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Design of Experiment Study on Cure Reactivities of a BMC Material Effected by Temperature, Levels of Peroxides and Inhibitors

by

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Abstract

Understanding how levels of peroxides, inhibitors and temperature affect cure is essential to optimizing formulations and processes for unsaturated polyester systems. These variables were studied by utilizing factorial design of experiment techniques. A typical Bulk Molding Compound (BMC) with an isophthalic acid based unsaturated polyester formulation was used in studying cure and flow properties. The formulation is targeted for elevated temperature molding applications. Spiral flow and cure properties such as gel time, inflection time and peak temperatures were measured. Effects of peroxides, inhibitors and temperature on spiral flow and cure characteristics are discussed.

Introduction

Deep understanding of raw material properties and functions, their relationships to molding process and part quality is imperative to developing robust products and maintaining high productivities. This is especially true in peroxide and inhibitor applications since they have strong relationships to process quality and efficiencies. For Bulk Molding Compound (BMC) in either injection or compression molding, engineers strive to design a formulation with the right material properties as well as to tailor it to process conditions. One of the tasks in doing this is to select peroxides and inhibitors so as to allow BMC materials to have enough flow to fill part details while ensuring efficient cure. Judiciously designed materials and molding conditions based on experimentation will result in improved quality, less scrap, fast new product development and trouble shooting strategies.

Organic peroxides generate free radicals on heating. Radicals are energetic species that initiate reaction of double bonds in unsaturated polyester resin and vinyl monomers, such as styrene to form cross-linked and thermally stable thermosetting networks [1]. Material flow properties of a BMC compound are determined by many factors such as cure reactivity, the amounts and intrinsic properties of resin, monomer, filler, glass and other additives. Cure reactivity depends upon factors like peroxides, their levels, proportion of monomer, crosslink density of the unsaturated polyester resin, inhibitors, temperature, etc. This study focuses on how peroxides, inhibitors, their levels, and temperature determine material flow as well as cure reactivity.

Peroxyesters and peroxyketals are the two most common classes of peroxides used in BMC and Sheet Molding Compound (SMC) [2]. For elevated temperature cured systems, a blend of initiators is generally recommended to achieve a constant rate of radical generation during curing. The ideal blend would consist of a mixture of low and medium and/or high activation temperature catalysts. Low activation temperature peroxides decompose at the beginning of curing triggered by external heat. As curing progresses, exothermic heat generated from curing will trigger medium and high activation temperature catalysts to continue and finish the cross-link reaction. General selection guidelines for peroxides are based on half-life data or experience. Some researchers have studied peroxide pot lives and cure activities using different levels of peroxide blends [2 - 5].

Generally a small amount of inhibitors is added in BMC to prolong compound shelf life and prevent pre-cure during molding. Typical inhibitors are quinones and their derivatives. Inhibitors also modify BMC flow characteristics, cure rate and degree of exothermic heat.

Quantitative knowledge of how catalysts, catalyst levels, inhibitors, molding temperatures and their interrelationships in affecting flow and cure properties of BMC materials is empirical and scarce. In order to comprehend the complex multi-dimensional representations of these factors as a whole, Design of Experiment (DOE) technique is required. DOE is proven in applications that have multiple and interactive factors [6]. Fractional and full factorial designs are utilized for this study.

Experiments

Materials

A typical isophthalic acid based unsaturated polyester BMC formulation is used. Dry chopped strand glass fiber of ¼” length comprised 15% of the formulation. Alumina trihydrate (ATH) was the only filler. Variables included in the study are typical peroxides and inhibitors used for BMC. Their loading levels are in parts-per-hundred resin (PHR). They are:

1. *tert*-Butyl peroxy-2-ethylhexanoate (TBPO). Trade names are: Trigonox 21C50, Luperox 26M50, etc.

2. 1,1-Di-(*tert*-amylperoxy)cyclohexane (TACH) Trade names are: Trigonox 122C80, Luperox 531M80, etc.
3. *tert*-Butyl peroxybenzoate (TBPB)
4. Butylated hydroxytoluene 40% (BHT)
5. para-Benzoquinone 5% (PBQ)
6. mono-*tert*-Butyl hydroquinone (TBHQ)25–30%

Instruments and Measurements

All experimental compounds were mixed in a laboratory Z blade mixer on a scale of 10 lb per batch. One compound batch is made for each experimental formulation. All responses are measured in triplicate. Material flow property is measured by molding BMC in a spiral flow mold installed in a transfer molding press. A specified weight of a compound is used in the spiral mold of ½” flow path. Reported flow length is measured in inches after the spiral part is demolded. Cure reactivity was tested on a CurePhase Dielectric Measurement System (DEA). A dielectric sensor is mounted on a 4” diameter compression mold. Two responses obtained from this test are gel time and inflection time. Both are measured in seconds. Inflection time is when curing is at its fastest rate. DEA can be run at different molding temperatures. Peak temperature is measured by a modified SPI Gel Test, in which compound is used as sample [7]. A typical compound was packed tightly in a test tube. A 1/8” diameter thermocouple probe was inserted into the middle of the compound. The test tube is placed in a high-temperature bath with a specified temperature setting. After the internal temperature of the compound reaches 150ºF, a timer will start. Temperature is recorded vs. time in minutes. Peak temperature is defined as the highest material internal temperature during cure. SPI gel time and interval time are another two responses obtained by the same test. SPI gel time is when the compound temperature reaches 10ºF degree higher than the bath temperature. Interval time is defined as the difference between peak time (time to reach the peak temperature) and SPI gel time. SPI test can be run at different temperatures.

Results and Discussions

Design of Experiment Study I

The purpose of this first design is to screen the most important factors in determining compound flow and cure properties. Design details of the experiment are shown in Table 1. Spiral flow and DEA were run at a constant temperature of 340ºF. This is a 2^{5-1}_{V} fractional factorial design with 5 factors, 2 levels, 16 experiments and resolution V [8]. SPI tests were conducted at 285ºF and 300ºF to study temperature effects.

Spiral flow and DEA results as measured in flow length, gel time and inflection time are summarized in Figure 1. Figure 2 shows the SPI test for SPI gel time, interval time and peak temperature. Figure 2 also includes a temperature variable. High slope in the graphs indicates greater impact of a factor on properties. The largest slope graphs in Figures 1 and 2 indicate catalyst TBPO is the most important factor in spiral flow and reactivity. It reduces flow, increases cure reactivity and reduces peak temperature. Bath temperature in the SPI test is also significant in SPI gel time and peak temperature. External bath temperature reduces gel time and increases peak temperature but is insensitive to SPI interval time. The next important factor is TACH for all responses except peak temperature. TBPB and BHT inhibitor did not show significance in this experiment except TBPB reduces peak temperature. This implies that TBPB is not effective in accelerating gel time and inflection time when TBPO and TACH are used. It may affect final cure time.

The next step is to study two-catalyst system and include the temperature variable for DEA. Catalysts TBPO and TACH are selected. Inhibitor BHT is fixed at a constant level.

Design of Experiment Study II

The purpose of this study is to understand how catalysts, inhibitors and temperature in a two-catalyst formulation affect cure and flow. Another goal is to compare two typical inhibitors, PBQ and TBHQ. Design details for factors and responses are listed in Table 2. Though the PHR levels for the two inhibitors are different, their effective concentration is about the same. Spiral flow, gel time, inflection time and peak temperature are the responses. Spiral flow was run at 340ºF. DEA test was run at 290 and 310ºF molding temperature. Peak temperatures are obtained by SPI test at 290 and 310ºF temperatures. For the spiral flow test this is a 2^{4}_{V} full factorial design with 4 factors (Inhibitor, inhibitor level, TBPO, TACH) 2 levels, resolution V and 16 experiments. For cure reactivity this is a 2^{5}_{V} full factorial design with 5 factors (all above plus temperature), 2 levels and 32 experiments. There are 16 compound mixes.

Spiral Flow Results

The spiral flow results are depicted in a variability chart in Figure 3. The left half of Figure 3 is for PBQ inhibitor formulations, and the right half is for TBHQ. Changes in spiral flow from one red box to another are affected by TBPO. Green boxes within red show spiral flow change due to TACH when TBPO is constant. Blue lines indicate changes caused by inhibitor level when both catalysts are constant. Combined DOE Least Square Fit analyses of Pareto Parameter Estimate and Interaction Plots have given results that can be summarized as follows:

1. In both inhibitor systems, TBPO is a significant factor when molding temperature is constant. The higher concentration of TBPO, the shorter the flow is.
2. TACH and its interaction with TBPO are the next important factors. An interaction plot is shown in Figure 4. When TBPO is low (red line), an increase of TACH loading decreases the spiral flow. However when TBPO is at high levels (blue line), the loading change for TACH does not affect spiral flow as much.
3. High PBQ levels result in long spiral flow, especially when TBPO is at low level. There are slight differences between the two inhibitors when TACH is at its high level. In this case PBQ is able to increase spiral flow. However TBHQ has very little influence on increasing spiral flow. The interaction plot of TACH and TBHQ in Figure 5 explains the above discussion.
4. An interactive 3-D contour graph can be drawn readily once DOE data is available. DOE prediction power is demonstrated in Figure 6 of such a graph. If a spiral flow of 35 inches is desired, for example, any combination of TBPO and TACH levels within the white band of the graph in Figure 6 is satisfactory. Inhibitor level is also included in the consideration. When inhibitor level is changed, the location of the white band changes. In short, DOE technique is able to provide versatile factor setting ranges to achieve a desired value in a response. Prediction power is one of the advantages DOE strategies have over the One-Factor-At-A-Time experiment technique.
5. Another approach to prediction is applying the mathematical models developed based on the experimental data. In order to verify the accuracy of the model, spiral flow predictions were made and compared to measured data. Green dots in Figure 7 represent predictions and black dots represent the three repeat measurements. They correlate very well.

Gel Time Results

Results for Gel Time are depicted in a variability chart in Figure 8. The description of the chart is similar to spiral flow. DOE analysis results can be summarized as follows:

1. TBPO is the most significant factor in determining Gel Time. The next import factors are molding temperature and TACH level. For the experimental inference space defined here, approximately a one second reduction in gel time can be achieved by either a 0.16 PHR increase in TBPO level or a 3ºF increase in molding temperature. In other words, controlling the mold temperature within ± 3ºF is as critical as controlling the TBPO level within ±0.16PHR.
2. There is an interaction between two catalysts that affects gel time. Figure 9 graphically describes the relationship. Catalyst TACH has a stronger effect on gel time when TBPO level is low than when TBPO level is high. This could have been caused by reaching a saturation level in total catalyst concentration.
3. PBQ inhibitor increases gel time as observed in Figure 8. PBQ has an interaction with TBPO as seen in Figure 10. PBQ has a stronger impact on gel time when TBPO is low (red line with higher slope) than when TBPO is at a high level. TBHQ inhibitor does not greatly increase gel time.
4. The prediction model developed was confirmed by the consistency between calculated and tested data. Figure 11 shows the data points predicted in green and experiment in black.

Inflection Time Results

DOE analysis results for inflection time are similar to those for gel time. Figure 12 illustrates the results in a variability chart.

1. TBPO is the most significant factor. The next important factors are molding temperature, TACH level and interaction between two catalysts. Similar to gel time, catalyst TACH has a stronger effect on inflection time when TBPO level is low than when the TBPO level is high.
2. PBQ increases inflection time more than TBHQ for long inflection time formulations. In other words, when either TBPO or temperature is high, PBQ does not affect inflection time very much. TBHQ effect on inflection time is insignificant in all situations.
3. The magnitude of the effects that peroxide catalysts and inhibitors have on gel time and inflection time are quite similar. Controlling gel time and inflection time independently by manipulating catalysts or inhibitors is not attainable in this system especially if a combination of long gel and short inflection time is desired.
4. The DOE prediction model developed was confirmed by close correlation between calculated and experimental data.

Peak Temperature Results

Peak temperature is directly related to internal heat generated and the reaction kinetics when curing. This is an important factor to consider in balancing mold temperature, catalysts and inhibitors to minimize internal cracking of thick parts. Figures 13 and 14 describe the relationship of peak temperature and all variables for PBQ and TBHQ systems, respectively. Figure 15 shows the variability chart.

1. Catalyst TBPO is significant in regards to peak temperature. TBPO reduces internal heat.
2. High mold temperature results in high peak temperature.
3. Both inhibitors increase peak temperatures.
4. Catalyst TACH does not affect peak temperature in PBQ systems. However TACH is more likely to increase peak temperature for TBHQ systems.
5. The prediction model developed was confirmed by the correspondence of calculated and experiment data shown in Figure 16.

Conclusions

The studies show that DOE techniques can be successfully used to understand how peroxides, inhibitors and temperature quantitatively affect flow characteristics and cure reactivities of BMC compounds. Interactions between different peroxides and between peroxides and inhibitors are reviewed. Prediction power is another result that only DOE can offer when multiple factors are changing at the same time. Using the traditional One-Factor-At-A-Time technique, it is difficult or impossible to learn about interactions. Using the Trial-and-Error approach does not foster learning and thus knowledge is not gained. In short DOE techniques make understanding complex relationships between factors and responses possible.

In summary the major findings are: 1.) TBPB may not be effective in BMC flow and gel time when TBPO and TACH are used. 2). TBPO is the most sensitive factor in spiral flow and cure. It reduces peak temperature. 3). Temperature has strong impacts on curing properties. 4). It is common to see interactions between TBPO and TACH. TACH is more significant when TBPO is low. 5). The effects of inhibitors and differences in performance between PBQ and TBHQ are situation dependent. Both inhibitors increase peak temperatures. PBQ increases flow and TBHQ does the same only when TACH is at low level. PBQ increase gel time especially when TBPO is low. TBHQ has much less effect on gel time.

Technologies for monitoring cure progress in manufacturing molds are readily available [9-10]. Laboratory scale test results can be directly correlated to manufacturing molding productivities and part qualities when such technologies are applied on both laboratory and manufacturing molds. It is advantageous to use DOE techniques in a manufacturing environment to comprehend the intricate relationships among productivity, part quality, raw material selections and molding process control parameters. Experiments, such as those presented here, provide a vast amount of knowledge and a foundation to optimize entire product operating systems consisting of formulations and molding processes to achieve maximum productivities.

Acknowledgements

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Table 1. Design Details of Experiment Study I

Variables	Low level PHR	High level PHR	Responses
TBPO	0	1	Spiral Flow (inch)
TACH	0.5	1.5	Gel Time (sec) and Inflection Time (sec) by DEA
TBPB	0	1	
BHT	0.1	0.3	
PBQ	0	0.3	
SPI Test Temperature	140 ºC	150 ºC	SPI Gel Time, Interval Time and Peak Temperature

Figure 1. DEA and Spiral Flow Results Prediction Profiler for DOE Study I

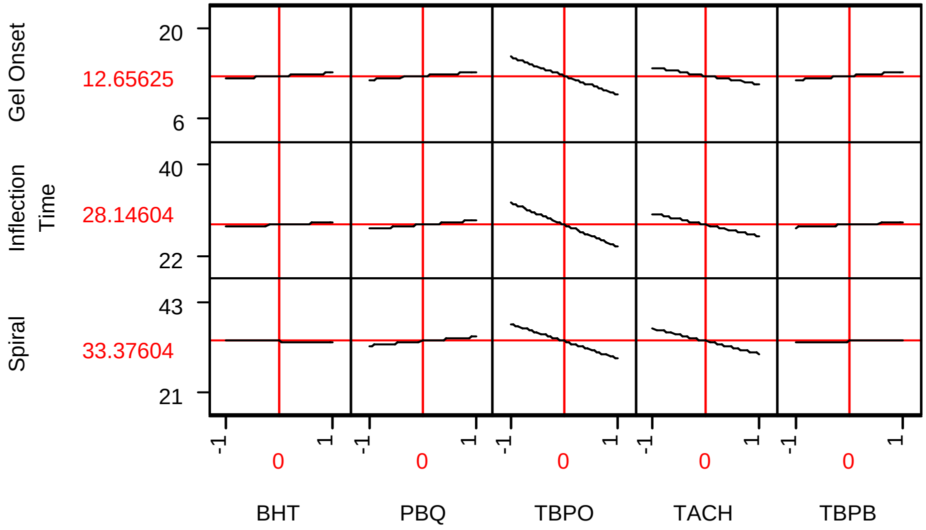


Figure 2. Prediction Profiler for DOE I SPI Peak Temperature Results

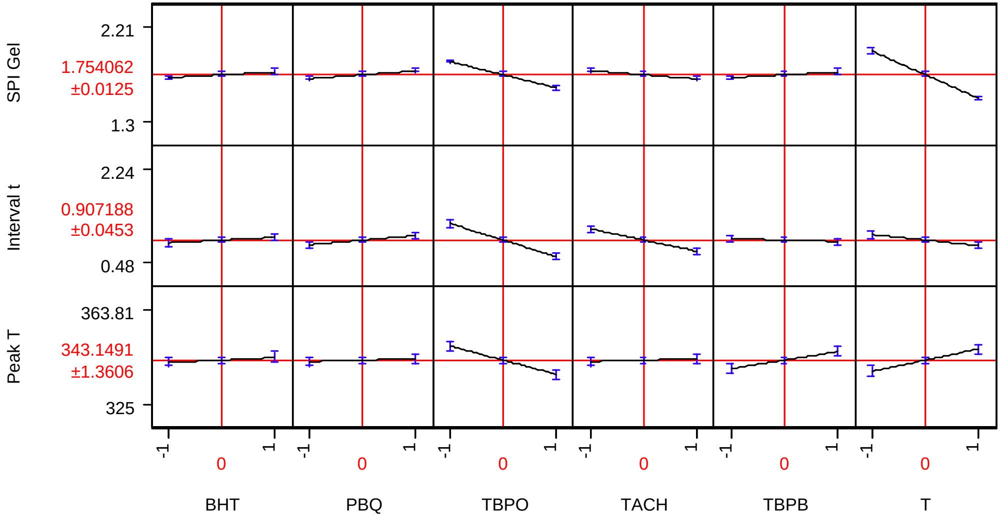


Table 2. Compound Formulation For Design of Experiment Study II

		Design Levels				Quantities in PHR				Responses
Run #	Pattern	PBQ	TBHQ	TBPO	TACH	PBQ	TBHQ	TBPO	TACH	
1	---+	-1		-1	1	0.00		0.00	2.00	Spiral Flow at 340 ºF
2	-+-+	1		-1	1	0.30		0.00	2.00	
3	--++	-1		1	1	0.00		1.50	2.00	
4	--+-	-1		1	-1	0.00		1.50	0.50	Gel Time, Inflection Time by DEA and Peak Temperature by SPI Gel test are run at two temperatures of 290 and 310 ºF
5	----	-1		-1	-1	0.00		0.00	0.50	
6	-++-	1		1	-1	0.30		1.50	0.50	
7	-+++	1		1	1	0.30		1.50	2.00	
8	-+--	1		-1	-1	0.30		0.00	0.50	
9	+--+		-1	-1	1		0.00	0.00	2.00	
10	++-+		1	-1	1		0.05	0.00	2.00	
11	+-++		-1	1	1		0.00	1.50	2.00	
12	+-+-		-1	1	-1		0.00	1.50	0.50	
13	+---		-1	-1	-1		0.00	0.00	0.50	
14	+++-		1	1	-1		0.05	1.50	0.50	
15	++++		1	1	1		0.05	1.50	2.00	
16	++--		1	-1	-1		0.05	0.00	0.50	

Figure 3. Variability Chart on Spiral Flow For DOE Study II

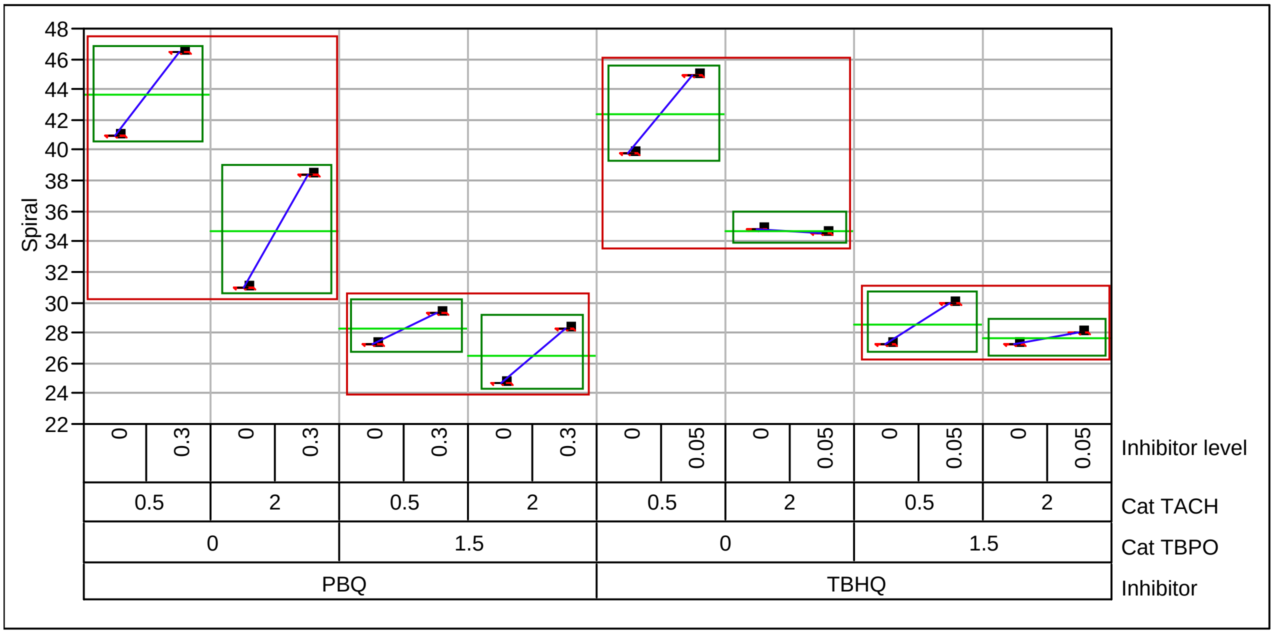


Figure 4. Spiral Flow Vs. TBPO and TACH Level

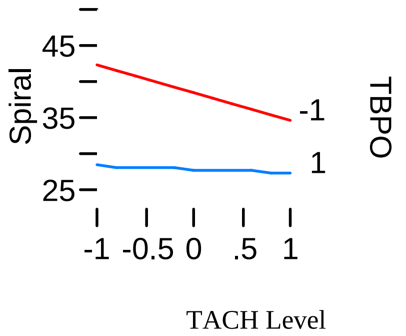


Figure 5. Spiral Flow Vs. TBHQ and TACH Level

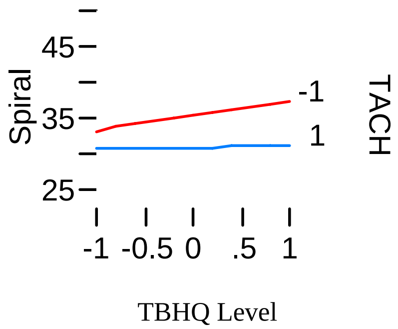
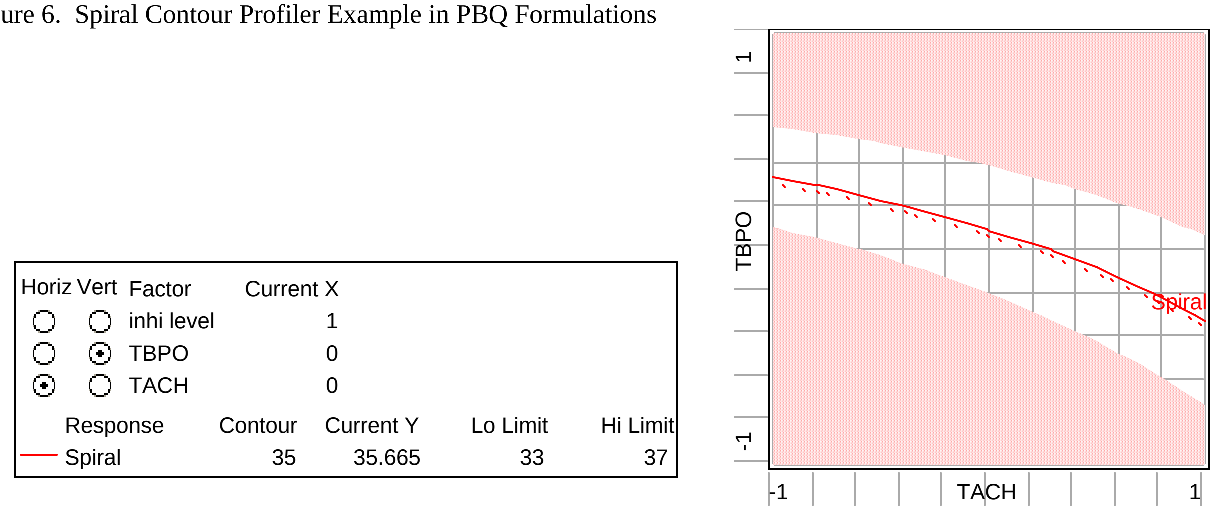


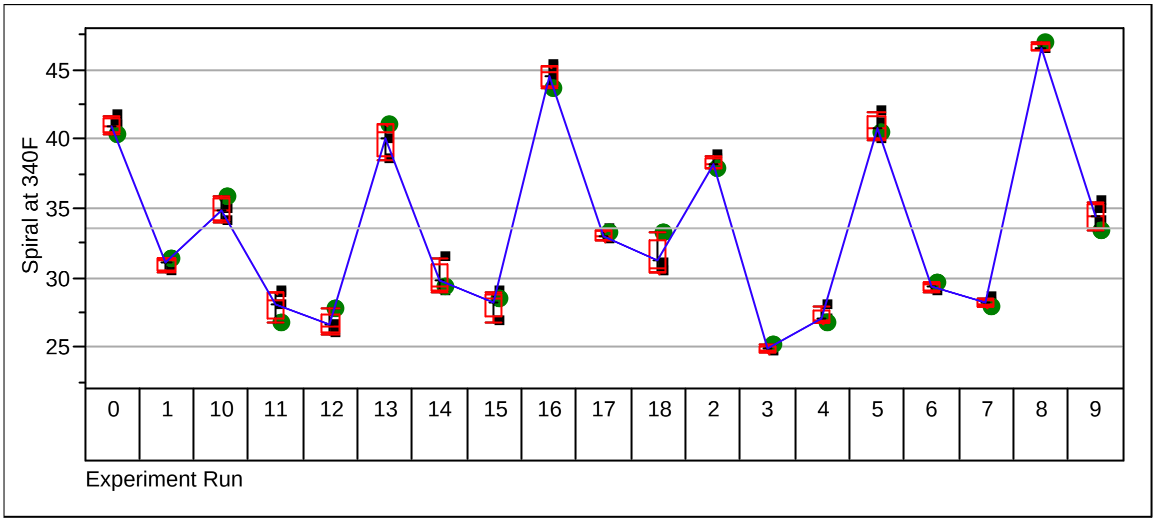
Figure 6. Spiral Contour Profiler Example in PBQ Formulations



Horiz	Vert	Factor	Current X
○	○	inhi level	1
○	●	TBPO	0
●	○	TACH	0

	Response	Contour	Current Y	Lo Limit	Hi Limit
—	Spiral	35	35.665	33	37

Figure 7. Spiral Flow Tested Data (Black Dots In Red Boxes) Compared To Predictions (Green Dots) by DOE II Model



*(The green data points are predictions based on the DOE model)

Figure 8. Variability Chart on Gel Time For DOE Study II

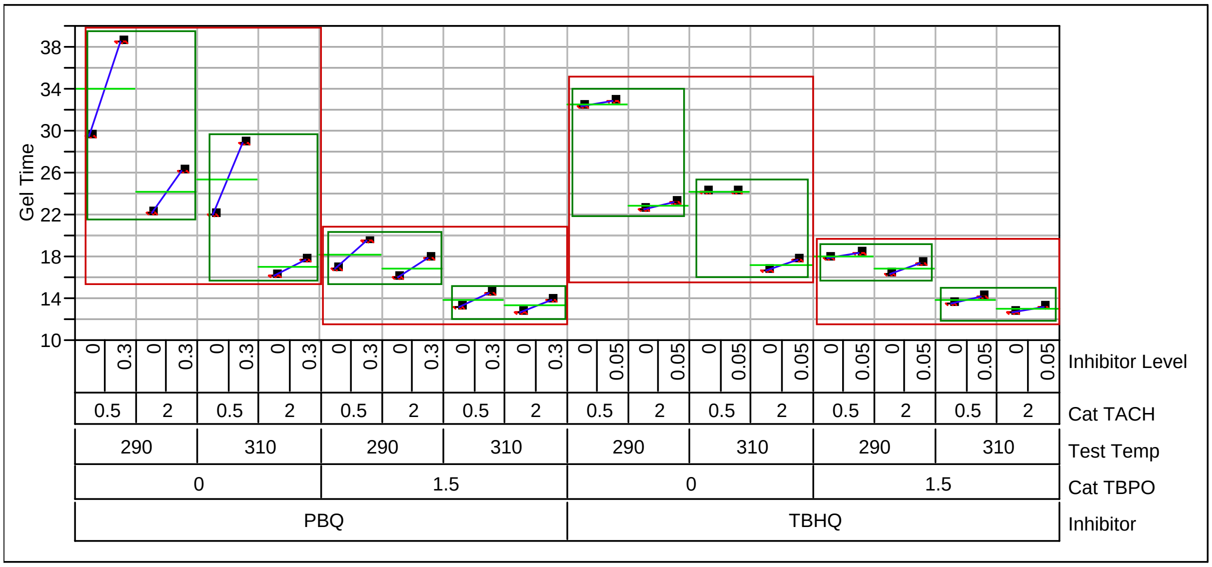


Figure 9. Gel Time Vs. TBPO and TACH Level

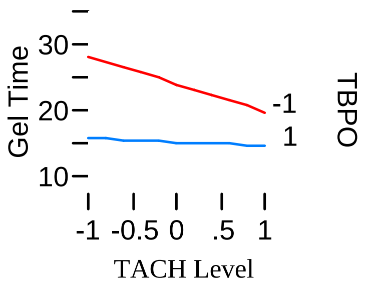


Figure 10. Gel Time Vs. TBPO and PBQ Level

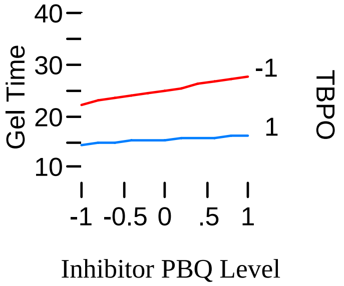


Figure 11. Gel Time Tested Data (Black Dots In Red Boxes) Compared To Predictions (Green Dots) by DOE II Model

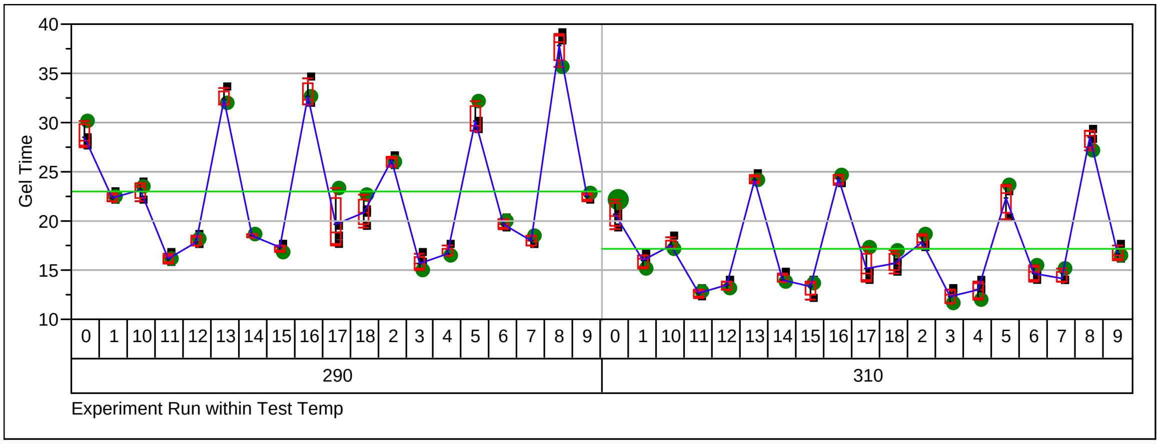


Figure 12. Variability Chart for Inflection Time Results

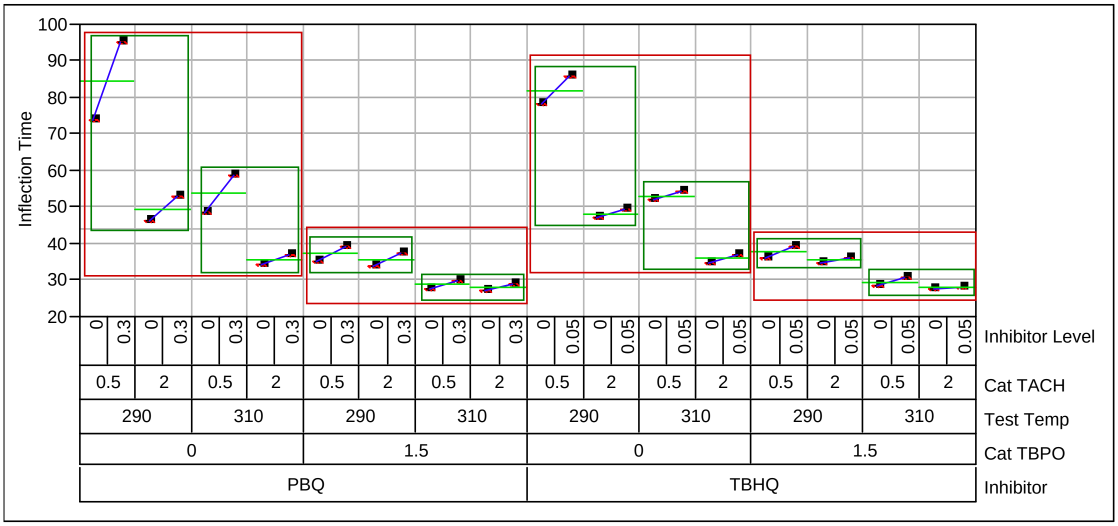


Figure 13. Prediction Profiler on Peak Temperature for PBQ System

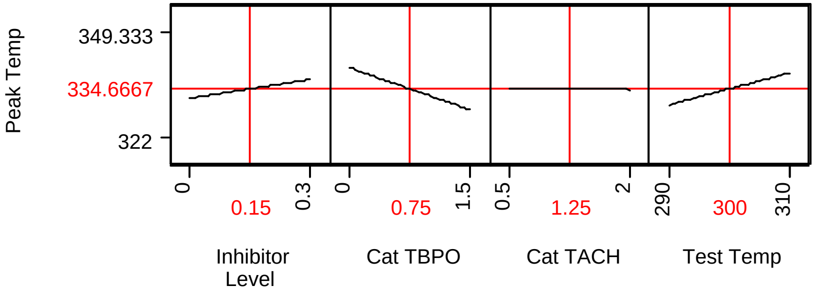


Figure 14. Prediction Profiler on Peak Temperature for TBHQ System

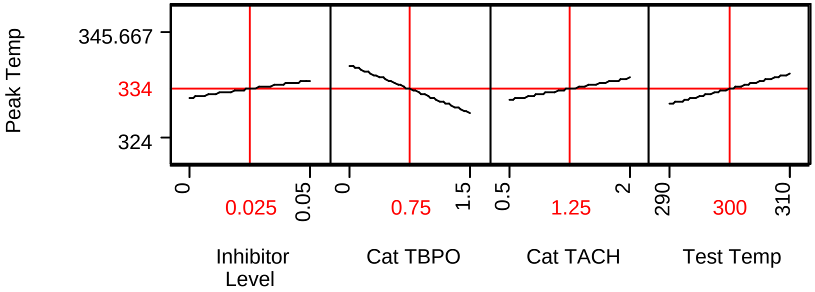


Figure 15. Variability Chart for Peak Temperatures

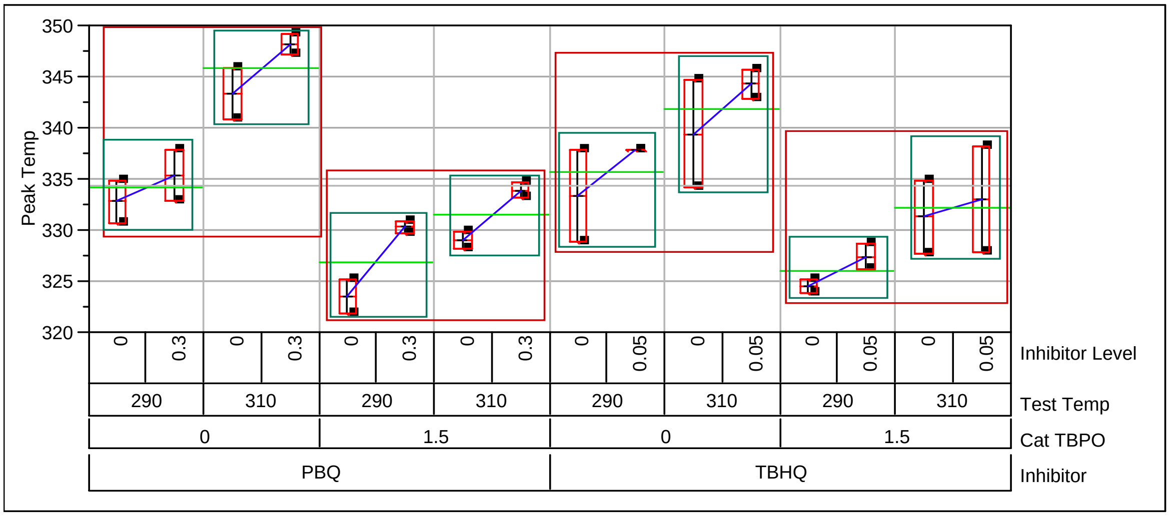


Figure 16. Peak Temperature Tested Data (Black Dots) Compared To Predictions (Green Dots) by DOE II Model