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Title: CHEMICAL ANALYSIS OF DC745 MATERIAL: DEV LOT 1 REINVESTIGATION; BARCODES P053387, P053388, AND P053389

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memorandum

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SUBJECT: CHEMICAL ANALYSIS OF DC745 MATERIAL: DEV LOT 1 REINVESTIGATION; BARCODES P053387, P053388, AND P053389

EXECUTIVE SUMMARY

This report serves as a follow up to our initial development lot 1 chemical analysis report (LA-UR-16-21970). The purpose of that report was to determine whether or not certain combinations of resin lots and curing agent lots resulted in chemical differences in the final material. One finding of that report suggested that pad P053389 was different from the three other pads analyzed. This report consists of chemical analysis of P053387, P053388, and a reinvestigation of P053389 all of which came from the potentially suspect combination of resin and curing agents lot. The goal of this report is to determine whether the observations relating to P053389 were isolated to that particular pad or systemic to that combination of resin and curing agent lot. The following suite of analyses were performed on the pads: Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FT-IR), and Solid State Nuclear Magnetic Resonance (NMR). The overall conclusions of the study are that pads P053387 and P053388 behave more consistently with the pads of other resin lot and curing agent lot combinations and that the chemical observations made regarding pad P053389 are isolated to that pad and not representative of an issue with that resin lot and curing agent lot combination.

INTRODUCTION

The purpose of this report is to determine if chemical differences observed in the original development lot 1 chemical analysis report (LA-UR-16-21970) were isolated to a single pad (P053389) or are truly representative of a particular resin lot and curing agent lot combination (Resin Lot 0007760082 and Curing agent Lot MKBR0087V). To achieve this goal, three pads from that resin lot/curing agent lot combination were analyzed; P053389 (original pad in DL1 study), P053388 and P053387. These pads are made of a composite material called DC745; generally, this material is a silicone elastomer that is reinforced with silicon-based fillers, silica and quartz. The silicone is comprised of dimethyl, methyl-phenyl, and methyl-vinyl siloxane repeat units. The following suite of analyses were performed on the pads: Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Nuclear Magnetic Resonance spectroscopy (NMR), and Fourier Transform-Infrared spectroscopy (FT-IR). TGA will be used to determine the thermal stability of the composites and filler content. DSC will be used to determine phase transitions within the composite. NMR will be used to examine the nature of the domains of the composite (crystalline, liquid-like, etc.). FT-IR probes the chemical bonding of the composite. Combining observations made through all of these analyses allows for an examination of the polymer structure, composite thermal stability, and composite composition.

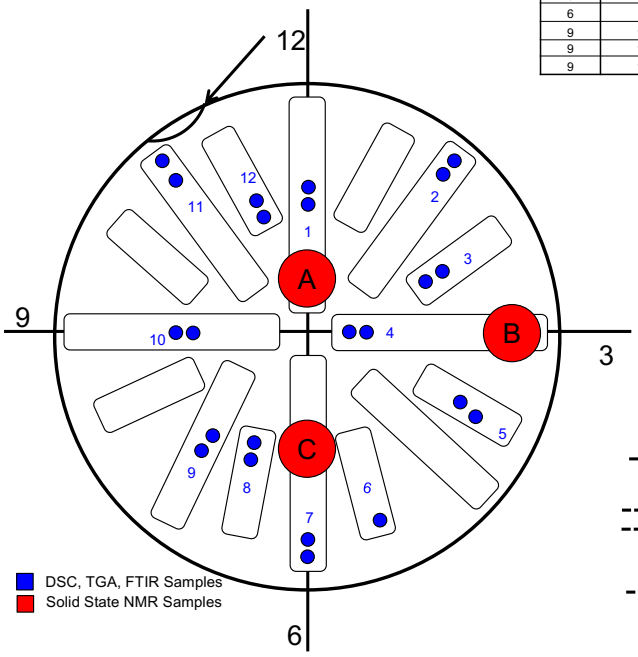
METHODS

Sampling

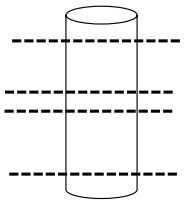
Small samples were cut from the pads according to the cut plan shown in **Figure 1**. This plan was chosen to ensure testing is representative of the pad as a whole. These small samples were sectioned into smaller samples appropriate for each chemical analysis. These sectioned samples were taken from the top, middle, and interior portions of the pad to see if variability was present in the depth of the samples. Each of these samples was subjected to various chemical analyses. For each analysis shown, the values are representative of an average of the samples run plotted with +/- one standard deviation. In most cases, the analyses of the 12 samples within a pad agreed well with each other; therefore, we can be confident that the data presented is representative of the pad as a whole.

Quad	Sample No	Rib	Position	Analysis
12	A	--	Center	Solid State NMR
3	B	--	Edge	Solid State NMR
6	C	--	Middle	Solid State NMR

Quad	Sample No	Rib	Position	DSC	TGA	FTIR
12	1	--	Center	Middle	Outside	Inside
12	2	B	Edge	Outside	Inside	Middle
12	3	C	Middle	Inside	Middle	Outside
3	4	--	Center	Middle	Outside	Inside
3	5	A	Middle	Outside	Inside	Middle
3	6	C	Edge	Inside	Middle	Outside
6	7	--	Edge	Middle	Outside	Inside
6	8	A	Center	Outside	Inside	Middle
6	9	B	Middle	Inside	Middle	Outside
9	10	--	Middle	Middle	Outside	Inside
9	11	B	Edge	Outside	Inside	Middle
9	12	C	Center	Inside	Middle	Outside



Two ¼" punches per sample #, as close together as possible. Position on rib follows an adapted procedure from thickness measurement BB6K0154, Birdsell, Hills "Requirements for Surveillance Testing of Polymer Components at the Kansas City Plant". Section 4.2.2. Punches are taken from 1 +/-0.5 cm from the position (Edge, Center, Middle).



For dividing punched sample for analytical testing: Outside and Inside are taken from ~1/8" inch of the edge of the sample. Middle is taken from the ~1/8" center of the sample.

Figure 1: Sampling plan for each component.

NMR

Samples were analyzed with a Magritek NMR Mouse instrument. This is a single-sided NMR designed for rapid relaxation measurements of materials with an added stage for profiling through samples. The B_1 magnetic field was measured to be 13.41 MHz and the $\pi/2$ pulse length was 6 µs at -7 dB power attenuation. For the CPMG experiment to measure the T_2^{eff}, 1000 echoes with a 200 µs echo time were acquired. Each data set is the accumulation of 1000 acquisitions with a T_1 delay of 600 ms (greater than $5*T_1$).

To determine the T_2^{eff}, the CPMG echo data was fit to a decaying exponential equation with two or three terms based on the results from the Inverse Laplace results. The form of the equation is:

$$y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2} + A_3 e^{-x/t_3}$$

with t_1, t_2, and t_3 as the T_2^{eff} for the crystalline and amorphous phases. Note the T_2^{eff} is reported as it is the observed relaxation mechanism that is being measured and has an additional inherent relaxation component due to magnetic field inhomogeneities. Percent crystallinity, rigid amorphous, and amorphous phases are determined from A_1, A_2, and A_3, respectively. As an example, and for the sake of simplicity $A_{1,2}$ and $t_{1,2}$ will be specified as the crystalline phases and the percent crystallinity will be determined by the equation:

$$\%\ crystallinity = \frac{(A_1)}{(A_1 + A_2 + A_3)} \times 100\%$$

FT-IR

FTIR spectra were collected using a Nicolet Avatar 360 FT-IR spectrometer with an ATR sample cell. Spectra were collected at 32 scans over a range of 400-4000 cm^{-1}.

TGA

Thermograms were collected using a Thermal Analysis TA-Q-5000-IR. Sample mass was approximately 10-20 mg. Samples were ramped at 10 °C/min to 750 °C under a nitrogen atmosphere. Thermogram analysis was accomplished using TA-Universal Analysis software.

DSC

Thermograms were collected using a Thermal Analysis TA-Q-20-a. Samples mass was approximately 10-20 mg. Samples were subjected to conventional DSC. The heating program for conventional DSC measurements was carried out as follows: 1) Samples were equilibrated at 35 °C 2) Ramped to -20 °C at 10 °C/min 3) Ramped to -150 °C at 5 °C/min 4) Held at -150 °C for 15 minutes 5) Ramped to 100 °C at 10 °C/min. Thermogram analysis was accomplished using TA-Universal Analysis software.

RESULTS AND DISCUSSION

Overall, the conclusions made in our initial development lot 1 chemical analysis report (LA-UR-16-21970) pointed to a marked difference between P053389 and the other three pads, P055663, P055660, and P055481. In general, the analyses all show that P053389 is less cross-linked or not as cured as the other three composites. The purpose of this report was to analyze two additional pads from the same resin and curing agent lot (P053387 and P053388) as P053389 and compare these results to the results from the initial development lot 1 chemical analysis report. Overall, P053387 and P053388 behaved more similarly to pads P055663, P055660, and P055481; therefore P053389 appears to be an outlier and not representative of some shortfallings of the resin and curing agent lot combination used to produce pads P053387, P053388, and P053389. The following sections will be discussed per analysis method.

TGA

TGA thermograms (Figure 2) show weight loss as a function of temperature. The data is also summarized in Table 1 and in bar graph form in Figures 3 and 4. In the original development lot 1 chemical analysis report P053389 seemed to have a lower onset of decomposition temperature compared to the other three pads analyzed. In this reevaluation report, it was observed that all the pads have very similar onset of decomposition temperatures as well as decomposition maximum temperatures. Furthermore, these results of all three pads analyzed in this report agree with pads from the other resin lot and curing agent lot combinations from the original chemical development lot 1 chemical analysis report. In that report TGA samples for P053389 were sampled according to a stand-alone report (LA-UR-15-29206), which seemed to introduce a sampling bias towards outer contour samples. When these plots were averaged and plotted +/- one standard deviation; the suspect surfaces seemed to sway the results. In this report, 12 plots (4 from the outer contour, middle and inner contour); therefore, the suspect surfaces were averaged in with nonsuspect surfaces and overall the effect appears muted when comparing

P053389 original data to P053389 redo data. P053389 redo data behaves quite similarly to P053387 and P053388.

All four samples have a very similar residue remaining at higher temperatures, showing that the filler content is nearly identical for the four samples. The residue remaining at high temperatures provides an estimate of the filler content of the composite. This residue is a combination of silicon-based filler that doesn't decompose at the temperatures studied and an amount of charred material. Previously, the filler content has been determined to be ~38 weight % via solvent extraction of the polymer[1]; therefore approximately 6% of the weight could be attributed to char. Modifying the gaseous environment in which the experiments are carried out to remove/reduce the char could reduce the experimental values determined in this study. However, these values are useful as a comparison between the samples.

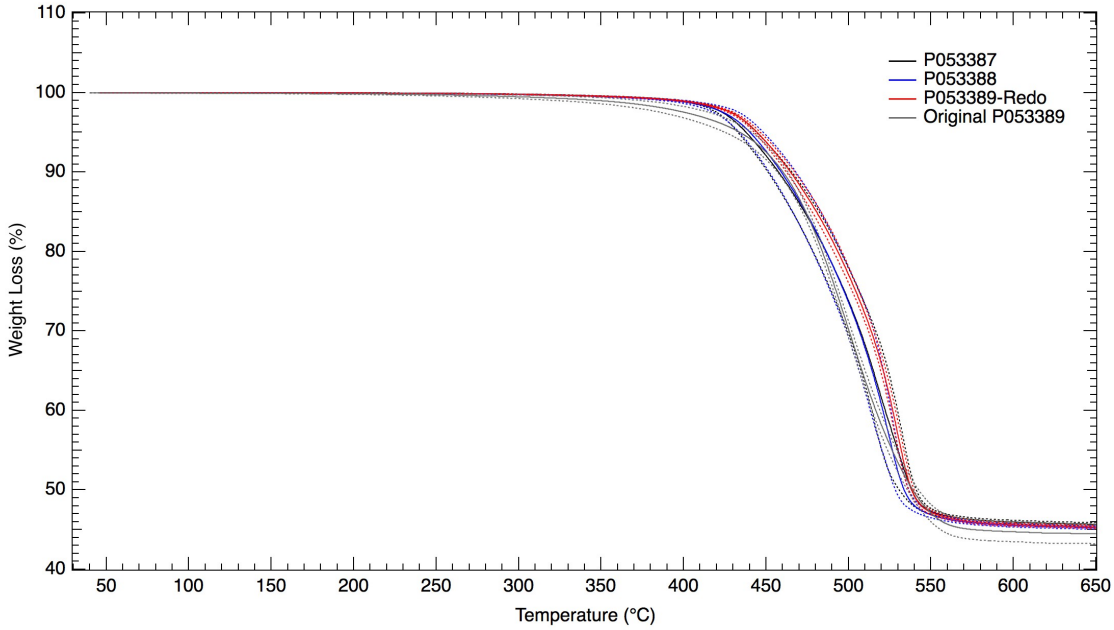


Figure 2: TGA thermograms showing weight loss as a function of temperature. Dashed lines represent +/- one standard deviation.

Sample		Onset of Decomposition (°C)	Decomposition Max (°C)	Residue @ 650 (°C)
P053387	Average	473.9	525.9	45.7
	Std. Dev.	10.7	8.3	0.2
P053388	Average	477.0	522.9	45.2
	Std. Dev.	9.4	6.6	0.2
P053389	Average	483.9	529.6	45.3
Redo	Std. Dev.	3.0	1.8	0.2
P053389*	Average	458.55	500.73	44.4
	Std. Dev.	0.86	1.57	1.02
P054481*	Average	466.12	507.2	44.24
	Std. Dev.	1.36	2.94	0.38
P055660*	Average	474.72	518.07	44.02
	Std. Dev.	1.58	3.1	0.22
P055663*	Average	475.1	517.64	43.64
	Std. Dev.	0.93	3.23	0.44

Table 1: TGA results showing onset and maximum temperature of decomposition and residue at 650 °C.

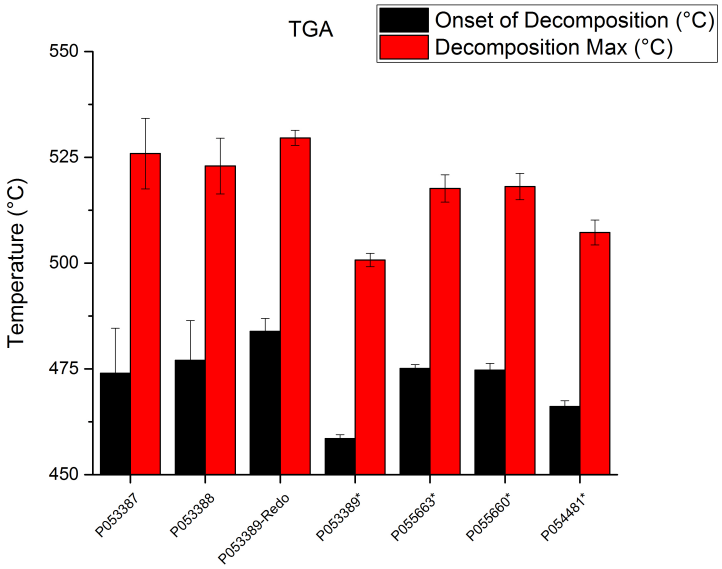


Figure 3: Onset of decomposition temperature and maximum decomposition temperature for all pads analyzed for this report shown alongside those analyzed in the original development lot 1 chemical analysis report (shown as*).

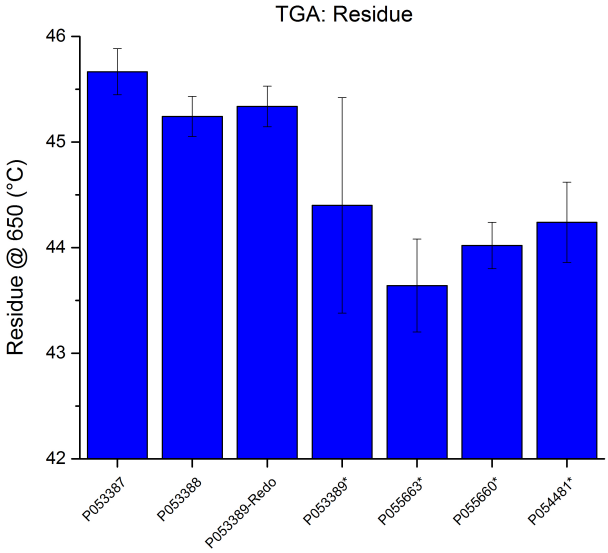


Figure 4: TGA residue for all pads analyzed for this report shown alongside those analyzed in the original development lot 1 chemical analysis report (shown as*).

DSC

The DSC results of the pads P053387, P053388, and P053389 show fairly similar results. These results also agree with all results from the previous development lot one chemical analysis study in which no differences were observed between the four pads tested. All thermal transitions are summarized in Table 2. Figures 5 and 6 show these transitions in bar graph to more easily compare across all 7 sets of data. The DSC is measuring bulk thermal properties, while differences observed in other methods may be subtle and usually limited to the surface of the pad, those subtleties are lost when measuring the bulk sample.

Sample		T_c			T_m		
		Onset (°C)	Max (°C)	ΔH_c (J/g)	Onset (°C)	Max (°C)	ΔH_f (J/g)
P053387	Average	-60.18	-62.73	12.37	-45.09	-39.93	12.03
	Std. Dev.	0.72	0.57	0.47	0.32	0.55	0.50
P053388	Average	-60.34	-63.00	11.96	-45.28	-40.45	11.94
	Std. Dev.	0.60	0.75	0.37	0.26	0.49	0.50
P053389	Average	-60.33	-62.96	12.43	-44.90	-39.77	12.05
Redo	Std. Dev.	0.76	0.56	0.67	0.36	0.72	0.40
P053389*	Average	-62.28	-67.36	12.84	-46.34	-42.99	12.03
	Std. Dev.	2.26	0.69	0.35	1.44	1.55	0.3
P054481*	Average	-59.88	-66.91	12.56	-46.39	-42.28	12.01
	Std. Dev.	3.01	1.50	0.53	0.17	0.32	0.55
P055660*	Average	-62.42	-66.91	12.50	-45.89	-41.93	12.09
	Std. Dev.	1.45	1.18	0.61	0.28	0.4	0.49
P055663*	Average	-63.06	-67.31	12.37	-46.39	-42.44	12.43
	Std. Dev.	1.45	0.77	0.49	0.19	0.32	0.63

Table 2: DSC results showing crystallization and melting temperatures of the four DC745 composites analyzed.

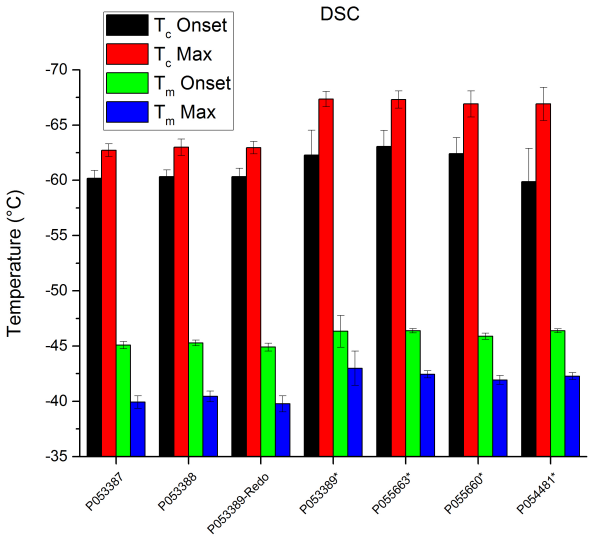


Figure 5: DSC thermal transition temperatures for all pads analyzed for this report shown alongside those analyzed in the original development lot 1 chemical analysis report (shown as*).

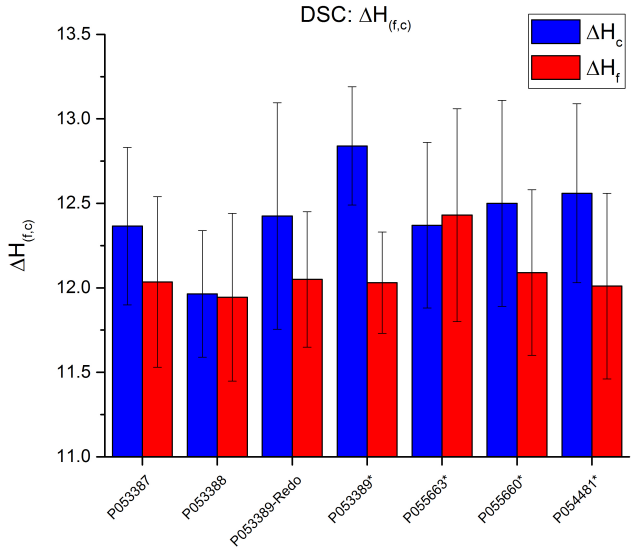


Figure 6: DSC heats of formation and crystallization for all pads analyzed for this report shown alongside those analyzed in the original development lot 1 chemical analysis report (shown as*).

NMR

T_2 measurements confirmed observations made in the original development lot 1 chemical analysis study and also confirm P053387 and P053388 trend with those observations. These observations include that NMR showed little difference between each pad. However, these T_2 studies did show that the variation in each phase for P053389 was much greater in the original study. The data is summarized in Table 3 and Figure 7.

	% Crystalline	% Crystalline (σ)	% Rigid Amorphous	% Rigid Amorphous (σ)	% Amorphous	% Amorphous (σ)
P053387	9.01	0.53	14.77	4.29	76.21	4.17
P053388	9.23	1.13	19.93	4.40	70.85	4.85
P053389-Redo	8.19	0.71	15.21	4.03	76.60	4.64
P053389*	8.00	1.28	19.04	11.56	72.96	12.78
P055481*	8.66	0.65	13.54	2.85	77.80	3.49
P055660*	8.28	0.77	11.00	0.97	80.72	1.61
P055663*	8.56	1.00	8.44	2.63	82.99	2.72

Table 3: T^2 study results for all for all pads analyzed for this report shown alongside those analyzed in the original development lot 1 chemical analysis report (shown as*).

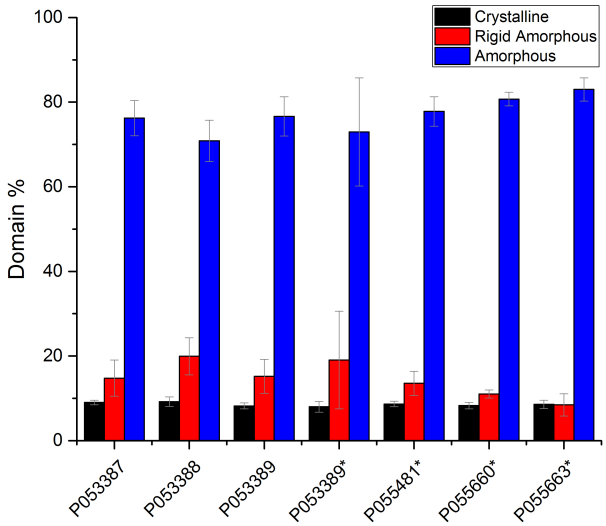


Figure 7: T^2 results for all pads analyzed for this report shown alongside those analyzed in the original development lot 1 chemical analysis report (shown as*).

FT-IR

As was the case for the original development lot 1 chemical analysis study, FT-IR was most helpful in determining chemical differences between the pads. Figure 8 shows all 12 IR spectra collected from each pad. These spectra all match fairly well suggesting the samples are relatively similar, but also a few features are different for pad P053389. The major peaks have been assigned according to Table 4.[2]

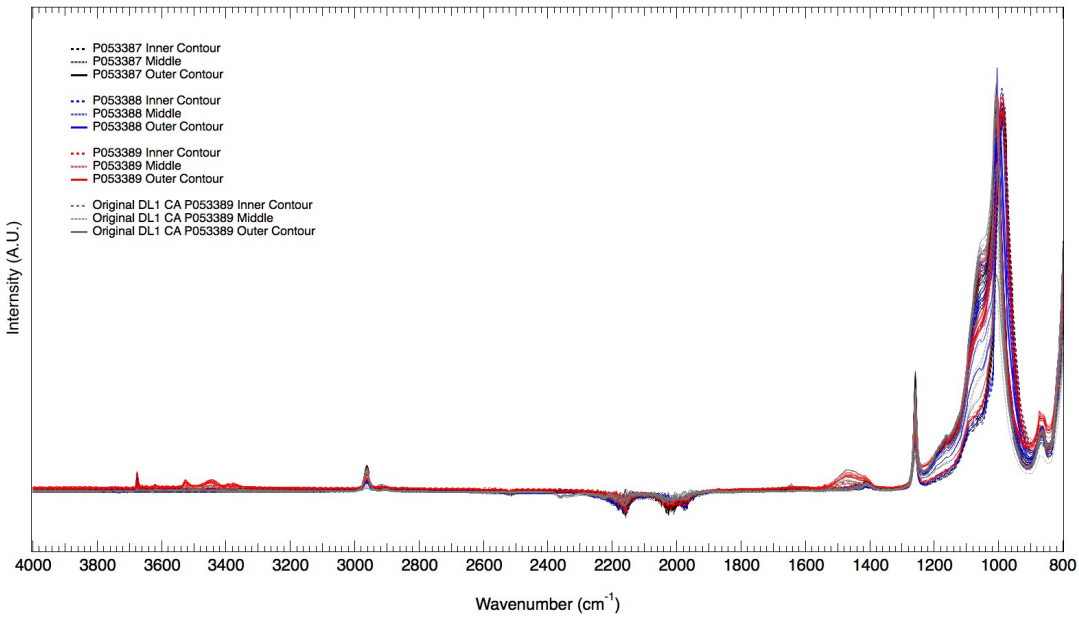


Figure 8: Representative IR spectra showing a fairly good overall match between each sample.

Wavenumber (cm^{-1})	Chemical Functionality
700	(C-H aromatic) Phenyl-Silicon
790	Si-CH_3
870	Si-CH_3
1006	Si-O-Si, polymer backbone
Shoulder @ 1070-1100	Quartz SiO_2
1257	Si-CH_3
1400-1490	C=C Si-C=C Vinyl (1410) C=C Aromatic (1450, 1500)
2840	Si-OCH_3
2960	C-H (methyl)

Table 4: Assignment of IR peaks

The FT-IR collected in this study also supports the observations made in the development lot one chemical analysis report. These main differences were observed in the C=C region and the –OH region. Figure 9a-c shows the C=C region, for all pads (A), both sets of data from P053389 (B), and only pads P053387 and P053388 (C). The peaks around 1410 cm^{-1} are attributed to the C=C stretch of a vinyl siloxane and peaks around 1440 cm^{-1} are attributed to the C=C aromatic stretch of the phenyl siloxane.[2,3] For some but not all of the samples analyzed from P053389 the peak at 1440 cm^{-1} is present whereas in other P053389 and all other samples from pads P053387, and P053388, do not show any peaks at 1440 cm^{-1}. Similarly, the Si-OH stretch region (peaks centered around 3550 cm^{-1}) show the same behavior (Figure 10). P053389 samples, which have a peak at 1440 cm^{-1}, also show peaks centered around 3550 cm^{-1}(Figure 10a,b). These peaks aren't seen in P053389 samples that don't have a peak at 1440 cm^{-1} or in P053387, and P053388 (Figure 10c). These peaks at 3550 cm^{-1} could be attributed to silanol groups in the polymer formed via side reactions or could be free silanol groups on the filler surface, suggesting weaker filler-

polymer interactions which would lead to a composite that would show degraded thermal properties and higher swelling as observed in this series of analyses. Finally, these irregularities in the IR spectra seem to occur with greater frequency on the pad surfaces.

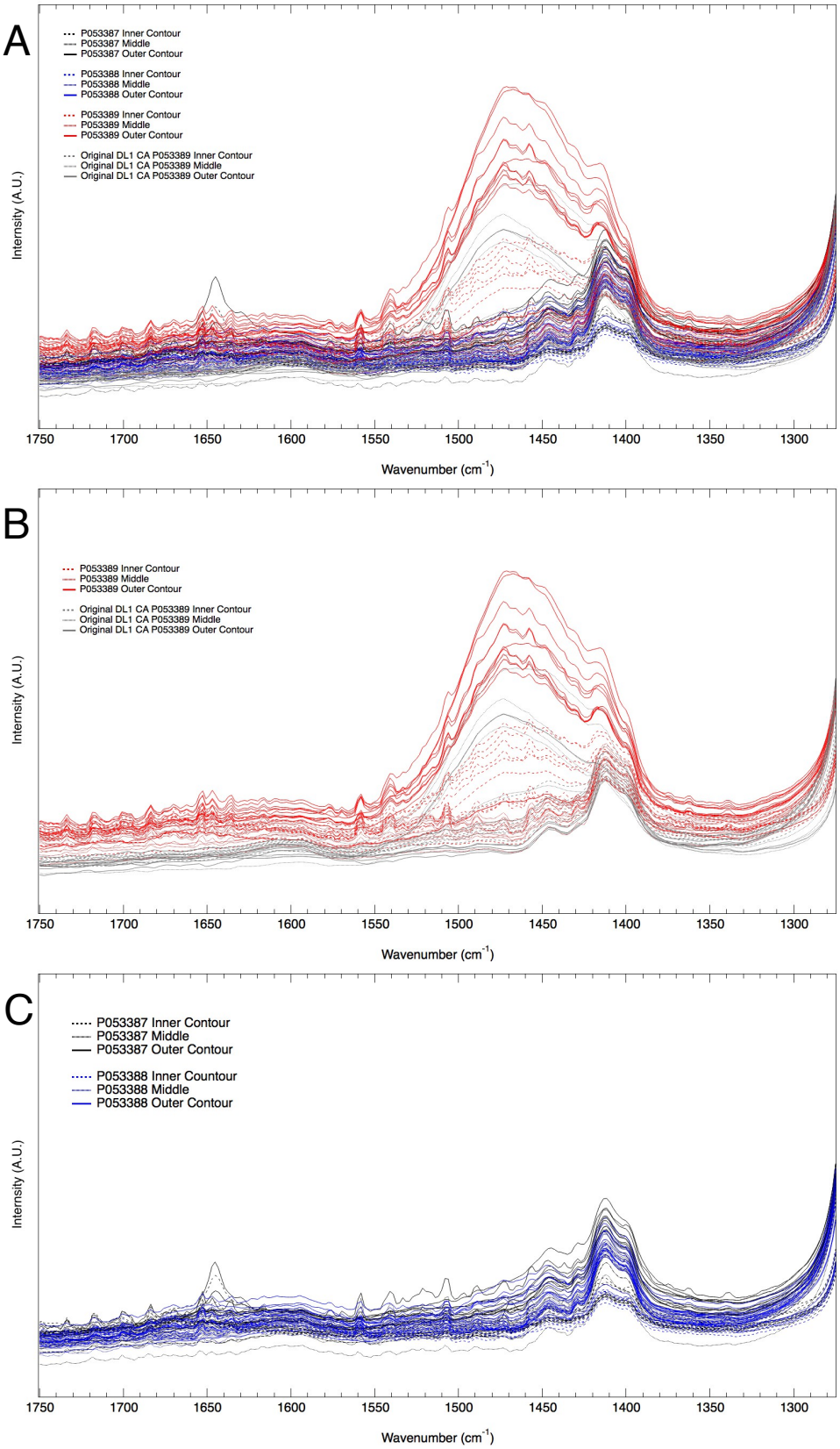


Figure 9: IR spectra of the alkene region: A) showing all samples. B) showing old and new P053389 samples. And C) showing P053387 and P05338 samples.

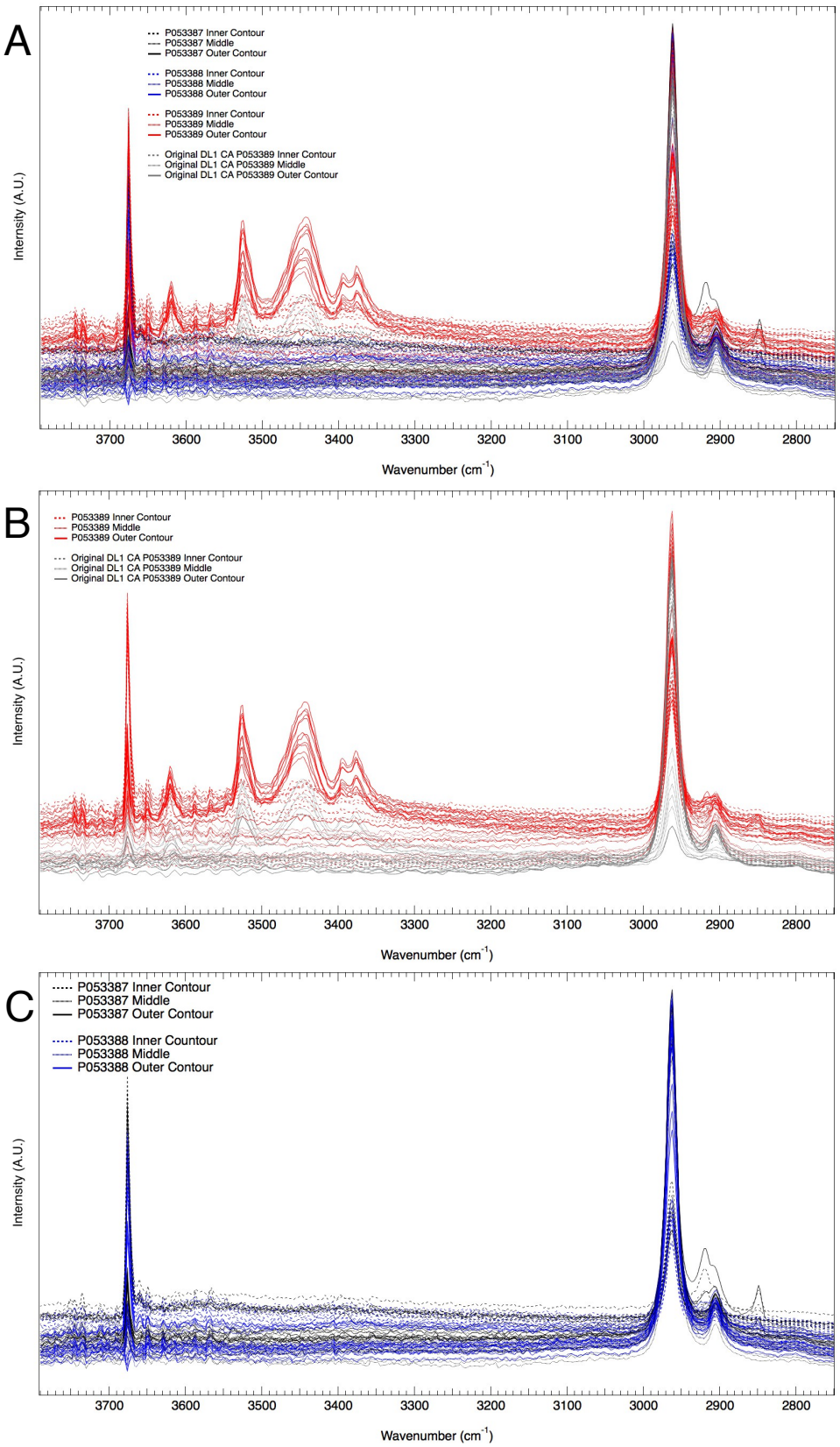


Figure 10: IR spectra of the silanol region: A) showing all samples. B) showing old and new P053389 samples. And C) showing P053387 and P05338 samples.

CONCLUSIONS

Two additional development lot 1 pressure pads (P053387 and P053388), along with a suspect pad (P053389) were subject to the suite of analyses that was used for the original development lot 1 pressure pad chemical analysis. These pads were analyzed by NMR, DSC, TGA, IR, and solvent swell studies to determine if different combinations of curing agent lot and resin lot changed the chemical/thermal properties of the composite. The purpose of this study was to determine if differences observed in P053389 were representative of the resin and curing agent lot combination used in production by comparing two additional pads from that resin and curing agent lot combination in addition to repeating the analysis of P053389. In general, P053389 continued to exhibit suspect behavior in each analysis while pads P053387 and P053388 performed quite similarly to all other pads in the initial development lot 1 pressure pad chemical analysis (P055481, P055660, and P055663). Therefore, we conclude that the suspect behavior observed in pad P053389 is not representative of some systemic problem associated with the resin and curing agent lot combination.

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[1] Ortiz-Acosta, D. Chemical Characterization of DC745U and the Peroxide Initiator, LA-UR-14-26854.

[2] A) Launder, P. *Infrared Analysis of Organosilicon Compounds: Spectra-Structure Correlations.* Silicone Compounds Register and Review, Edited by B. Arkles, 1987; B) Smith, A. L. *Infrared Spectra-structure Correlations for Organosilicon Compounds*. Spectro. Acta. 1960, v. 16, p. 87. C) Smith, B.C. Infrared Spectral Interpretation: A Systematic Approach, CRC Press, Boca Raton, 1999, p. 160.

[3] Andrianov, K.A, Radkina, A.Y., Leites L.A., Zavin, B.G. *Determining the Relative Content of Vinyl Groups in Various Polyvinyl(phenyl)siloxanes by IR Spectroscopy*. Vysokomol. Soyed . 1975, A17 No.3 p 682.