Modelling and optimization of a flexible poly(vinyl chloride) compound formulation for mine cables

Reinhard H. Fechter[1], Carl Sandrock[2], Ines Kühnert[3] and F.J.W.J. (Johan) Labuschagné[1,*]

[1]Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria, cnr Lynnwood Road and Roper Street, Hatfield 0028, South Africa

[2]Department of Chemical Engineering, University of Pretoria, cnr Lynnwood Road and Roper Street, Hatfield 0028, South Africa

[3]Department of Processing, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany

*Corresponding author email: johan.labuschagne@up.ac.za

Abstract

Developments by Labuschagné et al. [1] in the manufacture of Layered Double Hydroxides (LDHs) have led to a patent describing a new effluent free synthesis method. A promising application for the LDH is as an additive for a flexible poly(vinyl chloride) (PVC) compound used for the insulation for cables used in South African underground mines. Consequently, a new formulation is required. Unfortunately formulating a PVC compound is a complex problem. The purpose of the investigation is to develop a method that can be used to find an optimum PVC formulation where the material requirements are met while also allowing for the quantitative analysis of the effect of the ingredients on the material properties. This is achieved by modelling the thermal stability, fire retardancy and basic mechanical properties of the compound as a function of the relative proportions of the ingredients using 2nd order Scheffé polynomials. The empirical models are determined using statistical experimental design. Each model is interpreted using statistical analysis of the model terms which allows for the quantification of the effects and interactions of all the ingredients on the various response variables. The models are also used as constraints in the optimization of the PVC formulation for minimum cost. Parametric analyses are done to demonstrate how the optimization can be used to analyze the entire system taking into account the cost performance of the ingredients. Finally, it is demonstrated how the above approach requires significantly less time and labor to find an optimum formulation than the traditional approach.

1 Introduction

Poly(vinyl chloride) (PVC) is a commercially significant thermoplastic. With the use of a large variety of additives the properties of PVC can be modified and tailored to a specific application making it a very versatile plastic [2, 3]. One of the many types of additives used for PVC are Layered Double Hydroxides (LDHs). LDHs are clay like materials with a general structure that involves cationic layers, with a crystalline structure, that are connected with anions intercalated in between the cationic layers. LDHs are used as thermal stabilizers and fire retardants in PVC [4, 5]. Developments by Labuschagné et al. [1] in the manufacture of LDHs have led to a patent describing a new effluent free synthesis method. To make the LDHs produced using the new synthesis method commercially viable requires that they have product applications. One such application is as an additive for flexible PVC compound used for the insulation material for cables used in South African underground mines.

However this means that a new formulation is required that incorporates the LDH. The problem is that a PVC compound is a complex system where there are many interactions between the different additives. The problem is further complicated by the fact that the additives tend to have an effect on multiple properties of the PVC compound, and that the PVC compound is essentially a mixture system which means that changes in the proportion of a certain ingredient cannot be made independently. Traditionally PVC formulations are developed over many years by experienced PVC formulators using a predominantly best-guess trial and error approach. Although this has been used very successfully in the past it is not very flexible when it comes to introducing new additives. The traditional approach is also focused more on finding acceptable rather than optimum formulations.

The purpose of the investigation is to develop a method that can be used to find an optimum flexible PVC formulation for the insulation used for underground mine cables by varying the proportions of the ingredients included in the PVC compound. It is also required that the method facilitates the analysis of the effects and interactions of the various ingredients that are used.

An LDH manufactured using the effluent free method, a spherical fly ash filler and the industry standard primary thermal stabilizer, plasticizer, fire retardant, filler and PVC resin are used. The thermal stability, fire retardancy and basic mechanical properties of the PVC compound are modelled as a function of the mass fractions of the ingredients using statistical experimental design. The resultant empirical models are used to demonstrate how the system can be optimized and consequently analyzed using a parametric analysis. The experimental design is done using JMP™ Statistical Software, the experiments are conducted in a laboratory environment and the data analysis is done using programs written in Python programming language using Jupyter [6].

2 Optimization

2.1 Problem Statement

The problem is to minimize the production cost of a flexible PVC formulation, for the use in underground mine cables, while maintaining the desired material properties.

The production cost is selected as the objective because PVC is a commodity plastic and hence products, such as cable insulation, made from PVC are also commodity products [2]. One of the characteristics of commodity products is that they tend to have very narrow profit margins. Narrow profit margins mean that a significant increase in profits can be realized by even a small reduction in production costs [7].

2.2 Definition of Design Variables

The design variables are the relative proportions of the ingredients in the PVC compound formulation. In this case the mass fractions were varied. The actual ingredients that were used are not varied. The ingredients that were used for the PVC compound are shown in Table 1.

The PVC resin, Ca/Zn stabilizer, diisononyl phthalate (DINP) and fire retardant (FR) were selected so that achieving the desired properties required for an underground mine cable insulation or protective sheath was possible [8]. The Ca/Zn stabilizer, which consists of a mixture of Ca and Zn stearate, was included as a primary thermal stabilizer. This was necessary due to the fact that the only other thermal stabilizer, namely the LDH, only acts as a secondary stabilizer and so in theory cannot stabilize PVC in isolation [9, 10, 4]. The DINP was included because plasticization is necessary for the flexibility requirements of cable insulation [10]. The FR, which is the aluminum trihydrate (ATH) and Sb_2O_3 based one-pack, was added due to the stringent fire retardancy requirements for underground mine cables and due to the fact that DINP was included which is known to decrease the natural flame retardancy of PVC [11, 12]. The stearic acid coated $CaCO_3$ is not strictly necessary for achieving the desired material properties but was added as a filler due to its low cost [11]. All of these five ingredients discussed above were also selected because they are the industry standard used for flexible PVC compounds in South Africa.

The final two ingredients, namely the LDH and the fly ash, are not industry standard. The LDH was produced using the novel dissolution precipitation method [1] and was included as both a secondary stabilizer and FR [4, 5]. The fly ash was added as a spherical filler. It is a by-product of producing electricity with coal-fired power stations. In South Africa approximately 25 million tons of fly ash is produced in this way and only about 5 % of the fly ash is reused [13]. It is hypothesized that the spherical filler will be synergistic in the system by reducing the melt viscosity. It has also been successfully used as a cost reducing filler in other polymers [14].

Since there were seven ingredients there are seven design variables. The design variables will be represented by the vector **x**.

Table 1: PVC Compound Ingredients

Description	Trade Name	Source
Flexible grade PVC resin	PVC Resin S7106	Sasol
Stearic acid coated $CaCO_3$	Kulucote 2	Idwala
ATH and Sb_2O_3 one-pack	Flamex O	Associated Additives
Ca/Zn Stabilizer	Naftosafe PKN65119	Associated Additives
DINP	DINP	Isegen South Africa
LDH	Pyrogard	Greenfield Additives
Fly ash (spherical filler)	Plasfill-5	Ash Resources

2.3 Identification of the Objective Function

The objective function is given by

$$f = \sum_{i=1}^{7} c_i x_i \tag{1}$$

where **c** is the cost of each ingredient per unit mass and the objective f is the cost per unit mass of the flexible PVC compound. Other factors, besides the direct material costs, that are a function of the design variables and will affect the cost of the PVC compound, are assumed to be negligible or held relatively constant by the constraints which will be discussed in the following sections. These include factors such as the energy required to process the PVC compound or the abrasion of processing equipment by the compound.

2.4 Identification of Constraints

The first constraints are the logical constraints required because the system is a mixture which are the summation of equality constraint

$$\sum_{i=1}^{7} x_i = 1 \tag{2}$$

and the nonnegativity constraint

$$0 \leq x_i \quad i = 1,2,\ldots,7 \tag{3}$$

[15]. The rest of the constraints are to address the portion of the problem statement which requires that the desired material properties are maintained. The first material property which needs to be constrained is the thermal stability of the compound which is always a concern due to the inherent thermal instability of PVC through an autocatalytic degradation reaction [2, 10]. The second property is the fire retardancy of the compound. This is important due to the fire retardancy requirements of the target application. Finally, the basic mechanical properties of the compound need to be constrained which is necessary for two reasons. The first is that the target application requires that the material is flexible and has sufficient tensile strength [8]. The second reason is that if it is not constrained it is highly likely that a compound with poor mechanical properties will be the optimal solution due to the nature of optimization. This concept is in fact true for all three of the properties that are constrained, which is part of the reason why they were selected. It is also true for all three of these properties that the design variables have a significant effect on them.

The final requirement for the use of the above mentioned properties as constraints is that they are quantifiable in some way so that they can be mathematically related to the design variables **x** i.e. that the property can be described as a function of **x**. The constraints for each property are then defined as

$$p_{lower} \leq p(\mathbf{x}) \leq p_{upper} \tag{4}$$

where p is the value of the property and where the limit p_{lower} is used when the desired values for p are high and p_{upper} is used when the desired values for p are low.

The functions required for $p(\mathbf{x})$ are physical models that predict the properties of the PVC compound. Due to the complexity of the system and the lack of knowledge or clarity on the fundamental mechanisms of many of the components involved, first principal models or even semi empirical models do not exist and would require considerable effort to develop. Because of this empirical models are used as they require the least effort to develop and should be sufficient to optimize the system. Statistical design of experiments is used to develop the models.

3 Experimental Design

The aim of the statistical experimental design is to determine empirical models that can be used to describe the thermal stability, flame retardancy and basic mechanical properties of the PVC compound as a function of the design variables as described in the previous section.

3.1 Selection of the Response Variables

The experimental methods that are selected are shown in Table 2. Each experimental method does not necessarily result in only one response variable. The torque rheometer is selected because it is the most realistic indicator of thermal stability during processing. In addition to being able to determine the short and long term thermal stability time from the torque curves produced by the torque rheometer, the resting torque, which relates to processability, can also be determined [16, 2]. The Thermomat test does not simulate the processing conditions as well but requires less time and material than the torque rheometer test while still giving an indication of the stability time [17, 18]. A color measurement of pressed PVC samples is the final measurement used for thermal stability. It is the least accurate but does give an indication of the degradation that occurred during compounding (discussed further in the next section) and is relatively simple to determine [17]. The color stability itself is also often relevant due to aesthetic reasons but is not crucial for underground mine cables.

The Cone Calorimeter test, like the torque rheometer for thermal stability, gives the most complete information concerning fire retardancy with the closest simulation of a real fire. The Micro Cone Calorimeter (MCC) test is also done even though it gives less information and is not a good simulation of real fire behavior, in comparison with the Cone Calorimeter, because it requires less time, significantly less material and is less expensive to run. The final fire retardancy test that is used is the Limiting Oxygen Index (LOI) test which gives the least information but is used because it is still often a requirement for the specification of PVC products and compounds [19, 20].

Table 2: Experimental methods used to determine response variables

Property	Experimental Method
Thermal Stability	Torque Rheometer
	Thermomat
	Color
Fire Retardancy	Cone Calorimetry
	Micro Cone Calorimeter (MCC)
	Limiting Oxygen Index (LOI)
Mechanical	Tensile Test

The tensile test is used because it covers the basic mechanical properties of the compound. The elastic modulus, tensile strength and elongation at break can be determined [21].

3.2 Choice of Factors and Ranges

The factors for the experiment are the same as the design variables for the optimization defined in section 2.2. The ranges of the factors, or more generally the experimental space that will be used is a result of practical considerations of the testing methods which will be used to determine the response variables, and the system in general.

All of the testing methods with the exception of the torque rheometer require samples which are in the form of a PVC compound. This means that part of the sample preparation requires that the PVC and all the additives are compounded. The compounding was achieved using a laboratory twin-screw extruder. The twin-screw extruder can only process material that falls within a certain range of processing properties. Although the range of processing properties that it can handle is relatively broad it will definitely not be able to process all the possible combinations of the factors. Since the thermal degradation reaction of PVC is auto-catalytic it can proceed very rapidly after initiation. Ideally only compounds which are well within the processing limits should be used, however, in this case the experimental space needs to broad enough to make the empirical models meaningful by minimizing the effect of variance.

The following limits are proposed based on a number of existing commercial formulations found in the reference work by Wypych [11]. The limits are expressed in per hundred resin (phr) which is the traditional unit used in the PVC industry and in PVC research. The limits are shown in Table 3.

The lower limit on the mass fraction of PVC is to ensure that there is always enough PVC to form a PVC matrix. The upper limits of the filler, FR, LDH and spherical filler all limit the overall inorganic particulate loading. The lower limit on the stabilizer ensures that the system is always sufficiently stabilized to be extruded. The lower limit on the DINP ensures that there is always sufficient lubrication for the extrusions, whereas the upper limit ensures that the DINP does not approach the absorption limit of the PVC which is important for the high speed mixing step (which precedes the extrusion step). The exact upper limits for the FR, stabilizer and LDH are set more out of considering their relatively high cost and that they are generally effective even at low loadings. The upper limit on the spherical filler is set at a slightly conservative level since it is relatively untested as an additive for PVC.

3.3 Choice of Experimental Design

Since the system is a mixture and the experimental space is constrained there; are a number of options for the experimental design for example the extreme vertices, D-optimal and space filling designs. The problem with the extreme vertices and D-optimal design, in this case, is that all of the experimental points lie on the boundaries of the experimental space [15, 22, 23]. The overall aim of the experiment is to determine an optimum formulation which is more likely to be inside the experimental space than somewhere on the boundary. The solution is to use a space filling design which spreads the experimental points throughout the entire experimental space. The probability of having an experimental

Table 3: Limits for experimental space

	Limit (phr)	
Ingredient	Lower	Upper
PVC	0.4*	-
Filler	-	70
FR	-	20
Stabilizer	2	10
DINP	20	70
LDH	-	15
Spherical Filler	-	20

*Expressed as mass fraction i.e. not phr point close to the optimum, and hence having a better prediction in that region, is therefore increased.

The number of experimental points that are used needs to be greater than the number of parameters of the model, but is limited by the time and resources available to execute the experiment. In this investigation enough experimental points will be used to fit a 2nd order Scheffé polynomial. A Scheffé polynomial is essentially an ordinary polynomial which has been derived to take into account the mixture constraints [24]. The space filling design is generated using JMP™ statistical software.

3.4 Methods and Materials

3.4.1 Compound Preparation

Each experimental point represents a different PVC formulation which needs to be compounded. The compound preparation involves two steps, which are the high speed mixing and compounding step. The high speed mixing was done using a Zhangjiagang City Yili Machinery Co. SHR High Speed Mixer. The dry powder for each sample was then compounded using a CFam TX 28-P laboratory extruder which is a counter-rotating twin screw extruder.

3.4.2 Torque Rheometer

The torque rheometer tests were done according to ASTM D2538-02 using a Haake™ Polylab™ OS Rheomix. Type 600 roller rotors were used at a rotational speed of 50 rpm. The block temperature was set to 200 °C and 72 g of compound was used per sample.

The stability time, final degradation time and resting torque were determined from each torque curve using a program written in Python programming language using Jupyter [6]. The stability time is defined as the time from the first point that the torque is less than the threshold value of 3 N·m above the minimum value, to the first point after the minimum where the torque is greater than the threshold. The final degradation time is the time required to reach the maximum value in the torque curve starting at the same point as the stability time. The resting torque is calculated as the mean value of the torque during the stable time. An exponentially weighted moving average filter is used to decrease the effect of noise. The stability time and final degradation time are shown for sample 1 in Figure 1 as an example.

3.4.3 Thermomat

The Thermomat tests were done according to ISO 182-3 using a Metrohm 895 Professional PVC Thermomat. 0.5 g of PVC compound was used. A Thermomat temperature of 200 °C, nitrogen flow of 7 $l \cdot h^{-1}$ and 60 mL of distilled water was used.

The stability time is calculated using

$$t_{int} = \tau(\theta - 1)^{\frac{1}{\theta}}\left(1 - \frac{\ln(\theta)}{\theta - 1}\right) \quad (5)$$

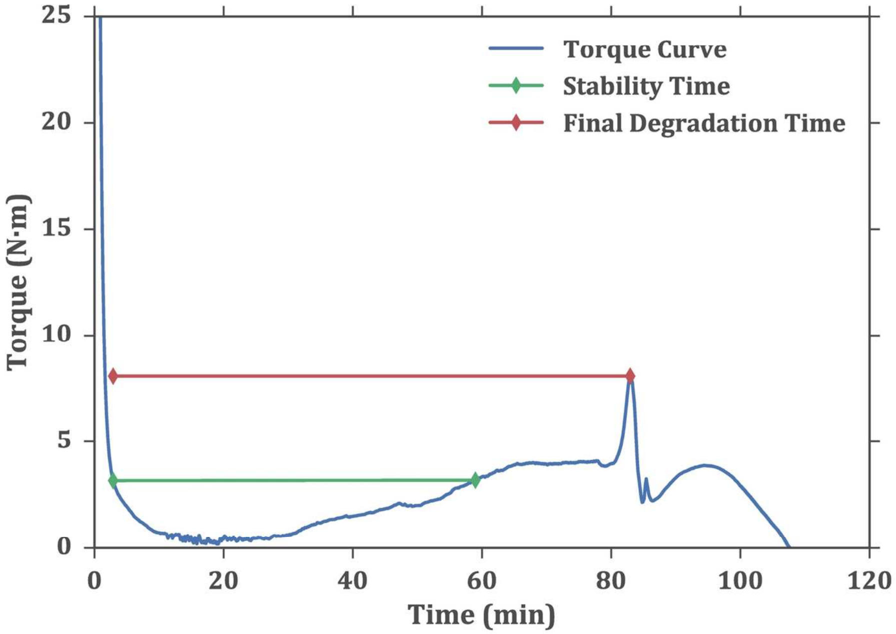

Figure 1: Torque rheometer curve for sample 1 showing the stability time and final degradation time

139x96mm (300 x 300 DPI)

where the parameters θ and τ are found by fitting the model

$$\sigma(t) = \sigma_{min} + mt + \beta \ln \left[1 + \left(\frac{t}{\tau} \right)^{\theta} \right] \tag{6}$$

to the conductivity curves for each sample [25]. The model fitting is done using a program written in Python programming language.

3.4.4 Color

The pressed sheets required for the Cone Calorimetry measurements (described in the following section) were also used to determine the color of each sample after compounding. The pressed sheets were photographed using a custom built rig that ensures that the camera is at a fixed height above the sample and that the light sources illuminate the sample at an angle of approximately 45°. A Nikon D60 camera was used with the white balance set to daylight and the color space set to sRGB. The light bulbs that were used are Phillips MASTER TL-D 90 De Luse 18W/965 1SL light bulbs. The specific light bulbs were selected because they are standard D65 illuminants.

The resultant images were analyzed using a program written in Python programming language. The program converts the image in to red, green and blue (RGB) color values. The RGB values are then converted to CIE tristimulus values which are then expressed as YI values using the equation

$$\mathrm{YI} = 100 \frac{1.28X - 1.06Z}{Y} \tag{7}$$

Finally the YI for each sample is taken as the mean value of the YI values for the entire image. The rig was designed and built and the analysis program was written by Wright [26].

3.4.5 Cone Calorimetry

The Cone Calorimetry measurements were conducted according to ISO 5660 1:2015. The samples were prepared by pressing the pelletized PVC compound into square sheets with a side length of 100 mm and a depth of 3 mm using a Vertex Hot Press. The actual testing was done using an FTT iCone Plus™ Calorimeter.

The following values were calculated by the Cone Calorimeter software for each sample: the peak heat release rate (pHRR) in kW/m^2, the total heat released (tHR) in MJ/m^2, the total smoke production (tSP) in m^2, the total mass lost (tML) in g, the time to ignition and pHRR in s and the maximum average rate of heat emission (MAHRE) in kW/m^2. The MAHRE value is used as a measure of the risk of a fire spreading to other objects in a fire situation.

3.4.6 MCC

The MCC measurements were done according to ASTM D7309 using an FTT FAA Micro Calorimeter. A sample mass of 50 mg was used. The tHR in kJ/g for the entire heat release rate curve and the pHRR in W/g, time and temperature at the pHRR and the tHR for each peak were determined using a program written in Python programming language.

3.4.7 LOI

The LOI measurements were done according to ASTM D2863 using a Stanton Redcroft™ LOI device. The samples were prepared by again pressing 100 mm by 100 mm by 3 mm sheets from the PVC compound pellets. The pressed sheets were then cut into several 3 mm by 3 mm by 100 mm rods which were then used for the LOI measurement.

3.4.8 Tensile Test

Unlike for the Color, Cone Calorimetry and LOI tests, pressed samples cannot be used for tensile testing. This is due to the fact that a pressed sheet is manufactured from pellets that melt onto each other rather than from a homogenous melt. If a pressed sheet is used for tensile testing mechanical failure will inevitably occur at the boundaries between pellets which means that the intrinsic tensile strength of the material cannot be determined. Therefore the samples for tensile testing were produced using injection molding. A Boy™ 22 A injection molding machine fitted with a specialized screw and barrel specifically designed for injection molding PVC was used.

The specialized screw is required to decrease the risk of rapid thermal degradation of the PVC during processing which would lead to irreparable damage to the screw and barrel. For example one of the features of the screw, that makes it appropriate for PVC, is that it does not have a reverse flow element, like most other injection molding screws, where material can accumulate and initiate degradation. To further decrease the risk of complete degradation during processing, the samples were ordered according to the final degradation time determined using the torque rheometer experiments. Samples with a final degradation time of less than 30 min were not used and the samples were injection molded in order of decreasing stability, i.e. the compounds with the least risk were injection molded first. Ordering the compounds in terms of thermal stability is in conflict with the randomization principle in experimental design [23] but is deemed necessary due to the high cost of the injection molding machine and specialized screw.

The pelletized PVC for each of the selected samples was dried under vacuum for 6 h at 60 °C before injection molding. The barrel has four thermostatically controlled heating zones which were set at 130 °C, 140 °C, 150 °C and 160 °C going from the feeding zone to the nozzle. A mold for the standard 1BA tensile bar was used and the mold temperature was set at 30 °C. For each sample the injection molding machine was run, discarding all the tensile bars produced, until the process stabilized. The exact values for process parameters such as cooling time and screw position required to achieve stable operation and satisfactory tensile bars were adjusted (usually for each sample) by an experienced operator. When the process was stable 15 tensile bars for tensile testing were produced and marked. After the 15 tensile bars for a certain sample were produced, the remaining material was ejected from the barrel and the above process was repeated. 15 tensile bars are required per sample because failure of the tensile bar outside of the testing zone can sometimes occur and measurements are usually done at least in triplicate with the mean reported [21].

The tensile testing was done according to ISO 527-2 using a Zwick™ tensile tester. A cross-head speed of 1 mm/min was used to determine the E modulus and a speed of 50 mm/min was used to determine tensile strength and elongation at break.

4 Results and Discussion

4.1 Model Selection

For every response variable a Scheffé polynomial is required that can be used to predict it as a function of the design variables. To definitively determine the 'best' Scheffé polynomial for each response variable requires that all possible variants of the Scheffé polynomial, with increasing model complexity, are tested using the data. For example, a 2nd order Scheffé polynomial has the form

$$y = \sum_{1 \le i \le q} \beta_i x_i + \sum_{1 \le i < j \le q} \beta_{ij} x_i x_j \tag{8}$$

where q is the number of factors in $\mathbf{x}$, y is the response and β are the model parameters. When $q = 7$ there are 28 model terms that can be used to construct a model; 7 first order terms and 21 interaction terms [24]. This means that for a model with a complexity of 1 (or in other words including only one term) there are 7 possible models taking into account the hierarchy principle (the hierarchy principle states that a higher order model term can only be included if the lower order terms it contains are also included in the model [23]). If the model complexity is 2 the number of possible models increases to 21 and then to 56 for 3 terms and 140 for 4 terms etc., increasing exponentially with increasing model complexity.

In total there are 2.35 million different possible models for the 2nd order Scheffé polynomial with $q = 7$. To validate all the possible models the data from the experiments described in sections 3.4.2 to 3.4.8 is collected into a single data set where each row represents a sample, identified by its sample number, and each column represents a response variable. The data for each column is normalized to be between -1 and 1 using the following transformation

$$y^* = 2\left(\frac{y - \mathbf{y}_{min}}{\mathbf{y}_{max} - \mathbf{y}_{min}}\right) - 1 \tag{9}$$

where y^* is the scaled response value and $\mathbf{y}_{max}$ and $\mathbf{y}_{min}$ are the maximum and minimum value for that particular response variable. The particular range of -1 to 1 for the normalisation is selected so that in the hypothetical situation where a response variable has no relation to the design variables, the true mean will be 0 and the resultant model parameters for the true Scheffé model will all be 0 as well.

The design variables can be expressed in a similar way with each row representing a sample number and each column representing a design variable. The interaction terms for the 2nd order Scheffé polynomial can be included as additional columns to form the matrix X

$$X = \begin{bmatrix} x_{1,PVC} & \cdots & x_{1,sph.fill} & x_{1,PVC}x_{1,fill} & \cdots & x_{1,LDH}x_{1,sph.fill} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ x_{53,PVC} & \cdots & x_{53,sph.fill} & x_{53,PVC}x_{53,fill} & \cdots & x_{53,LDH}x_{53,sph.fill} \end{bmatrix} \tag{10}$$

This simple transformation will allow linear regression to be used when validating the models rather than non-linear regression. Linear regression is significantly faster than non-linear regression which is important due to the number of models which need to be validated.

The model for each response variable can then be expressed as

$$\mathbf{y} = X\boldsymbol{\beta} + \boldsymbol{\epsilon} \tag{11}$$

where $\boldsymbol{\beta}$ is a column vector of the model parameters and $\boldsymbol{\epsilon}$ represents the measurement error for each sample. Estimates of the model parameters, referred to as $\hat{\boldsymbol{\beta}}$, can then be determined using ordinary least squares. For each model that is tested only the relevant columns of X are used. Similarly if there is data missing for a certain sample of $\mathbf{y}$ that row is excluded for X and $\mathbf{y}$.

Therefore for each response variable $\mathbf{y}$ is constructed, all possible models are generated and X is augmented for each model. All of the possible models are then scored using k-fold cross validation (a validation technique that is used to evaluate the predictive ability of a model [27]) with $k = 3$. To minimise any effects on the score resultant from the order in which the experiments were conducted, the order of the samples is randomized before splitting into the different folds for each response variable. This is only done once per response variable so that the scores on different models can be compared. The scoring results can be illustrated by plotting the highest score for each level of model complexity. An example of this is shown in Figure 2 for the final degradation time measured with the torque rheometer.

The k-fold score figures for the response variables that are predicted well tend to have a similar shape to the example shown in Figure 2. The score increases, plateaus and then eventually decreases due to overfitting. The plateau effect means that it is possible to choose a model with a complexity that is significantly lower than the model with the best score, without decreasing the score significantly. This is favored due to the fact that models with lower complexity with close to the maximum possible score are more likely to indicate the true behavior of the response variables. Therefore the model that is selected is defined as the model with the lowest complexity where the maximum score is less than 5 % greater than the score of that model. The model with the maximum score and the model that is selected for the final degradation time are indicated on Figure 2.

In this case a model with 9 terms is selected rather than a model with 13 terms. The models for all the response variables are selected using this method.

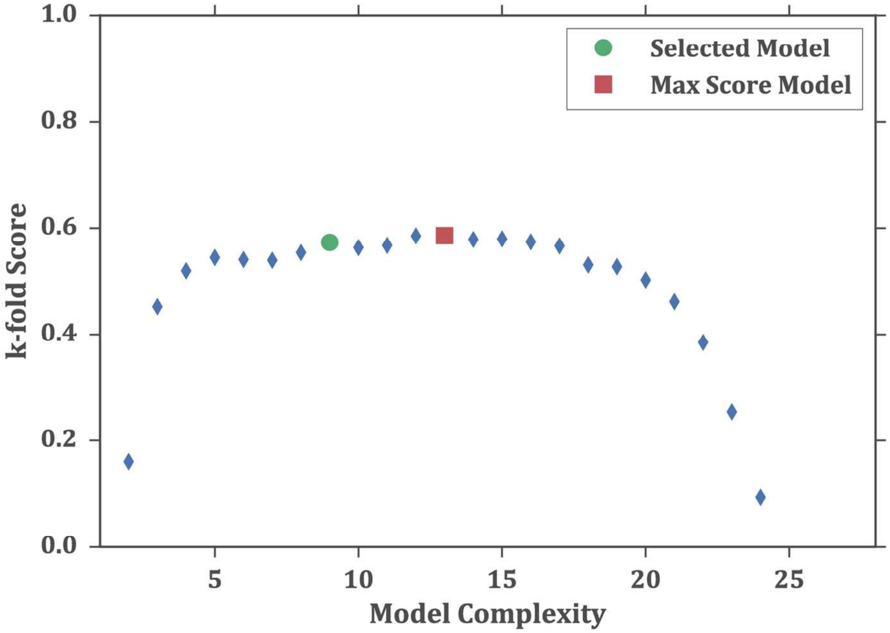

Figure 2: k-fold score curve showing the selected model and the model with the highest scores

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4.2 Model Analysis

4.2.1 Statistical Significance of Model Terms

Each of the specific models that is selected contains information about the relationship between the design variables and the response variable. The statistical significance of each term can be analyzed using the t-statistic. The statistical significance of a model term can be interpreted as the contribution of that term to the changes in the response variable, or in other words its importance to the response variable. This is demonstrated again using the final degradation time response variable. The t-values for the terms of the selected model are shown in Figure 3

The terms are sorted according to the absolute value of the t-statistic or in other words from the most significant to the least significant term. Positive t-statistics correspond to positive model terms and negative t-statistics to negative terms. Note also that an absolute t-statistic of less than 2 corresponds to a p-statistic greater than 0.05 and hence, a confidence in the statistical significance of less than 95 %.

It is clear from Figure 3 that the most important term is the synergistic interaction between the LDH and DINP. This is interesting as the positive effect of LDHs on long term thermal stability of PVC is well documented but has never been linked to the amount of DINP in a formulation. This implies that there is a mechanism in which the DINP assists the LDH in performing its stabilizing action. This already demonstrates the value of statistical experimental design over doing traditional one-factor-at-a-time experiments, which are the norm in literature on the use of LDH as a PVC additive. Further analysis reveals that there is relatively strong evidence of antagonism between the LDH and primary stabilizer. This is contrary to what is reported in literature for LDHs in general which are specifically mentioned as synergists to primary stabilizers. There is also some evidence of synergism between the LDH and the spherical filler which supports the hypothesis stated in section 2.2.

The analysis demonstrated above shows how statistical experimental design can be used to draw conclusions about the behavior of all the included design variables and their interaction with each other over the entire experimental space. To make the same observations using the favored one factor-at-a-time experiments, where changes in the phr of a single ingredient are made, would take an impractically large number of experiments. A similar analysis can be conducted for every response variable. It is important however that the k-fold score of the model is considered. If the predictive ability of the model is very poor it is unlikely that conclusions made using the model parameters will be meaningful. For the example of the thermal degradation time the score for the selected model is 0.573 (the maximum score is 1). While this is not particularly high the variance involved with torque rheometer measurements is expected to be high and hence the prediction scores will be lower than for response variables with low variance.

4.2.2 Sensitivity Analysis

It is clear from the analysis above that the overall effect of a particular ingredient on a particular response variable can be dependent on the mass fractions of the other ingredients, due to the interaction terms. To determine the overall effect of each ingredient

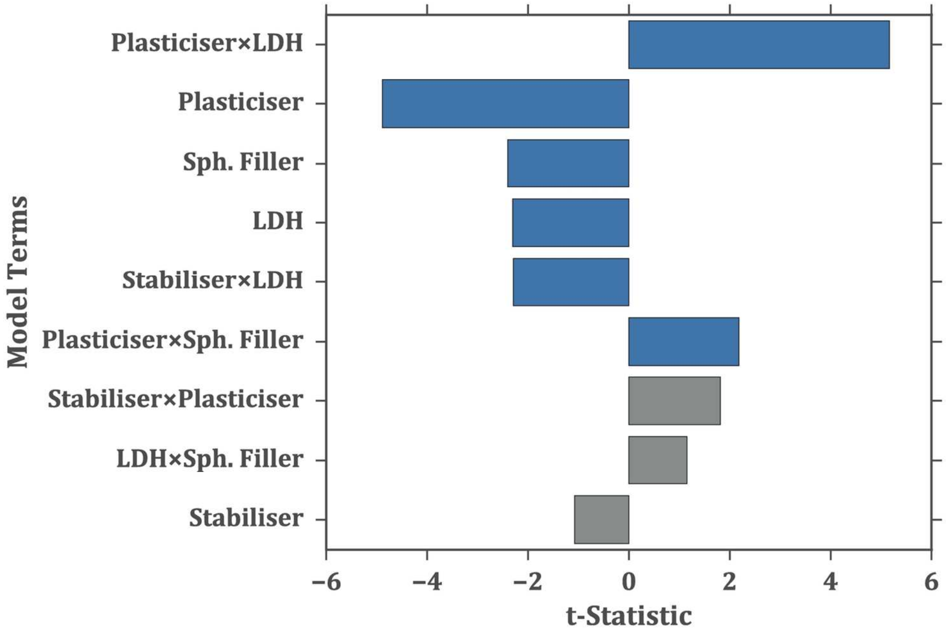

Figure 3: t-statistics for the model terms for the final degradation time measured by the torque rheometer, blue bars indicate confidence above 95 % in the relevance of the parameter and the grey bars indicate confidence below 95 %

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a sensitivity analysis of the response variable at a certain formulation can be used. The sensitivity of a response variable to the ingredients can be determined using the partial derivatives. For example the model for the final degradation time given as

$$y^* = -6.5x_{stab} - 4.6x_{DINP} - 12.3x_{LDH} - 8.6x_{sph.fill} + 60.5x_{stab}x_{DINP} - 206x_{stab}x_{LDH} + 114.9x_{DINP}x_{LDH} + 39.6x_{DINP}x_{sph.fill} + 50x_{LDH}x_{sph.fill} \quad (12)$$

has the following partial derivatives

$$\frac{\partial y^*}{\partial x_{PVC}} = \frac{\partial y^*}{\partial x_{fill}} = \frac{\partial y^*}{\partial x_{FR}} = 0 \quad (13)$$

$$\frac{\partial y^*}{\partial x_{stab}} = -6.5 + 60.5x_{DINP} - 206x_{LDH} \quad (14)$$

$$\frac{\partial y^*}{\partial x_{DINP}} = -4.6 + 60.5x_{DINP} + 114.9x_{LDH} + 39.6x_{sph.fill} \quad (15)$$

$$\frac{\partial y^*}{\partial x_{LDH}} = -4.6 - 206x_{stab} + 114.9x_{DINP} + 50x_{sph.fill} \quad (16)$$

$$\frac{\partial y^*}{\partial x_{sph.fill}} = -8.6 + 39.6x_{DINP} + 50x_{LDH} \quad (17)$$

The values of the partial derivatives at a certain formulation show the effect of making a very small increase in the relevant ingredient. This is interpreted as the sensitivity of the model and is a very useful method to analyze the effects of the ingredients on the different response variables. This is demonstrated for selected response variables using an example formulation based on an existing PVC cable formulation [11]. The sensitivities of the thermal stability at the example formulation, in terms of the torque rheometer measurements of short and long term stability, are shown in Figure 4.

Note that the sensitivities for the final degradation time shown in Figure 4 are calculated using equations 13 to 17. The strong influence of the primary and secondary stabilizers on the thermal stability in general is clear. The primary stabilizer, however, has a stronger influence on the short term stability than the LDH whereas the LDH has a stronger influence on the long term stability which is to be expected.

It is important to note, however, that the sensitivity analysis shows the effect of an independent change in each of the design variables. This is not possible in a mixture due to the mixture constraint (it is theoretically possible to calculate the partial derivative while taking the mixture constraint into account, however, in this investigation the 'straight' partial derivative is used for expediency). Consider, for instance, the sensitivity analysis of the final degradation time shown in Figure 4. The final degradation time is not sensitive to

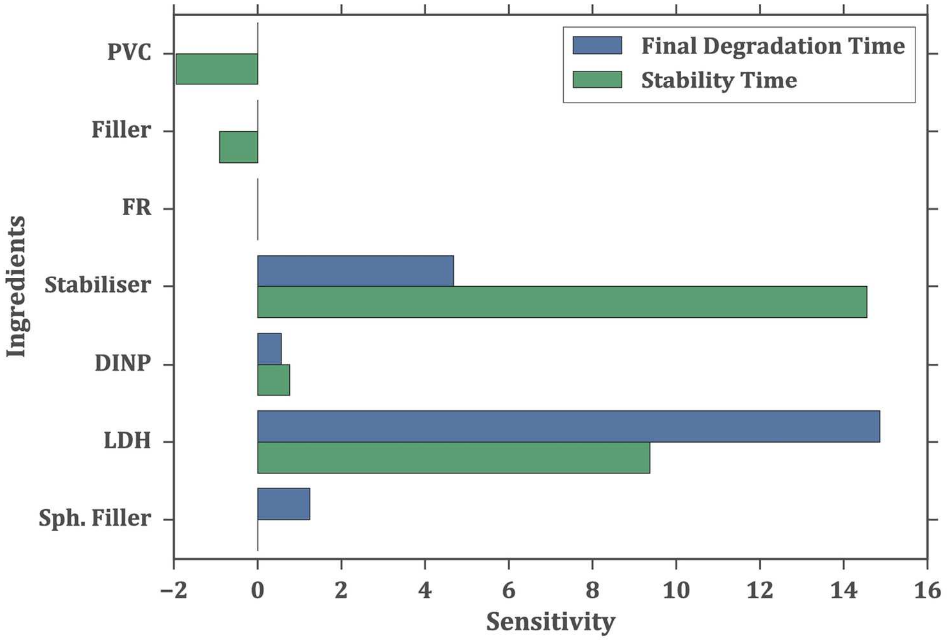

Figure 4: Thermal stability sensitivities at the example formulation

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the amount of FR, however if the mass fraction of FR is changed then the mass fraction of at least one other ingredient needs to change to maintain the mixture constraint. If the amount of Filler or PVC is adjusted to absorb the change in FR there will be no effect on the final degradation time since they also do not have an effect on the final degradation time according to the model. However if the mass fraction of any of the other ingredients is changed the final degradation time will change. In the case where a response variable is sensitive to all of the remaining ingredients it is impossible to change the mass fraction of the ingredient in question without changing the response variable.

This is particularly important when making adjustments to a formulation in the traditional units of phr. This is due to the fact that a change in phr of an ingredient relates to an increase in the mass fraction of the ingredient in question, while the mass fractions of the remaining ingredients are decreased together, to a lesser extent, with only their ratios maintained. This is illustrated in Figure 5 where the effect of a 1 phr increase for each of the ingredients on the scaled response variables for Figure 4 is shown.

Figure 5 shows one of the inherent problems created by using phr as unit for PVC compound mixtures. Take for example a formulator that needs to increase the fire retardancy of the example formulation. If the formulator simply increases the phr of the FR sufficiently to achieve the desired fire retardancy properties the final degradation time will decrease. If the final degradation time of the example formulation was on the limit of what is acceptable (which is true if the formulation is an optimum formulation) then the new formulation will fail the thermal stability requirements. These unwanted changes make it near impossible for a person to find an optimum formulation when multiple response variable requirements are present and only changes in the phr of ingredients are made or by using only data generated using one-factor-at-a-time experiments with changes in phr. Even finding acceptable formulations can be a challenge, requiring time and an experienced formulator. It also shows how one-factor-at-a-time experiments using changes in phr can be misleading and/or skewed. Consider for instance a one-factor-at-a-time experiment where FR is varied and the effect on thermal stability is analyzed. The results in isolation would seem to indicate that the FR has an effect on the thermal stability whereas in reality the FR has no effect, which is clear from Figure 5.

It is also important to note that Figure 4 and Figure 5 are quite similar, especially when it comes to the most significant ingredients for the thermal stability which are the primary stabilizer and the LDH. This shows one of the advantages of using phr as a unit for PVC formulations. If a formulator has no information about which of the other ingredients affect the response variable, or other response variables, a change in phr of one ingredient is a way of minimizing the necessary change in any particular other ingredient.

The sensitivities for the fire retardancy and mechanical properties at the example formulation (shown in Figure 6 and Figure 7) can be similarly analyzed. From Figure 6 the importance of the FR to the pHRR and MAHRE measurements is clear (take note that low pHRR, MAHRE and tSP values are desired). It is also clear that an increase in DINP is detrimental to the fire retardancy of the example formulation. It is interesting to note that the LDH has no effect on the pHRR and MAHRE values but has a significant effect on the tSP. Based on this evidence the LDH can only be classified as a smoke suppressant and not as a true fire retardant.

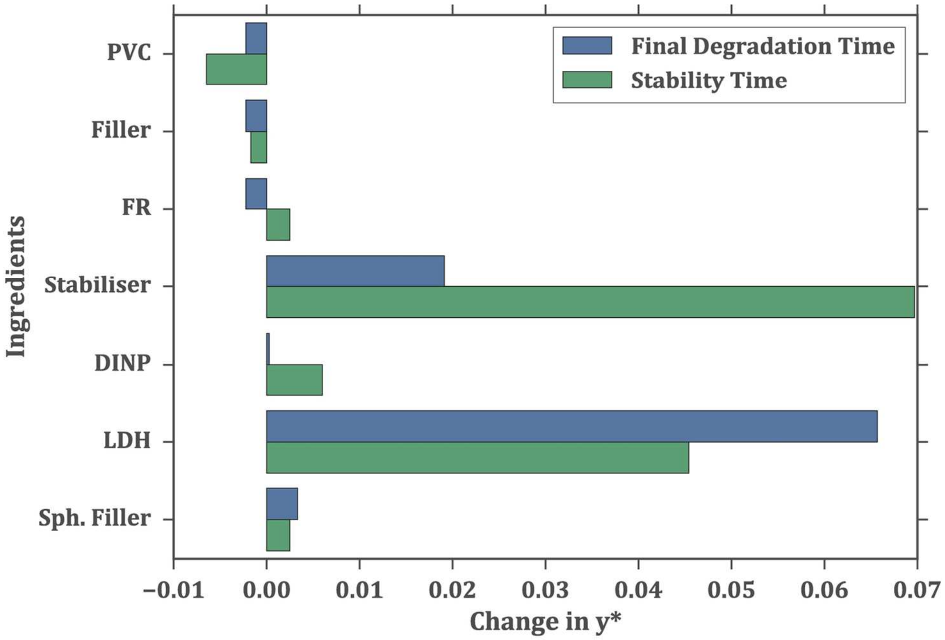

Figure 5: Change in y* for thermal stability induced by a 1 phr increase for each ingredient

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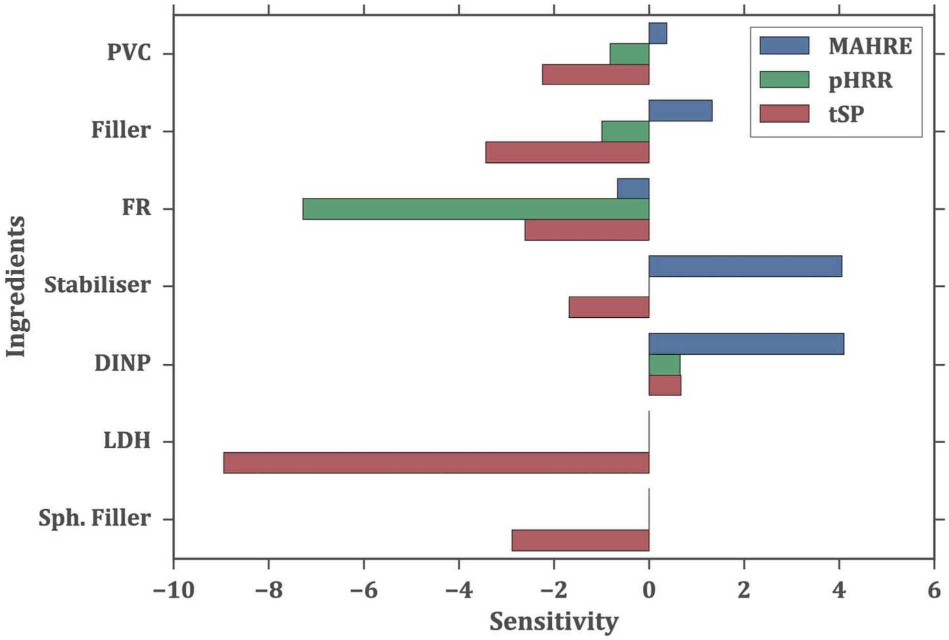

Figure 6: Fire retardancy sensitivities at the example formulation

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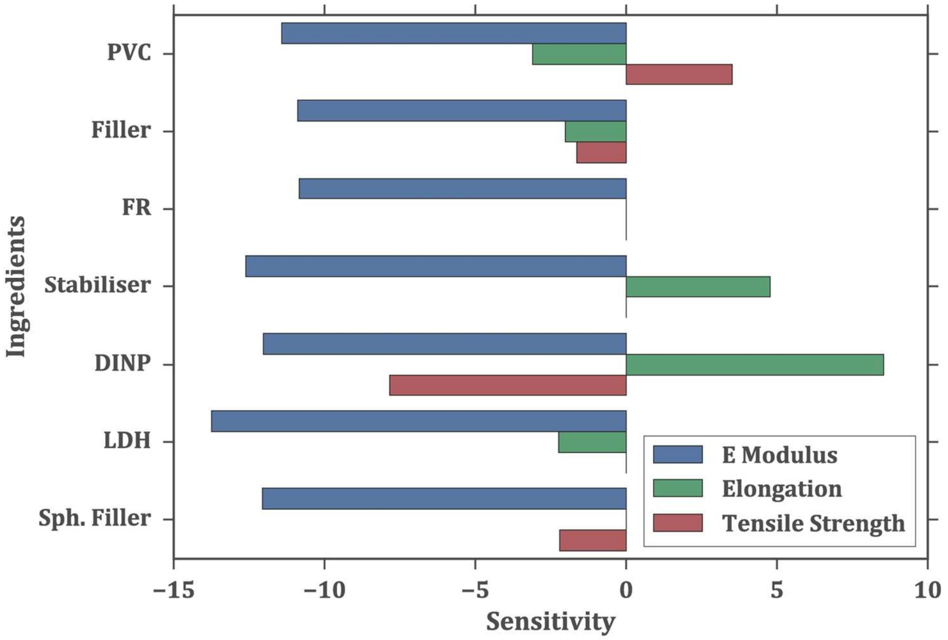

Figure 7: Mechanical property sensitivities at the example formulation

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The interpretation of the elongation and tensile strength sensitivities shown in Figure 7 is simple. It shows how the DINP increases elongation and decreases tensile strength while the PVC has exactly the opposite effect. It also shows how all of the inorganic additives (except the FR which has no effect) have a negative effect on at least one of the two mechanical properties. This shows for instance that the LDH cannot be used without considering the adverse effects it has on the elongation at break of the material. The interpretation of the sensitivities for E is not as straight forward when considering the mixture constraint. Since E is almost equally sensitive to all of the ingredients the change in E is based on the relative sensitivities of all of the ingredients that change (with a minimum number of two ingredients changing).

4.3 Optimization

Analyzing each response variable using the model statistics is useful. Optimization on the other hand can be used to analyze the entire system, as well as its more obvious function of finding an optimum solution for a given set of conditions.

4.3.1 Optimum Solution

The optimization can be summarized as follows: minimize

$$f = \sum_{i=1}^{7} c_i x_i \tag{1}$$

subject to

$$\sum_{i=1}^{7} x_i = 1 \tag{2}$$

$$0 \leq x_i \quad i = 1,2,\dots,7 \tag{3}$$

$$p_{lower} \leq p(\mathbf{x}) \leq p_{upper} \tag{4}$$

$$0.4 \leq x_{PVC} \tag{18}$$

$$x_{fill} \leq 0.7 x_{PVC} \tag{19}$$

$$x_{FR} \leq 0.2 x_{PVC} \tag{20}$$

$$0.02 x_{PVC} \leq x_{stab} \leq 0.1 x_{PVC} \tag{21}$$

$$0.2 x_{PVC} \leq x_{DINP} \leq 0.7 x_{PVC} \tag{22}$$

$$x_{LDH} \leq 0.15x_{PVC} \tag{23}$$

$$x_{sph.fill} \leq 0.2x_{PVC} \tag{24}$$

The details for equations 1 to 4 are found in sections 2.3 and 2.4. Equations 18 to 24, which represent the limits to the design space for the experimental design, are included so that extrapolation of the empirical models is not possible. The objective depends on the values that are used for the ingredient costs $\mathbf{c}$ and the limits on the material properties p_{lim}. In reality the costs of the ingredients vary depending on their availability and the size of the order or contract etc. The costs used here are based broadly on the expected costs of the various ingredients (in South Africa) to give a realistic demonstration of the optimization. Note that since the LDH is not a commercial product a rough cost estimate is used. The estimated costs that are used are shown in Table 4.

The limits on the properties are also estimated, taking into account the requirements for underground mine cables. An experienced PVC formulator would be able to determine more exactly what the required property settings should be. For this example only the most relevant response variables, using the most comprehensive measuring technique, are limited. The limits used as well as the maximum and minimum measured values and k-fold score for each of the selected response variables is shown in Table 5.

The range of the measured values is shown to provide some context for the limit values. The k-fold scores are shown because it is important to take into account the accuracy of the model prediction when setting the property limits. This is due to the fact that optimization by its nature will push against the active constraints. This means, for instance, that the predicted final degradation time of the optimum solution is likely to be 80 min. However the model describing the final degradation time has a k-fold score of 0.57 which is not particularly high. This means that there is an associated prediction error and that it is distinctly possible that the real final degradation time for the optimum formulation is less than 80 min. To avoid this safety factors need to be introduced in the property limits and the required size of the safety factors can be gaged using the k-fold score. For instance, the elongation and tensile strength at break are predicted very well, both having a k-fold score of 0.92, which means significantly lower safety factors are required.

The optimum solution is found using a constrained non-linear optimization algorithm called Sequential Least Squares Quadratic Programming (SLSQP). Multiple starts are used, with randomly generated $\mathbf{x}_0$ values for each start, to increase the chance of finding the global optimum. The optimum solution for the settings shown in Table 4 and Table 5 is shown in Table 6. All the response variable values are shown in Table 7 with the response variables which are included in the constraints and the values which are constrained in bold.

Table 7 allows for the inspection of all of the response variable values at the optimum formulation. If a value which is currently not constrained is not satisfactory a limit on that value can simply be included. Note however that adding constraints, if they are active, will always lead to an increase in the objective function. It is also important to note that it is

Table 4: Estimated costs for PVC formulation ingredients

Ingredient	Cost (R/kg)
PVC	15
Filler	8
FR	48
Stabilizer	45
DINP	30
LDH	40
Spherical Filler	3

Table 5: Property limits for optimization including the range of measured values and k-fold scores

Equipment	Response Variable	Max	Min	p_{lim}	k-fold Score
Torque Rheometer	Stability Time (min)	141.4	8.5	$\geq \mathbf{25}$	0.58
	Final Degradation Time (min)	346.9	12.6	$\geq \mathbf{80}$	0.57
Cone Calorimeter	MARHE (kW/m^2)	179.2	12.1	$\leq \mathbf{85}$	0.89
	pHRR (kW/m^2)	242.8	60	$\leq \mathbf{125}$	0.7
Tensile Test	E (MPa)	1917.7	23.6	$\leq \mathbf{300}$	0.86
	Elongation at Break (%)	114.8	9.8	$\geq \mathbf{50}$	0.92
	Tensile Strength at Break (MPa)	29.5	10.6	$\geq \mathbf{18}$	0.92

Table 6: Example optimum formulation

Ingredient	Mass Fraction (%)	phr
PVC	53.19	100
Filler	3.34	6.3
FR	10.04	18.9
Stabilizer	1.06	2.0
DINP	18.99	35.7
LDH	2.73	5.1
Spherical Filler	10.64	20.0
Objective Function (R/kg)		20.65

Table 7: Response variable values at the example optimum solution

Equipment	Response Variable	Max	Min	Value	*k*-fold Score
Torque Rheometer	**Stability Time (min)**	141.4	8.5	32.2	0.58
	Final Degradation Time (min)	346.9	12.6	**80**	0.57
	Resting Torque (N·m)	8.7	-1.9	3.9	0.61
Thermomat	Stability Time (min)	451.4	0	50.6	0.41
Color	YI	140.8	-4.9	44.7	0.63
Cone Calorimeter	**MARHE (kW/m^2)**	179.2	12.1	**85**	0.89
	pHRR (kW/m^2)	242.8	60	**125**	0.70
	t to pHRR (s)	460	25	132.1	0.65
	t to Ignition (s)	216	13	58.5	0.36
	tHR (MJ/m^2)	56.6	6.3	29.6	0.76
	tSP (m^2)	18.1	3.7	12.5	0.66
LOI	-	37.7	23.2	35.4	0.91
MCC	pHRR 1 (W/g)	388.3	85.7	245.3	0.88
	pHRR 2 (W/g)	92.6	54.0	71.6	0.75
	tHR (kJ/g)	20	10.1	12.7	0.85
	tHR Peak 1 (kJ/g)	12.4	3.7	6.1	0.96
	tHR Peak 2 (kJ/g)	8.9	5.2	7.3	0.35
	T pHRR 1 (C)	294.9	248.3	249.3	0.78
	T pHRR 2 (C)	467.9	451.9	455.8	0.35
	t to pHRR 1 (s)	314	228.5	250.6	0.24
	t to pHRR 2 (s)	506.5	426.5	466.4	0.00
Tensile Test	E **(MPa)**	1917.7	23.6	149.1	0.86
	Elongation at Break (%)	114.8	9.8	**50**	0.92
	Tensile Strength at Break (MPa)	29.5	10.6	19.5	0.92

possible that adding or increasing a constraint will mean that there is no solution, in which case the constraints need to be relaxed.

It is interesting to note that for the above case the constraints

$$x_{sph.fill} \leq 0.2x_{PVC} \tag{24}$$

$$0.02x_{PVC} \leq x_{stab} \tag{21}$$

are active. This indicates that if the models are extrapolated it is possible to further reduce f by including more spherical filler or less primary stabiliser. However, extrapolation decreases the confidence in the predicted values. Extrapolating purely empirical models is always questionable even if steps are taken to avoid overfitting.

4.3.2 Parametric Analysis

Parametric analysis involves determining the influence of changes in the input settings on the optimal solution. It can be used to analyze the system as a whole. Fortunately for this system the optimization is very simple requiring no more than a few seconds to find a solution. This makes it possible to perform very detailed parametric analyses. Two example analyses are used to demonstrate how they can be performed and how useful they are.

4.3.2.1 Change in Response Variable Constraint Value

It may be of interest to determine how a change in the limit set on a response variable will influence the formulation and the objective function. This can be done by running the optimization at different limits for the response variable in question while keeping the rest of the settings the same. This will be demonstrated for the final degradation time. All other settings are kept constant at the values shown in Table 4 and Table 5 (referred to as Case 0 in the following discussion). The objective and the mass fractions as a function of the limit on the final degradation time are shown in Figure 8 and Figure 9 respectively.

Figure 9 shows how parametric analysis can reveal the complex interplay between the PVC compound ingredients with changing conditions. It is clear that the LDH has an important role to play in increasing the final degradation time but that it is not the only ingredient that is changed to achieve an optimum formulation. Complex behavior such as this can only be revealed by taking into account the entire system, particularly taking into account the cost performance of the ingredients. It is also important to note that parametric analysis of this system is not restricted to two dimensions, or what is effectively a one-factor-at-a-time approach, as was used for the above examples. This was done simply to demonstrate the principle and to make the interpretation of the analysis easier.

4.3.2.2 Change in Response Variables Constrained

The response variables that are constrained can also be changed. This is of interest for this study due to the different methods used to measure the thermal stability and the fire retardancy. In terms of thermal stability the values for Thermomat stability time and YI are both satisfactory for Case 0 where the Torque Rheometer final degradation time is

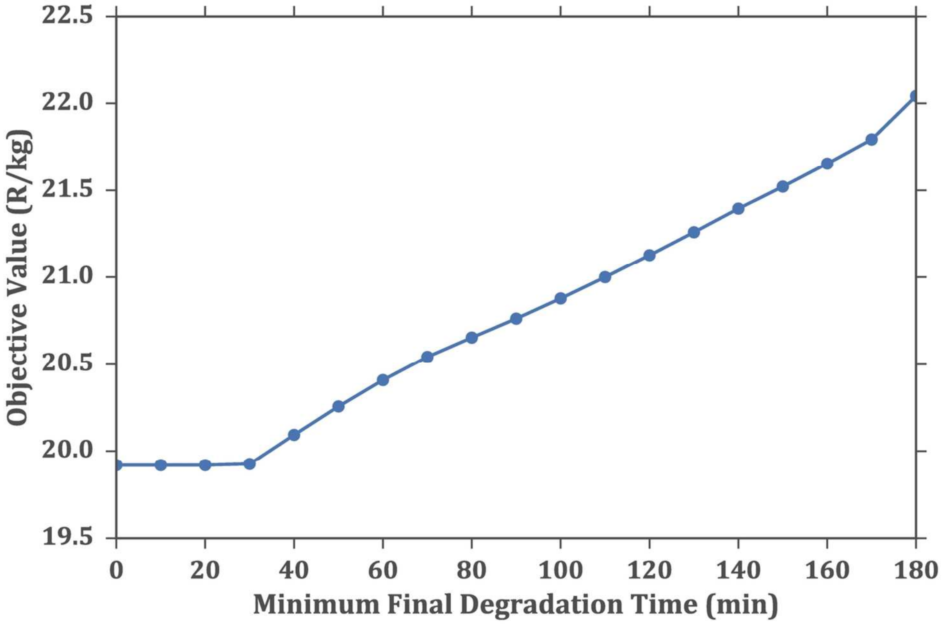

Figure 8: Parametric analysis for minimum final degradation time showing objective function value

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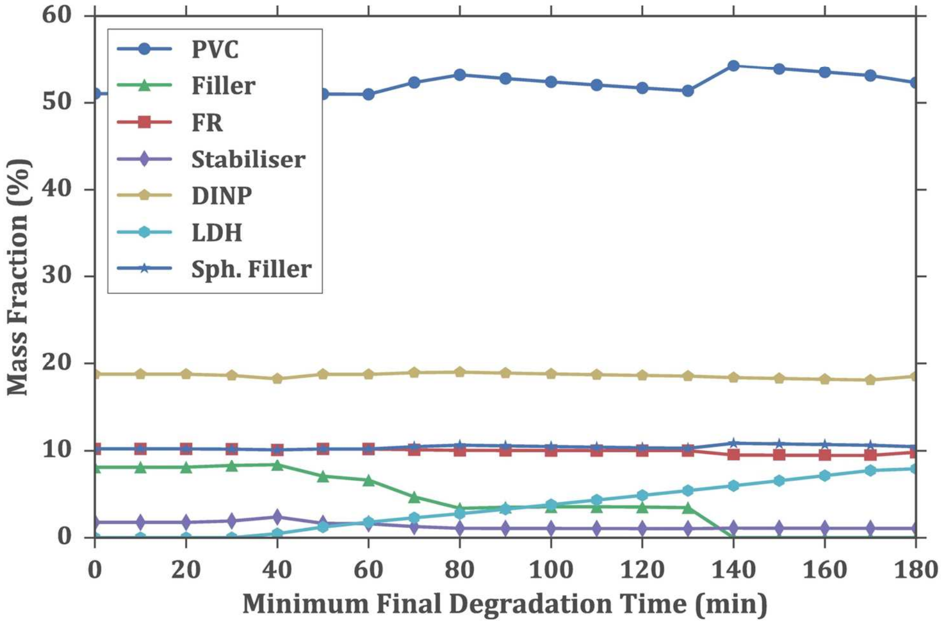

Figure 9: Parametric analysis for minimum final degradation time showing formulation

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Table 8: Optimum formulation where Thermomat rather than Torque Rheometer response variables are constrained

	Mass Fraction (%)	
Ingredient	Case 0	Case 1
PVC	53.19	52.07
Filler	3.34	6.76
FR	10.04	10.19
Stabilizer	1.06	1.56
DINP	18.99	19.01
LDH	2.73	0
Spherical Filler	10.64	10.41
Objective Function (R/kg)	20.65	19.96

Table 9: Response variable values for thermal stability

Equipment	Response Variable	Value		k-fold
		Case 0	Case 1	Score
Torque Rheometer	Stability Time (min)	32.2	19.2	0.58
	Final Degradation Time (min)	**80**	27.07	0.57
	Resting Torque (N·m)	3.9	4.2	0.61
Thermomat	Stability Time (min)	50.6	**55**	0.41
Color	YI	44.7	10.2	0.63

constrained. This shows that the measurements are linked. However if the Torque Rheometer response variables are not constrained and instead only the Thermomat stability time is constrained the final degradation time is no longer satisfactory. The optimization results for this case (referred to as Case 1), with the Thermomat stability time constrained to a minimum of 55 min, are shown in Table 8 and Table 9

It is clear that the Thermomat stability time is not a complete representation of the thermal stability behaviour. This is expected due to the fact that it is a static and not a dynamic test like the Torque Rheometer. It fails to capture the long term stabilizing abilities of the LDH so that it is not included in the formulation. The YI can also be shown to be an insufficient measure of long term thermal stability.

The different measurement techniques for fire retardancy can be similarly investigated. It is of particular interest to determine if the less time consuming and complicated LOI and MCC measurements are sufficient to describe the fire retardancy of the system. However this requires a more detailed investigation of the system beyond the scope of this investigation, but is recommended for future work due to the fact that the data set is well suited to such an investigation.

4.4 Implementation

All of the calculations and analyses described in sections 4.1 to 4.3 were done using code written in Python programming language using Jupyter [6]. The model validation was done using scikit-learn [28] and the model statistics were calculated using Statsmodels [29]. The optimization of the system was done using SciPy [30].

4.5 Labor and Time Savings

The utility of the models is demonstrated extensively in the previous sections. Another important aspect of using statistical experimental design, that has not been highlighted, is the efficiency with which it uses experimental data. This is important due to the fact that real experiments will always use resources i.e. there will always be an associated cost of performing the experiments.

For instance a resource which is particularly relevant for the experiments used in this study is the time required. Consider, for instance, the time required in this investigation for the Torque Rheometer, Cone Calorimeter and Tensile Tests which is shown in Table 10.

Consider a hypothetical situation where a formulator wishes to find an optimum formulation of the same system, using only the traditional one-factor-at-a-time experiments with changes in phr and a sequential next-best-guess approach. There is a set requirement for the thermal stability, fire retardancy and tensile properties that needs to be reached. Say the formulator uses a known formulation as a starting point. The properties are then ordered and a certain core ingredient to change for each property is selected. Say the LDH for stability, the FR for fire retardancy and the DINP for the mechanical property are selected.

The phr of LDH in the formulation is changed first. For example say that 5 additional formulations are used with each formulation tested using the torque rheometer. Since the

Table 10: Number of days required to obtain Torque Rheometer, Cone Calorimeter and Tensile Test data

Process/Equipment	No. Samples	No. Samples/Day	No. Days
High Speed Mixing	53	20	3
Compounding	53	12	5
Torque Rheometer	46	4	12
Pressing	40	15	3
Cone Calorimeter	40	15	3
Injection Molding	27	8	4
Tensile Test	27	7	4
		Total	**34**

Table 11: Number of experiments and amount of time required for example of next-best-guess approach using one-factor-at-a-time experiments

	No. of Runs/Batches							
Process/Equipment	LDH	FR	DINP	Filler	Sph. Filler	Total	No. Samples /Day	No. Days
High Speed Mixing	1		6	1		8	20	1
Compounding	6	6	6	6	6	30	12	3
Torque Rheometer	18			18	18	54	4	14
Pressing		18		18	18	54	15	4
Cone Calorimeter		18		18	18	54	15	4
Injection Molding			18	18	18	54	8	7
Tensile Test			18	18	18	54	7	8
							Total	**41**

torque rheometer is known to have a high variance the formulator uses triplicate measurements on each formulation therefore requiring 18 runs. Since only the phr of LDH is changed (and not that of the DINP) only one batch of high speed mixing (i.e. making one dry mix) is required. The formulator analyses the results and chooses a new base formulation satisfying the thermal stability requirement. The formulator then repeats the above process for the FR and Cone Calorimeter experiments and the DINP and tensile experiments.

The formulator then decides to increase the Filler amount to decrease the overall cost of the formulation having fulfilled the material requirements by running one-factor-at-a-time experiments for all three response variables. A new base formulation is again chosen such that the material requirements are still achieved. This is repeated with the Spherical Filler. The process described above is summarized in Table 11 including a calculation of the approximate amount of time required.

At this point in the hypothetical example more time has already been spent than what is shown in Table 10. At best the formulator has found an improved formulation (i.e. with a lower cost) which satisfies the requirements. This formulation is, however, highly unlikely to be the optimum formulation. To find the optimum formulation would require many more iterations of the type of processes described above, and even if the optimum is found it is difficult to prove that it is indeed the optimum using data generated in this way. In addition to this if the property requirements are subsequently changed a portion if not the entire experimental process needs to be repeated. In summary the proper use of optimization and statistical experimental design not only makes it possible to find an optimum formulation for a range of different requirements, it also requires significantly less labor and time to get to an optimum solution.

5 Conclusions

5.1 Response Variable Models

It can be concluded that the response variables describing the thermal stability, fire retardancy and basic mechanical properties as a function of the mass fractions of the PVC compound ingredients (i.e. the formulation) can be modelled effectively using 2nd order Scheffé polynomials. The particular empirical models for each response variable, selected and evaluated for predictive ability using k-fold cross validation, can be interpreted using statistics to make deductions about the relationship between the response variables and the formulation. The interaction terms in the 2nd order Scheffé polynomial are particularly useful in identifying synergistic and antagonistic relationships between ingredients.

This principle is demonstrated using the model selected to describe the final degradation time measured by the torque rheometer. The model shows clearly that there is a synergistic relationship between DINP and the LDH which has the greatest influence on the final degradation time. There is also evidence that supports the hypothesis that the LDH and spherical filler are synergists. Finally it is interesting to note that there is relatively strong evidence of antagonism between the LDH and primary stabilizer which is contrary to what is reported in literature. These conclusions show the value of using statistical experimental design over the one-factor-at-a-time experiments favored in the literature on LDH as a PVC additive.

The interaction terms in the models mean that the effect of a certain ingredient is dependent on the mass fractions of the other ingredients. Sensitivity analysis can be used to determine the overall effect of a very small independent change in the mass fraction of an ingredient on a response variable at a given formulation. Sensitivity analyses of selected response variables at an example formulation are used as a demonstration. The example sensitivity analysis for the long and short term thermal stability shows the strong influence of the primary stabilizer and the LDH. It also shows how the primary stabilizer has a stronger influence on short term stability while the LDH has a stronger influence on long term stability.

The sensitivity analyses for the fire retardancy of the example formulation shows that the FR is the most important ingredient in terms of reducing the pHRR and MAHRE values. It also shows that an increase in the DINP has a detrimental effect on fire retardancy. Interestingly the LDH only has an effect on the tSP value, which means that in this case the LDH can only be classified as a smoke suppressant and not as a true fire retardant. The sensitivity analysis of the mechanical properties shows how the DINP increases elongation and decreases tensile strength while the PVC has exactly the opposite effect. It also shows how all of the inorganic additives (except the FR which has no effect) have a negative effect on at least one of the two mechanical properties. This shows for instance that the LDH cannot be used without considering the likely adverse effects that it has on the elongation at break.

5.2 Optimization

It can also be concluded that the models make it possible to minimize the cost of the PVC compound by varying the formulation. The optimum formulation is a function of the costs of the various ingredients and the limits which are placed on the response variables. To analyze the system as a whole, parametric analysis can be used. The number of different analyses which can be done is very large and depend on the specific questions which need to be answered. Some basic analyses demonstrate the usefulness of parametric analysis and highlight some interesting aspects of the system.

The value of the limit on a response variable can be changed. An analysis of this type, where the Torque Rheometer final degradation time is varied, reveals the complex interplay between the PVC compound ingredients with changing conditions.

The parametric analysis on this system can also be used to determine the completeness of the different measuring techniques used to describe the thermal stability and fire retardancy of the PVC compound. It is demonstrated that the Torque Rheometer is the only measuring technique for thermal stability, of those used in this study, to differentiate between the long term and short term stability. This means, for instance, that it is the only measuring technique which can capture the long term stabilizing effects of LDH. The different measurement techniques for fire retardancy can be similarly investigated.

Finally it can be concluded that using proper statistical experimental design over the traditional one-factor-at-a-time experiments leads to significant time and labor savings.

This is due to the efficiency with which statistical experimental design uses experimental data.

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