Optimization of Fire Retardants in a Formulations of Intumescent Fire Retardant Coatings for Steel Structure via a D-optimal Mixture Design Based on Response Surface Methodology

Jian HU*

Department of Chemical Engineering, Sichuan Vocational College of Chemical Technology, Luzhou China

*Corresponding author

Keywords: Response surface methodology, Design of experiments, Mixture experiments, Analysis of variance, Computer aided experimental design, D-optimal design, Fire retardant coating.

Abstract. Response surface methodology (RSM) is a very efficient tool to provide a good practical insight into developing new process and optimizing them. This methodology could help engineers to raise a mathematical model to represent the behavior of system as a convincing function of process parameters. Many experiments in research and development in the paint preparation involve mixture components. These are experiments with mixtures in which the experimental factors are the components of a mixture and the response variable depends on the relative proportion of each components, but not on the absolute amount of the mixture. Thus the mixture components cannot be varied independently. Optimizing the formulations for a preparation of intumescent fire-resistant coating requires the fire resistant effectiveness of several fire retardants combinations to be determined. We discuss the design and analysis of these types of experiments, presents a D-optimal design methodology for computer aided experimental design for fire retardant coating formulations involve mixture components, exemplifies the benefits of using design of experiments(DOE) together with statistical software package to facilitate the formulating of recipe for structural steelworks. Goal of this paper is to encourage greater utilization of information technology in paint preparation research and development.

Introduction

The use of fire-resistant coatings is one of the most efficient ways to protect materials against fire[1]. Intumescent fire-resistant systems are chemical compounds which, when heated, melt, bubble and form a foamed char which acts as insulation for underlying steel structures[2]. Intumescent fire-retardant coatings composition usually contain three fundamental active ingredients: a carbon source (such as pentaerythritol-PER), a blowing agent (most often melamine-MEL), an acid source (generally ammonium polyphosphate-APP), and they are linked together by a binder such as polymer materials.

Optimizing the formulations for a preparation of intumescent fire-resistant coating(IFRC) requires the fire resistant usefulness of several fire retardants collaboration to be confirmed. Three fire retardants were tested in this study: ammonium polyphosphate, pentaerythritol and melamine. Their fire resistant effects were evaluated using the fire-resistance tests of the International Organization for Standardization (ISO) [3]. From a limited number of experiments, a D-optimal mixture design was used to give a maximum of information. The main objective of the research presented here was to carry out multivariate analysis upon data from the experiment design based on Design Expert® software. We analyze our investigation results with the help of the MODDE software and to formulate coatings convincing requirements of the ISO 834-1:1999.

Multivariate analysis is a statistical tool that can be used to determine the contributing effect(s) of and identify relationships between independent variables and dependant variables in a multivariable system. A dependant variable is an uncontrolled variable which is being predicted or explained by one or more independent variables. An independent variable is a quantity which can be controlled (altered) and used as a predicting or explanatory variable for a dependant variable. Independent
variables include factors such as composition of the ingredients in formulations of the fire-resistant coatings. This system of analysis has been used on prior information based on historical experiments to cut down the vast amounts of experiments involved in the development and optimization of the IFCR formulation. For this research a readily available statistical package called MODDE (Umetrics, Sweden) was used.

This paper investigates some of the key issues for applying and understanding mixture experiments. We consider different models for the mixture components and select an appropriate design for a particular model, the analysis suitable for the experiment resulting from the design will be considered. We propose a particular model with up to quadratic terms in the mixture components, quadratic terms for the process variables and first and second order interaction terms between mixture and process variables, and propose a strategy for building and testing this model. Examples of flame-retardant coating involving both mixture and mixture–process experiments are shown.

The Basics of Mixture Experiment

Mixture experiments, of which the property studied depends on the proportions of the components present, but not on the amount of the mixture[4]. In a q-component mixture (q≥3) let \( x_i \) be the proportion (by volume, or by weight, or by moles, etc.) of the jth component in the mixture. When expressed as fractions of a mixture, the proportions are nonnegative and sum to one or unity, so that:

\[
x_i \geq 0 (i = 1,2,\ldots,q), x_1 + x_2 + \ldots + x_q = 1
\]  

(1)

The factor space is thus a regular \((q - 1)\)-dimensional simplex (triangle for \( q = 3 \), tetrahedron for \( q = 4 \)).

By virtue of the above restriction, the totality of the unrestricted factor space of \( n \) dimensions has been reduced to an \((n - 1)\) dimensional simplex. The \( n \) components of this system are called mixture variables. If in addition to the mixture variables certain other variables which are not bounded by the restriction Eq.1, are present in the system, they are called process variables [5].

As with standard response surface methods, common model choices are based on lower-order polynomials to model the relationship between the factors and the response \( \mu \). However, the constraint in Eq.1 leads to some modification of the basic models to allow for unique estimation of the model parameters. The standard first-order linear model used in response surface methods:

\[
\mu = \beta_0 + \beta_1 x_1 + \ldots + \beta_k x_k
\]  

(2)

does not have unique estimates for the parameters, \( \beta_0, \beta_1, \ldots, \beta_k \). The preferred solution to this overparameterized model is to remove the intercept term, \( \beta_0 \), since its usual interpretation as the value of the response when all factors are set to zero has no meaning under the constraint in Eq.1. The second-order model where \( \beta_{ij} \) is the curvature term of independent variable[6]:

\[
\mu = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_i x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{i<j} \beta_{ij} x_i x_j + \varepsilon
\]  

(3)

needs to be modified to compensate for the constraint in Eq.1. The pure quadratic terms, \( \beta_{ii} x_i^2 \), are redundant, and hence can be removed from the model, leading to the general form:

\[
\mu = \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{i<j} \beta_{ij} x_i x_j + \varepsilon
\]  

(4)

and \( \beta_{ij} \) is the interaction coefficient between variables \( x_i \) and \( x_j \). \( k \) is the number of factors and \( x_i \) are the coded variables. \( \varepsilon \) represents the statistical random error in \( \mu \) that are mutually independent in the statistical sense, often assuming it to have a normal distribution with mean zero and common variance \( \sigma^2 \).
An Example of a Mixture Experiment

In paint industry, the intumescent coatings are to be formulated mainly from six ingredients, the silicone-acrylate emulsion resin as a binder which is fixed at 36.4% of the mixture, the nano-titanium dioxide as a nanometer filler which is fixed at 6% and nano-aluminum hydroxide as nano-flame retardants which is fixed at 4% respectively, an ammonium polyphosphate(APP) (used to be an acid source), a pentaerythrite(PER) (used to be a carbon source), and a melamine(MEL) (used to be a blowing agent). Since the resin a binder and nano-titanium dioxide and nano-aluminum hydroxide have fixed percentage in the mixture, no experimentation with these components is required. In addition to this constraint, the other ingredients have restrictions on their relative contribution to the mixture:

\[22.6\% \leq x_1 \leq 32.3\%
\]
\[11.7\% \leq x_2 \leq 21.4\%
\]
\[5.4\% \leq x_3 \leq 9.6\%
\]
\[x_1 + x_2 + x_3 = 53.6\%\]  

(5)

For our experiment with three components, the second-order model has the form as Eq.3. Typically we wish to obtain some measure of pure error and lack of fit for the process. Pure error measures how much variability is expected if the same experimental set-up is run multiple times. Lack of fit checks the adequacy of the model and provides feedback as to whether additional terms are required in the model. The statistical software package, Design-Expert® 10.0 (Stat-Ease, Inc.), can construct optimal designs for a variety of constrained and unconstrained mixture regions and models:

\[
\mu = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3
\]

(6)

If we did not have constraints on the three variable components beyond their total proportions, the ideal design for the second-order model would be the simplex design shown in Table 1 (where \(x_1, x_2, x_3\) are labelled A, B, C). To obtain this design, under the Mixture option, we would request a simplex centroid design with three components. Since we have the components fixed at 46.4% we would set the remaining variable components to sum to 0.536. Using the recommended sample size in Design-Expert®, we allocate four degrees of freedom to lack-of-fit testing and four degrees of freedom for estimating pure error. Table 1 contains the Design Summary where the experiment would be run that was obtained by requesting a D-Optimal design from Design-Expert® with 16 runs for the unrestricted region.

Table 1. Design summary of 16-runs.
An Response Modeling and Multivariate Analysis

The fire-resisting time of IFRC was modelled by polynomial equations and taken as the measured response variable. These mathematical model equations depending on various factors and their interaction.

With the aid of the MODDE statistical software package, the main variables effects and interactions between response variables were ascertained from the tested results and are listed in Table 2.

We proposed an useful graphical methods that can be used to pre-experimental planning and to analyze experiment designs regarding prediction variance by aids of Design Expert® software package, with inputs, experimental variables, and responses all clearly labeled, the graphical results showed in Figure 1 and Figure 2.

There are graphical methods that can be used to evaluate mixture–process designs with respect to prediction variance.

In Fig. 1 and Fig. 2, both process variables are set at their low levels. A low level was chosen for blending time to help speed up the process. A numerical optimization can be performed to find the mixture–process combination with the highest fire-resisting time values. In this case, we could also find the maximum graphically. A coating formulation with 14.5% APP, 3.6% MEL, 12.9% PER, and particle size 0.1mm will yield a flame-retardant coating with a predicted fire-resisting time of 26.31.

A 95% confidence interval for the predicted fire-resisting time is (21.84, 41.59).

Conclusion

In this study, previous investigations have been used in the establishment of mathematical model, observational data that have been collected routinely by historical process operating personnel based on prior experiments. Multivariate design via a D-optimal mixture regulation based on response surface methodology is used to build a few supplementary investigation work so that be able to obtain a satisfactory predictive capability of the consequent model. A series of graphical methods used to pre-experimental designs planning with the help of complex computer software systems via response surface methodology. A confirmative test procedure indicate that a development process which utilizes the D-optimal methodology making the best of the investigation data gathered from the DOX which mathematical models with equivalent predictive power are given using fewer experiments. It is critical where investigations can be time consuming and very costly to perform for a given quantities of experiment information gathered.

<table>
<thead>
<tr>
<th>Effects</th>
<th>Regression coefficient</th>
<th>Sum of squares of partial regression</th>
<th>Value of contribution degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_0$</td>
<td>57.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>5.12</td>
<td>66.8</td>
<td>8.42%</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>-7.54</td>
<td>127</td>
<td>16.95%</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>8.44x10^{-2}</td>
<td>75.0</td>
<td>10.96%</td>
</tr>
<tr>
<td>$\beta_{12}$</td>
<td>-0.328</td>
<td>107</td>
<td>13.23%</td>
</tr>
<tr>
<td>$\beta_{13}$</td>
<td>0.290</td>
<td>123</td>
<td>19.77%</td>
</tr>
<tr>
<td>$\beta_{23}$</td>
<td>5.54x10^{-3}</td>
<td>141</td>
<td>17.5%</td>
</tr>
<tr>
<td>$\beta_{123}$</td>
<td>-7.87x10^{-4}</td>
<td>159</td>
<td>20.48%</td>
</tr>
</tbody>
</table>
Design-Expert Software
Component Coding: Actual
Highs/Lows inverted by U_Pseudo coding
Factor Coding: Actual
Original Scale
Fire-resisting time (min)
- Design Points
- Design points above predicted value
- Design points below predicted value

Fire-resisting time (min) = 29.7
Std # 6 Run # 4
X1 = A: APP = 14.451
X2 = B: MEL = 3.600
X3 = C: PER = 12.949
Actual Factors
D: particle size = 0.1
E: grinding time = 90

Figure 1. Contour plot of the response model of the paint development.

Figure 2. 3D Surface of the response model of the paint development.

References
