)$$
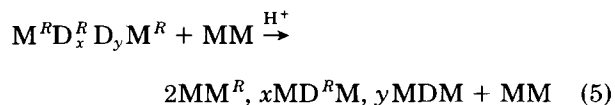
R = alkyl, hydride, aryl, etc. The products of the degradation of the initial hydride fluid are shown in eq. (6):

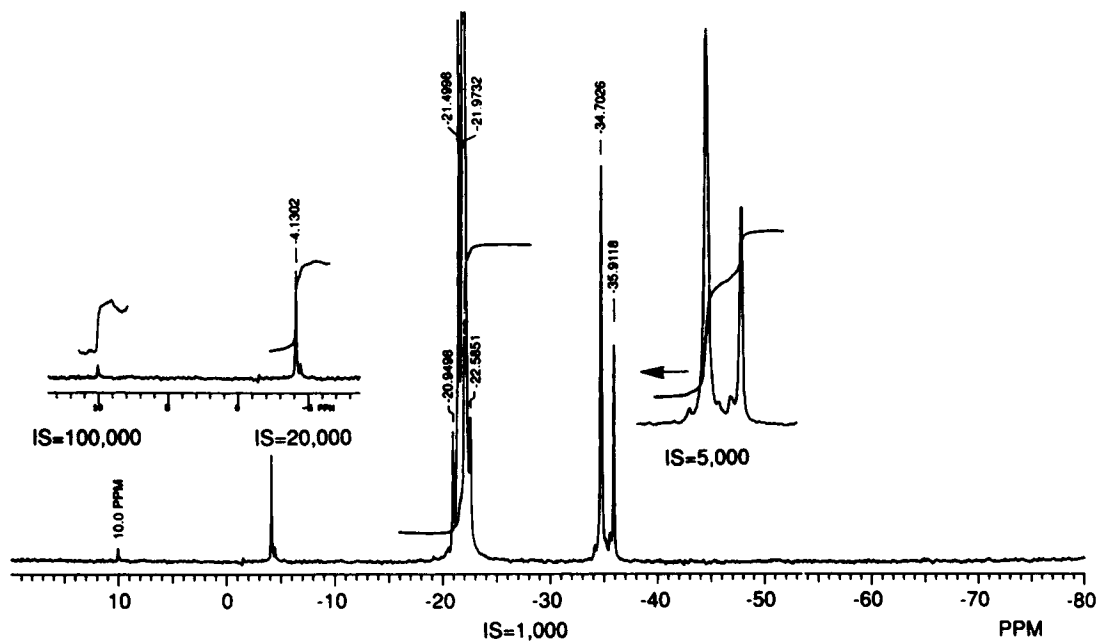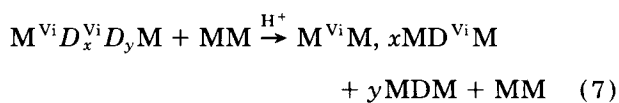$$MD_x^H M^H + MM \xrightarrow{H^+} x MD^H M + MM^H + MM \qquad (6)$$

Figure 7   Solution ^{29}Si-NMR spectrum of uncured Sample III.

The degradation scheme for a silicone polymer containing both terminal and on-chain vinyl groups is shown in eq. (7):

$$M^{Vi}D_x^{Vi}D_yM + MM \xrightarrow{H^+} M^{Vi}M, \ xMD^{Vi}M$$

$$+ yMDM + MM \quad (7)$$

Degradation of an uncured formulation containing SiH, Si(Vi) (terminal and on-chain), and catalyst yields MM, MDM, MD^{Vi}M, MM^H, MD^{H}M, MD^{Vi}M, and M$_3$T, the last of which arises from hydrolysis of a D^H group in the presence of platinum. In addition to the above products that arise from capping of either M or D groups, the cross-links are
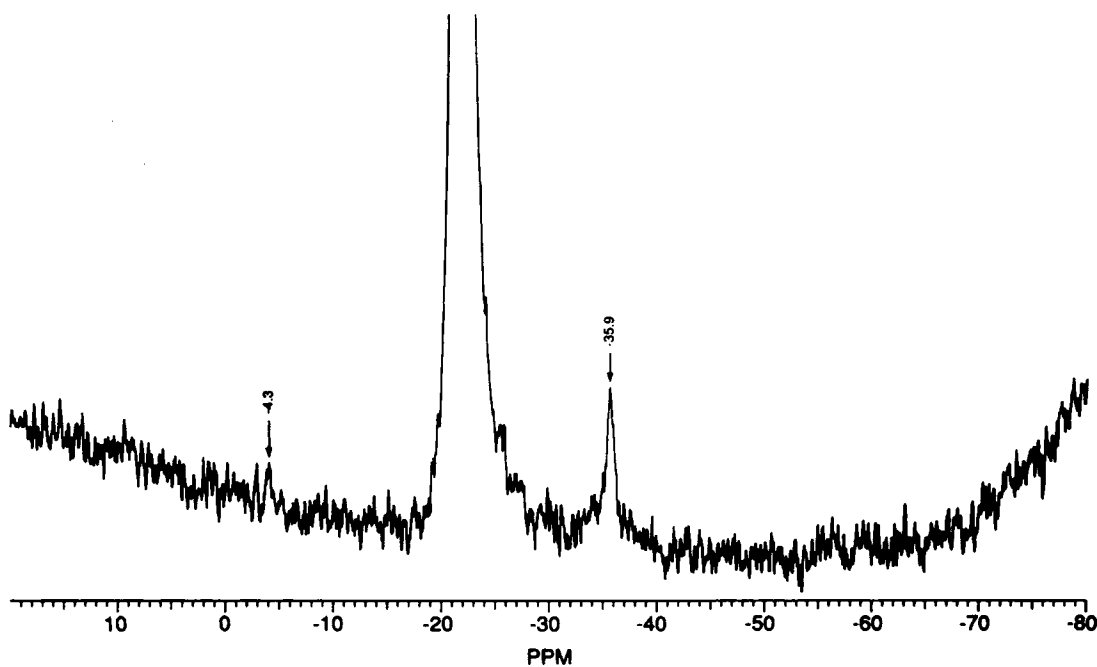

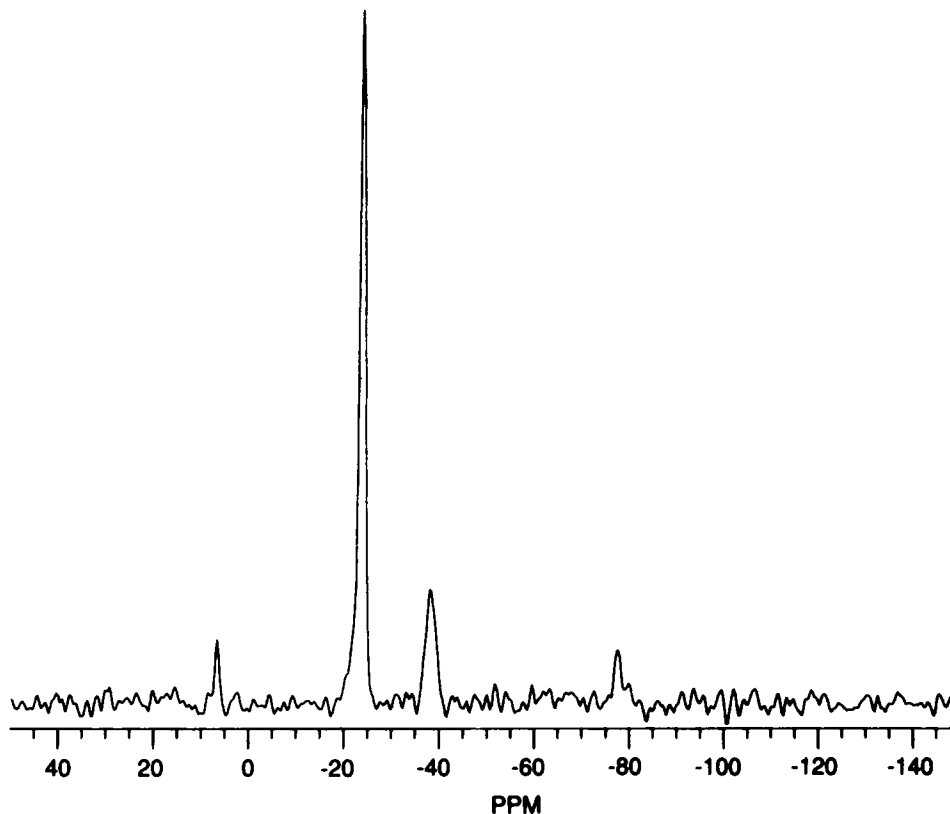**Figure 8**   Solution ^{29}Si-NMR spectrum of cured Sample III.

Figure 9   Solid-state ^{29}Si-CPMAS-NMR spectrum of cured Sample III.

also capped by this procedure. Three types of cross-links can be formed from systems that contain M^H and D^H subunits and M^{Vi} and D^{Vi} subunits: those arising from reaction of M^{Vi} with M^H to give

$$\overline{M \quad M},$$

those from M^{Vi} with D^H or M^H with D^{Vi} to give

$$\overline{M \quad D},$$

and those from D_{Vi} with D^H to give

$$\overline{D \quad D}.$$

In addition, there are two isomers possible for each cross-link depending on whether hydrosilylation occurs at the α or β position. The products of the degradation reaction of the cross-links are

$$\overline{M M \quad M M}, \ \overline{M D M \quad M M}, \text{ and } \overline{M D M \quad M D M}$$

and their β isomers.

The reconstructed chromatogram from the gas chromatography–mass spectrometry (GC–MS)

(isobutane chemical ionization) analysis of a degraded coating prepared from Sample I is shown in Figure 10. Most of the enormous excess of hexamethyldisiloxane was diverted away from the mass spectrometer in the interface. Switching this "bypass" off results in the split peak for hexamethyldisiloxane in the chromatogram. Unreacted D^H in the cured network is indicated by the presence of MD^HM in the chromatogram of the degraded sample. It is also apparent that a small amount of D^H has undergone hydrolysis by the presence of M_3T. The majority of cross-links are formed between D^H units and M^{Vi} units. A very small amount of cross-linking occurs between M^H and M^{Vi} subunits.

$$\overline{MDM \quad MDM}$$
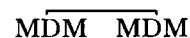
results from reaction of D^{Vi} groups with the D^H. The identifications of the components from the spectra as obtained by both electron impact and chemical ionization are based on spectra of known reference materials and their relative retention times.

To positively identify the peaks due to the vinyl-hydride cross-links, electron ionization and isobu-
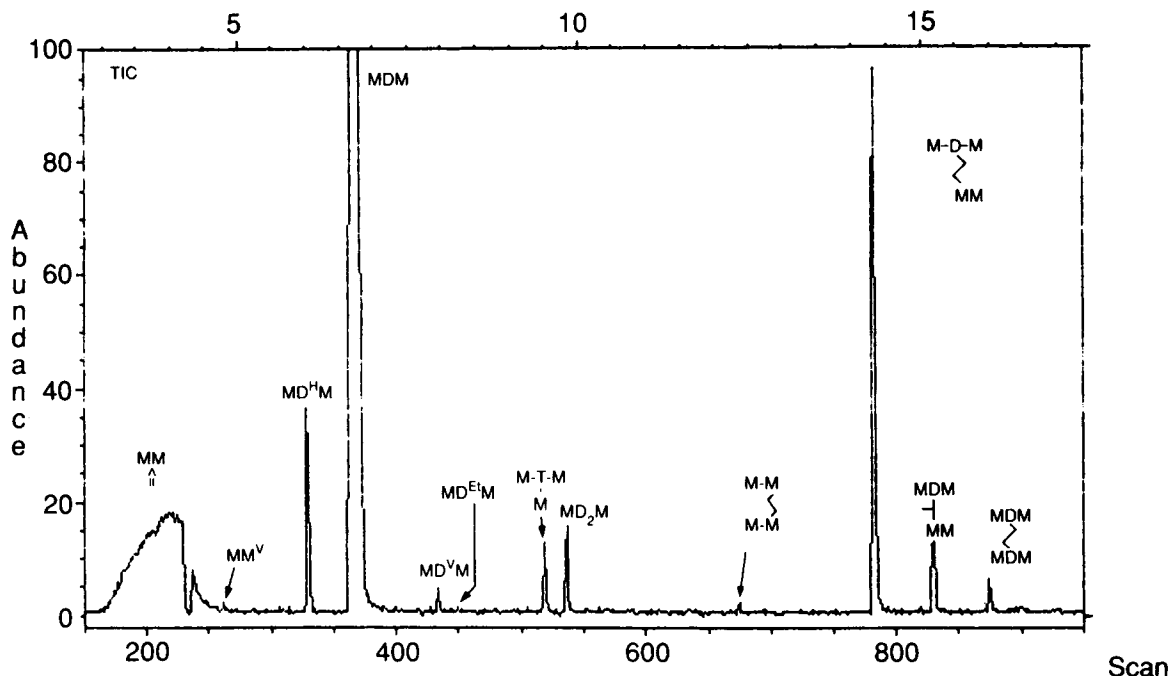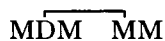
**Figure 10**   Reconstructed chromatogram (GC–MS) of degraded Sample I.

tane chemical ionization spectra were acquired by GC–MS for standards that were prepared by Pt-catalyzed hydrosilylation of vinyl and hydride starting materials. The major product of MW 396 formed from reaction of MM^{Vi} with MD^HM is

$$\overline{MDM\ \ MM}$$

and the minor product is

$$MDM$$
$$\vert$$
$$MM$$

The EI mass spectrum of the major product contains diagnostic ions at m/z 396 (molecular ion), 381 (loss of methyl), and 221 [due to cleavage of the $Si—(CH_2—CH_2)—$ bond]. In this spectrum, m/z 221 is of much greater abundance than are the larger mass ions. The CI spectrum contains ions at m/z 397 (MH), 396 (M), and the base peak at 307 (the loss of the elements of trimethylsilanol). In contrast, the EI spectrum of the minor product contains no signal at m/z 396, and the peak due to methyl loss is of approximately equal abundance as the peak at m/z 221. The CI spectrum contains no ions at m/z 396, but m/z 397 and 307 remain as before. The spectra and their relative retention times match with the data from the degraded coating. Neither of the isomeric structures

$$MDM$$
$$\vert$$
$$\overline{MDM\ \ MM}\quad\text{and}\quad MM$$
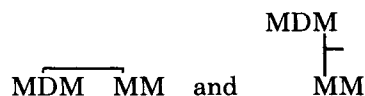
as formed from the reaction of MM^{Vi} with MD^HM exhibits molecular ions in their EI mass spectra. The spectrum of the compound formed by hydrosilylation at the β position exhibits a much more abundant m/e 221 as compared to the peak at m/e 381, but the peak at m/z 381 for the spectrum of the compound formed by hydrosilylation at the α position is more abundant than is the peak at m/e 221. The spectra for the two isomers formed by hydrosilylation at the α position could only be distinguished by retention time differences.

The vinyl–hydride cross-linked compounds, which contain 6 silicon atoms, exhibit analogous fragmentation behavior. Of all the isomers, only

$$\overline{MDM\ \ MDM}$$
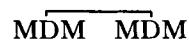
exhibits a molecular ion at m/z 470 in its EI mass spectrum and m/z 470 in its isobutane CI mass spectrum. Compounds formed by silylation at the α position exhibit peaks at m/z 221 that are by far the most abundant in their EI spectra, but the peaks due to methyl loss are of similar abundance to the m/z 221 peak for compounds formed by silylation at the β position. All of the isobutane CI spectra exhibit M^H ions at m/z 471 and their base peaks
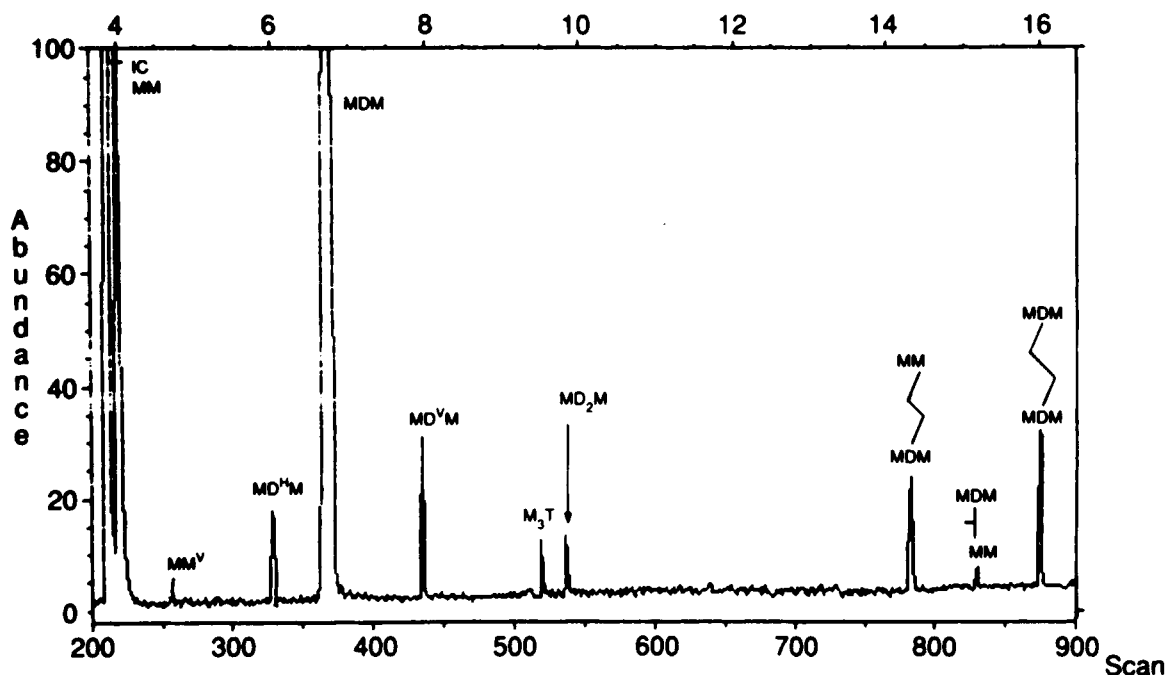
Figure 11 Reconstructed chromatogram (GC–MS) of degraded Sample III.

are m/z 381. Fortunately, the combination of retention times and spectral differences could be used to resolve all isomers if present. The peaks from the degraded coatings are not vinyl siloxanes because the isobutane CI spectra of vinyl siloxanes generally exhibit abundant peaks for protonated molecular ions and/or ions due to loss of vinyl and/or methyl groups, but not for ions from the apparent loss of trimethylsiloxy groups.

A reconstructed chromatogram from the GC–MS (isobutane CI) analysis of the degradation of a "well-cured" coating prepared from Sample III is shown in Figure 11. Surprisingly, a large amount of both D^H and D^{Vi} groups remain unreacted in the cured coatings, as evidenced by large amounts of $MD^{Vi}M$ and MD^HM. Additionally, the majority of cross-links occur between D^H and D^{Vi} groups. Chromatograms of less well cured samples show the same features as Sample I and II, respectively, although fewer cross-links are present.

Analysis of the degradation products of Sample I, after allowing the coating to age for 2 weeks prior to degradation, indicated a decrease in SiH functionality in agreement with the FTIR data. Additionally, an increase in M_3T is seen, indicating that SiH groups are undergoing hydrolysis and perhaps condensation with time. There is also a slight increase in cross-links of the type originating from

reaction of M^{Vi} units with D^H units. The GC of Sample III after aging also shows a decrease in D^H content and a small decrease in D^{Vi} content. An increase is seen in both cross-links arising from reactions of M^{Vi} with D^H and D^{Vi} with D^H. The aged, less well cured Samples II and IV followed the same trends as the well-cured Samples I and III, respectively.

The amount of residual functionality had a profound influence on the values obtained for the release force when the coatings were laminated against acrylic adhesives. The results in Table III indicate that less well cured samples gave higher release values (greater adherence) than do well-cured samples. Additionally, Sample I gave much lower release values than those of Sample III, which has a higher vinyl content. These results indicate that both re-

Table III Release Values for Laminated Silicone Coatings (g/2 in.)

Sample	1 Week	3 Weeks	4 Weeks
I	66	60	52
II	127	87	62
III	510	266	226
IV	618	288	237

sidual hydride and residual vinyl groups can result in high release values. It is likely that acrylic groups in the adhesive can undergo a hydrosilylation reaction with residual SiH groups to give a chemical bond between the adhesive and the release coating. Additionally, we have found that in model studies Si(Vi) groups accelerate the free radical polymerization of acrylates. Thus, it is also possible that this reaction may also contribute to acrylic weld.

CONCLUSION

We have developed several techniques to determine the network structure of platinum-catalyzed addition cure silicone-release coatings. FTIR has been successfully employed to determine hydride functionality concentration. ^{29}Si CPMAS NMR has provided additional information about the network structure. Methodology to determine the nature of cross-links has been developed in which the network is degraded by acid in the presence of excess hexamethyldisiloxane and GC–MS is used for characterization. The effect of residual functionality on network properties has also been discussed.

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