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THE IMPACT OF RELEASE AGENTS ON PULTRUDED FRP

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ABSTRACT:

A common practice for pultruders is to increase the release agent level in the resin mix when issues such as die wear occur. The purpose of this paper is to understand the potential impact of this increased release agent level on select performance properties. It is important that the Pultruder understand their limitations for process adjustments. Two different releases will be considered in this paper.

INTRODUCTION

Mold releases are generally proprietary blends of fatty acids, organic phosphate compounds and glycerides. Pultrusion resin mixes, whether polyester, vinyl ester, phenolic, epoxies or urethane all contain some form of mold release. The chemical composition of the mold release often changes with the choice of polymer in the resin mix. Pultrusion resin mixes typically contain a polymer, accelerator or hardener, filler, mold release, flame retardants as appropriate and pigment. All pultruders consider mold releases to be an invaluable processing aid but pultruders can have the mistaken impression that "if some is good, more is better". Production personnel, who do not test the manufactured product, may have a tendency to desire extra release to resolve a current manufacturing problem.

This paper will study the use of different levels of two release agents designated as Release "X" and Release "Y". Release "X" is a general purpose release of an acidic nature with pH of approximately three. Release "Y" is also a general purpose release but has been neutralized to yield a pH of approximately five. Release agent suppliers have been evolving their technology to develop less acidic releases in response to die wear and other processing concerns. Also studied in this paper is the potential impact of the choice of filler, whether clay, calcium carbonate, or aluminum trihydrate (ATH). The amount of filler was maintained throughout this experiment and only the chemistry of the filler was changed. The mat and roving ratio was also maintained with the same polyester resin type and level and with the same initiator level throughout this experiment. The three factors studied were: release agent type, release agent level, and filler chemistry.

EXPERIMENTAL DESIGN

The base experimental design used was a Taguchi L_4 (2^3) format to evaluate the three factors using four trials.

The Taguchi method is a partial factorial design of experiments whose purpose is to reduce the amount of overall testing. This paper will also illustrate how to apply this partial factorial design of experiment technique. Typically, the partial factorial approach is an initial experiment to identify the most dominant factor(s).

Experimental Design No. 1 on (Table No. 1) has four trials labeled "A, B, C, D". "R_A, R_B, R_C, R_D" are the experimental response using the various resin mix combination found in "A, B, C, D". The experimental responses can be the viscosity, gel times, mechanical properties, etc. The evaluation of the effect of the different factors in the properties measured is illustrated below. Define:

- d_L = difference in the experimental results for the property measured caused by the difference in the release level.
- d_R = difference in the experimental results for the property measured caused by the difference in the release type ("X" or "Y").
- d_F = difference in the experimental results for the property measured caused by the difference in the filler chemistry.

Specifically, for Experimental Design No. 1

- d_L = average test result difference at the 1.0-phr level minus the average test result difference at the 2.5-phr level. Experimental runs "A" and "B" were run using the 1.0-phr level and experimental runs "C" and "D" were run at the 2.5-phr level.

$$d_L = \frac{1}{2}(R_A + R_B) - \frac{1}{2}(R_C + R_D) \quad (1)$$

The "Y" release agent was used on experimental trials "A" and "C" and the "X" release was used on experimental "B" and "D". The d_R is similarly calculated as:

$$d_R = \frac{1}{2}(R_A + R_C) - \frac{1}{2}(R_B + R_D) \quad (2)$$

And the impact of the filler is calculated as:

$$d_F = \frac{1}{2}(R_A + R_D) - \frac{1}{2}(R_B + R_C) \quad (3)$$

As an example, the test results (responses) for the LW (lengthwise or 0°) compressive strength as measured by ASTM D695 for the four composites of "A" through "D" were:

R_A = 76.5-ksi
R_B = 64.1-ksi
R_C = 54.8-ksi
R_D = 59.8-ksi

This individual composite test data is found on Table No. 2. The level difference using equation (1) for d_L:

$$d_L = \frac{1}{2}(76.5 + 64.1) - \frac{1}{2}(54.8 + 59.8)$$

d_L = 70.3 - 57.3 = 13-ksi

Or, for the difference caused by the release agent level compared to the overall test average is.

$d_L \div$ AVERAGE = 13 ÷ 63.8 = .204 (20.4%)

The interpretation is that the change in release level from 1.0-phr to 2.5-phr had an average reduction of 20.4% in the 0° compressive strength. The fact that Trial A was substantially higher might suggest there are combination effects involved with the filler.

A second partial factorial experimental design was performed labeled as Experimental Design No. 2 on Table No. 1. Essentially, two more trials, "E" and "F", were added with different filler (ATH). The analysis proceeded in the same manner as Experiment No. 1.

RESULTS

Table No. 2 contains the property test results including the resin mixes results for all of the experiments. The 0°/90° (lengthwise/crosswise) D695 compressive properties and D2344 short beam shear was measured. Each of these properties will be discussed in detail.

90° (CROSSWISE) COMPRESSIVE STRENGTH

This information is found in Table No. 3 and Graph No. 1. The analysis of both Taguchi of design of experiments suggests that the lower release agent level between 1.0-phr and 2.5-phr would produce higher 90° compressive strength properties. One theory for the reduction in strength is that the excess release agent level degrades the bond between the glass and the resin matrix by coating the glass to some extent. It is beyond the scope of this paper to confirm this theory.

The effect of the release agent type and the filler chemistry is less than 50% of the main effect and is not considered significant in the first order of approximation. By "not being considered significant" it is meant that the effect is too small to be considered when developing an initial resin mix formula. It should be noted that release agent "Y" with a clay formulation produced the highest mechanical property results when compared to release agent "Y" with the carbonate. The strength contribution from the filler is not discussed in detail (Taguchi only indicates which factors are significant); however, this would be an excellent topic for a future paper.

90° (CROSSWISE) COMPRESSIVE MODULUS

This information is found in Table No. 4 and Graph No. 2. Here the Taguchi analysis indicates that the two significant factors are both the lower release agent level (between 1.0 and 2.5-phr) and the clay filler compared to the carbonate. However, these factors are approximately 10% or less. The type of release agent is not a significant factor with the crosswise compressive modulus which may be more reinforcement controlled.

0° (LENGTHWISE) COMPRESSIVE STRENGTH

This information is found in Table No. 5 and Graph No. 3. Two significant factors from the analysis are the lower release agent level and the clay filler. Graph No. 3 illustrates the substantial drop in lengthwise compressive strength at the 1.5-phr level with the "Y" release agent type and the clay filler. The "X" release agent level appears not to have the same significant drop, although there's an overall reduction using the carbonate filler. One potential interpretation from this and other graphs is that the choice in release agent level and the choice of filler will both potentially impact properties and detailed experiments must be made to determine the appropriate combinations.

0° (LENGTHWISE) COMPRESSIVE MODULUS

This information is found in Table No. 6 and Graph No. 4. The most significant factor is the filler type and this is less than 5% of the average response. None of these factors are considered an issue with the 0° compressive modulus.

90° (CROSSWISE) SHORT BEAM SHEAR

This information is found in Table No. 7 and Graph No. 5. The difference is probably not strong enough to be statistically different in any of the Taguchi experiments.

0° (LENGTHWISE) SHORT BEAM SHEAR

This information is found in Table No. 8 and Graph No. 6. The lower release agent level is the most dominant factor with the clay/carbonate Taguchi, the "Y" release agent and the carbonate is preferred. With the clay/ATH Taguchi, only the release agent level is an issue.

180°F SPI PROPERTIES

This information is found in Table No. 9 and Graph No. 7. While the Taguchi analysis indicates some difference the actual change appears to be relatively small.

VISCOSITY

This information is found in Table No. 10 and Graph No. 8. For the clay/carbonate Taguchi, the higher release agent level has a higher viscosity. Carbonate produces an inherently lower viscosity than the clay. This study indicated that further data was required and a separate bench mix study was made.

The follow up viscosity study was designed to fully investigate the effects of the various chemistries of the fillers in relation to the two mold releases when combined in a typical resin mix formulation. Because viscosity was the only parameter of interest, initiators were not used. Initiators themselves increase resin mix viscosity and it was important to take their effect out of the equation so the only effect would be from the presence of the mold release.

A general polyester resin was used for the tests. The viscosity of the neat resin at 25°C was tested and found to be 3,875-centipoise. All formulations were tested from the same lot of resin on the same day by the same person. The pH of the neat resin was tested using pH paper with a range of one to fourteen and found to be approximately five. The pH of the releases was also tested with the same pH paper, and given earlier in this paper.

Table No. 11 shows the layout of the formulations tested. All values corresponding to the chemical component listed at the left column are given in parts per hundred resin (phr). The viscosity is given in centipoise and was tested using RVF spindles. All resin mixes were tested at 25°C. Mixes 1-3 and 10-12 were tested without any mold release at all to establish a baseline viscosity for comparison purposes.

Graph No. 9 shows the increase in viscosity over the baseline viscosity for each given filler loading and release type. It should be noted that the value of the base viscosity (Mix 1-3 & 10-12) has been subtracted from each corresponding mix.

At the 20-phr filler loading and 1.5-phr release level, there was an increase in viscosity in going from a neutralized release to the more acidic release. This was expected and is due to the acid-base reaction of calcium carbonate in the presence of an acid:

$$CaCO_3 + 2H^+ \rightarrow H_2CO_3 + Ca^{+2}$$

This was evidenced in the mix by the increased amount of foaming seen in the mixes containing the calcium carbonate. The mixes with the neutralized release also foamed, though not as bad as the ones in the presence of the more acidic release. There was even slight foaming (compared with the clay or ATH formulations) in the calcium carbonate mix that had no release which could be due to the fact the resin was on the acidic side of the scale with a pH of approximately five.

A slight increase was seen in the aluminum trihydrate {$Al(OH)_3$, aka $Al_2O_3xH_2O$} formulation as well when going from the neutralized release to the more acidic release. Perhaps it, too, is being neutralized by the presence of the acid. It was interesting to note that the clay formulation saw a decrease in viscosity when going from a more neutral to more acidic release.

At the 50-phr filler loading and 1.5-phr release level, the effect of going to a more acidic release produced an even larger viscosity rise – about 10,000-centipoise. The same effect was seen with the ATH formulation, with a difference of around 5,000-centipoise. Again we saw a slight decrease in the clay formulation when going to a more acidic mold release. Of particular interest to any pultruder running high levels of filler is that with a more acidic mold release, the calcium carbonate mix produced the highest viscosity of all three fillers. It would suggest that a more neutral release would be warranted to reduce viscosity unless one is running clay filler.

The right end of Graph No. 9 shows the effect of doubling the release agent at 50-phr filler loading level. Sometimes pultruders will add more mold release if they are running higher filler loadings and having trouble with pull force. This data shows adding more release is not a particularly good idea – especially if one was using clay filler. We again see an increase in viscosity in both the calcium carbonate and aluminum trihydrate fillers when going from a more neutral to a more acidic release. The viscosity of the clay mixes increases dramatically. To simulate what might happen in a production situation, the mixes containing 3-phr of release were developed by adding an additional 1.5-phr of release to mixes 13-18.

SUMMARY OF RESULTS

To summarize the results, a more acidic mold release can have an increase in resin mix viscosity if the formulation contains calcium carbonate or aluminum trihydrate (ATH). At higher filler loadings, this becomes even more important as pultruders attempt to achieve lower viscosity levels for improved wet out, lower pull force, and higher line speeds. While a formulator may be tempted to increase the mold release level to overcome processing problems, this can actually increase the viscosity further.

From a mechanical property perspective, careful consideration should be given to the choice of release agent type, level and filler chemistry as all three can impact both structural and processing performance.

Table No. 1

EXPERIMENTAL DESIGN No. 1

RUN NO	RELEASE LEVEL	RELEASE TYPE	FILLER TYPE	RESPONSE
A	1.0-phr	Y	CLAY	R_A
B	1.0-phr	X	CARB	R_B
C	2.5-phr	Y	CARB	R_C
D	2.5-phr	X	CLAY	R_D

EXPERIMENTAL DESIGN No. 2

RUN NO	RELEASE LEVEL	RELEASE TYPE	FILLER TYPE	RESPONSE
A	1.0-phr	Y	CLAY	R_A
E	1.0-phr	X	ATH	R_E
F	2.5-phr	Y	ATH	R_F
D	2.5-phr	X	CLAY	R_D

TABLE No. 2

COMPOSITE	ASTM	A	B	C	D	E	F	G	H	I	J
Filler		Clay	Carbonate	Carbonate	Clay	ATH	ATH	Clay	Clay	Carbonate	Carbonate
Release		Y	X	Y	X	X	Y	X	Y	Y	Y
Release level (phr)		1.0	1.0	2.5	2.5	1.0	2.5	1.5	2.0	1.5	2.0
Filler level (phr)		23.2	23.2	23.2	23.2	23.2	23.2	23.2	23.2	23.2	23.2
90° Compressive Strength (ksi)	D695	22.6	20.6	18.5	18.8	22.6	20.1	22.0	22.5	18.5	18.4
90° Compressive Modulus (msi)	D695	1.27	1.15	1.06	1.16	1.19	1.01	1.20	1.22	0.96	1.00
0° Compressive Strength (ksi)	D695	76.5	64.1	54.8	59.8	68.5	58.6	78.1	69.5	54.4	62.7
0° Compressive Modulus (msi)	D695	4.35	4.16	4.18	4.27	4.06	4.10	4.17	4.22	3.93	4.20
90° Short Beam Shear (ksi)	D2344	3.36	3.09	3.16	2.94	3.18	2.94	3.16	3.30	2.91	3.13
0° Short Beam Shear (ksi)	D2344	5.70	5.65	5.46	5.48	5.42	4.58	4.80	5.25	4.97	5.50
SPI GEL											
Gel (min)		0.62	0.43	0.71	0.49	0.68	0.66	0.56	0.50	0.37	0.37
Peak (°F)		349	363	393	354	340	356	350	353	361	362
Interval (min)		1.18	1.15	0.74	1.11	1.28	1.06	1.18	1.22	1.19	1.22
VISCOSITY (cps)		4690	4180	3810	7160	5440	6180	5270	6150	4460	4610

Table No. 3

PROPERTY: CW COMPRESSIVE STRENGTH (ksi)

GRAPH No. 1

TAGUCHI	No. 1	TAGUCHI	No. 2	LEVEL (phr)	Y/CLAY	Y/CARB	X/CARB	X/CLAY	X/ATH	Y/ATH
LEVEL	2.95	LEVEL	3.15	1	22.6		20.6		22.6	
TYPE	0.85	TYPE	0.65	1.5	22	18.5				
FILLER	1.15	FILLER	-0.65	2	22.5	18.4				
AVERAGE	20.13	AVERAGE	21.03	2.5		18.5		18.8		20.1
% LEVEL	14.66	% LEVEL	14.98							
% TYPE	4.22	% TYPE	3.09							
% FILLER	5.71	% FILLER	-3.09							

Table No. 4

PROPERTY: CW COMPRESSIVE MODULUS (msi)

GRAPH No. 2

TAGUCHI	No. 1	TAGUCHI	No. 2	LEVEL (phr)	Y/CLAY	Y/CARB	X/CARB	X/CLAY	X/ATH	Y/ATH
LEVEL	0.10	LEVEL	0.15	1	1.27		1.15		1.19	
TYPE	0.01	TYPE	-0.03	1.5	1.2	0.96				
FILLER	0.11	FILLER	0.12	2	1.22	1				
AVERAGE	1.16	AVERAGE	1.16	2.5		1.06		1.16		1.01
% LEVEL	8.62	% LEVEL	12.53							
% TYPE	0.86	% TYPE	-3.02							
% FILLER	9.48	% FILLER	9.94							

Table No. 5

PROPERTY: LW COMPRESSIVE STRENGTH (ksi)

GRAPH No. 3

TAGUCHI	No. 1	TAGUCHI	No. 2	LEVEL (phr)	Y/CLAY	Y/CARB	X/CARB	X/CLAY	X/ATH	Y/ATH
LEVEL	13.00	LEVEL	13.30	1	76.5		64.1		68.5	
TYPE	3.70	TYPE	3.40	1.5	78.1	54.4				
FILLER	8.70	FILLER	4.60	2	69.5	62.7				
AVERAGE	63.80	AVERAGE	65.85	2.5		54.8		59.8		58.6
% LEVEL	20.38	% LEVEL	20.20							
% TYPE	5.80	% TYPE	5.16							
% FILLER	13.64	% FILLER	6.99							

Table No. 6

PROPERTY: LW COMPRESSIVE MODULUS (msi)

GRAPH No. 4

TAGUCHI	No. 1	TAGUCHI	No. 2	LEVEL (phr)	Y/CLAY	Y/CARB	X/CARB	X/CLAY	X/ATH	Y/ATH
LEVEL	0.03	LEVEL	0.02	1	4.35		4.16		4.06	
TYPE	0.05	TYPE	0.06	1.5	4.17	3.92				
FILLER	0.14	FILLER	0.23	2	4.22	4.2				
AVERAGE	4.24	AVERAGE	4.20	2.5		4.18		4.27		4.1
% LEVEL	0.71	% LEVEL	0.48							
% TYPE	1.18	% TYPE	1.43							
% FILLER	3.30	% FILLER	5.48							

Table No. 7

PROPERTY: CW SHORT BEAM SHEAR (ksi)

GRAPH No. 5

TAGUCHI	No. 1	TAGUCHI	No. 2	LEVEL (phr)	Y/CLAY	Y/CARB	X/CARB	X/CLAY	X/ATH	Y/ATH
LEVEL	0.18	LEVEL	0.33	1	3.36		3.09		3.18	
TYPE	0.25	TYPE	0.09	1.5	3.16	2.91				
FILLER	0.02	FILLER	0.09	2	3.3	3.13				
AVERAGE	3.14	AVERAGE	3.11	2.5		3.16		2.94		2.94
% LEVEL	5.58	% LEVEL	10.63							
% TYPE	7.81	% TYPE	2.90							
% FILLER	0.80	% FILLER	2.90							

Table No. 8

PROPERTY: LW SHORT BEAM SHEAR (ksi)

GRAPH No. 6

TAGUCHI	No. 1	TAGUCHI	No. 2	LEVEL (phr)	Y/CLAY	Y/CARB	X/CARB	X/CLAY	X/ATH	Y/ATH
LEVEL	0.70	LEVEL	1.03	1	5.7		5.64		5.42	
TYPE	0.52	TYPE	0.19	1.5	4.8	4.97				
FILLER	-0.46	FILLER	0.09	2	5.25	5.5				
AVERAGE	5.32	AVERAGE	5.05	2.5		5.46		4.48		4.58
% LEVEL	13.16	% LEVEL	20.42							
% TYPE	9.77	% TYPE	3.77							
% FILLER	-8.65	% FILLER	1.78							

Table No. 9

PROPERTY: SPI GEL TIME (min)

GRAPH No. 7

TAGUCHI	No. 1	TAGUCHI	No. 2	LEVEL (phr)	Y/CLAY	Y/CARB	X/CARB	X/CLAY	X/ATH	Y/ATH
LEVEL	-0.08	LEVEL	0.08	1	0.62		0.43		0.68	
TYPE	0.21	TYPE	0.06	1.5	0.56	0.37				
FILLER	-0.02	FILLER	-0.12	2	0.5	0.37				
AVERAGE	0.56	AVERAGE	0.61	2.5		0.71		0.49		0.66
% LEVEL	-13.33	% LEVEL	12.24							
% TYPE	36.44	% TYPE	8.98							
% FILLER	-2.67	% FILLER	-18.78							

Table No. 10

PROPERTY: VISCOSITY (cps)

GRAPH No. 8

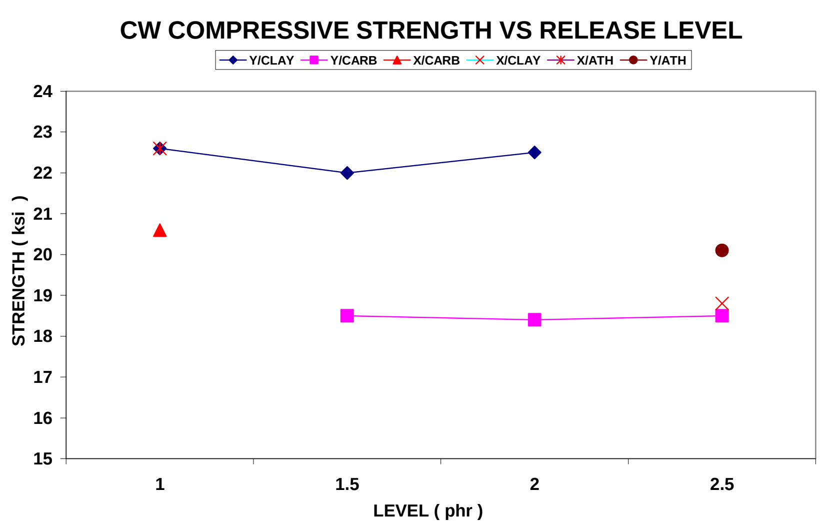
TAGUCHI	No. 1	TAGUCHI	No. 2	LEVEL (phr)	Y/CLAY	Y/CARB	X/CARB	X/CLAY	X/ATH	Y/ATH
LEVEL	-1050.00	LEVEL	-1605.00	1	4690		4180		5440	
TYPE	-1420.00	TYPE	-865.00	1.5	5270	4460				
FILLER	1930.00	FILLER	115.00	2	6150	4610				
AVERAGE	4960.00	AVERAGE	5867.50	2.5		3810		7160		6180
% LEVEL	-21.17	% LEVEL	-27.35							
% TYPE	-28.63	% TYPE	-14.74							
% FILLER	38.91	% FILLER	1.96							

Table No. 11

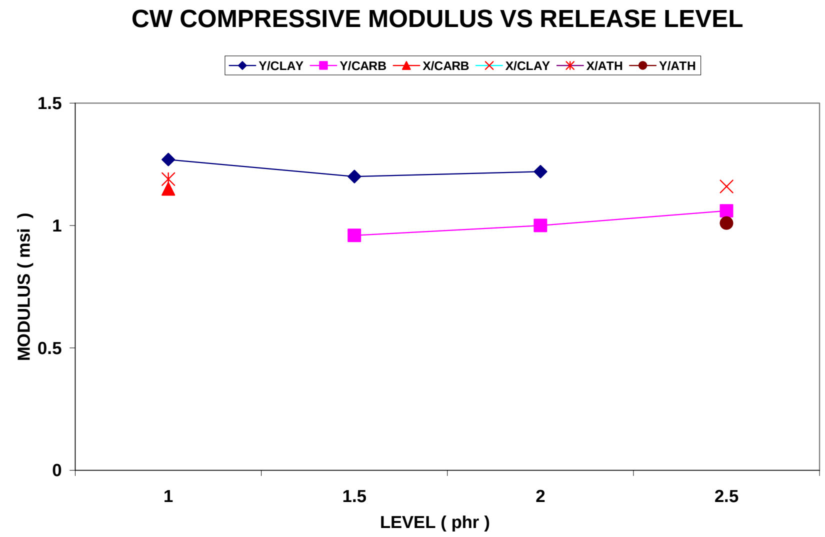
(phr of):	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7	Mix 8	Mix 9
Polyester Resin	100	100	100	100	100	100	100	100	100
Calcium Carbonate	20	---	---	20	---	---	20	---	---
Kaolin Clay	---	20	---	---	20	---	---	20	---
ATH-st	---	---	20	---	---	20	---	---	20
"Y" Release	---	---	---	1.5	1.5	1.5	---	---	---
"X" Release	---	---	---	---	---	---	1.5	1.5	1.5
VISCOSITY (cps)	5,500	6,540	5,690	7,380	10,220	7,620	10,080	8,540	8,460
(phr of):	**Mix 10**	**Mix 11**	**Mix 12**	**Mix 13**	**Mix 14**	**Mix 15**	**Mix 16**	**Mix 17**	**Mix 18**
Polyester Resin	100	100	100	100	100	100	100	100	100
Calcium Carbonate	50	---	---	50	---	---	50	---	---
Kaolin Clay	---	50	---	---	50	---	---	50	---
ATH-st	---	---	50	---	---	50	---	---	50
"Y" Release	---	---	---	1.5	1.5	1.5	---	---	---
"X" Release	---	---	---	---	---	---	1.5	1.5	1.5
VISCOSITY (cps)	8,420	15,350	9,560	11,060	23,650	12,580	21,600	23,200	18,000
(phr of):				**Mix 19**	**Mix 20**	**Mix 21**	**Mix 22**	**Mix 23**	**Mix 24**
Polyester Resin				100	100	100	100	100	100
Calcium Carbonate				50	---	---	50	---	---
Kaolin Clay				---	50	---	---	50	---
ATH-st				---	---	50	---	---	50
"Y" Release				3	3	3	---	---	---
"X" Release				---	---	---	3	3	3
VISCOSITY (cps)				16,980	35,700	16,550	25,850	34,750	21,750

* ATH-st refers to surface treated ATH

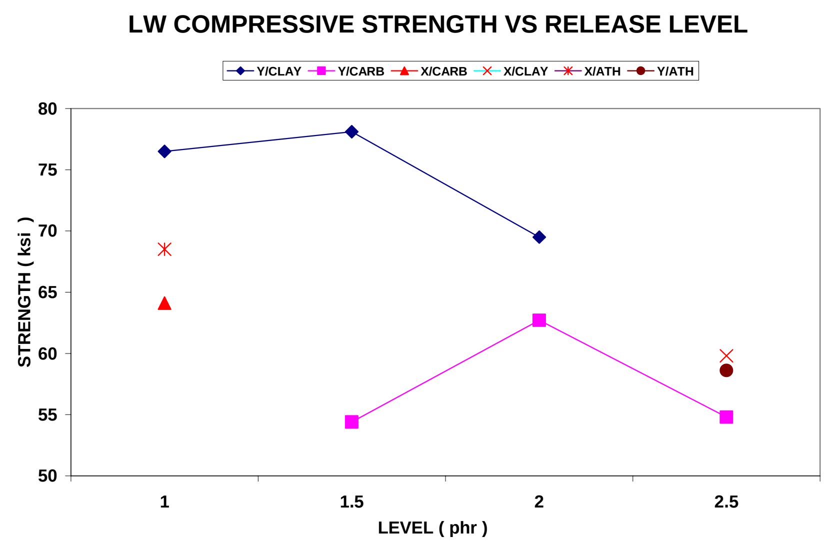
Graph No. 1



Graph No. 2



Graph No. 3



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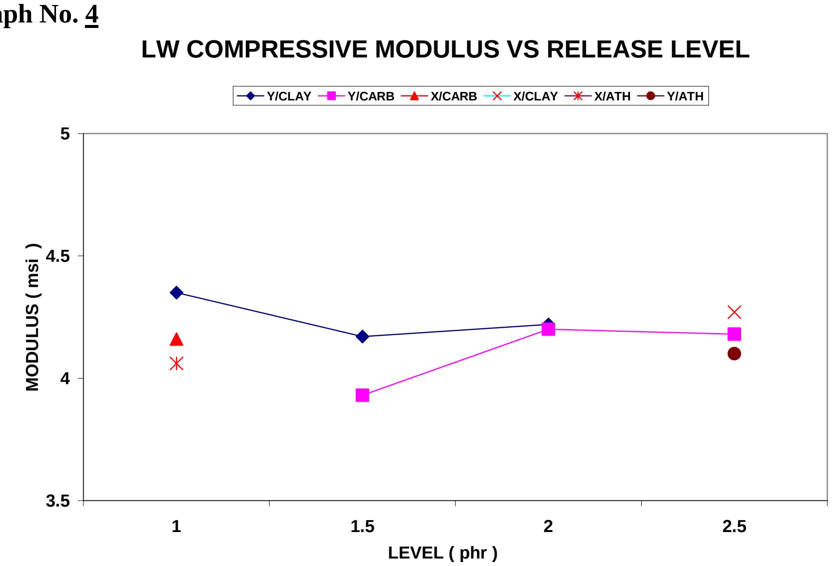

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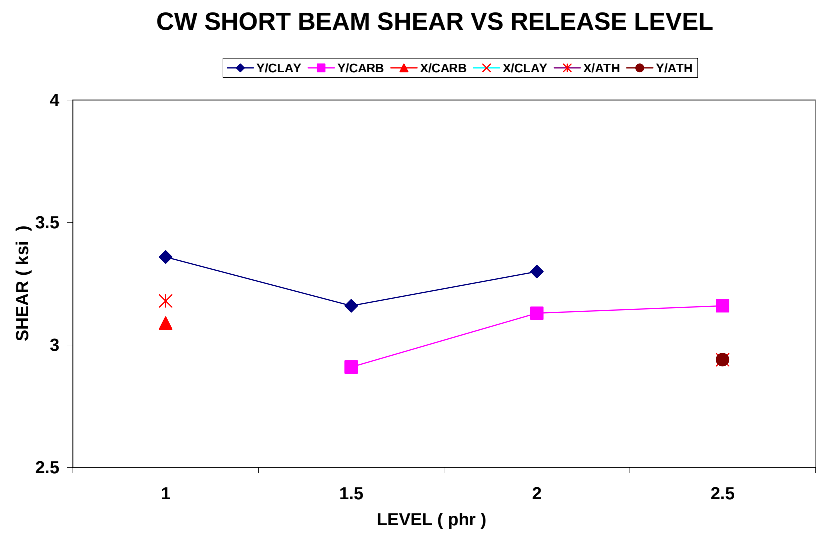
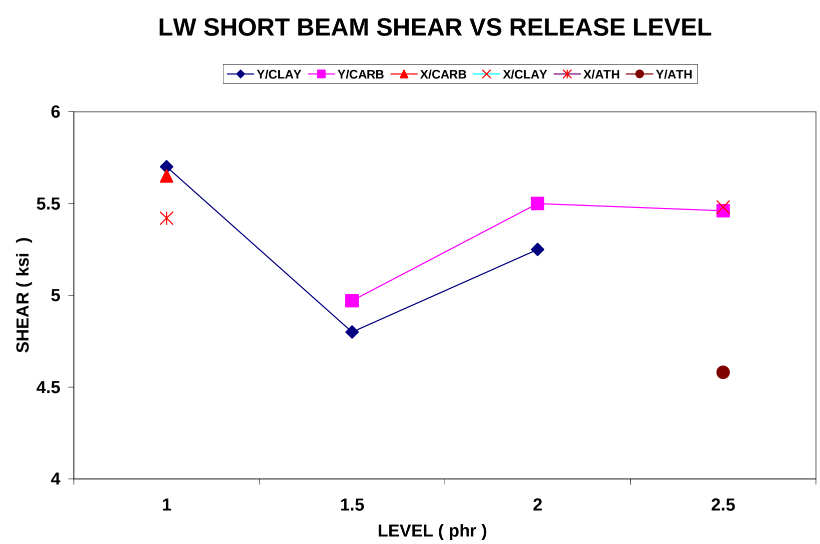
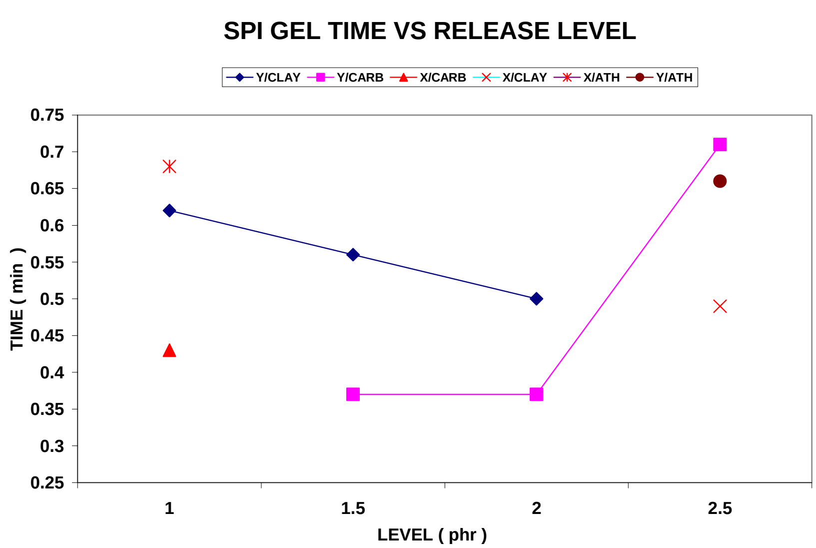


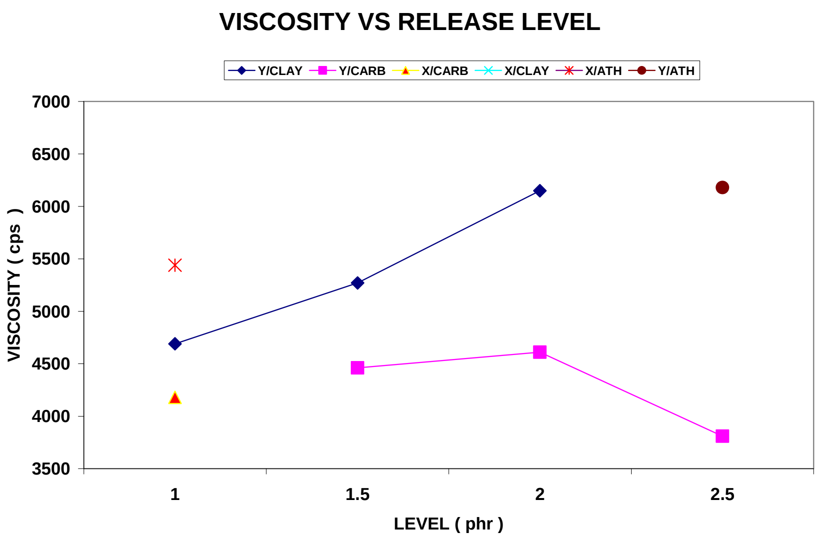
Graph No. 6



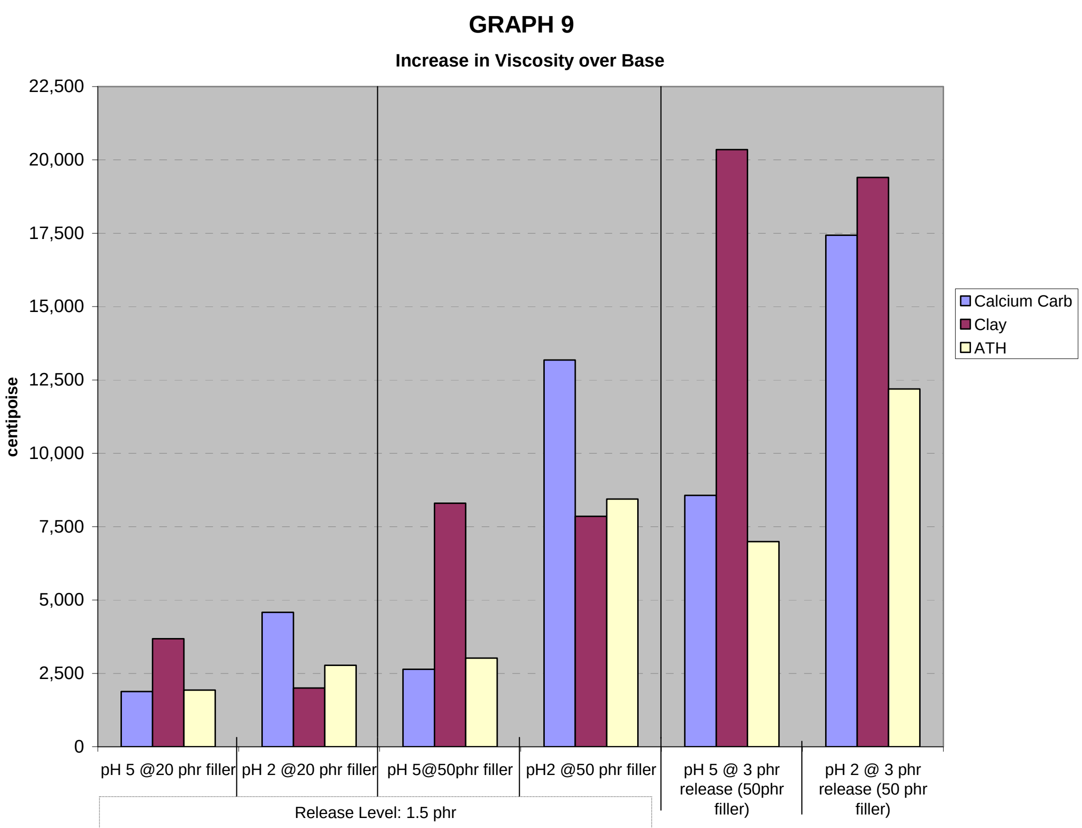
Graph No. 7



Graph No. 8



VISCOSITY VS RELEASE LEVEL
Y/CLAY
Y/CARB
X/CARB
X/CLAY
X/ATH
Y/ATH
7000
6500
6000
5500
5000
4500
4000
3500
VISCOSITY (cps)
1
1.5
2
2.5
LEVEL (phr)



GRAPH 9
Increase in Viscosity over Base
22,500
20,000
17,500
15,000
12,500
10,000
7,500
5,000
2,500
0
centipoise
Calcium Carb
Clay
ATH
pH 5 @20 phr filler
pH 2 @20 phr filler
pH 5@50phr filler
pH2 @50 phr filler
pH 5 @ 3 phr release (50phr filler)
pH 2 @ 3 phr release (50 phr filler)
Release Level: 1.5 phr