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A statistical approach for adjusting the gel time and cure properties of high-performance unsaturated polyester resins

Abstract

The objective of this study is to demonstrate the use of statistics in a four-variable experiment (initiator, promoter, copromoter and inhibitor) to obtain desired gel time and Barcol hardness properties for high-performance unsaturated polyester resins. Two different levels of investigation will be presented: The "starting from scratch" method and the "short-cut" method. The principal benefit of this statistical approach is that the experimenter will obtain a broader knowledge or a more general "feel" for the cure properties of a resin rather than the less useful "specific answer to a specific question."

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A statistical approach for adjusting the gel time and cure properties of high-performance unsaturated polyester resins

The Fiberglass Reinforced Plastics Industry (FRP) has advanced greatly since its early days. The original propylene glycol/ orthophthalic resins have been used in many different market areas. However, as the demands placed on the general-purpose resin became more severe, the performance properties of unsaturated polyester resins had to improve. The consumer asked for better corrosion resistance, weatherability, flexibility and hydrolytic stability than the standard general-purpose resin could provide. This demand prompted the development and commercialization of high-performance resins.

The improved properties of high-performance resins are related to their chemical structure. The more steric hindrance introduced into the polymer backbone, the better its corrosion resistance. Fewer beta-hydrogens or ether linkages result in better weatherability. However, "What is offered with one hand can be taken with the other hand" is a statement that is very appropriate. The same chemical structure changes that provide the desired performance properties can alter the cure properties of a resin. The challenges that today's resin chemist must meet are to provide a reliable cure system for the high-performance unsaturated polyester resin and to define the operating limitations for that system.

Experimental details

In each study, a single batch of resin was used. The resins were based on Eastman TMPD™ glycol (TMPD™/PG/ IPA/MA) and Eastman NPG™ glycol (NPG™/IPA/MA). Both resins were initially inhibited with 100 ppm hydroquinone, which was carried through the entire study and was part of the final cure system. A 6% Co (cobalt octoate) solution and Lupersol DDM-9 MEKP (methyl ethyl ketone peroxide) were used. All the inhibitor and copromoter solutions were used as 10% solutions in Eastman™ TEP (triethyl phosphate).

Each cure experiment was run on a 100 gram sample of resin, which was divided in two aliquots after the addition of the four-component cure system. These two samples provided a 50 gram Sunshine gel time evaluation and a 50 gram Barcol hardness evaluation from a 1/8-in casting. The Barcol hardness reported was the average of five readings. The temperatures at the sites of the gel time and Barcol hardness testing were recorded and evaluated as uncontrollable variables for each study.

The "starting-from-scratch" method

This process would be the method of choice with a high-performance resin requiring a totally new cure system. The target for this study was to develop a cure system for a specific Eastman TMPD™/ISO resin that gives a gel time of approximately 35 minutes and a 2.5 hour Barcol hardness of at least 15 for a 1/8-inch casting. It was assumed that the cure system had to be based on Co and MEKP to have general acceptance by the FRP industry. Therefore, the first step was to perform a two-by-two statistically designed experiment with the Co and MEKP variables. Figures 1a and 1b show the results of this work.

The first conclusion from this data is that the desired cure properties cannot be obtained with the simple two-component system. In fact, while the desired gel time of 35 minutes was reached (see Figure 1a), none of the cure systems showed a measurable 2.5 hour Barcol hardness (see Figure 1b). The only indications for possible acceptable cure were the 168 hour Barcol hardness readings. Since the differences in the 168-hour responses were insignificant, the center point values of 0.5% Co and 1.0% MEKP were chosen for the next level of analysis.

Figure 1a Gel time, minutes

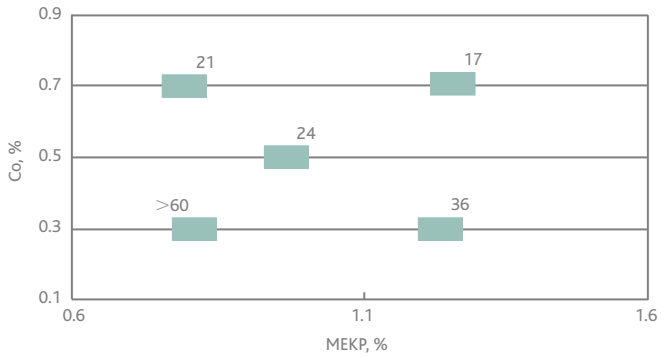
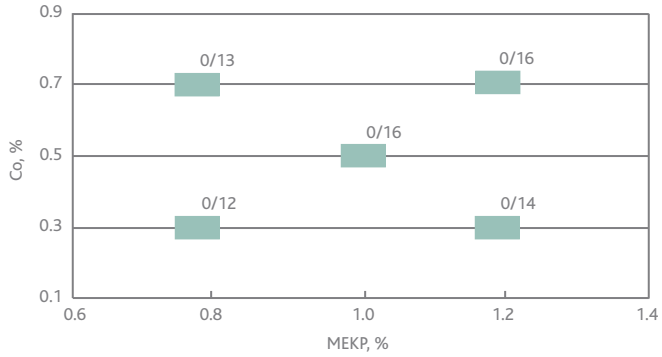


Figure 1b 2.5/168-hour Barcol hardness



From these initial results, it was necessary to choose between two very different paths — the choice between investigating the inhibitor or investigating the copromoter. Since the first part of this work demonstrated that the desired gel time was achievable, the more difficult 2.5-hour Barcol hardness property was pursued; therefore, copromoter was the next variable investigated. The following copromoters were evaluated at various levels with the above stated levels of Co and MEKP held constant: Eastman™ DMAA (dimethylacetoacetamide), Eastman™ EAA (ethyl acetoacetate), Eastman™ MAA (methyl acetoacetate), Eastman™ AAA (acetoacetanilide), DMA (dimenthylaniline), and PDEA (pheny-idiethanolamine). A total of 17 experiments were performed during the copromoter selection stage. Table 1 shows some of the more pertinent results.

Table 1 **Copromoter selection***

Copromoter	Gel time, minutes (GT)	Time to peak exotherm, minutes (TPE)	Peak exotherm temperature, °F (PET)	Time, hours to Barcol hardness of 15
Eastman™ EAA	12	7	295	>30
Eastman™ MAA	10	12	336	>30
PDEA	5	6	310	>24
DMA	3	4	346	1.3
Eastman™ DMAA	4	6	361	<1

**All of the experiments reported in this table used Co, MEKP, and copromoter at 0.5%, 1.0%, and 0.5% respectively.*

Based on this data, copromoters DMA and DMAA were selected due to their ability to give acceptable 2.5-hour Barcol hardness. The need now was to maintain this Barcol hardness while stretching the gel time back out to the desired 35 minutes using an inhibitor.

The following inhibitors were evaluated at various levels with the copromoter (DMA or DMAA) held at 0.5%, and the Co and MEKP held at the previously chosen levels of 0.5% and 1.0%, respectively: Eastman™ HQ (hydroquinone), Eastman™ THQ (toluhydroquinone), Eastman™ MTBHQ (mono-t-butylhydroquinone) and Eastman™ DTBHQ (di-t-butylhydroquinone). A total of 52 experiments were performed during this stage of the study. Table 2 shows some of the more pertinent results.

Table 2 Inhibitor selection*

Copromoter	Gel time, minutes (GT)	Time to peak exotherm, minutes (TPE)	Peak exotherm temperature, °F (PET)	Time, hours to Barcol hardness of 15
DMAA at 0.5%:				
Eastman™ HQ	55	8	283	>24
Eastman™ THQ	38	7	330	1 – 3
Eastman™ MTBHQ	37	6	295	>24
Eastman™ DTBHQ	8	8	331	<1
DMA at 0.5%:				
Eastman™ HQ	>60	—	—	>24
Eastman™ THQ	>60	—	—	>24
Eastman™ MTBHQ	55	13	296	>24
Eastman™ DTBHQ	15	24	196	>24

**All of the experiments reported in this table used Co, MEKP, and copromoter at 0.5%, 1.0%, and 500 ppm respectively.*

The final selection of copromoter and inhibitor for the four-component system under study was DMAA and THQ. The second choice combination was DMA and HQ. Examination of the data in Table 2 shows that the target value was achieved. We now have a specific cure package that we know will perform adequately with this resin system. However, a statistically designed experiment is required to define the performance boundaries for the Co/ MEKP/ DMAA/ THQ cure system.

The experimental design chosen for this four-variable cure system was a four-by-four matrix (16 experiments) with eight star points (8 experiments) and center points replicated eight times (8 experiments). This resulted in a total of 32 experiments conducted over a period of four days. Two center point and two satellite experiments with four matrix experiments were done each day. The center point experiments were performed at the beginning and end of each day to show the variability of the system. The levels of the variables used are shown in Table 3:

Table 3 Variable levels

	Low	Center point	High
Co, %	0.4	0.5	0.6
MEKP, %	0.9	1.0	1.1
DMAA, %	0.4	0.5	0.6
THQ, ppm	350	500	650

The responses evaluated were gel time (GT), time to peak exotherm (TPE), peak exotherm temperature (PET) and hours to a Barcol hardness of 5 (BH5), 10 (BH10), 15 (BH15), 20 (BH20), 25 (BH25) and 30 (BH30). Barcol hardness readings were recorded to a maximum of 24 hours. A mathematical combination for the total Barcol hardness from BH5 to BH30 was also determined. This term, BHALL, is an indication of the overall Barcol hardness reached for each experiment.

Regression analysis was used to interpret the data. The use of this statistical technical allowed this complex four-variable system to be analyzed. Statistical Analysis Systems (SAS) from a main frame computer was used to analyze the data. Other software programs for use on personal computers are being evaluated and should be applicable.

The degree and direction (positive or negative effect) of influence for each variable of the cure system were determined. A positive effect for a variable indicated that an increase in the variable (i.e. THQ) increase the corresponding response (i.e. GT). Table 4 summarizes the degree and direction of the variable influence for the main responses of interest.

Examination of these results provides the following preliminary conclusions within the variable limits of the experiment:

1. Co has a major effect on all of the main responses. It appears that the addition of Co shortens the GT while accelerating the cure — a normally undesirable response. The desired effect is to shorten the cure without extending or shortening the GT.
2. MEKP has an insignificant effect on all the main responses.
3. DMAA has a major effect on the Barcol hardness properties and an insignificant effect on GT. This implies that the addition of more DMAA will decrease the cure time without affecting the GT.
4. THQ has a major effect on GT and minor effect on the Barcol hardness properties. This is not the ideal situation, but a response in the right direction.

While it appears that the desired general trends have been identified, examining the data more closely reveals an imbalance of data points for the Barcol hardness response. The vast majority of the Barcol hardness readings are less than ten hours. Therefore, the study was repeated with the variable limits shifted to obtain a better balance of Barcol hardness readings. This stage of the study indicated the following changes were needed to obtain an increase in desirable Barcol hardness readings:

1. Co was increased slightly to assist in obtaining the desired overall Barcol hardness.
2. The usage range for MEKP was expanded slightly to ascertain the effect of this variable with a wider level of MEKP concentrations.
3. The level of DMAA was increased the most because it appeared to be specific for the Barcol hardness property.
4. The THQ level was increased slightly to counteract the effect of the Co increase, thus attempting to maintain the GT at the desired 35-minute target.

Table 4 **Degree of variable influence on responses**

Response	Major	Minor	Insignificant
Gel time (GT)	Co (−),THQ (+)	—	MEKP, DMAA
Time to peak exotherm (TPE)	Co (−)	THQ (+), DMAA (−)	MEKP
Peak exotherm temperature (PET)	No statistically significant model for this response		
Barcol hardness all (BHALL)	Co (−), DMAA (−)	—	MEKP, THQ
Barcol hardness (BH15)	Co (−), DMAA (−)	THQ (+)	—
Barcol hardness (BH20)	DMAA (−), Co (−), MEKP (−), DMAA (−), THQ (+)	Co (−), THQ (+)	MEKP

These changes led to the variable limits for the second statistically designed experiment shown in Table 5.

The design and experimental execution for the second stage of this study were identical to the first stage. SAS analysis was again used to interpret the data. Table 6 summarizes the degree and direction of variable influence on the main responses of interest.

Preliminary examination of these results showed that the number of usable Barcol hardness readings had increased from 17% to 60%. This provided a good balance of Barcol hardness readings to define the "operating window" for the cure system. The trends identified for the variables were:

1. Co and MEKP shared a nearly equal status as being a major influence on all of the main responses. The only exception was GT, in which MEKP had a minor effect while Co had a major effect. This indicated that an increase of MEKP would increase the cure of the resin more than it would decrease the GT, while the same increase in Co would probably decrease the GT to a greater extent.
2. As in the first stage of the study, DMAA was still the most effective way to increase the Barcol hardness cure without affecting the GT.
3. THQ appeared to be the only component that would allow the increase of the GT without having a major effect on the cure. It should be noted that this is not the ideal solution because THQ does still have a minor effect on cure.

This statistical approach to problem-solving offers the experimenter the option to use the mathematical models generated to predict the responses obtained within the variable limits of the experiment. The last part of this statement "within the variable limits of the experiment" is most important. The prediction models are generated from the experimental responses which were bracketed by the variable limits; therefore, the models are only good within these limits.

Table 5 Variable limits

	Low	Center point	High
Co, %	0.5	0.6	0.7
MEKP, %	0.85	1.0	1.15
DMAA, %	0.6	0.7	0.8
THQ, ppm	500	600	700

Table 6 Degree of variable influence on responses

Response	Major	Minor	Insignificant
Gel time (GT)	Co (−)	MEKP (−), THQ (+)	DMAA
Time to peak exotherm (TPE)	Co (−) MEKP (−)	THQ (+)	DMAA
Peak exotherm temperature (PET)	No statistically significant model for this response		
Barcol hardness all (BHALL)	Co (−), MEKP (−), DMAA (−)	THQ (+)	—
Barcol hardness (BH15)	Co (−), MEKP (−), DMAA (−)	—	THQ
Barcol hardness (BH20)	Co (−), MEKP (−), DMAA (−), THQ (+)	—	—

The "short cut" method

This method offers the experimenter a "short-cut" when a full statistically designed experiment is not desired or justified. An example could be a resin cure system which works well most of the time, but still has the occasional problem. In other words, you are satisfied with the cure components, but the "operating window" is not fully defined.

An Eastman NPG™/ISO resin was chosen for this study. Since the cure components were already defined, the experimental testing was initiated with the statistically designed experiment. The short-cut method allowed the running of only ten experiments (one day's work) as compared to 32 required by the previous method. This method used only eight of the experiments from the four-by-four matrix with the center point run twice. Selection of the proper eight experiments was critical and because of the complexity of a four-variable system, consulting with a statistician or good statistics textbook may be necessary [1]. In a much simpler three-variable system, one would choose either the x's or the o's.

To take the "true short-cut," the experiment would be done on just the x's or the o's. Both of the two possible sets of statistically designed studies were performed to illustrate the advantages and disadvantages of the "short cut" method. The variable limits for this statistically designed experiment are shown in Table 7.

The design, experimental execution and analysis for these studies were exactly the same as the "starting-from-scratch" method. Table 8 summarizes the degree and direction of variable influence on the main responses of interest for both studies.

Table 7 Variable limits

	Low	Center point	High
Co, %	0.4	0.6	0.8
MEKP, %	0.9	1.1	1.3
DMAA, %	0.4	0.6	0.8
THQ, ppm	400	600	800

Table 8 Degree of variable influence on responses

Response	Major	Minor	Insignificant
Part 1			
Gel time (GT)	No statistically significant model for this response		
Time to peak exotherm (TPE)	Co (−)	MEKP (*), DMAA (−)	THQ
Peak exotherm temperature (PET)	No statistically significant model for this response		
Barcol hardness all (BHALL)	Co (−)	DMAA (−), THQ (+)	MEKP
Barcol hardness (BH15)	Co (−)	DMAA (−), THQ (+)	MEKP
Barcol hardness (BH20)	Co (−), THQ (+)	MEKP (*), DMAA (−)	—
Part 2			
Gel time (GT)	Co (−)	MEKP (*), THQ (*)	DMAA
Time to peak exotherm (TPE)	MEKP (*)	Co (*), DMAA (*)	THQ
Peak exotherm temperature (PET)	No statistically significant model for this response		
Barcol hardness all (BHALL)	No statistically significant model for this response		
Barcol hardness (BH15)	Co (−)	THQ (+)	MEKP, DMAA
Barcol hardness (BH20)	No statistically significant model for this response		

**Regression analysis was unable to determine the direction of influence for this particular response.*

The first observation from this data is that less information is gained when using the "short-cut" method. Regression analysis is unable to determine the direction of influence for a number of the responses. There are also more cases of no statistically significant models for responses than with the previous method; however, some generalizations can still be made:

1. Co exhibits a major influence on all of the responses, but still not in the most practical manner.
2. MEKP appears to be the least important variable with its most influential role as a minor contributor to GT.
3. DMAA has a minor effect on Barcol hardness properties while showing an insignificant effect on GT. This may be a good tool for adjusting Barcol hardness without affecting GT.
4. THQ exhibits a minor influence on all of the responses indicating that THQ (as in the case of Co) may not be very useful for adjusting the resin's cure properties.

The approach demonstrated in the "short cut" method illustrates that "when less data is collected, less information is usually obtained." It is important to remember that normally the experimenter would perform only part 1 or part 2 in this method. If more precise knowledge is required, it is suggested that a full statistically designed experiment be performed.

Conclusions

The use of statistically designed experimentation and analysis has allowed identification of trends or generalizations from very complex four-variable investigations. This form of experimentation may appear lengthy. However, through its careful planning, a true understanding of a resin cure system can be gained. These methods of experimentation lend themselves to cure study work because multiple-cure experiments can be performed in a relatively short time (one day to one week). The answers one desires may not always be forthcoming, but a better understanding of the system will always be achieved with a minimum of experimental work. The following are conclusions on the two methods discussed in this paper:

The "starting-from-scratch" method

This method is very intensive and methodical. It is suggested when the cure-system need is complex and important to the commercial feasibility of the resin product; however, the final product of this method of investigation is a broader knowledge of the effects of the variables. In the case of the Eastman TMPD™/ISO resin, a cure system using Co and MEKP that is consistent and reproducible was identified.

The "short-cut" method

This method uses the same basic techniques as the "starting-from-scratch" method; however, the amount of experimentation is decreased to save laboratory effort. The amount of knowledge obtained is also decreased proportionately. This method is suggested for taking a "quick-and-dirty" look at determining the "operating window" for a resin cure system. It may be a prelude to a full-fledged statistically designed experiment.

The methods discussed in this paper are examples of how to work smarter. When experimentation is designed based on statistics, rather than random choice, more useful information is gained. This information will translate into knowledge and understanding, instead of uncorrelated facts.

One observation that must be stated is that conclusions derived from this study are resin specific. No general statements on cure systems for all types of resins can be postulated at this time.

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