Optimization of Fire Retardants and Multivariate Analysis of the Formulations based on Response Surface Methodology for Intumescent Fire-retardant Coatings via a D-optimal Mixture Design

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Abstract. Response surface methodology (RSM) could help scholar and academician to raise a mathematical model representing the behavior of system as a function of process parameters to be convinced. This methodology is a very efficient tool to provide a good practical perceptiveness into developing and optimizing a new process. Optimizing the formulations for a preparation of intumescent fire-resistant coating requires the fire resistant effectiveness of several fire retardants combinations to be determined. This paper investigates the design and analysis of mixture experiments in paint preparation, we discuss a computer aided experimental design via a D-optimal design methodology for fire retardant paint recipe include mixture ingredients, illustrate the advantages of facilitating the formulation of ingredients for fire-retardant coatings by using statistical software package together with the design of experiments (DOX).

1. Introduction

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). 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.

The use of fire-resistant coatings is one of the most efficient ways to protect materials against fire[1,2]. 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[3]. 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[4,5].

In the product development process of IFRC, the variety determination of fire retardants and paint quantities of components is usually done by experiments which often demands a great amount of development work and may be very expensive and time consuming. Factorial designs of experiments demands less resource such as experiments material consumption, time of product development, etc., It is very important since experiments can be very costly for a given amount of experiment information obtained[6]. The purpose of our study was to evaluate the effectiveness of a D-optimal mixture design for ascertaining the optimal composition of an intumescent fire-retardant coatings [7,8].

A chapter in the ISO 834-1:1999 is devoted to the fire-resistance tests. The resisting time test is designed to evaluate the fire-resisting performance of intumescent fire-retardant coatings during its use[9].

2. Specimens Preparation and Fire-resistance tests according to the ISO

Ammonium polyphosphate(APP, Shifang Changfeng Chemical Co., Ltd), pentaerythritol(PER, Sichuan Tianhua Chemical Co., Ltd), and melamine(MEL, Yunnan Yuntianhua Co., Ltd) and titanium dioxide(TiO₂, Chengdu Kelong Chemical Reagent Factory), silicone-acrylate emulsion(solid content 50%, Beijing Donglian Chemical Co., Ltd). CS-12 coalescent (Chisso Corporation, Japan).

Silicone-acrylate emulsion, APP, MEL, PER, TiO₂, CS-12 coalescent and water were mixed by laboratory sanding machine. The prepared fire-retardant coatings were brushed onto the external face of a metal sample plate. The same operation was repeated several times until the target thickness of the paint film was obtained at room temperature.

In order to determine the heat insulation of fire-retardant coatings, fireproof examination was executed. During the detection of the paint product, the coated steel structure plates were burned in exposed gas flame, flame temperature increased according to the standard time-temperature curve [10]. The time when the average temperatures of the backside steel plate reached 300°C was defined as fire-resisting time.

The experimental equipment for determining the fire-resisting time is shown in Figure. 1. To ensure reliable and stable temperature measurements along steel plate thickness, the tip of thermocouple was set on the point at half of the sample thickness, thus make certain that the sample plate with good thermal connection state of the thermocouple.
3. **Methodology of the Experiments Design**

Design of Experiment (DOX) is a well organized technique that is used to promote determining the relationship among several factors affecting a process and ascertaining the outcome of that process. Well-designed experiments through DOX are used widely in the engineering world, such as product design & development, evaluation of material properties[11], component & system tolerance determination, process characterization & optimization, etc.

When we planning, conducting & analyzing an experiment in building a DOX with better understanding of the experiment system, there are several interrelated steps as follows: 1) Recognition of & statement of problem (The aims is to obtain optimal fire protective performance of fire-proofing paints in this investigation). 2) Choice of factors, levels, and ranges of variation (In our study, the major influential factors were MEL (Factor1), PER (Factor2), APP (Factor3)). 3) Selection of the response variables (It is fire-resisting time of the prepared intumescent fire-retardant coatings in our study). 4) Choice of design that is well matched with the investigation goals, test accuracy of measurements, amount of factors, and has a reasonable cost (In this multivariate formulation design, we chose D-optimal design as DOX methodology[12]). 5) Conducting the experiment. 6) Statistical analysis (The experiment designs were generated and evaluated through the medium of Design Expert® software package). 7) Drawing conclusions, recommendations.

Ten experiment runs were performed by selecting the unrestricted form of the mixed model, ten -runs D-optimal design with data are shown as in the Table 1.

| Run   | Factor1 MEL(g) | Factor2 PER(g) | Factor3 APP(g) | 50%silicone-acrylate emulsion (g) (35wt%) |
|-------|----------------|----------------|----------------|----------------------------------------|
| SAMP01| 7.83           | 14.5           | 77.6           | 107.7                                  |
| SAMP02| 29.0           | 9.68           | 61.3           | 107.7                                  |
| SAMP03| 2.50           | 47.5           | 50.0           | 107.7                                  |
| SAMP04| 26.6           | 32.5           | 40.8           | 107.7                                  |
| SAMP05| 57.0           | 10.1           | 32.9           | 107.7                                  |
| SAMP06| 11.1           | 63.0           | 25.8           | 107.7                                  |
| SAMP07| 44.3           | 36.3           | 19.4           | 107.7                                  |
| SAMP08| 82.3           | 4.33           | 13.4           | 107.7                                  |
| SAMP09| 23.0           | 69.1           | 7.80           | 107.7                                  |
| SAMP10| 63.4           | 34.1           | 2.53           | 107.7                                  |
4. 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:

\[
\mu = \beta_0 + \beta_1 X_1 + \ldots + \beta_n X_n + \beta_{12} X_1 X_2 + \ldots + \beta_{xyz} X_x X_y X_z
\]  

(2)

Where \( \beta \) means fire-resisting time, \( X_i \) means the ration of factor, \( n, i, j, \ldots, x, y, z = 1 \sim 3 \)

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.

| Effects \((\beta_0, \beta_{ij} \text{ and } \beta_{xyz})\) | Regression coefficient | Sum of squares of partial regression | Value of contribution degree |
|------------------------------------------------|------------------------|-------------------------------------|-----------------------------|
| \(\beta_0\)                                      | 57.8                   | -                                   | -                           |
| \(\beta_1\)                                      | 5.12                   | 66.8                                | 8.42%                       |
| \(\beta_2\)                                      | -7.54                  | 127                                 | 16.95%                      |
| \(\beta_3\)                                      | 8.44×10^{-2}           | 75.0                                | 10.96%                      |
| \(\beta_{12}\)                                   | -0.328                 | 107                                 | 13.23%                      |
| \(\beta_{13}\)                                   | 0.290                  | 123                                 | 19.77%                      |
| \(\beta_{23}\)                                   | 5.54×10^{-3}           | 141                                 | 17.5%                       |
| \(\beta_{123}\)                                  | -7.87×10^{-4}          | 159                                 | 20.48%                      |

Fig. 2. Contour plot of the response model of the paint development
5. 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.

References
[1] H.L. Vandersall. Intumescent Coating Systems, Their Development and Chemistry [J].J. Fire Flamm.,1971 2 97~140.
[2] J.A. Rhys. Intumescent Coatings and Their Uses [J]. Fire Material, 1980 4 154~156.
[3] R. Delobel, M. LeBras, N. Ouassou et al. Thermal Behaviors of Ammonium Polyphosphate-epentaerythritol and Ammonium Pyrophosphate-pentaerythritol Intumescent Additives in Polypropylene Formulations [J]. J. Fire Sci. 1990 8 85~108.
[4] M. Jimenez, S. Duquesne, S. Bourbigot. Intumescent Fire Protective Coating: Toward a Better Understanding of Their Mechanism of Action [J]. Thermochim. Acta. 2006 449 16~26.
[5] S. Duquesne, S. Magnet, C. Jama, R. Delobel. Intumescent Paints: Fire Protective Coatings for Metallic Substrates [J]. Surf. Coat. Technol. 2004 180–181 302–307.
[6] Douglas C. Montgomery. Design and Analysis of Experiments, 7th Edition [M]. New York: John Wiley & Sons, 2009.
[7] R. Lanouette, J. L. Valade1, J. Thibault. Optimization of an Alkaline Peroxide Interstage Treatment of Jack pine (Pinus banksiana lamb.) Using a D-optimal Design [J]. Can. J. Chem. Eng. 1997 75 70~78.
[8] Yang, Y. K., Tzeng, C. J., Yang, R. T. and Hsieh, M. H. Study on Tribological Behaviors of Short Glass Fiber and Polytetrafluoroethylene Reinforced Polycarbonate Composites via a D-optimal Mixture Design [J]. Polym. Adv. Technol. 2011 22: DOI: 10.1002/pat.1744

[9] ISO 834-1:1999 on http://www.iso.org/iso/home.htm

[10] S. Duquesnea, S. Magnetb, C. Jama, R. Delobel. Thermoplastic Resins for Thin Film Intumescent Coatings Towards a Better Understanding of Their Effect on Intumescence Efficiency [J]. Polym. Adv. Technol. 2005 88 63–69.

[11] M. Trifkovic, M. Sheikhzadeh, K. Choo, S. Rohani. Experimental and Statistical Study of the Effects of Material Properties, Curing Agents, and Process Variables on the Production of Thermoplastic Vulcanizates [J]. J. Appl. Polym. Sci. 2010 118 764–777.

[12] Kai tai Fang, Yuan Wang: Number-theoretic methods in statistics [M]. Washington: Chapman & Hall/CRC, 1994.