Pultrusion Exotherm Study Gauge Sensitivity And Application To Process Engineering Problems

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ABSTRACT

The Pultrusion Die Exotherm Test is broadly used and discussed in the pultrusion industry. In this test, a thermocouple is inserted in the wetted, moving reinforcement laminate and is pulled through a pultrusion die. The curve of temperature vs. die position is used to interpret reaction kinetics in the die, and often applied to process engineering and quality control problems. In this study, the authors have executed the Die Exotherm Test on numerous dies, the results are examined to establish gauge sensitivity of this test method, and comments on accuracy are offered. Comparisons are made between die exotherm data and DSC as well as SPI gel data. These analysis techniques are then applied in a designed experiment to optimize initiator levels for a common channel profile relative to cost, productivity, and product performance.

BACKGROUND

Pultrusion is an efficient process for the continuous manufacture of composite articles of constant cross-section. In this process, reinforcements and surface veils are pulled through a resin-in-impregnation bath or chamber and then into a heated die. The cured composite is continuously pulled from the die through the use of traction (caterpillar) or reciprocating clamp pullers, and then cut to length by a flying cut-off saw timed to the speed of the process. A wide range of reinforcements and resins can be pultruded, but most commonly, E-glass reinforcements are combined with saturated polyester surface veils, and unsaturated polyester resins employing styrene as both diluent and crosslinking agent. Peroxide initiators are incorporated in the resin mixture to initiate cure/crosslinking. They decompose when exposed to heat to initiate free-radical reactions between styrene and the sites of unsaturation in the polyester alkyd. The styrene crosslinks tie the polyester alkyd together to create a 3-dimensional network. The result is a thermoset matrix that is hard and stiff, making it very suitable for pultruded structural profiles. Typically multiple (in this case, 3) peroxide initiators are employed, as each decomposes at progressively higher temperatures with very short half-lives under typical process conditions. Many factors are known to affect the cure reaction, which in turn influences both the cosmetic and structural quality of pultruded profiles. These include material parameters (such as resin chemistry, reinforcements, the chemistry and concentration of peroxide initiators and other additives), and process parameters (including location and set-point of heaters, die mass and heat flux, and puller speed). Since materials selection and productivity both have significant impact on cost, it is important to have a means of optimizing all of the above relative to the required degree of cure for the part. Since there is no known continuous monitor for degree of resin cure, pultruders commonly employ the "Die Exotherm Test" to obtain a fingerprint of the thermal profile in the moving laminate within the die. This fingerprint then relates to the cure reaction underway in the matrix resin. In this procedure, a sacrificial thermocouple is inserted in the moving reinforcement laminate upstream of the die, and recording is initiated as the sensing junction enters the die. As this study will highlight, the interpretation of the resulting exotherm curves can be complex.

The Die Exotherm Test has been discussed in prior literature. Examples are: Sumerak et. al., who demonstrated the utility of the measurement technique in solving process engineering prob-

lems related to line speed [1], part quality [2], and die design [3]. Vaughan et. al [4] have used differential scanning calorimetry to characterize resin formulations, and predict the cure profile and die exotherm curve with the use of a numerical model. However, the authors are not aware of any literature that addresses the reliability of the measurement technique itself.

Example exotherm curves are shown in Figure 1. Here, 9 runs (3 replicates performed by each of three operators) are overlaid on the same graph. What is immediately obvious is the significant degree of variation between these 9 replicates, though all 9 were performed on the same pultrusion run within a span of 30 minutes. This begs the question: How consistent and thus reliable is the method? A fundamental prerequisite to the use of any test method for engineering analysis or process control is to establish an acceptable Gauge Repeatability and Reproducibility, or GR&R. [The formulas for GR&R are shown in Figure 2.] In other words, it is necessary that the variations between measurements performed by the same operator (repeatability) and the variation operator-to-operator (reproducibility) measuring the same object is much less than the part-to-part variation. Otherwise, variation in the gauge may be interpreted as a real change in the object or process being studied, leading to incorrect conclusions. For purposes of this paper, we will focus on "% Study Variation", which is that variation associated with distinguishing differences between process conditions or resin formulations. In this case, gauge variation should be no more than 30% of the total variation. It should also be noted that even tighter requirements (no more than 10% gauge variation) should be applied to "tolerance variation". Tolerance variation is employed when the gauge is intended to establish the acceptability of a product for release to the customer, based on customer acceptance criteria.

PURPOSE
In this paper, we establish the repeatability and reproducibility of the Die Exotherm Test through a statistical "Gauge R&R" study, and then apply the technique to the solution of a process engineering problem: the optimization of peroxide concentrations in a polyester resin system. A designed experiment with three initiators at two levels is ana-

lyzed relative to full-section deflection and exotherm data. An attempt is also made to relate exotherm measurements to other thermal characterization techniques, differential scanning calorimetry, and SPI Gel data.

METHOD
This study employed a 3.15" X 1.17" X 0.120" channel section commonly used as ladder rail. The composite laminate was comprised of 2 layers of polyester veil, and 3 layers of 1 oz/yd2 E-glass continuous filament mat, sandwiching two layers of unidirectional E-glass rovings. The resin was an unsaturated polyester resin containing 30% by weight styrene. Other additives included 3 peroxide initiators, inorganic fillers, orange pigment dispersion, and a commercially available internal lubricant. This laminate was pultruded at 84"/min through a steel die, 56" in length first 8" comprises an un-heated injection chamber. The 48" cure chamber is heated in three zones by surface-mounted electrical resistance heaters set to 250, 350 and 330 degrees Fahrenheit in zones 1 through 3 respectively. Exotherm measurements were made by inserting a 30 gauge Teflon coated Type K thermocouple into the center mat layer, such that the sensing junction would be centered on the height and the thickness of the channel flange. Temperature was continuously recorded with an Omron OM3000 data logger at an interval of 200 milliseconds. Recording was initiated at the time the sensing junction entered the die. DSC measurements were made with a Mettler TC 10A (heating rate=10oC/min, sample size=9.5-15.5 mg). The SPI gel time measurements were made according to Draft ASTM Protocol dated 4-19-2002. In both the DSC and SPI test protocols, duplicate runs were averaged. Full section deflection measurements were made by supporting a pair of channels with flange tips facing each other on a 108" span, centered under a 1" dia. loading bar. The channels were fixtured with 0.5" thick plastic plates spaced 12" apart along the entire length. The loading fixture was equipped with Satec control and data collection software, and rails were loaded to 250 lbs. Displacement of the loading bar was continuously logged, and the peak deflection reported. Statistical analysis was performed using Minitab statistical analysis software, with alpha=0.1.

GAUGE R&R

Initially, 7 pultrusion runs were performed at two locations (AOC and Werner) with a consistent resin formula. On each run, 9 replicate exotherm measurements were performed, three operators each made three measurements. The twisted thermocouple junction was inserted into the moving center mat, approximately 5/8" from the edge of the mat (determined by eye by each operator). A black mark was made on the moving reinforcement pack, which would be visible at the die face. When the black mark reached the die face, recording was initiated until after the black mark exited the die.

The data from both locations was analyzed separately for Gauge R&R using Minitab statistical software. Data from both locations failed to pass the GR&R. For peak position, the study variation was 51% of the total variation, and for peak temperature, the study variation was 55%. It was hypothesized that there was insufficient consistency when positioning the thermocouple by eye roughly 5/8" from the edge of the mat. In addition, because of shifting or stretching of the non-woven materials (particularly the veil) in the laminate prior to the die, it was believed that the black mark on the surface of the laminate was not a sufficiently consistent means of timing the entrance of the thermocouple into the die. The exercise was therefore repeated with additional 8 runs at one location only. Again in these trials, 9 replicate measurements were obtained with three operators each making three measurements. However, three revisions were made to the measurement technique:

1. The exposed twisted junction was trimmed to the same length on each wire.
2. The wires were measured a fixed distance from the sensing junction to a reference point on the infeed, and marked with a piece of tape. Recording was initiated when the tape mark crossed the reference point on the infeed tooling.
3. A sheet metal gauge was fabricated to consistently locate the thermocouple 5/8" from the edge of the center mat. This was to improve the consistency of locating the sensing junction within the center of the channel flange.

These three revisions to the test method proved valuable, as the gauge error for peak position was reduced to 30%. This established the procedure as an acceptable gauge for peak position. However, the error for peak height was not improved. This necessitates the use of a "workaround gauge", wherein the % gauge variation can be reduced by the inverse of the square root of the number of replicate results averaged. Therefore, to cut the variation in half, it is necessary to average the results of at least 4 measurements. Nine replicates were averaged for the pultrusion trials in the DOE initiator study, though 4 would have been sufficient.

INITIATOR STUDY

A designed experiment was performed to optimize the levels of three peroxide initiator concentrations relative to peak exotherm (location and height), channel deflection, and cost. The three initiators, with their respective high and low concentrations, are listed below:

DOE Initiator Concentrations (pph based on resin)		
Initiator	High	Low
Di-(2-ethylhexyl)peroxydicarbonate; 75% assay ("A")	0.6	0.4
t-Amyl peroxy(2-ethylhexanoate); 95% assay ("B")	0.4	0.2
t-Butyl Peroxybenzoate; 98% assay ("C")	0.2	0.1

The goal was to match or improve upon the performance of a control formulation (incorporating a different initiator system) at minimum cost. The cost function is B>A>C. Table 1 contains the results of the die exotherm tests, full section deflection, DSC and SPI Gel data for all 8 combinations of A-B-C. Also listed are the control, and one follow-up formulation, which were predicted from the DOE analysis to be an optimum.

First, we attempt to correlate the die-exotherm data to the two most commonly used thermal analysis methods for thermoset polyesters: DSC and SPI Gel test. High pultrusion line speeds, (requiring high cure rates) are generally associated with early die peak exotherm position, as well as a low DSC onset temperature, and short SPI gel time. However, as Figures 3 and 4 reveal, it is found that with this dataset, no direct correlation can be drawn between the die exotherm peak position and either DSC onset temperature, or SPI gel time. This is implied by the degree of scatter in these X-Y plots. Similarly, there is no simple correlation between die exotherm peak

temperature and DSC peak temperature, SPI peak temperature, or DSC Delta H. In these cases, the scatter plots are excluded because they look very similar to those in Figures 3 and 4. Therefore, there is no simple relationship between these three thermal analysis techniques, though all three are commonly employed in the pultrusion industry as means of characterizing the cure reaction. The authors are aware that Vaughan et. al. [4] have used kinetic parameters extracted from DSC data to successfully model the die exotherm profile; however, this requires the execution of a numerical model, and is accurate only at relatively low pultrusion rates (up to 60"/min). The relationship is sufficiently complex that little comparison can be made on the basis of onset and peak temperature, or even Delta H data, alone.

While there is no simple relationship that can be drawn between these data sets, the DOE did show several strong dependencies that can be discussed. The DOE analyses are presented here in two formats: Pareto charts (with alpha=0.1, i.e. 90% confidence) and tabulated coefficients of the predictor equation (in coded units, i.e. +1 and -1 representing high and low concentrations respectively). When reading the Pareto charts, any bars that cross the dashed lines represent factors that are statistically significant at alpha=0.1. The largest bars represent the variable with the greatest significance. The coefficients, up to 3-way interactions, are listed in Table 2. These coefficients fit the equation shown at the top of Table 2. The larger the coefficient, the greater the effect. Positive coefficients have a positive effect on the parameter of interest when the product of the highs and lows is positive, and negative effect when the product is negative. The corollary is also true: negative coefficients reducing the effect when the product of [A][B][C] is positive. Any factors that fail the test for statistical significance are highlighted in Table 2.

Peak exotherm position in the die was most influenced by level of initiator B (Figure 5). It was also influenced by A and AB combinations. While it is somewhat accepted that higher levels of low temperature initiator (A) tend to have the greatest affect on moving the peak location towards the die entrance, this was not seen in this study. Possibly the variation in the level of A was too small to adequately effect a significant change. By contrast, DSC onset (Figure 6) was most strongly influenced by A, with high levels of A significantly reducing DSC onset temperature. B had a weak positive influence on onset temperature. The peak exotherm height

(Figure 7) does follow convention with a strong positive influence by initiator C (i.e., increasing C increases peak exotherm temperature). By comparison, DSC Delta H (Figure 8) is affected by all three initiators, with C making the strongest (and positive) impact on Delta H. While early die exotherm peak position is desirable, high peak temperature is most often undesirable. High temperatures have been associated with quality defects such as internal cracking and small (so called "popcorn") surface blisters. While high peak exotherm temperature is generally believed to be a necessary by-product of fast reactions (early peak position), this study suggests that an optimum balance between peak position and peak temperature is possible through selection of initiators. Minimizing C minimizes heat evolved and thus peak temperature, but has little impact on peak position.

Deflection data (Figure 9) was the most confounding. The DOE analysis suggested that all three initiators had a positive effect on deflection (i.e., higher levels of initiator leading to lower stiffness). The effect of A and B was weak, while the effect of C was strong. This result is completely counter intuitive; however, studying the run order (see Table 1: run order in the DOE is left to right, excluding the control) reveals that the pultruded sections from the first three successive runs all showed higher deflection than the rest. Therefore, we suspect a run-order dependency resulting from placement or orientation of reinforcements, which is generally recognized to have a much more significant effect on stiffness than does resin cure, unless the resin is grossly under cured. Unfortunately, these three runs all had high C, which would confound the DOE analysis relative to deflection if in fact, as suggested above, there was a more significant source of variation to be blamed for the high deflections. If however the data is valid (as the low residual error in the DOE analysis suggested), then it may be possible that secondary reactions occurring under high temperature conditions resulting from high C produce detrimental (lower stiffness) products. No experts in polyester chemistry could suggest any such chemical mechanisms, and therefore we reserve judgment until the results can be corroborated by a repeat study.

The DOE analysis would suggest that the combination of A]=H, [B]=H, and [C]=L makes the best selection (from within the region of concentrations studied) if the goal is earliest peak position with lowest

peak height. On the other hand, if the goal is to most closely match the performance of the control at minimum cost, then the H/L/L combination is suggested. Considering that B is the costliest of the 3, and that the influence of C on peak the high and low (0.3 pph) and C was eliminated entirely (zero). Table 2 shows that this combination resulted in the earliest peak position of any, moderate peak temperature, and low deflection (high stiffness). Unfortunately, the absence of C also resulted in low surface luster making the product rejectable.

CONCLUSIONS

It is found that the Die Exotherm Test can make a suitable gauge for formulation studies with acceptable error if care is taken to ensure consistency of thermocouple placement. The level of consistency required is greater than that generally observed by the authors to be common industry practice, and therefore we make the call for consistent practice in order to provide a platform for data comparison. Even at that, the error seen in peak temperature suggests that multiple runs (in this case at least 4) need be averaged in order to have confidence in the results. It is also found that there is no direct correlation between peak exotherm data and other thermal analysis techniques commonly employed by the industry: DSC and SPI Gel. Analysis of a DOE performed with 3 initiators at 2 levels reveals that die exotherm data can be used to optimize initiator formulations, and the analysis of DSC data also provides corollary information.

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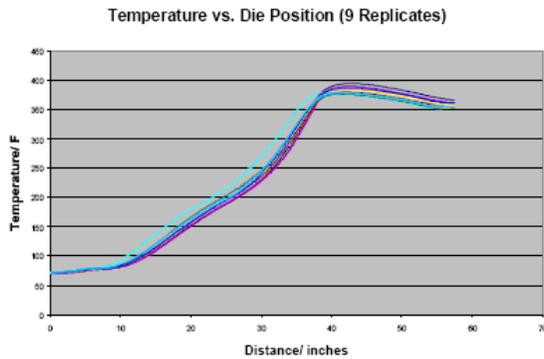
Figure 1.

Temperature vs. Die Position (9 Replicates)

Figure 2.

$$\% StudyVar = \frac{\sqrt{(repeatability)^2 + (reproducibility)^2}}{TotalVariation} \times 100$$

Where (*repeatability*) is the sum of squares within an operator

$$SS_W = \sum_{j=1}^{g} \sum_{i=1}^{n_j} \left(x_{ij} - \overline{x_j}\right)^2 ,$$

(*reproducibility*) is the sum of squares between operator subgro

$$SS_B = \sum_{j=1}^{g} n_j \left(\overline{x_j} - \overline{\overline{x}}\right)^2$$

and *TotalVariation* is the overall or total sum of squares

$$SS_T = \sum_{j=1}^{g} \sum_{i=1}^{n_j} \left(x_{ij} - \overline{\overline{x}}\right)^2$$

Wherein:

x = data point.
g = number of operators.
n = number of points for the respective operator.
$\overline{x_j}$ = the subgroup mean for the respective operator.
$\overline{\overline{x}}$ = the grand average.

Figure 3.

Die Exotherm Peak Position vs. DSC Onset Temperature

Figure 4.

Die Exotherm Peak Position vs. SPI Gel Time

Figure 5.

Pareto Chart of the Standardized Effects
(response is Peak Pos, Alpha = .10)

Figure 6.

Pareto Chart of the Standardized Effects
(response is DSC Onse, Alpha = .10)

Figure 8.

Pareto Chart of the Standardized Effects
(response is DSC Delt, Alpha = .10)

Figure 7.

Pareto Chart of the Standardized Effects
(response is Peak Ht., Alpha = .10)
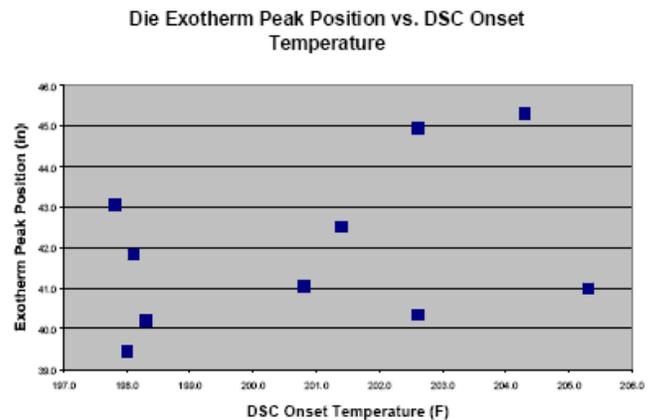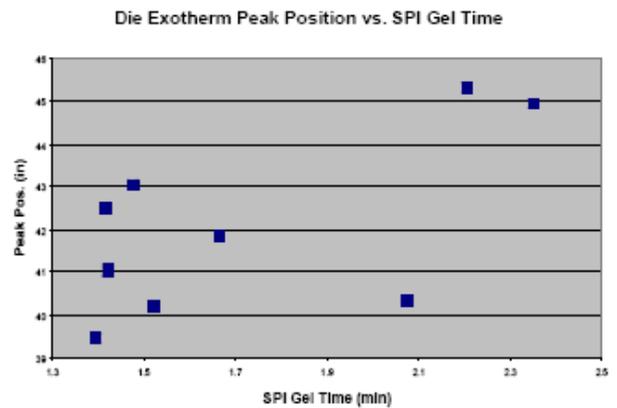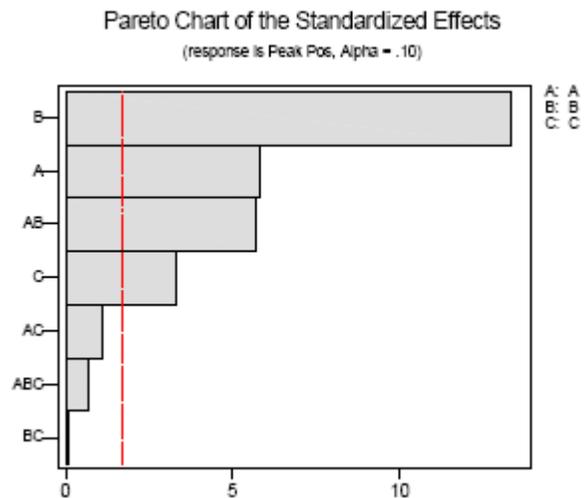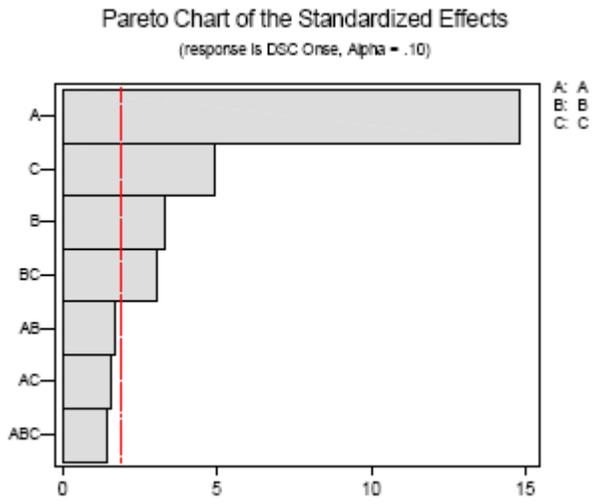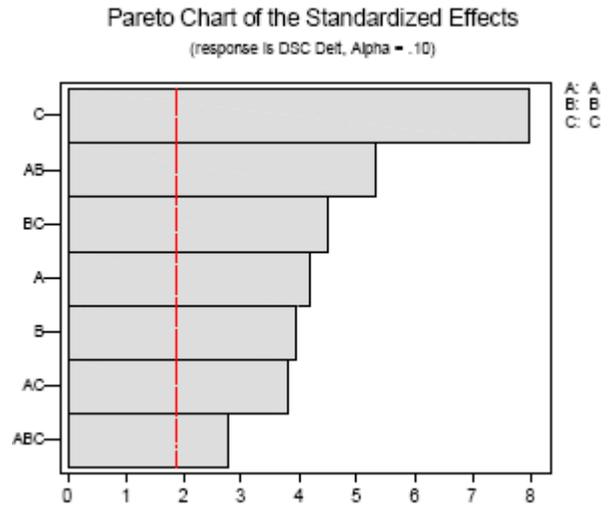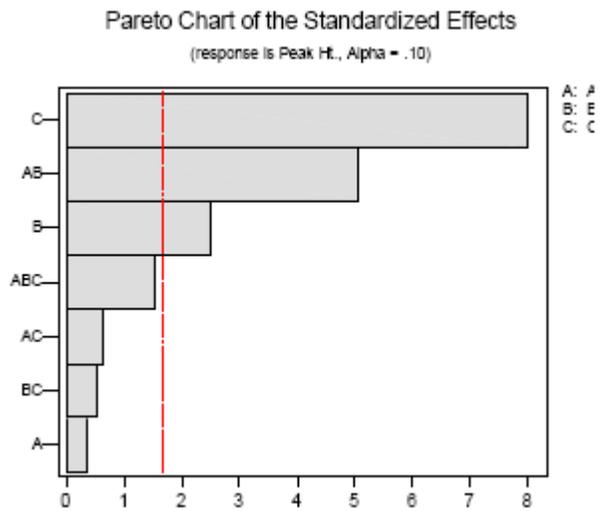
Table 1: Formulations and Data										
	Control	DOE								Follow-up
A		H	L	H	H	L	L	H	L	H
B		L	H	H	L	L	H	H	L	M
C		H	H	H	L	H	L	L	L	"0"
Deflection Data (in)										
Full-Section Deflection (in)	1.04	1.09	1.09	1.16	1.05	1.05	1.06	1.03	1.06	1.04
Thermocouple (Die Exotherm) Data										
Peak Height (^{o}F)	386	401	404	399	388	395	395	382	378	386
Peak Position (in)	42.5	41.8	40.4	40.2	43.1	45.0	41.0	41.1	45.3	39.5
DSC Data										
Onset (^{o}F)	201.4	198.1	202.6	198.3	197.8	202.6	205.3	200.8	204.3	198.0
Peak (^{o}F)	212.7	212.5	218.5	212.4	210.2	219.9	227.3	215.2	236.5	210.6
Delta H (J/g)	300.4	306.4	308.6	301.5	295.5	301.1	294.4	255.7	295.2	292.5
SPI Gel Data										
Gel time (min)	1.42	1.67	2.08	1.52	1.48	2.35	1.42	1.42	2.21	1.40
Total Time (min)	2.25	2.16	2.95	2.36	2.31	3.31	3.51	2.22	3.36	2.18
Peak T (^{o}F)	355.0	369.5	364.0	358.0	354.5	370.0	361.5	357.0	362.0	349.0

Table 2: Estimated Coefficients for the equation (Response=A[A]+B[B]+C[C]+A*B[A][B]+….) where [A], [B], [C] are in coded units (+1/-1)					
Response	Peak Position	Peak Height	DSC Onset	DSC Delta H	Deflection
Constant	42.23	392.62	201.17	294.79	1.074
A	-0.68	-0.33	-2.46	-5.04	0.009
B	-1.57	2.20	0.55	-4.77	0.010
C	-0.39	7.00	-0.82	9.61	0.025
A*B	0.67	-4.42	0.28	-6.42	0.026
A*C	-0.13	0.56	0.26	4.57	0.019
B*C	0.01	-0.48	-0.51	5.40	0.016
A*B*C	0.08	1.34	-0.24	3.32	0.007

    =factors which are not statistically significant