

# Addition-Cured Silicone Adhesive Technology: Vinyl Silicone Crosslinker

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## SYNOPSIS

Silicone pressure-sensitive adhesives prepared from a platinum-catalyzed, high solids silicone composition are described. The adhesive compositions consist of an MQ siloxane resin, vinyl- and hydride-terminated silicone fluids, and a multifunctional vinyl silicone crosslinker. In this study, multifunctional vinyl silicone crosslinkers of various structures, including linear polymers, T, TQ, and Q resins, were prepared and evaluated for their effect on the adhesive properties of cured silicone pressure-sensitive adhesives. Additionally, the activity of these multifunctional vinyl silicones in hydrosilylation reaction was investigated. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Silicone pressure-sensitive adhesives (PSAs) have traditionally been made by compounding a resinous siloxane copolymer of M ( $R_3SiO_{1/2}$ ) and Q ( $SiO_{4/2}$ ) units with a high-molecular-weight polydimethylsiloxane or poly(dimethyl-co-diphenyl)-siloxane gum at a selected resin-to-gum ratio. For ease of processing, these silicone PSAs are supplied as solutions in such volatile solvents as toluene and xylene. Depending on the types of converting equipment, these silicone PSAs are further diluted to a relatively low solids level (30–55 wt %) and a crosslinking peroxide is added. For example, when a knife-over-roll coater is used, the viscosity of the adhesive mixture can be in the range of 10,000–30,000 cps, whereas, a reverse-roll coater is capable of processing the same adhesive mixture at a viscosity of 3000–10,000 cps. Occasionally, such additives as pigments and fillers are also compounded into the silicone adhesive mixtures for the manufacturing of various finished PSA tapes and labels. To these precompounded silicone PSAs, the compounders and converters are given limited formulational flexibility in the design of adhesive tape properties.

It was recently reported that silicone PSAs with useful properties were obtained from a reactive, high solids silicone composition.<sup>1–4</sup> This technology uses low-viscosity, reactive silicone fluids plus a MQ resin with a small amount of solvent. The composition is cured via a platinum-catalyzed addition reaction to give a structured silicone adhesive with promising properties. The key compositional parameters governing the adhesive properties include the chain length of silicone oligomers, SiH to Si-vinyl stoichiometric ratio, type, and amount of multifunctional crosslinkers.

In this study, linear silicone polymers, TQ and Q siloxane resins having  $M^{vi}$  and  $D^{vi}$  vinyl functionalities were prepared and incorporated as crosslinkers into a high solids silicone system. Effects of the type and concentration of these vinyl-containing crosslinkers on PSA properties were investigated. Additionally, the reactivity of the vinyl silicones during the hydrosilylation reaction with Karstedt's Pt catalyst was also investigated.

## EXPERIMENTAL

### Silicone Nomenclature

The nomenclature of silicones in this study follows the system used in the silicone industry and literature.<sup>5</sup> The formulas and symbols for silicones are listed in Table I. For example, the letters M, D, T,

**Table I Formula, Functionality, and Shorthand of Silicone Notation**

Formula	Functionality	Symbol
$(\text{CH}_3)_3\text{SiO}_{1/2}$	Mono	M
$(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiO}_{1/2}$	Mono	$\text{M}^{\text{vi}}$
$(\text{CH}_3)_2(\text{H})\text{SiO}_{1/2}$	Mono	$\text{M}^{\text{H}}$
$(\text{CH}_3)_2\text{SiO}_{2/2}$	Di	D
$(\text{CH}_2=\text{CH})(\text{CH}_3)\text{SiO}_{2/2}$	Di	$\text{D}^{\text{vi}}$
$(\text{CH}_3)(\text{H})\text{SiO}_{2/2}$	Di	$\text{D}^{\text{H}}$
$(\text{CH}_3)\text{SiO}_{3/2}$	Tri	T
$(\text{OH})\text{SiO}_{3/2}$	Quadri	$\text{Q}^{\text{OH}}$
$\text{SiO}_{4/2}$	Quadri	Q

and Q represent mono-, di-, tri-, and quadrifunctional monomer units; monomer units are the silicones bonded to one, two, three, and four oxygen atoms, individually.  $\text{M}^{\text{vi}}$  and  $\text{D}^{\text{vi}}$  represent dimethylvinylsiloxy and methylvinylsiloxy units, respectively. The short-handed formula and structure for the silicones and the siloxane resins for the high solids silicone compositions are shown in Table II.

### Preparation of Vinyl Silicones

#### $\text{M}^{\text{vi}}\text{D}_x\text{D}_y^{\text{vi}}\text{M}^{\text{vi}}$ Linear Polymer

A low  $\text{D}^{\text{vi}}$  containing polymer  $\text{M}^{\text{vi}}\text{D}_{21.5}\text{D}_{0.28}^{\text{vi}}\text{M}^{\text{vi}}$  and a high  $\text{D}^{\text{vi}}$  containing polymer  $\text{M}^{\text{vi}}\text{D}_{175.9}\text{D}_6^{\text{vi}}\text{M}^{\text{vi}}$  were synthesized for the study. These two linear vinyl crosslinkers were prepared according to the following procedure: A mixture of the stoichiometric amounts of tetramethyldivinyl disiloxane, octamethylcyclotetrasiloxane ( $\text{D}_4$ ), and tetramethyltetra vinyl cyclotetrasiloxane ( $\text{D}_4^{\text{vi}}$ ) were equilibrated with a catalytic amount of KOH for 6 h at  $150^\circ\text{C}$ , then neutralized to slight acidity. The equilibrated polymer mixtures were further vacuum stripped at  $150^\circ\text{C}$  to remove volatiles. The structure of the resulting silicone polymers was determined by  $^{29}\text{Si}$ -NMR.

#### $\text{M}_x\text{D}_y^{\text{vi}}\text{TQ}$ Resin

This TQ-type resin was prepared by the process described below. The following silanes-xylene blend was fed over 7 min to a nitrogen-purged, 3-L Morton flask containing 700 mL water while under vigorous agitation and maintained at  $60^\circ\text{C}$  maximum temperature: 278.3 g tetraethylorthosilicate, 200.0 g methyltrichlorosilane, 56.6 g methylvinylchlorosilane, 232.2 g trimethylchlorosilane, and 263 g xylene. After 30 min of vigorous agitation, the mixture was thoroughly washed with water, then phase separated. The organic phase was heated to reflux at  $145^\circ\text{C}$  to remove volatiles. The mixture was further catalyzed with KOH and condensed at  $145^\circ\text{C}$  for 3 h. After cooled down, the resin mixture was neutralized to about 10 ppm HCl and filtered. The product was vacuum stripped at  $150^\circ\text{C}$ ,  $< 0.5$  mmHg pressure for 1 h and gave a soft, tacky gummy resin. The resin had the composition, identified by  $^{29}\text{Si}$ -NMR, of  $\text{M}_{0.59}\text{D}_{0.13}^{\text{vi}}\text{T}_{0.51}\text{Q}_{0.49}$ . The gel permeation chromatography (GPC) analysis gave the following results:  $M_n = 1560$ ,  $M_w = 4020$ , and a polydispersity of 2.6.

#### $\text{M}_x\text{D}_y^{\text{vi}}\text{Q}$ Resin

A Q-type resin of  $\text{M}_{0.678}\text{D}_{0.114}^{\text{vi}}\text{Q}$  composition was prepared as follows: A mixture of 321.4 g sodium silicate and 574.7 g water was added over 10 s to a 3-L Morton flask containing 161.5 g 37% HCl and 358 g water while under vigorous agitation. This was followed by the addition of 378.1 g isopropyl alcohol over 10 s. Then the following silanes-xylene blend was charged over 80 s: 133.0 g trimethylchlorosilane, 29.2 g methylvinylchlorosilane, and 89.9 g xylene. The mixture was heated to reflux for 2 h, then cooled to an ambient temperature, and washed with additional 113.4 g xylene. The lower acidic layer was discarded. The remaining hydrolysate catalyzed with KOH and refluxed at  $145^\circ\text{C}$  for 3 h. The mixture was cooled to ambience, neutralized to a slightly acidic state, and filtered. The resulting mixture was vacuum dried and yielded a resinous white solid powder.

**Table II Common Formulas and Structure of Silicones and Siloxanes**

Formula	Structure
$\text{M}^{\text{vi}}\text{D}_x\text{M}^{\text{vi}}$	$(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiO}-((\text{CH}_3)_2\text{SiO})_x-\text{Si}(\text{CH}_3)_2\text{CH}_2=\text{CH}$
$\text{M}^{\text{vi}}\text{D}_x\text{D}_y^{\text{vi}}\text{M}^{\text{vi}}$	$(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiO}-((\text{CH}_3)_2\text{SiO})_x-((\text{CH}_2=\text{CH})(\text{CH}_3)\text{SiO})_y-\text{Si}(\text{CH}_3)_2(\text{CH}_2=\text{CH})$
$\text{M}^{\text{H}}\text{D}_x\text{M}^{\text{H}}$	$(\text{CH}_3)_2\text{HSiO}-((\text{CH}_3)_2\text{SiO})_x-\text{SiH}(\text{CH}_3)_2$
$\text{M}_x\text{D}_y^{\text{vi}}\text{TQ}$	$[(\text{CH}_3)_3\text{SiO}_{1/2}]_x[(\text{CH}_2=\text{CH})(\text{CH}_3)\text{SiO}_{2/2}]_y\{(\text{CH}_3)\text{SiO}_{3/2}\}\{\text{SiO}_{4/2}\}$
$\text{M}_x\text{D}_y^{\text{vi}}\text{Q}$	$[(\text{CH}_3)_3\text{SiO}_{1/2}]_x[(\text{CH}_2=\text{CH})(\text{CH}_3)\text{SiO}_{2/2}]_y\{\text{SiO}_{4/2}\}$
$\text{M}_x\text{M}_y^{\text{vi}}\text{Q}$	$[(\text{CH}_3)_3\text{SiO}_{1/2}]_x[(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiO}_{1/2}]_y\{\text{SiO}_{4/2}\}$

### $M_xM_y^iQ$ Resin

An  $M^{vi}$  containing siloxane resin of  $M_{0.71}M_{0.12}^iQ$  composition was prepared by a process similar to the procedure for the  $MD^{vi}Q$  resin. A Morton flask containing 252.4 g 37% HCl and 465.9 g water was maintained at 15°C with vigorous agitation. The following reagents were added in order: 1391 g sodium silicate with 401.5 g water and 756.2 g isopropanol. The following silanes-xylene blend was then added over 7 min: 258.9 g trimethylchlorosilane, 17.2 g dimethylvinylchlorosilane, and 90 g xylene. After 2 h of reflux at 84°C, the mixture was cooled to an ambient temperature and phase separated. The hydrolysate was diluted with 227 g xylene, catalyzed with KOH, and then further reflux condensed for 4 h at 145°C. The resulted solution was neutralized to about 10 ppm HCl, filtered through a Celite filter pad to give a clear resin solution. The solution was vacuum dried and gave a white solid powder. The GPC analysis gave the following result:  $M_n = 3020$ ,  $M_w = 7782$ , and a polydispersity of 2.58.

### NMR Spectroscopic Characterization

$^{29}Si$ -NMR measurements were carried out on solutions of these silicone polymers in deuterated chloroform  $CDCl_3$  at approximate 40% w/v concentration, which was doped with chromium acetylacetonate. Solution samples in a Teflon polytetrafluoroethylene tube were placed in a Varian XL-300 FT NMR spectrometer operating at 59.6 MHz. All chemical shifts were assigned with respect to TMS (tetramethylsilane) standard. A  $CDCl_3$  solvent blank in the Teflon tube was run to subtract the background signal in the Q region of the NMR spectra. The structures of these polymers were determined based on proper integrations of the assigned peaks.

### Preparation of High Solids Adhesive Composition

High solids silicone compositions in this study were prepared according to the method reported in the references<sup>1,2</sup> with the following components: a hydride-terminated silicone fluid  $M^H D_{128.4} M^H$ , a vinyl-terminated silicone fluid  $M^{vi} D_{120} M^{vi}$ , and a siloxane MQ resin having a M/Q ratio of 0.7 to 1 and 2 wt % silanol (provided in toluene solution). Appropriate amounts of these components along with a vinyl crosslinker silicone of choice were homogeneously mixed. Toluene was vacuum stripped to give a mixture of about 90 wt % solids. These high solids mixtures were further catalyzed with Karstedt's Pt catalyst prior to coating.

### Adhesive Preparation and Testing

The high solids compositions were applied using a universal knife coater over 1 mil polyester film substrate, to give a 1.5–2 mil dried adhesive, and cured for 3 min at 150°C. The cure quality of cured silicone PSAs was evaluated by determining if residue occurred when the adhesives were removed from steel and glass substrates.

The peel adhesion property of the cured adhesive tapes was measured by performing a 180° peel against a clean steel plate after the adhesive-steel laminates were allowed to dwell for 20 min. The measurement was done according to ASTM D3330 at a rate of 12 in./min. The probe tack adhesion was measured according to ASTM D2979-88 using a Polyken Probe Tack Tester (TMI Testing Machines Inc.) at a contact pressure of 14.5 psi, a probe movement rate of 1 cm/s, and a dwell time of 1 s. A repeated test study showed that the peel adhesion test has an accuracy of  $\pm 1$  ounce/in, and the probe tack testing has an accuracy of  $\pm 50$  g/cm<sup>2</sup>. The consistency in adhesive thickness and the cleanliness of the probe and steel plate are the keys to good test reproducibility.

### Differential Scanning Calorimetry Study on Vinyl Silicones

The reactivity of the vinyl silicones in a Pt-catalyzed hydrosilylation reaction was investigated using a methylhydrogen silicone fluid SS4300C (manufactured by GE Silicones). This methylhydrogen silicone fluid contains 1.63% hydrogen by weight. A silicone fluid of  $M^{vi} D_{24.8} M^{vi}$  composition [2.66 wt % vinyl content and a vinyl equivalent weight (VEW) of 1015 g] was employed as a reactive diluent for the preparation of these otherwise solid or gummy materials in the study. Vinyl crosslinkers of interest were first dissolved in the  $M^{vi} D_{24.8} M^{vi}$  diluent fluid to form a 50/50 blend by weight. The blend was further catalyzed with 80 ppm Karstedt's Pt catalyst and 0.5 wt % (or otherwise as indicated) dimethyl maleate (DMM) inhibitor. Differential scanning calorimetry (DSC) experiments were conducted on a Perkin-Elmer DSC-7 system under a constant nitrogen purge. The DSC measurements were performed from 30 to 200°C at a rate of 10°C/min, using 10–15 mg samples of the catalyzed formulations in open aluminum pans. The amount of heat released,  $\Delta H$  in joules/gram, was calculated by integrating the area under the peak(s) to the baseline of the DSC curves and normalized to the sample weight. The DSC profile for the  $M^{vi} D_{24.8} M^{vi}$  reactive

diluent was also included for reference. To obtain good reproducibility on DSC profiles and the subsequent calculations, the optimal conditions include a sample weight around 10–15 mg and a constant heating rate of 10°C/min. The higher the heating rate, the higher the exotherm temperature locates. In order to compare the reactivity among the vinyl silicones, it is important to maintain constant DSC conditions. A repeated DSC survey under the same conditions suggested that the exothermic peaks occurred with 1°C accuracy.

## RESULTS AND DISCUSSION

### Vinyl Crosslinker Type and Properties

The structure and the vinyl characteristics of the vinyl functional silicones synthesized for this study are summarized in Table III. The structures were based on <sup>29</sup>Si-NMR analyses. The weight percent vinyl content (wt % vinyl) is the ratio of the total weight of vinyl groups to the weight of the host silicone polymer. The VEW is the molecular weight of silicone per one equivalent of vinyl group, and was calculated based on the derived structure.

As shown in Table III, both linear silicone polymers are dimethylvinylsiloxy-terminated poly-(dimethyl-co-diphenyl)siloxanes.  $M^{vi}D_{21.5}D_{0.28}^{vi}M^{vi}$  is a low  $D^{vi}$  containing crosslinker having 12 mol % of the total vinyl groups as on-chain methylvinyl siloxane units. On the other hand,  $M^{vi}D_{175.9}D_6^{vi}M^{vi}$  is a high  $D^{vi}$  polymer having 75 mol % of the total vinyl groups as methylvinyl siloxane units.  $M_{0.59}D_{0.13}^{vi}T_{0.51}Q_{0.49}$  is a TQ-type resin in which all the vinyl functionalities are on-chain methylvinyl siloxane  $D^{vi}$  units.

Of the four Q-type three-dimensional resins,  $M_{0.678}D_{0.114}^{vi}Q$  and  $M_{0.62}D_{0.12}^{vi}Q$  are the siloxane resins consisting of M,  $D^{vi}$ , and Q repeat units.  $M_{0.648}M_{0.076}^{vi}Q$  and  $M_{0.71}M_{0.12}^{vi}Q$  are the siloxane resins

comprising M,  $M^{vi}$ , and Q repeat units. The <sup>29</sup>Si-NMR spectra of the selected silicones are plotted in Figure 1.

### Hydrosilylation Reactivity Study by DSC

The reactivity of the vinyl silicones during the hydrosilylation reaction with a hydride silicone fluid was evaluated by determining the “maximal reaction heat” detected by DSC. The maximal reaction heat of a vinyl silicone is defined as the highest amount of “heat of reaction” released during the reaction between the vinyl silicone and SS4300C methylhydrogen silicone fluid in a series of DSC experiments. The DSC experiments were performed on the formulated mixtures containing proper amounts of the vinyl silicone, the reactive diluent, and the hydride silicone fluid, wherein the SiH to Si-vinyl stoichiometric ratio was varied systematically. Illustrated in Figure 2 are the DSC scans of the hydrosilylation reaction between the  $M_{0.71}M_{0.12}^{vi}Q$  vinyl silicone resin (at a 50/50 blend with  $M^{vi}D_{24.8}M^{vi}$  diluent fluid) and the hydride silicone fluid at SiH to Si-vinyl ratios from 1.12 to 2.17. Also illustrated in Figure 2 are the  $T_{95}$  readings, which are defined as the temperatures at which 95% of the total heat of reaction were observed.

The heat of reaction property, or  $\Delta H$  in joules/gram, in each DSC profile was obtained by integrating the area under the peak(s) to the baseline, then normalized to the sample weight. The heat of reaction  $\Delta H$  was also converted into joules/mole equivalent vinyl unit by normalizing the value in joules/gram against the  $\langle \text{VEW} \rangle$  (i.e., averaged vinyl equivalent weight) value of the vinyl silicone blend.

To derive the maximal reaction heat value for a specific vinyl silicone, a correlation curve between the hydrosilylation reaction heat and the SiH/Si-vinyl stoichiometric ratio was established. As illustrated in Figure 3 for  $M_{0.71}M_{0.12}^{vi}Q$  siloxane resin, the

**Table III Vinyl Crosslinker Type and Properties**

Crosslinker	Vinyl Type	Wt % Vinyl	VEW	Property
$M^{vi}D_{21.5}D_{0.28}^{vi}M^{vi}$	12% $D^{vi}$ , 88% $M^{vi}$	3.4	790	Liquid
$M^{vi}D_{175.9}D_6^{vi}M^{vi}$	75% $D^{vi}$ , 25% $M^{vi}$	1.57	1720	Liquid
$M_{0.59}D_{0.13}^{vi}T_{0.51}Q_{0.49}$	$D^{vi}$	2.86	944	Gummy
$M_{0.678}D_{0.114}^{vi}Q$	$D^{vi}$	2.47	1093	Solid
$M_{0.62}D_{0.12}^{vi}Q$	$D^{vi}$	2.7	1000	Solid
$M_{0.648}M_{0.076}^{vi}Q$	$M^{vi}$	1.72	1570	Solid
$M_{0.71}M_{0.12}^{vi}Q$	$M^{vi}$	2.65	1019	Solid

maximal reaction heat of 100.5 J/milli eq. was observed at a SiH to Si-vinyl ratio of 1.81. The same treatments were given to each vinyl crosslinker. The correlation curves for some vinyl silicones are plotted in Figure 3. The results are summarized in Table IV.

It was noted that the heat of reaction increased with the SiH/Si-vinyl stoichiometric ratio, and peaked at a SiH to Si-vinyl ratio of well above 1 for all the vinyl functional silicones. However, the hydrosilylation reactivity of these silicones was rather different and appeared to be structure dependent. Based on the  $\Delta H$  in joules/milli equivalent shown in Table IV, the following observations were made: (a) the linear vinyl crosslinkers were more reactive than the resinous vinyl crosslinkers; (b) among the resinous crosslinkers, TQ-type siloxane resin was more reactive than the Q-type resin; and (c) the vinyl group of the terminal dimethylvinylsiloxy  $M^{vi}$  type was more reactive than that of the on-chain methylvinylsiloxy  $D^{vi}$  type.

From a reaction mechanism viewpoint, silicone structure (linear, TQ, and Q types) affects sterically the accessibility of these vinyl groups to Pt catalyst and the activation energy for Pt to form a complex with vinyl functionalities. Linear silicone fluids are highly flexible and the on-chain  $D^{vi}$  units are readily assessable due to highly free rotating Si—O bonds on the main chains. These characteristics made the linear vinyl silicone fluids reactive during the hydrosilylation reaction. The more rigid the crosslinker type, the more difficult it is thermodynamically, for the formation of Pt catalyst–vinyl complex.<sup>6,7</sup> Therefore, the steric hinderance associated with the T and Q units of these siloxane resins made these vinyl groups less accessible to Pt catalyst during the addition reaction.

The effectiveness of dimethyl maleate (DMM) on delaying the hydride-vinyl addition reaction was apparent throughout the silicones investigated. As illustrated in Figure 4 the value of  $T_{95}$  (i.e., the temperature at which 95% of the total reaction heat

registered) was plotted against the SiH/Si-vinyl ratio. It appears the hydrosilylation reaction rate, indicated by  $T_{95}$ , clearly is a function of the SiH/Si-vinyl stoichiometric ratio. The influence of the DMM inhibitor concentration on the hydrosilylation kinetics is clearly illustrated.

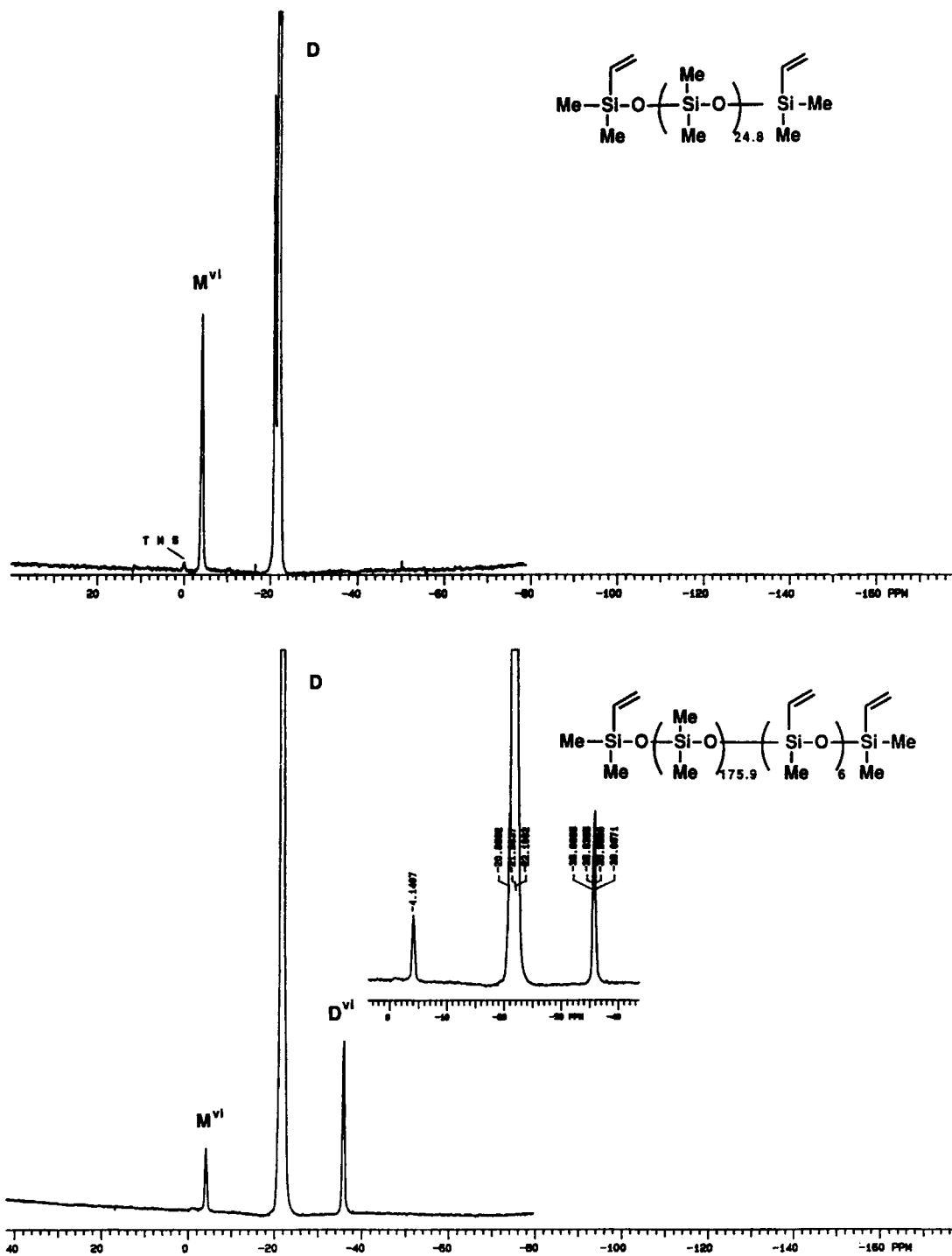
### Addition Cure Stoichiometry and Adhesive Properties

To investigate how the SiH/Si-vinyl stoichiometry affects the properties of the cured adhesive, a series of high solids silicone compositions were prepared with a SiH to Si-vinyl ratio ranging from just under 1.0 to about 15. The adhesives contained an approximate 58 wt % of an MQ siloxane resin. The remaining silicone components in the adhesives comprised appropriate amounts of a dimethylhydrogensiloxy-terminated silicone fluid  $M^H D_{128.4} M^H$ , a dimethylvinylsiloxy-terminated silicone fluid  $M^{vi} D_{120} M^{vi}$ , and vinyl silicone crosslinker  $M_{0.59} D_{0.13} T_{0.51} Q_{0.49}$ , the vinyl crosslinker maintained at approximate 21 mol % level. The properties of the cured silicone adhesives are shown in Table V.

While the adhesive film prepared from the composition at 0.98 SiH/Si-vinyl ratio showed high peel adhesion value, the weak cohesive strength left a slight residue on the steel plate. The best peel adhesion property was observed at a stoichiometric ratio of 1.28. As the stoichiometric ratio further increased, the peel and tack adhesion properties decreased. When the SiH/Si-vinyl ratio was 14.7 and higher, the cured adhesives no longer had sufficient structural integrity and left residue on steel and glass substrates. Therefore, the addition-curable, high solids compositions need to be formulated at a SiH/Si-vinyl ratio of above 1 to give PSAs with useful properties. The optimal stoichiometry is empirically determined for each of the vinyl silicone crosslinker of choice to prepare a high solids silicone composition with desirable peel and tack adhesions.

**Table IV** Hydrosilylation Reactivity Properties of Vinyl Crosslinkers

Crosslinker	$\langle \text{VEW} \rangle$ (blend, g)	$\Delta H$ , J/milli eq.	$\Delta H$ , J/g	SiH/Si-vinyl (at $\Delta H_{\text{max}}$ )
$M^{vi} D_{24.8} M^{vi}$	1015	115.5	113.8	1.58
$M^{vi} D_{175.9} D_6^{vi} M^{vi}$	1368	119.6	87.4	1.96
$M_{0.71} M_{0.12}^{vi} Q$	1017	100.5	98.8	1.81
$M_{0.59} D_{0.13}^{vi} T_{0.51} Q_{0.49}$	980	97.1	99.1	2.01
$M_{0.678} D_{0.114}^{vi} Q$	1054	91.3	86.6	1.65



**Figure 1**  $^{29}\text{Si-NMR}$  spectra of (a)  $M^{\text{vi}}D_{24.8}M^{\text{vi}}$  and  $M^{\text{vi}}D_{175.9}D_6^{\text{vi}}M^{\text{vi}}$  linear silicones and (b)  $M_{0.71}M_{0.12}^{\text{vi}}Q$ ,  $M_{0.678}D_{0.114}^{\text{vi}}Q$ , and  $M_{0.59}D_{0.13}^{\text{vi}}T_{0.51}Q_{0.49}$  resinous vinyl siloxanes.

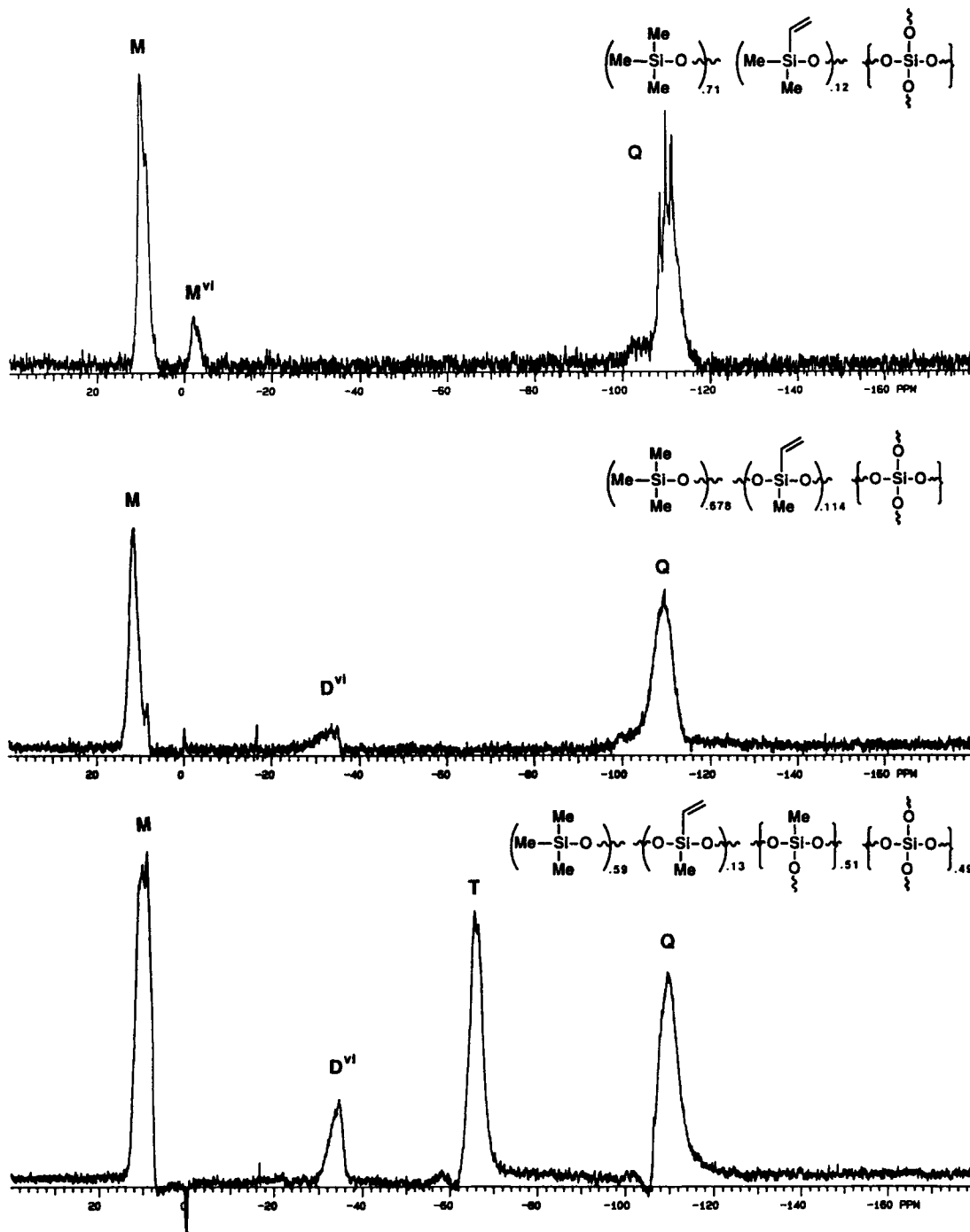
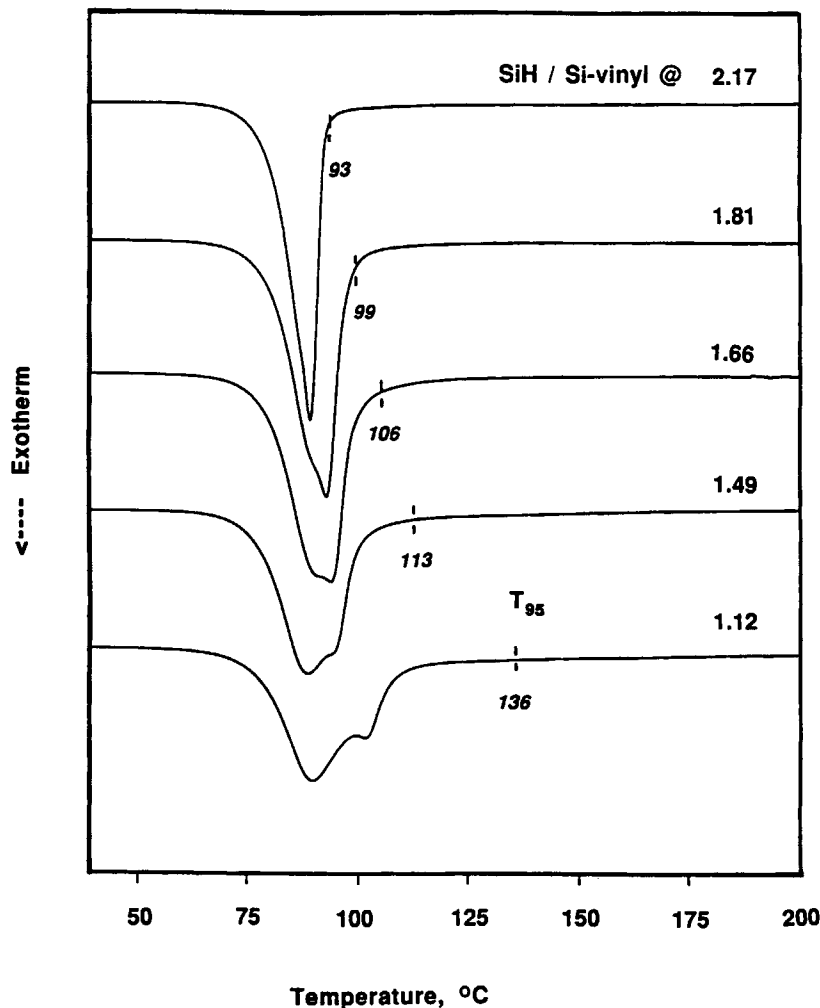


Figure 1 (Continued from the previous page)

### Vinyl Crosslinker Level and Properties

A multifunctional vinyl crosslinker in an addition-curable silicone composition is vital to the formation

of a three-dimensional structure. Generally, the more crosslinker present, the higher the degree of crosslinking that occurs in the adhesive. How the increase in the degree of crosslinking affects the



**Figure 2** DSC scans of the Pt-catalyzed hydrosilylation between  $M_{0.71}M_{0.12}Q$  vinyl silicone (in a 50/50 blend with  $M^{vi}D_{24.8}M^{vi}$  diluent) and a methylhydrogen silicone fluid.

properties of cured silicone PSAs is not well documented.

The vinyl groups of the multifunctional silicone compete with the  $M^{vi}$  vinyl groups of the  $M^{vi}D_{120}M^{vi}$  for the SiH groups in the high solids silicone system. It is the multifunctional vinyl silicone that contributes to the formation of a cured matrix through simultaneous chain extension and crosslink branching reactions.<sup>4</sup> Therefore, the type and level of the vinyl crosslinker used in the high solids composition affect the extent of crosslink branching in the cured adhesive, as well as the properties of the cured PSA. Illustrated in Table VI is a series of addition-cured silicone adhesives in which the amount of the vinyl crosslinker,  $M_{0.59}D_{0.13}^{vi}T_{0.51}Q_{0.49}$ , was varied to give

21.5 to 100 mol % of the total vinyl groups needed for the mixture. The SiH/Si-vinyl ratio, the averaged  $\langle VEW \rangle$ , and the MQ resin content for these compositions are tabulated in Table VI, along with the adhesive properties.

As the mole percent of the crosslinker increased, the relative content of on-chain  $D^{vi}$  vinyl units increased, and the corresponding terminal  $M^{vi}$  vinyl (of  $M^{vi}D_{120}M^{vi}$ ) units decreased. Thus, the degree of crosslinking of the cured adhesive proportionally increased, as suggested by the decreasing  $\langle VEW \rangle$  value. This resulted in a cured adhesive with lowered flexibility and reduced pressure sensitivity. The peel and probe tack adhesion properties reduced correspondingly.



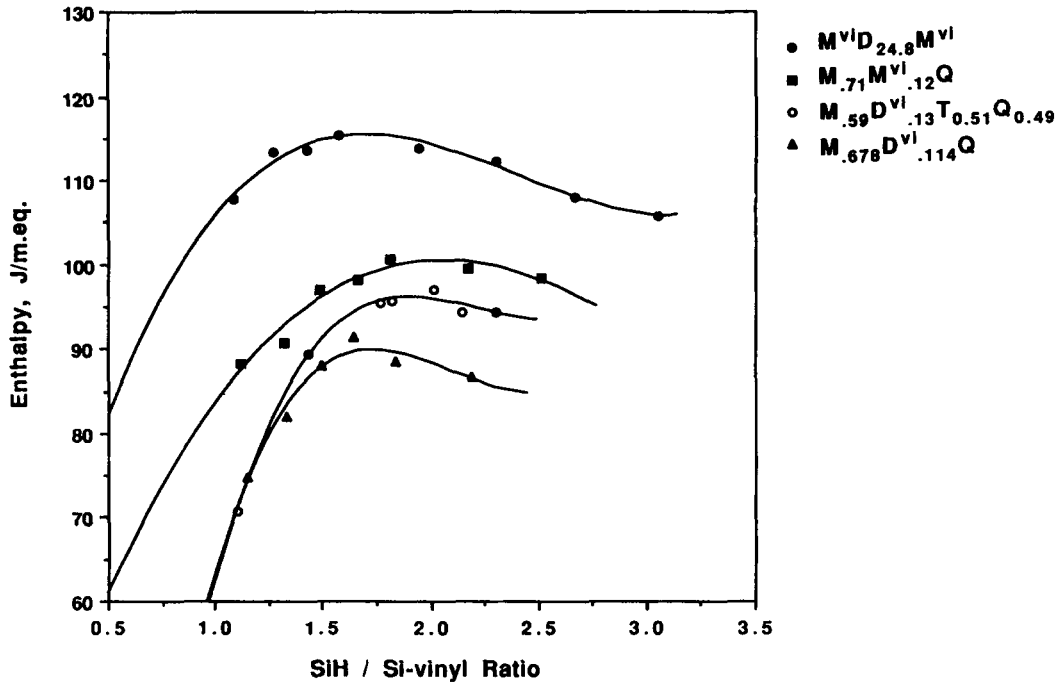


Figure 3 Hydrosilylation reaction enthalpy of vinyl silicones with a methylhydrogen silicone fluid as a function of SiH to Si-vinyl stoichiometric ratio.

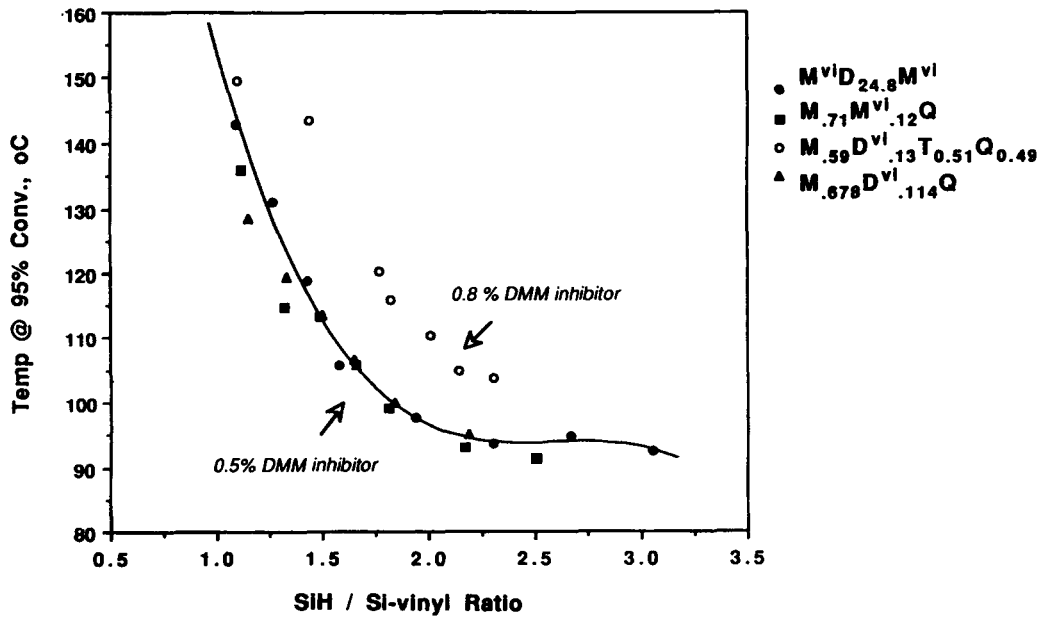


Figure 4  $T_{95}$ , the temperature at which 95% of the total reaction heat was registered, of vinyl silicones as a function of SiH to Si-vinyl ratio and the level of DMM inhibitor.

**Table V Stoichiometry Effect on Cured Adhesive Properties ( $M_{0.59}D_{0.13}^{vi}T_{0.51}Q_{0.49}$  as crosslinker)**

SiH/Si-vinyl	Mol. % X-ker	<VEW>	Peel, oz/in.	Tack, g/cm <sup>2</sup>	Cure Quality
0.984	21.4	3335	51 <sup>a</sup>	466	Slight residue
1.28	21.5	3332	39	478	No residue
4.93	21.3	3345	28	268	No residue
9.85	21.3	3345	26	290	No residue
14.7	21.5	3332	< 10	n/a	Residue

<sup>a</sup> Cohesive failure observed.

### Vinyl Crosslinker Type and Adhesive Properties

It has been shown that the type and the structure of vinyl silicone crosslinker affected the reactivity during the hydrosilylation reaction. From a product design viewpoint, the primary purpose of the study is to evaluate how key adhesive properties are affected by the type of silicone crosslinker. In order to compare these vinyl silicone crosslinkers, the prepared vinyl functional siloxanes were incorporated into the high solids silicone compositions while the overall SiH to Si-vinyl stoichiometric ratio was maintained at near 1.3. The other key design parameters shown in Table VII are the specific molar content of the vinyl groups of the crosslinker and the weight percent MQ for each formulation. These adhesives were heated for 3 min at 150°C to allow sufficient curing. The peel adhesion and probe tack properties of the cured adhesives are displayed in Table VII.

Among the vinyl silicones investigated, the adhesive formulated with  $M^{vi}D_{21.5}D_{0.28}^{vi}M^{vi}$  silicone fluid showed heavy residue transfer and gave the weakest cohesive strength. This vinyl silicone crosslinker has only 12 mol % of the total vinyl groups as  $D^{vi}$  vinyl and 88 mol % as  $M^{vi}$  vinyl. Thus it provides very light crosslinking. Contrasting to  $M^{vi}D_{21.5}D_{0.28}^{vi}M^{vi}$ , the linear vinyl silicone  $M^{vi}D_{175.9}D_6^{vi}M^{vi}$  gave highly crosslinked adhesive structure, since it carries 75

mol % of the total vinyl groups as  $D^{vi}$  vinyl. This resulted in an adhesive with good pressure-sensitive properties.

Overall, the vinyl siloxane resin crosslinkers gave cured silicone PSAs with better adhesive properties than the linear polymer crosslinker  $M^{vi}D_xD_y^{vi}M^{vi}$ . It is desirable to design a multifunctional vinyl silicone with three-dimensional, resinous characteristics since it imparts better adhesive properties than the linear silicones. As shown in Table VII, silicone PSAs with excellent peel adhesion were obtained when a TQ- or Q-type resin crosslinker was used. The peel adhesion properties of these high solids silicone systems correlate with the type of vinyl crosslinker in the following descending order:  $M_{0.648}M_{0.076}^{vi}Q$ ,  $M_{0.678}D_{0.114}^{vi}Q > M_{0.59}D_{0.13}^{vi}T_{0.51}Q_{0.49} > M^{vi}D_{175.9}D_6^{vi}M^{vi}$ .

### CONCLUSIONS

Multifunctional vinyl silicones of linear, TQ-, and Q-type resinous structures were synthesized and evaluated as crosslinkers for a Pt-catalyzed addition-cured, high solids silicone adhesive system. In addition to the weight percent MQ resin content, the adhesive properties of this high solids silicone system depend strongly on the SiH to Si-vinyl stoichiometric ratio, the type of multifunctional vinyl silicone, and the vinyl crosslinker concentration. It was found that TQ- and Q-type resinous crosslinkers gave cured silicone PSAs with better adhesive properties than the linear silicone crosslinker  $M^{vi}D_xD_y^{vi}M^{vi}$ . Among the crosslinker type investigated, the peel and probe tack adhesion properties of cured PSAs decreased in the following order:  $M_{0.648}M_{0.076}^{vi}Q$ ,  $M_{0.678}D_{0.114}^{vi}Q > M_{0.59}D_{0.13}^{vi}T_{0.51}Q_{0.49} > M^{vi}D_{175.9}D_6^{vi}M^{vi}$ .

The hydrosilylation reactivity of these vinyl functional silicones with a methylhydrogen silicone fluid was investigated using DSC. The following observations were made: (a) the linear vinyl cross-

**Table VI Effect of Vinyl Crosslinker Concentration on PSA Properties ( $M_{0.59}D_{0.13}^{vi}T_{0.51}Q_{0.49}$  as crosslinker)**

Mol % X-ker	SiH/ Si-vinyl	<VEW>	Wt % MQ	Peel, oz/in	Tack, g/cm <sup>2</sup>
21.5	1.28	3332	57.3	39	478
52.0	1.22	2450	56.4	30	404
69.4	1.22	1875	55.7	30	374
79.1	1.39	1590	55.6	25	312
100.0	1.37	944	54.5	25	306

**Table VII Vinyl Crosslinker Type and Adhesive Properties**

Crosslinker	% X-ker (mol)	SiH/Si-vinyl	Wt % MQ	Peel (oz/in.)	Tack (g/cm <sup>2</sup> )
M <sup>vi</sup> D <sub>21.5</sub> D <sub>0.28</sub> <sup>vi</sup> M <sup>vi</sup>	20.0	1.30	57.5	38 <sup>a</sup>	490 <sup>a</sup>
M <sup>vi</sup> D <sub>175.9</sub> D <sub>8</sub> <sup>vi</sup> M <sup>vi</sup>	19.2	1.31	57.0	31	348
M <sub>0.59</sub> D <sub>0.13</sub> <sup>vi</sup> T <sub>0.51</sub> Q <sub>0.49</sub>	21.5	1.28	57.3	39	478
M <sub>0.678</sub> D <sub>0.114</sub> <sup>vi</sup> Q	15.6	1.37	57.5	41	590
M <sub>0.62</sub> M <sub>0.12</sub> <sup>vi</sup> Q	20.0	1.30	57.4	36	426
M <sub>0.648</sub> M <sub>0.076</sub> <sup>vi</sup> Q	22.1	1.27	57.0	40	376

<sup>a</sup> Slight residue noted.

linkers were more reactive than the resinous vinyl crosslinkers; (b) among the resinous crosslinkers, the TQ-type siloxane resin was more reactive than the Q-type resin; and (c) the vinyl group of the terminal dimethylvinylsiloxy M<sup>vi</sup> type was more reactive than that of the on-chain methylvinylsiloxy D<sup>vi</sup> type. It is viewed that the steric hinderance associated with the T and Q units of these siloxane resins made these vinyl groups less accessible to Pt catalyst during the addition reaction.

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