INVESTIGATING EFFECTS OF RELEASE COATING COMPOSITION ON CURE PROFILE AS MEASURED BY DSC

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Introduction

Cure of a series of platinum catalyzed addition cured solvent free release coatings was characterized by differential scanning calorimetry. A novel method of plotting the conversion vs temperature during a constant heating rate temperature ramp experiment yielded a straight line with the slope interpreted as the rate of reaction. Thinking of coating cure as being a two-step process consisting of initiation as measured by the 1% conversion temperature and onset temperature followed by a rapid crosslinking reaction allowed for separating the factors that dictate the initiation or onset temperature and the factors that effect rate of crosslinking following initiation. Finally, the temperature at which full cure is achieved can be measured and be shown to be affected by the factors controlling onset as well as rate of reaction.

DSC Characterization of Release Coating Cure

Differential Scanning Calorimetry (DSC) is a well-known thermal analysis technique that measures the heat flow into or out of a sample as function of the sample's temperature. The exothermic nature of the hydrosilylation reaction responsible for forming crosslinks between vinyl functional siloxane polymers and SiH functional crosslinkers is ideal for study by DSC. Samples consisted of a specific vinyl functional base polymer, specific SiH functional crosslinker and a platinum catalyst mixed to give a desired SiH/SiVi ratio as well as platinum content. A drop of the sample after thorough mixing was weighed into an open-top aluminum pan and then placed into the DSC along with an empty open-top aluminum reference pan. The sample and reference pan were heated from 30 degrees Celsius to 150 degrees Celsius as a constant heating rate of 10 degrees Celsius per minute. The heating and of the sample and reference were carried out in an inert nitrogen environment. The resultant sharp exothermic peak resulting from the hydrosilylation or "cure" reaction was then analyzed using peak integration and running integral analysis found in the standard instrument software functions.

DSC Cure Characterization by Peak Integration

A typical DSC thermogram detailing the cure reaction of a platinum catalyzed solvent free silicone release coating will show a flat base line followed by a well-defined exothermic peak and a return to the base line. Figure 1 shows a typical thermogram for a drop of a release coating heated from 30 degrees C to 150 degrees Celsius at a constant heating rate of 10 degrees Celsius per minute.

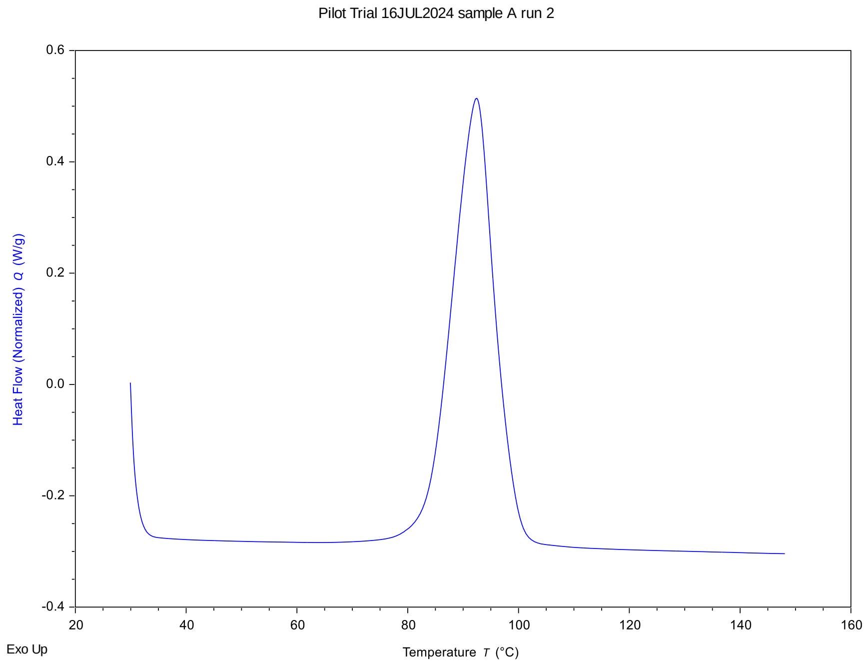

Figure 1: DSC thermogram showing exothermic cure of a silicone release coating.

The thermogram shows the heat flow out of the sample due to the exothermic nature of the cure reaction in units of Watts per gram on the Y axis as a function of the temperature in degrees Celsius displayed on the X axis. The thermogram shows deflection from the baseline starting around 70 degrees Celsius indicating the initiation of the cure process followed by a sharp increase in heat flow which reaches a maximum between 90 and 95 degrees Celsius followed by completion near 115 degrees Celsius as the heat flow curve returns to the baseline. The first step in numerical analysis of the results is to perform a peak integration analysis which yields a total heat flow as the area under the curve as well as a peak exotherm temperature and onset temperature. Figure 2 shows a typical peak integration result for cure of a silicone release coating.

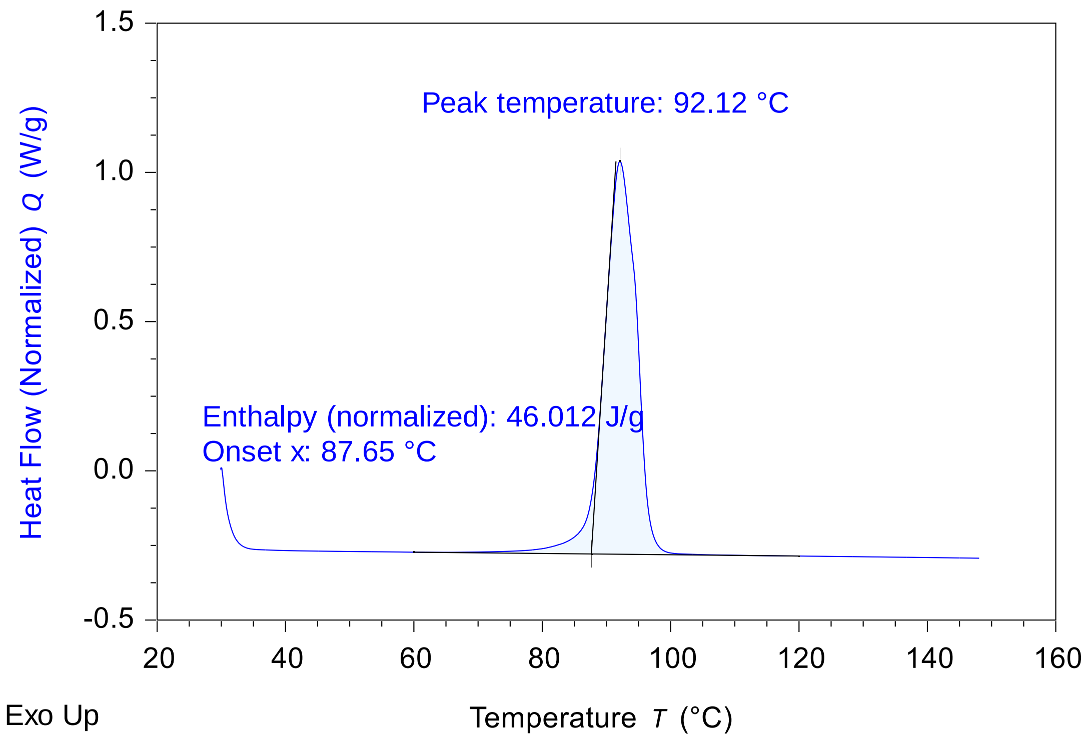

Figure 2: Peak Integration results for a silicone release coating cured in a DSC.

The results in figure 2 show that the sample evolved 46.0 Joules of energy per gram of sample during the cure reaction with an onset temperature of 87.65 degrees Celsius and a peak temperature of 92.12 degrees Celsius. The heat of reaction or total area under the curve is a great measure of the crosslink density formed during cure. It is useful to think of the total energy released during cure as being proportional to the number of crosslinks formed by the addition of a Si-H functional group from a crosslinker polymer across a Si-Vi group from the vinyl functional base polymer. This will become readily apparent when we compare the heat of reaction of short chain end blocked vinyl functional base polymer with relatively higher vinyl content per gram to longer chain end blocked vinyl functional base polymers with lower vinyl content per gram. The crosslink density effects the viscoelastic properties of the finished release liner and measured phenomena such as release profile or release force vs peel speed. The onset temperature is found by extending the tangent line to the curve at the inflection point down to where it intercepts the baseline. This serves as one measure of the temperature at which the reaction starts as we heat the sample from 30 degrees Celsius. Platinum catalyzed release coatings contain an inhibitor which prevents the formulation from curing at room temperature, allowing components to be mixed as well as pumped to a coating head and applied to a substrate in a liquid form. Following application of the coating to the substrate, it is heated in an oven resulting in breaking the platinum-inhibitor complex and allowing cure at elevated temperature. The peak temperature of the exotherm corresponds to the temperature of maximum heat flow rate or maximum rate of reaction. The running integral analysis will provide the temperature corresponding to 1% of total reaction and 5% of total reaction that are used along with the onset temperature from the peak integration as measures of reaction initiation temperature.

DSC Cure Characterization by Running Integral

Just as integrating the area under the curve for the complete cure reaction yields the total heat of reaction, we can integrate the partial area under the curve from the initiation of the reaction to any temperature above the initiation and below the completion temperatures. This allows for determining the temperature corresponding to 1% cure, 5% cure, 50% cure and 95% cure. Figures 3 through 6 show the running integral analysis for a single sample cured in a DSC with the point on the curve corresponding to 1%, 5%, 50% and 95% cure respectively. We can express the following equations.

Heat of Reaction = $\int_{T_0}^{T_f} Q(T)\, dT$ (1)

Partial Heat of Reaction = $\int_{s=T_0}^{s=T} Q(S)dS$ (2)

Equation 1 gives the total heat of reaction as found using peak integration function depicted in figure 2. Equation 2 is a function that can be used to find the value of T corresponding to any desired partial heat of reaction. In particular we will be interested in finding the temperatures corresponding to 1%, 5%, 50% and 95% cure. The percent cure is found by dividing equation 2 by equation 1. This is very easy to do graphically using the running integral analysis function. Figures 3 through 6 show the running integral analysis for a cure profile corresponding to 1%, 5%, 50% and 95% cure respectively.

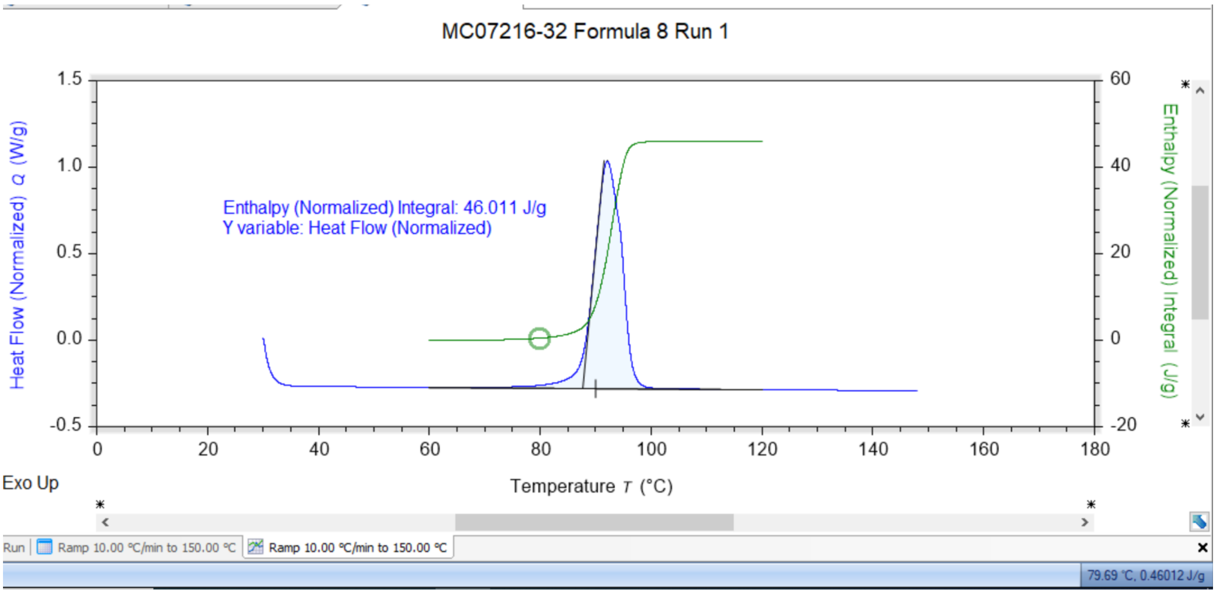

Figure 3: Running integral analysis showing that T = 79.69C when heat evolved is 0.46 J/g

Note in figure 3 that the total heat of reaction was 46.01 Joules per gram as determined by peak integration analysis. One percent of the total heat of reaction is 0.46 J/g and the running analysis shows that when the temperature was 79.69 C that the total heat evolved up to that point was 0.46 J/g.

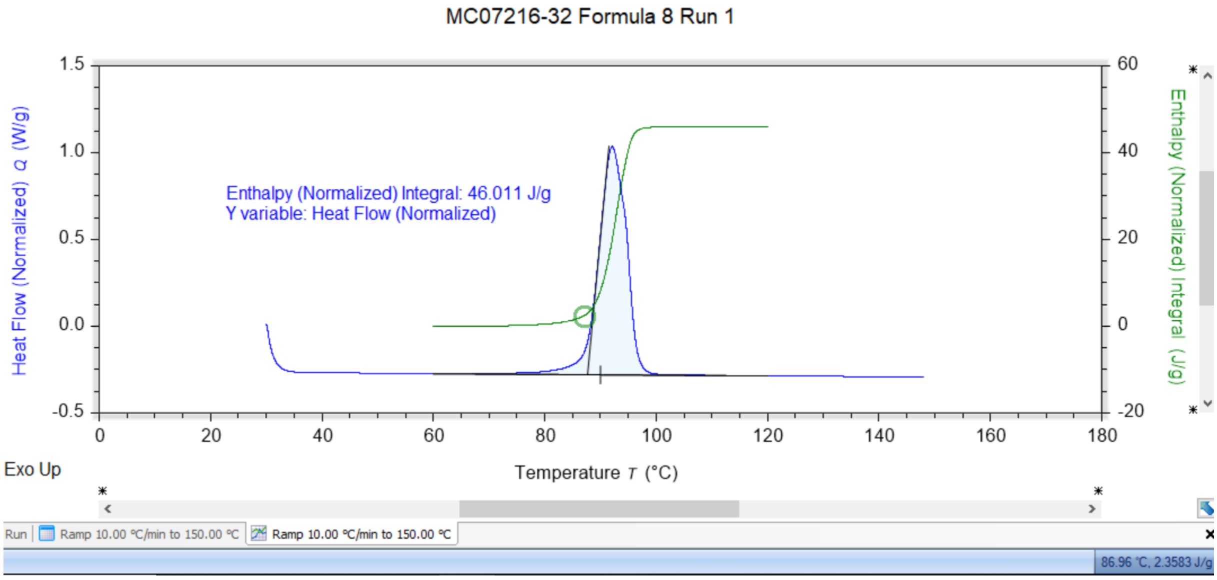

Figure 4: Running integral analysis showing 5% of reaction occurred at 86.96 degrees C.

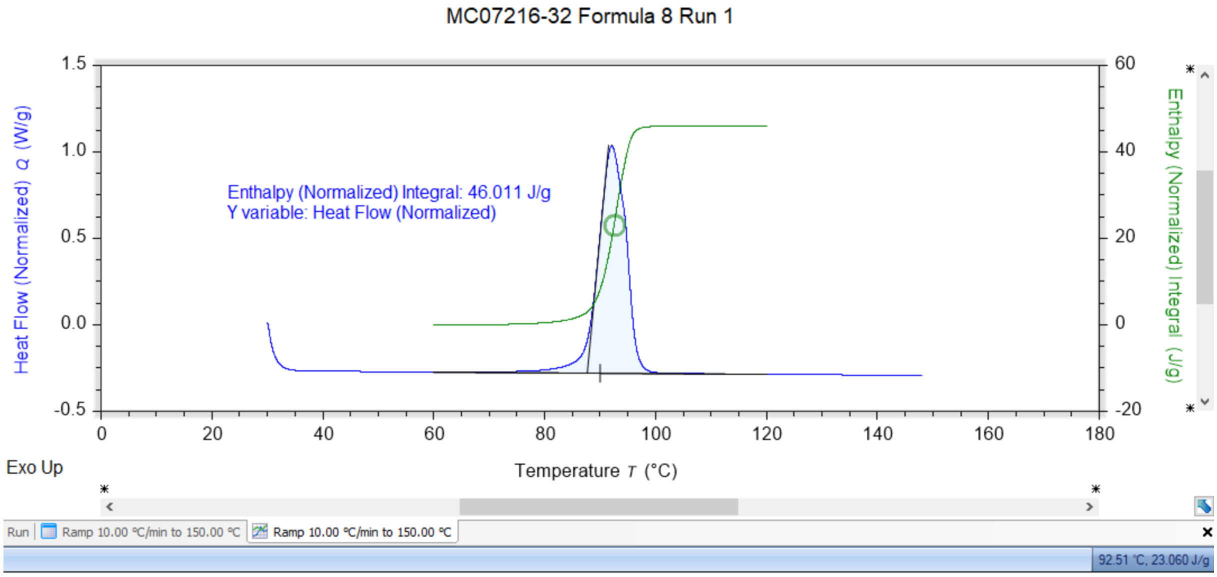

Figure 5: Running integral analysis showing 50% of total heat evolved at 92.51 degrees C.

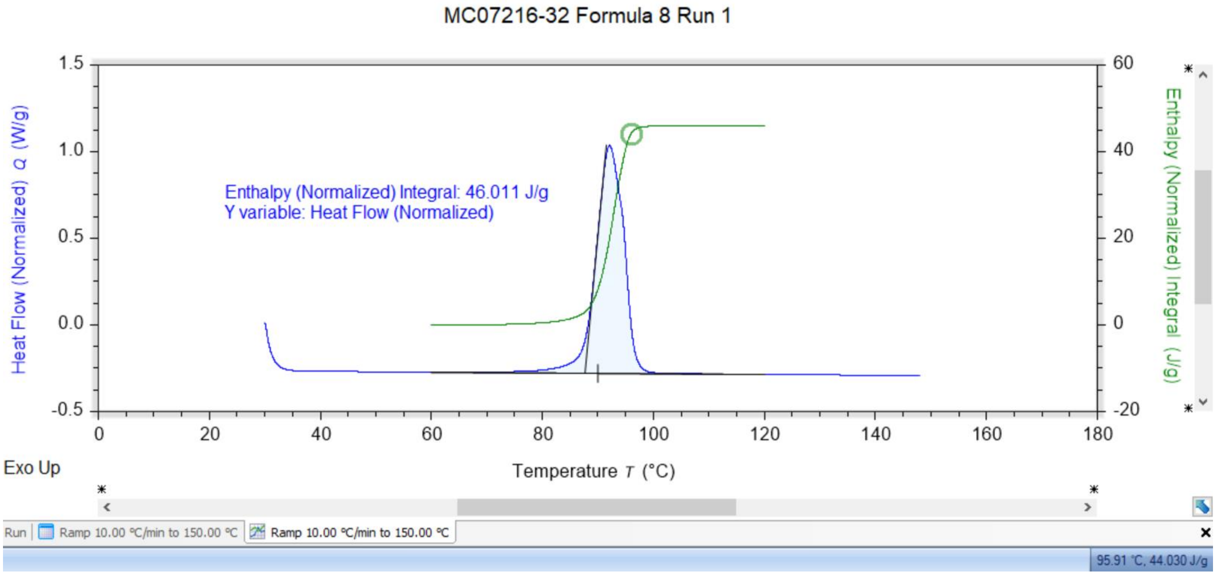

Figure 6: Running integral analysis showing 95% of total heat evolved occurred at 95.91 degrees C.

Rate of Reaction from Plots of Percent Conversion vs Temperature

The running integral analysis allowed for determining the temperature corresponding to 5%, 50% and 95% of the total evolved heat. These fractional conversions plotted against temperature yield a linear plot with a slope giving the rate of reaction. Figure 7 shows a plot of conversion vs temperature for three of the coating formulations investigated in this work. Note that one of the coatings cures at lower temperature than the other two. The two that initiate reaction near the same temperature have distinctly different slopes or rate of reaction.

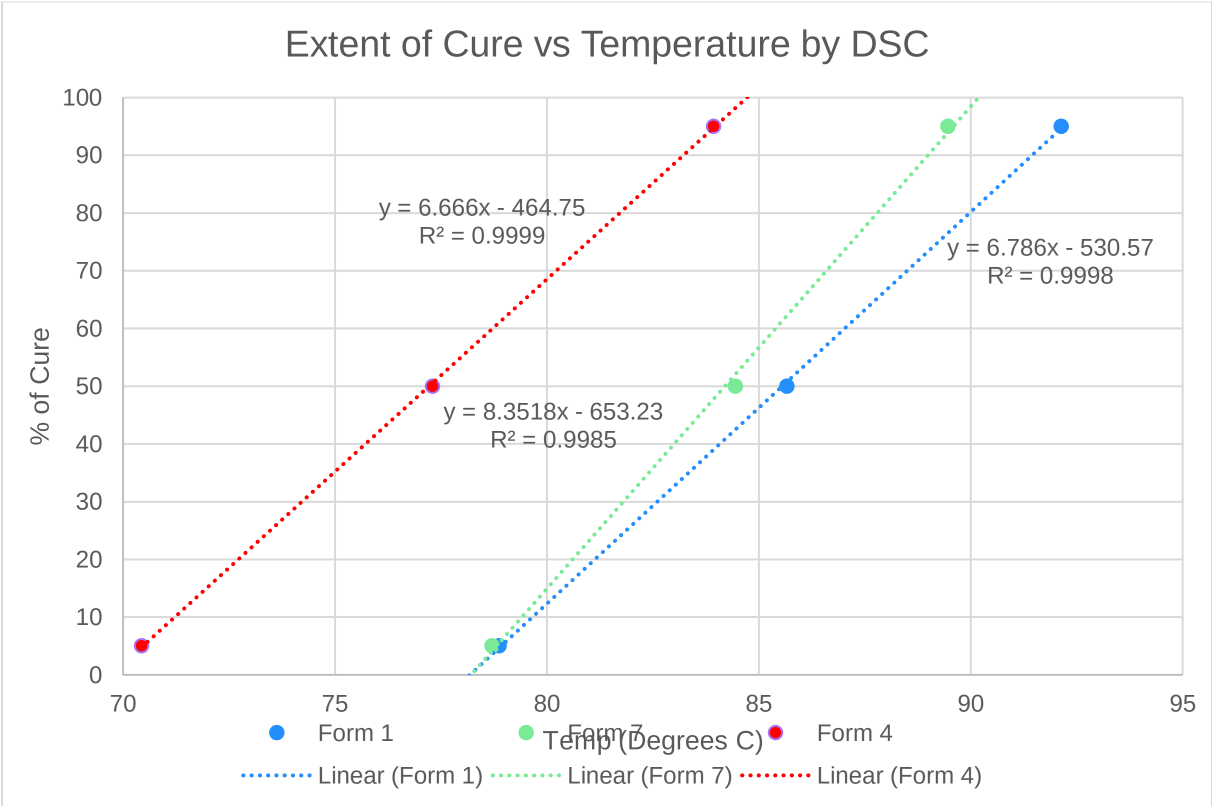

Figure 7: Plot of % conversion vs temperature for three different release coatings formulas.

The results in figure 7 are highly interesting. Formula 4 achieved 5% conversion near 71 degrees Celsius and had a rate slope of 6.67 per degree Celsius. Formulas 1 and 7 had delayed initiation of cure achieving 5% conversion near 78 degrees Celsius. While formulas 1 and 7 initiated reaction at the higher temperature, it is observed that formula 1 has a rate slope of 6.79 per degree Celsius and thus similar to formula 4. Formula 7 has a steeper slope and thus faster rate of cure with a slope of 8.35 per degree Celsius. The DOE carried out to explore the effect of formula composition will show the input factors that determine the observed cure phenomena.

Taguchi L12 Experimental Design

The Taguchi L12 experimental design is a very efficient method to investigate up to 11 independent or input variables and their effect on one or more dependent or output variables. The variables investigated in this experimental design include vinyl content of the vinyl end blocked base polymer, crosslinker architecture, inhibitor content of the base polymer, platinum loading of the formula and SiH/SiVi ratio. Table 1 shows the respective low setting value and high setting value for each of the five input variables.

Input Variable	Low Setting (-1)	High Setting (+1)
Vinyl Content Base Polymer	0.0185 mols Vi/100g	0.04 mols Vi/100g
Platinum Loading	60 parts per million	100 parts per million
Inhibitor Loading	800 parts per million ECH	1500 parts per million ECH
Crosslinker Architecture	Copolymer	Homopolymer
SiH/SiVi Ratio	1.3 mols SiH/mol SiVi	1.7 mols SiH/mol SiVi

Table 1: Low and high setting values for the five input factors

Note that the copolymer crosslinker contains 0.01052 mols SiH per gram and the homopolymer crosslinker contains 0.0158 mols SiH per gram. Table 2 shows the experimental array as dictated by the L12 design.

Run	Base Polymer	Crosslinker Architecture	Inhibitor Loading	Platinum Loading	SiH/SiVi Ratio
1	Low Vinyl	Copolymer	800	60	1.3
2	Low Vinyl	Copolymer	800	60	1.3
3	Low Vinyl	Copolymer	1500	100	1.7
4	Low Vinyl	Homopolymer	800	100	1.7
5	Low Vinyl	Homopolymer	1500	60	1.7
6	Low Vinyl	Homopolymer	1500	100	1.3
7	High Vinyl	Copolymer	1500	100	1.3
8	High Vinyl	Copolymer	1500	60	1.7
9	High Vinyl	Copolymer	800	100	1.7
10	High Vinyl	Homopolymer	1500	60	1.3
11	High Vinyl	Homopolymer	800	100	1.3
12	High Vinyl	Homopolymer	800	60	1.7

Table 2: Experimental array for Taguchi L12 design with five input variables.

Experimental Analysis

The output variables analyzed from the twelve experimental runs detailed in the design in table 2 include the heat of reaction, initiation temperatures as defined by the 1% conversion and onset temperatures, the rate slope from plots of conversion vs temperature from 5% to 95% conversion and finally the temperature at which complete cure is achieved. Due to the asymptotic nature of the running integral approaching 100% cure, the 95% conversion temperature is used as a measure of the final cure state. The primary interest of this investigation is to determine how choice of base polymer, crosslinker, platinum and inhibitor content and SiH/SiVi ratio effect both the initiation temperature and rate of reaction which combine to dictate the temperature at which we achieve final cure. In addition, it is of interest to determine how these choices effect the final crosslink density as measured by heat of reaction.

Heat of Reaction as a Function of Release Coating Formulation

The heat of reaction, measured in units of Joules per gram, is proportional to the number of crosslinks formed by the hydrosilylation cure reaction per gram coating. It is highly likely that the dominant factor therefore will be the concentration of vinyl groups as dictated by the choice of base polymer and the ratio of crosslinker to base polymer given by the SiH/SiVi ratio. Table 3 gives the measured heat of reaction as well as the individual formulas for all 12 experimental runs.

Run	Base Polymer	Crosslinker	Inhibitor	Platinum	SiH/SiVi	Heat of Reaction
1	Low Vinyl	Copolymer	800	60	1.3	22.46
2	Low Vinyl	Copolymer	800	60	1.3	22.08
3	Low Vinyl	Copolymer	1500	100	1.7	22.16
4	Low Vinyl	Homopolymer	800	100	1.7	25.96
5	Low Vinyl	Homopolymer	1500	60	1.7	25.79
6	Low Vinyl	Homopolymer	1500	100	1.3	20.79
7	High Vinyl	Copolymer	1500	100	1.3	45.32
8	High Vinyl	Copolymer	1500	60	1.7	45
9	High Vinyl	Copolymer	800	100	1.7	43.92
10	High Vinyl	Homopolymer	1500	60	1.3	46.38
11	High Vinyl	Homopolymer	800	100	1.3	45.19
12	High Vinyl	Homopolymer	800	60	1.7	46.43

Table 3: Heat of Reaction by DSC

As expected, comparing runs 1 through 6 with the low vinyl base polymer to runs 7 through 12 with the high vinyl base polymer shows a sharp increase in heat of reaction for the high vinyl formulations.

Table 4 and Figure 8 are the Response Table for Means and Main Effects Plot for Means for each of the five input factors as related to the measured heat of reaction.

Response Table for Means

Level	Base Polymer	XL Type	Inhib Load	Platinum Load	SiH/Vi
1	23.39	35.73	36.75	37.17	35.99
2	45.37	35.09	34.24	33.89	34.88
Delta	21.98	0.64	2.51	3.28	1.11
Rank	1	5	3	2	4

Table 4: Response Table for Means for Heat of Reaction by DSC

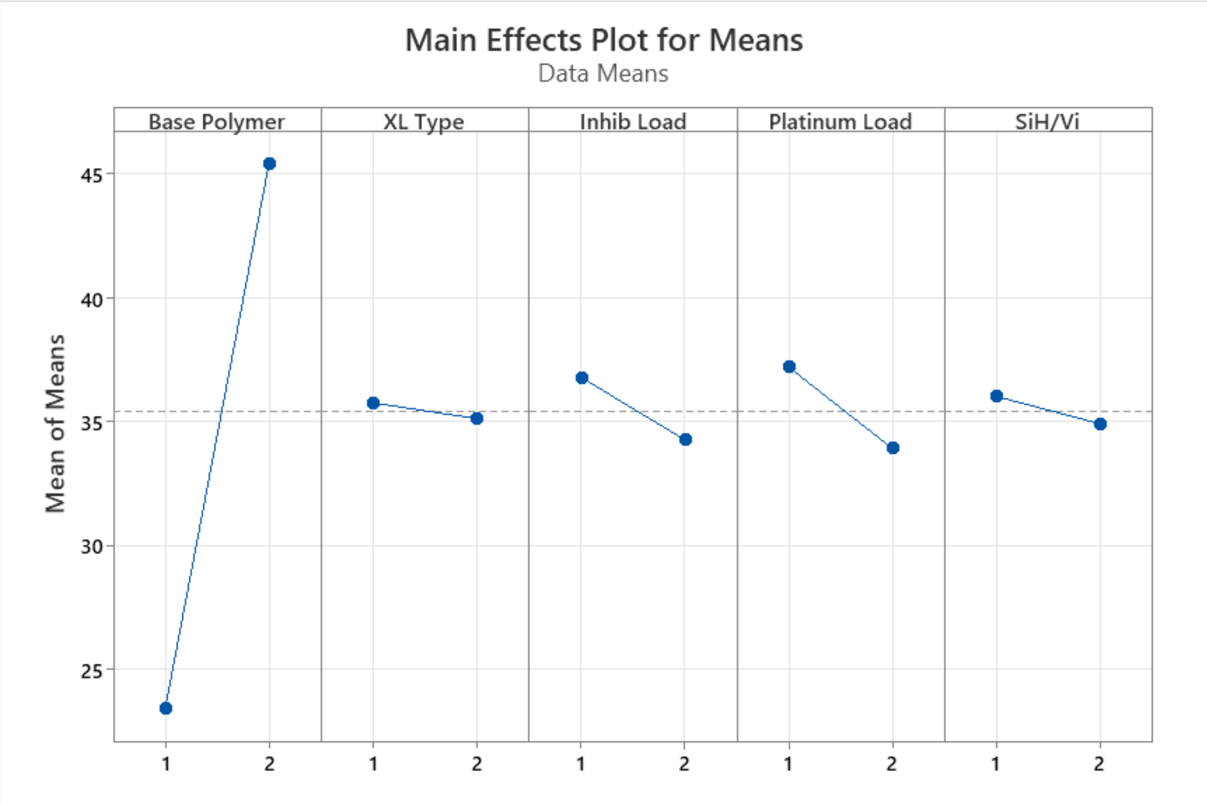

Figure 9: Main Effects Plot for Means for Heat of Reaction by DSC

The main effects plot for means in figure 9 is a graphical representation of the data in table 3. Table 3 ranks the effects from 1 (strongest) to 5 weakest by computing the mean for the six experiments ran at the low setting of the input factor and the six runs at the high setting of the input factor. The heat of reaction increased from an average of 23.39 Joules per gram with the low vinyl base polymer to an average of 45.37 Joules per gram with the high vinyl base polymer. Interestingly the weakest input factors were the SiH/SiVi ratio and the crosslinker type. The tradeoff for efficiency of an L12 design is the inability to compute a p statistic to measure statistical significance of an observed difference between the average of the six experiments at the low setting and six experiments at the high setting for each of the five input variables.

The Temperature at 1% Conversion and Onset Temperature as Measures of Reaction Initiation

The early stages of the reaction involve breaking thermal dissociation of the platinum-inhibitor complex and associated addition of SiH to SiVi functional groups to start the formation of a network polymer. Table 5 shows the 1% conversion temperature and onset temperature for each of the twelve experimental runs.

Run	Base Polymer	Crosslinker	Inhibitor	Platinum	SiH/SiVi	T (1%)	T onset
1	Low Vinyl	Copolymer	800	60	1.3	74.11	77.5
2	Low Vinyl	Copolymer	800	60	1.3	73.88	77.33
3	Low Vinyl	Copolymer	1500	100	1.7	82.78	83.25
4	Low Vinyl	Homopolymer	800	100	1.7	65.30	69.32
5	Low Vinyl	Homopolymer	1500	60	1.7	79.05	84.5
6	Low Vinyl	Homopolymer	1500	100	1.3	73.94	77.9
7	High Vinyl	Copolymer	1500	100	1.3	72.97	78.5
8	High Vinyl	Copolymer	1500	60	1.7	81.67	87.69
9	High Vinyl	Copolymer	800	100	1.7	60.2	66.36
10	High Vinyl	Homopolymer	1500	60	1.3	80.51	88.2
11	High Vinyl	Homopolymer	800	100	1.3	65.31	70.53
12	High Vinyl	Homopolymer	800	60	1.7	73.40	79.49

Table 5: 1% Conversion temperature and onset temperature in degrees Celsius

Table 6 and figure 10 show the Response Table for Means and Main Effects Plot for Means for the temperature corresponding to 1% conversion.

Response Table for Means

Level	Base Polymer	XL Type	Inhib Load	Platinum Load	SiH/Vi
1	75.01	74.32	67.64	77.72	73.34
2	72.34	72.92	78.49	70.08	73.73
Delta	2.67	1.40	10.85	7.64	0.39
Rank	3	4	1	2	5

Table 6: Response Table for Means for 1% Conversion Temperature by DSC

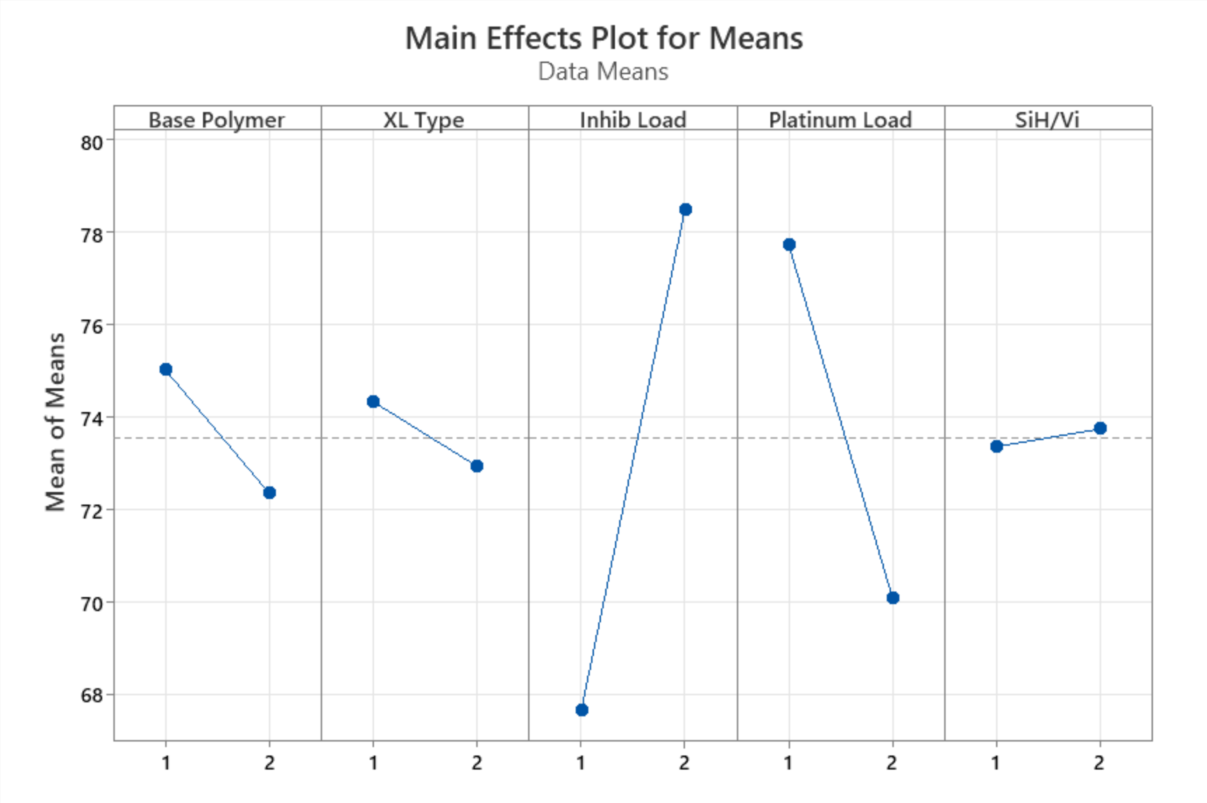

Figure 10: Main Effects Plot for Means for 1% Conversion Temperature by DSC

The inhibitor content of the base polymer and platinum loading of the formula are by far the strongest effects on the temperature at which the reaction starts and achieves 1% of the total crosslinking as measured by heat of reaction. The low setting for the inhibitor shows a 1% conversion average temperature of 67.64 degrees Celsius while the high setting shows an average of 78.49 degrees Celsius. The average for the low and high levels of platinum loading were found to be 77.72 degrees Celsius and 70.08 degrees Celsius. The base polymer showed a decrease of 2.67 degrees Celsius in going from the low vinyl to high vinyl settings and the contributions from the XL type and SiH/SiVi ratio were much smaller than the dominant effects from the inhibitor and platinum loading.

Table 7 and Figure 11 show the Results Table for Means for and Main Effects Plots for Means for the onset temperature as measured by DSC.

Response Table for Means

Level	Base Polymer	XL Type	Inhib Load	Platinum Load	SiH/Vi
1	78.48	78.64	72.62	83.46	78.51
2	78.46	78.32	83.34	74.31	78.44
Delta	0.02	0.32	10.72	9.15	0.07
Rank	5	3	1	2	4

Table 7: Response Table for Means for Onset Temperature

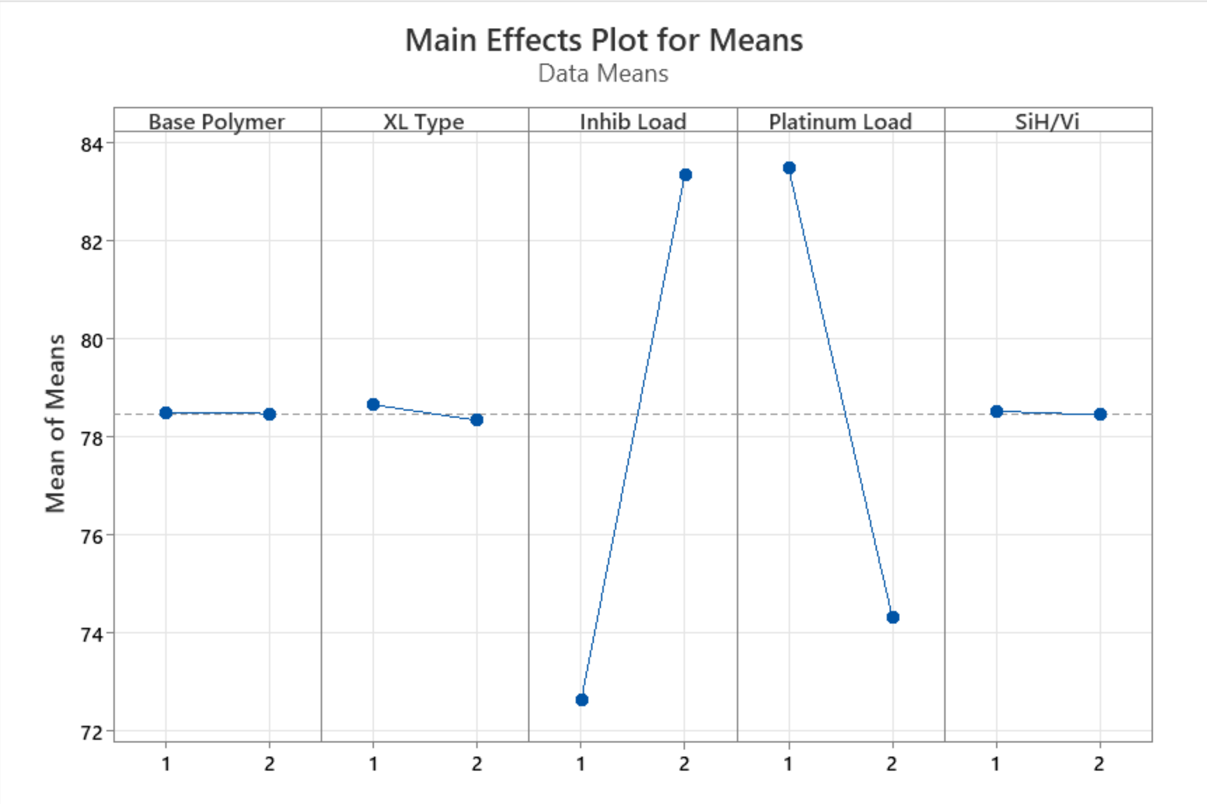

Figure 11: Main Effects Plot for Means for Onset Temperature as noted by DSC

A cursory glance at the main effects plot for means for the onset temperature in figure 11 tells the definitive tale that the inhibitor content and platinum loading control the onset temperature of the cure reaction with virtually no effect from the base polymer vinyl content, the crosslinker type or SiH/SiVi ratio. Increasing the inhibitor content shifts the reaction to higher temperature while increasing the platinum shifts it to lower onset temperature. It is safe to say that the choice of inhibitor level and platinum content of a formula will determine when the reaction starts while heating.

The Rate of Reaction as Determined by the Slope of the Conversion vs Temperature Plot

We have observed that the initiation of the cure reaction is dictated by the choice of inhibitor and platinum level in the release coating formulation. Following volatilization of the inhibitor we would expect it to play no role in the crosslinking kinetics. Table 8 shows the measured rate of reaction as defined by the slope of the conversion vs temperature plot for each of the 12 experimental formulations.

Run	Base Polymer	Crosslinker	Inhibitor	Platinum	SiH/SiVi	Rate Slope
1	Low Vinyl	Copolymer	800	60	1.3	6.79
2	Low Vinyl	Copolymer	800	60	1.3	6.53
3	Low Vinyl	Copolymer	1500	100	1.7	6.15
4	Low Vinyl	Homopolymer	800	100	1.7	6.67
5	Low Vinyl	Homopolymer	1500	60	1.7	6.35
6	Low Vinyl	Homopolymer	1500	100	1.3	6.21
7	High Vinyl	Copolymer	1500	100	1.3	8.35
8	High Vinyl	Copolymer	1500	60	1.7	10.34
9	High Vinyl	Copolymer	800	100	1.7	9.18
10	High Vinyl	Homopolymer	1500	60	1.3	5.93
11	High Vinyl	Homopolymer	800	100	1.3	6.06
12	High Vinyl	Homopolymer	800	60	1.7	8.88

Figure 12: Rate of Reaction for each of the 12 experimental formulations

Table 8 and Figure 13 show the Response Table for Means and the Main Effects Plot for Means for the rate of reaction.

Response Table for Means

Level	Base Polymer	XL Type	Inhib Load	Platinum Load	SiH/Vi
1	6.408	8.136	7.490	7.632	6.642
2	8.123	6.683	7.222	7.103	7.928
Delta	1.715	1.453	0.268	0.529	1.286
Rank	1	2	5	4	3

Table 8: Response Table for Means for rate of reaction

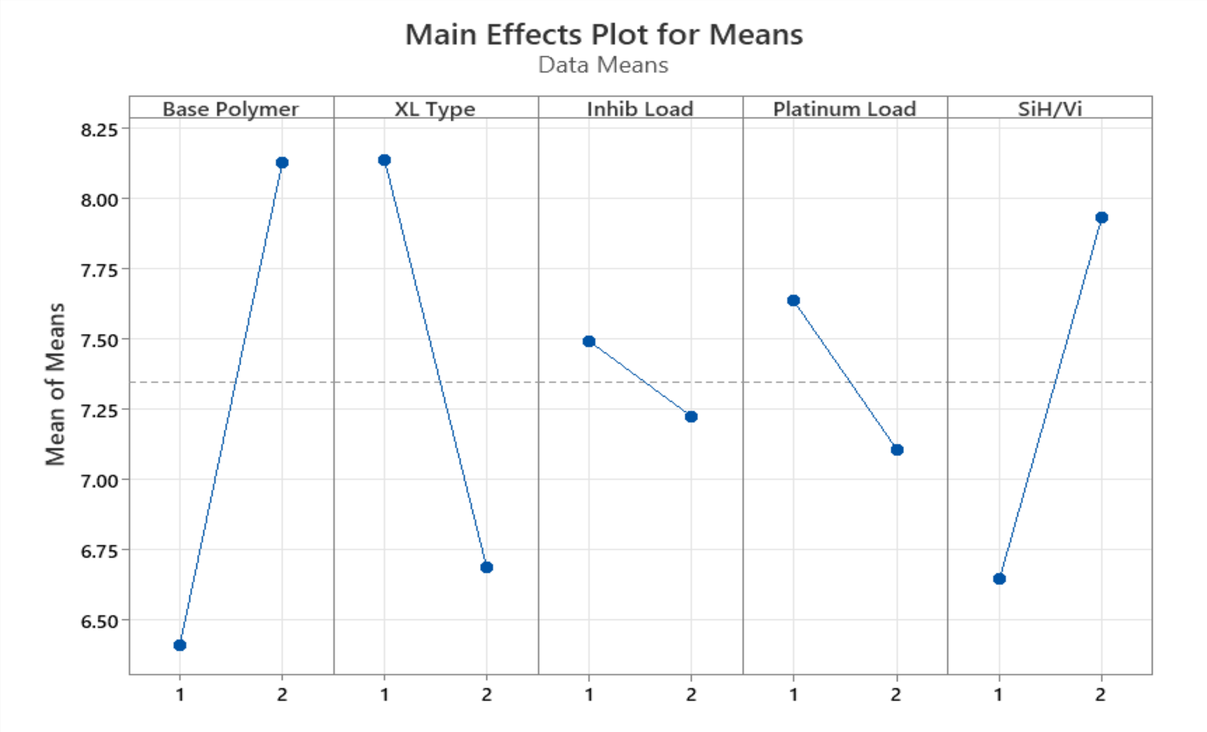

Figure 13: Main Effects Plot for Means for Rate of Reaction as measured by DSC

The results clearly show that the inhibitor content is weakest effect as expected. The platinum level is interestingly the second weakest input factor and would indicate that increasing the platinum content would decrease the rate of reaction. This would be interesting to explore in a full factorial DOE, which would allow for determining a statistical significance along with a magnitude of the effect. Of great interest here is that the rate of reaction is faster for the shorter chain, higher vinyl content base polymer and this is the strongest effect. This fits well with the rule of thumb that shorter chain base polymer react faster and actually gives a numerical estimate of the effect. The second strongest effect was found to be the crosslinker type with the lower SiH copolymer crosslinker giving a higher rate of reaction than the higher SiH content homopolymer. This gives experimental proof to the rule of thumb that copolymer crosslinkers cure faster. The third strongest factor is the SiH/SiVi ratio with increasing the relative content of crosslinker giving a faster cure reaction. Again, another oft cited rule of thumb is proven true and the magnitude of the effect made measurable.

Approaching Final Cure as Measured by the 95% Conversion Temperature

It has been shown experimentally that the inhibitor and platinum loading of the formula determine the temperature at which we observe the onset of reaction. The base polymer, followed by the crosslinker type and the SiH/SiVi ration impact the rate of reaction between 5% and 95% conversion. The two effects of when the reaction starts followed by how fast it proceeds will determine the temperature at which full cure is observed.

Table 9 shows the experimental results for the temperature at which 95% conversion is observed for each of the 12 experimental runs.

Run	Base Polymer	Crosslinker	Inhibitor	Platinum	SiH/SiVi	T 95% Cure
1	Low Vinyl	Copolymer	800	60	1.3	92.13
2	Low Vinyl	Copolymer	800	60	1.3	92.43
3	Low Vinyl	Copolymer	1500	100	1.7	99.85
4	Low Vinyl	Homopolymer	800	100	1.7	83.93
5	Low Vinyl	Homopolymer	1500	60	1.7	99.89
6	Low Vinyl	Homopolymer	1500	100	1.3	93.68
7	High Vinyl	Copolymer	1500	100	1.3	89.46
8	High Vinyl	Copolymer	1500	60	1.7	95.82
9	High Vinyl	Copolymer	800	100	1.7	75.27
10	High Vinyl	Homopolymer	1500	60	1.3	102.83
11	High Vinyl	Homopolymer	800	100	1.3	85.63
12	High Vinyl	Homopolymer	800	60	1.7	89.4

Table 9: 95% Conversion temperature as measured by DSC

Response Table for Means

Level	Base Polymer	XL Type	Inhib Load	Platinum Load	SiH/Vi
1	93.93	90.54	85.30	96.04	92.78
2	89.73	92.56	96.92	87.97	90.69
Delta	4.19	2.02	11.62	8.07	2.08
Rank	3	5	1	2	4

Table 10: Response Table for Means for 95% conversion temperature by DSC

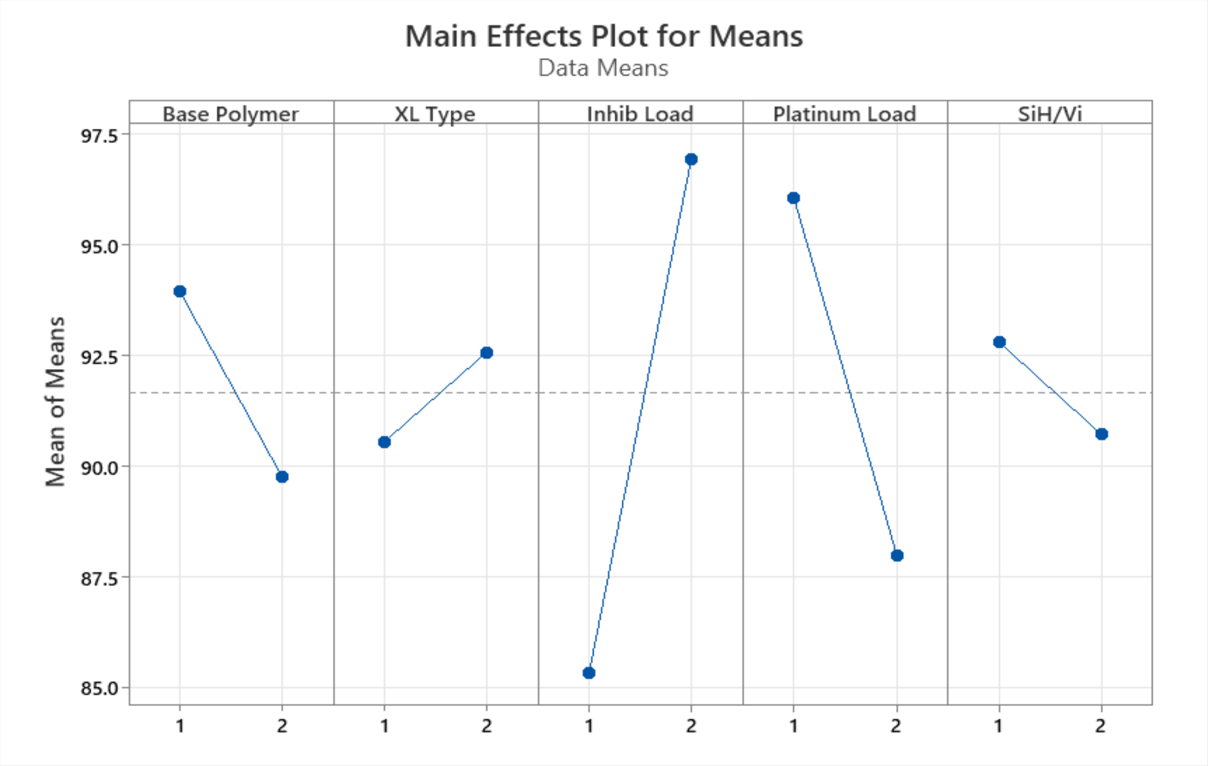

Figure 14: Main Effects Plot for Means for 95% Conversion Temperature

The main effects plot in figure 14 clearly shows that the inhibitor content is the strongest effect followed by platinum loading. The choice of base polymer is the third strongest effect while the crosslinker type and SiH/SiVi ratio have nearly the same magnitude of shift on the 95% conversion temperature.

Conclusions

Differential Scanning Calorimetry is a good tool for measuring the effect of formulating choices on rate of cure. The novel method developed here of plotting the % Conversion vs temperature as determined by running integral analysis of the cure exotherm during a constant heating ramp experiment yields a numerical measure of the rate of reaction. Application of an L12 Taguchi design allowed for determining the effect of base polymer vinyl content, crosslinker type, inhibitor loading, platinum content and SiH/SiVi ratio on the initiation of reaction, the rate of reaction and achieving full cure. The onset has been shown to be solely a function of the inhibitor loading and the platinum content while the rate of reaction after onset is controlled by the vinyl content of the base polymer, the type of crosslinker and the SiH/SiVi ratio.