Modelling and Optimisation of Flexible PVC Compound Formulation for Mine Cables

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Synopsis

The thermal stability, fire retardancy and basic mechanical properties, as a function of the mass fractions of the poly(vinyl chloride) (PVC) compound ingredients, can be modelled using 2nd order Scheffé polynomials. The empirical models for each response variable can be determined using statistical experimental design. The particular models for each response variable, which are selected for predictive ability using k-fold cross validation, can be interpreted using statistical analysis of the model terms. The statistical analysis of the model terms can reveal the synergistic or antagonistic interactions between ingredients, some of which have not been reported in literature. The interaction terms in the models also mean that the effect of a certain ingredient is dependent on the mass fractions of the other ingredients. Sensitivity analysis can be used to examine the overall effect of a change in a particular formulation on the response variables.

The empirical models can be used to minimise 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 analyse the system as a whole, parametric analysis can be used. The number of different parametric analyses which can be done is very large and depends on the specific questions which need to be answered. Parametric analysis can be used to gain insight into the complex behaviour of the system with changing requirements, as a decision making tool in a commercial environment or to determine the completeness of the different measuring techniques used to describe the thermal stability and fire retardancy of the PVC compound. Statistical experimental design allows for the above methods to be used which leads to significant time and labour
savings over attempting to reach the same conclusions using the traditional one-factor-at-a-time experiments with changes in the phr of an ingredient.

It is recommended that the data generated for this investigation is analysed in more detail using the methods outlined for this investigation. This can be facilitated by making the analysis of the data (and therefore the data itself) more accessible through a usable interface. The data set itself can also be expanded to include new ingredients requiring very few additional experiments. If a PVC compound that contains none of the ingredients that were used in this investigation is of interest a new separate data set needs to be generated. This can be done by following the same procedure used in this investigation. In fact the method that is used in this investigation can be generalised to optimise the proportions of the ingredients of any mixture.

Keywords: PVC, mine cables, statistical experimental design, mixture optimisation
Acknowledgements

• My supervisors, Dr. Johan Labuschagne and Carl Sandrock
• Dr. Ines Kühnert, Dr. Andreas Leuteritz, Martin Zimmermann, Andreas Scholze and Yvonne Spörer of the Leibniz-Institut für Polymerforschung Dresden e.V.
• Harry Wright, Gerard James, Chirlene Botha and Isbe van der Westhuizen of the Institute of Applied Materials at the University of Pretoria
• Dr. Manfred Scriba and Gertrude Makgatho of the CSIR
• National Research Foundation of South Africa
• University of Pretoria StudyAbroad Bursary Programme
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Nomenclature

c Cost of ingredient R/kg
D Design variables matrix
E Elastic Modulus MPa
f Objective function value R/kg
k Number of folds for k-fold cross-validation
m Empirical conductivity model slope μS/(cm·min)
n Degree of Scheffé polynomial
N Number of terms
Ne Number of experimental points
p Material property value
plim Limit on material property value
q Number of components
t Time min
T_g Glass transition temperature °C
tint Time at intercept min
v_T Cross-head speed mm/min
X CIE tristimulus value
x Mass fraction
X Transformed design variable matrix
x_{DINP} Mass fraction of DINP
x_{fill} Mass fraction of filler
x_{FR} Mass fraction of FR
x_{LDH} Mass fraction of LDH
x_{PVC} Mass fraction of PVC
x_{sph.fill} Mass fraction of spherical filler
x_{stab} Mass fraction of primary stabiliser
Y CIE tristimulus value
y Response variable value
\[ y \] Response variable value vector
\[ y^* \] Scaled response variable value
\[ YI \] Yellowing Index
\[ y_{\text{min}} \] Minimum response variable value
\[ y_{\text{max}} \] Maximum response variable value
\[ Z \] CIE tristimulus value

Greek

\[ \beta \] Empirical conductivity model constant \( \mu \text{S/cm} \)
\[ \beta \] Model parameters vector
\[ \hat{\beta} \] Estimated model parameter vector
\[ \beta_i \] Scheffé polynomial linear parameter
\[ \beta_{ij} \] Scheffé polynomial two-way interaction parameter
\[ \beta_{ijk} \] Scheffé polynomial three-way interaction parameter
\[ \gamma_{ij} \] Scheffé polynomial antisymmetric two-way interaction parameter
\[ \epsilon \] Measurement error vector
\[ \theta \] Empirical conductivity model constant
\[ \sigma \] Conductivity \( \mu \text{S/cm} \)
\[ \sigma_{\text{min}} \] Conductivity offset \( \mu \text{S/cm} \)
\[ \tau \] Empirical conductivity model constant \( \text{min} \)
1 Introduction

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. One of the many types of additives used for PVC are Layered Double Hydroxides (LDHs). LDHs are used as thermal stabilisers and fire retardants in PVC. Developments by Labuschagne et al. (2006) 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 are not independent. 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.
A Ca-Al LDH manufactured using the effluent free method, a spherical fly ash filler and the industry standard primary thermal stabiliser, plasticiser, 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 optimised and consequently analysed 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 programmes written in Python programming language.
2 Theory

2.1 PVC

PVC is a commercially important and versatile thermoplastic which is synthesised using free-radical polymerisation of the vinyl chloride monomer (Wilkes, et al., 2005). PVC is the third most produced polymer in the world after polyethylene (PE) and polypropylene (PP). In 2013 the estimated global consumption of PVC was 39.3 million tonnes (Ceresana Research, 2014). Since the commercialisation of PVC in the 1930s the PVC industry has grown in spite of a number of challenges such as developing non-toxic thermal stabilisers and plasticisers (Braun, 2004). This pattern of increasing growth is still relevant with a predicted increase of 3.2% per year in the global demand for PVC (Ceresana Research, 2014).

Many of the interesting and unique aspects of PVC are due to the fact that it contains chlorine. The chemical structure of PVC is shown in Figure 1.

![Chemical Structure of PVC](image1)

Figure 1: Chemical Structure of PVC (Wilkes, et al., 2005)

The chlorine content of PVC by mass is approximately 58 %, meaning that PVC requires significantly less natural gas and oil as a raw material than other major polymers such as PP and PE, which are completely hydrocarbon based (Wilkes, et al., 2005). PVC is also an important chlorine sink. Chlorine is produced primarily as a by-product of the production of sodium hydroxide which is used in many industries as a strong base (Braun, 2004). In terms of the material properties the
presence of the chlorine atom makes PVC moderately polar and inherently flame retardant (Wilkes, et al., 2005).

2.1.1 Additives

The polarity of PVC combined with its amorphous structure make it compatible with a large number of different additives (Braun, 2004). The additives perform essential functions during processing of the PVC and influence the properties of the final product (Wypych, 2009).

2.1.1.1 Thermal Stabilisers

The presence of the chlorine in PVC, although helpful in many aspects, also results in an autocatalytic thermal degradation reaction. The degradation reaction is initiated by the release of labile chlorine from unstable chlorine groups such as allylic and tertiary chlorides which are a result of structural irregularities in the polymer (Wilkes, et al., 2005) (Schiller, 2015). During the thermal degradation hydrogen chloride (HCl) is released and double bonds are formed. The HCl acts as a catalyst for the degradation reaction (Bacaloglu & Fish, 1995). The thermal degradation reaction for neat PVC occurs below typical processing temperatures of 170 °C to 220 °C making it impossible to process PVC without the use of thermal stabilisers (Gupta, et al., 2009).

Stabilisers are grouped in two basic categories: primary and secondary stabilisers. Primary stabilisers react with the allylic chlorides preventing the initiation of the degradation reaction. Due to the autocatalytic nature of the degradation, once the process is initiated it accelerates very quickly. The primary stabilisers are essential for the inhibition of the initial step to maintain early stability. A number of primary stabilisers are available commercially including mixed metal stabilisers and organotins (Bacaloglu & Fisch, 2000).
Secondary stabilisers are substances which have the ability to scavenge HCl. The removal of HCl cannot prevent the initial degradation step but inhibits the abovementioned auto-catalytic degradation. This means that a secondary stabiliser used in isolation cannot give short term stability, but provides good long term stability (Bacaloglu & Fisch, 2000). LDHs and Zeolites are two materials commonly used as secondary stabilisers (Gupta, et al., 2009).

To obtain PVC with short and long term stability primary and secondary stabilisers are often combined (Bacaloglu & Fisch, 2000). The choice and amount of additives used together to form a so called ‘stabilisation package’ is important due to the fact that synergistic and antagonistic interactions between different stabilisers are common (Schiller, 2015).

2.1.1.2 Plasticisers

Plasticisers are substances that are incorporated into PVC to increase its flexibility and workability. The general plasticiser for PVC must contain a polar and non-polar chemical group. The polar part of the plasticiser molecule is able to bind with the polar PVC molecule while the non-polar part of the molecule limits the interaction of the PVC molecules with each other through van der Waal’s forces. The non-polar part of the molecule also creates additional free volume and provides some lubrication. All of these mechanisms contribute to the plasticisation of the PVC (Wilkes, et al., 2005).

The most commonly used chemicals for the plasticisation of PVC are phthalate esters, constituting approximately 87% of all PVC plasticisers (Schiller, 2015). The polar carbon-chloride bond \((\text{C}^5\text{+} - \text{Cl}^5\text{-})\) in PVC is particularly attracted to the carbonyl bond \((\text{C}^5\text{+} = \text{O}^5\text{-})\) in esters while the aliphatic side chain of the ester is the non-polar part of the molecule (Wilkes, et al., 2005). Traditionally diethylhexyl
phthalate (DEHP or DOP) was the most commonly used phthalate but it has been mostly replaced by diisononyl phthalate (DINP) (Schiller, 2015).

Plasticisers have a significant effect on both the processing of PVC and the final PVC part. During processing the plasticiser reduces internal friction and adhesion to metal surfaces (which can be a problem due to the polarity of PVC) through its lubricating effect while also decreasing the required processing temperature. In the final part the plasticiser reduces the elastic modulus $E$, tensile strength and glass transition temperature while increasing the elongation at break, bending strength and antistatic properties. The easy incorporation of plasticisers into PVC result in a broad range of compounds with different flexibilities from rigid PVC with no plasticiser to highly flexible PVC compounds that can be tailored to specific and varying applications (Schiller, 2015). A distinct disadvantage of using plasticisers, which are generally used in significant quantities in flexible PVC formulations, is that (with the exception of phosphoric acid esters) plasticisers are highly flammable (Wypych, 2009).

2.1.1.3 Fire Retardants

PVC is inherently fire and flame retardant. The high chlorine content means that there is less fuel available for combustion in contrast to completely hydrocarbon-based polymers such as PE which burn readily. The chlorine in the PVC also removes hydrogen as a fuel source from the condensed phase, through a radical trapping mechanism, producing HCl (in addition to the HCl produced through thermal degradation). The HCl in turn dilutes the gas phase decreasing the oxygen concentration (Wilkes, et al., 2005). The final fire retarding mechanism that is inherent to PVC is the formation of a char. Char formation is a desirable property for fire retardancy because the char acts as a barrier to heat and to the release of volatiles, which decreases the fuel available to the flame. Char formation also decreases smoke production (Wypych, 2008). Due to this inherent fire retardancy
rigid PVC does not require fire retarding additives. In flexible PVC compounds, however, fire retardants are required due to the flammability of the plasticisers as discussed in Section 2.1.1.2 (Wypych, 2009).

The main fire retardant used for flexible PVC is antimony trioxide (Sb$_2$O$_3$). During combustion Sb$_2$O$_3$ forms antimony trichloride (SbCl$_3$) which acts as a flame inhibitor by trapping radicals in a similar mechanism to the PVC itself (Levchik & Weil, 2005). Sb$_2$O$_3$ is generally added to PVC in relatively low concentrations. The other flame retardant additive used frequently in PVC is aluminium trihydrate (ATH). In contrast to Sb$_2$O$_3$ relatively high concentrations of ATH are required to have a reasonable effect on the flame retardancy (Wypych, 2009). Fortunately ATH is relatively cheap and so is used effectively as a functional filler. ATH and other mineral fire retardant fillers (such as magnesium hydroxide (Mg(OH)$_2$) which is also used in PVC) work through two different mechanisms. The first is through the release of water during combustion which dilutes the combustible pyrolysis products in the gas phase. The second is by providing a substantial inorganic residue which promotes the formation of a char and provides a barrier to heat and mass transfer (Levchik & Weil, 2005).

2.1.1.4 Fillers

Fillers are the most abundantly used additives by mass in PVC and other polymers. The main purpose of fillers is to reduce the overall material cost of a polymer compound (Wypych, 2009). The most commonly used filler in all polymers including PVC is calcium carbonate (CaCO$_3$). The main advantages of CaCO$_3$, which make it popular as a mineral filler, are its low cost, low hardness, wide range of possible particle size distributions, its low refractive index and high whiteness (Wilkes, et al., 2005). The main disadvantage of using CaCO$_3$ is that it contains no chemical groups in its structure which interact, through van der Waals forces, with the PVC matrix. This results in a decrease in the mechanical performance of the
compound and makes it more difficult to process. A common way to decrease the adverse effects of CaCO₃ and other mineral fillers is to surface treat them with a compatibiliser. The CaCO₃ also has a low packing density which means that for flexible PVC compounds more plasticiser is required (Wypych, 2009).

2.1.2 Applications

PVC is the most versatile plastic currently known. Its versatility is primarily as a result of its polarity which makes plasticisation possible (discussed in section 2.1.1.2). PVC applications vary from rigid construction products such as pipes, sidings and window profiles to semi-rigid flooring and wall coverings to flexible products such as medical tubing and cable insulation (Wilkes, et al., 2005). The broad range of applications is also a consequence of the large variety of other additives that can be incorporated into PVC (discussed in section 2.1.1) and some of PVC's unique properties. These properties include its resistance to environmental attack, particularly against exposure to hydrocarbons, and its tendency to crosslink rather than undergo chain scission during degradation from oxidation or UV exposure. These properties make it particularly suited to applications with a long service life. The main applications as a percentage of PVC production in Europe in 2014 are shown in Figure 2 (European Council for Vinyl Manufacturers, 2014).
2.1.2.1 Cables for Underground Mines

One application where PVC is used is for the sheathing (also referred to as jacketing) and insulation of low voltage power cables in underground mines. Cables in underground mines need to be flexible, protected from mechanical damage, fire resistant, corrosion resistant and resistant against oils and other hydrocarbons. The fire retardancy requirements are particularly stringent due to the confined spaces found in mines (Khastgir, 2009).

Cable jackets are primarily made from four different types of materials:

- Fibrous materials
- Rubber and rubber-like materials
- Metallic materials
• Thermoplastics

Thermoplastic jackets have some fundamental physical and financial advantages over the other more traditional jackets (Shoemaker & Mack, 2012). The two thermoplastics used most commonly are PVC and PE (Shoemaker & Mack, 2012) (Pabla, 2011) (Joshi, 2008).

In general PVC is well suited as an insulating and protective sheath material for wires and cables due to its good dielectric strength, fire retardancy, low weight and durability. The versatility of PVC compound means that it can be tailored to the specific operating conditions of many wire and cable applications by changing the formulation (Wilkes, et al., 2005).

2.1.3 Processing

2.1.3.1 Compounding

In almost all polymer processes the quality of the final part is influenced by the quality of the mixing of all the different constituents of the polymer compound. In polymer science there are two defined forms of mixing namely distributive and dispersive mixing (Osswald, 2010). The aim of distributive mixing is to improve the spatial distribution of the ingredients without overcoming the cohesive forces to break down agglomerates. Dispersive mixing has to overcome cohesive forces so that it can break down agglomerates into their primary particle sizes. Dispersive mixing is effectively a more rigorous and finer version of distributive mixing (Murphy, 2001).

Due to some of the unique features of PVC and the various additives that are used, the compounding of PVC is generally performed in two steps; a powder mixing step that is predominantly distributive followed by a dispersive compounding
step. The powder mixing step is done for a number of reasons. The first is to disperse the different particulate additives and the PVC resin powder. The second is to heat the PVC resin to a temperature above its glass-transition temperature \(T_g = 82 \, ^\circ\text{C}\) so that the plasticiser (which is typically a liquid) is rapidly absorbed by the PVC resin particles. This is achieved using a high speed shear mixer. For high speed mixing the dry PVC resin powder, particulate additives and liquid plasticiser are added to the mixer. At room temperature the diffusion rate of the plasticiser into the PVC is very low so that initially, during mixing, a wet, caked powder is formed. The temperature of the caked powder increases as the mixing progresses due to the friction that is generated. As the temperature of the powder increases the diffusion rate of the plasticiser into the PVC increases. When the temperature rises to just above \(T_g\) the plasticiser is rapidly absorbed and a dry powder is formed. It is important that the mixing time is only as long as it takes for all the plasticiser to be absorbed. If mixing continues after a dry powder has been formed the temperature of the powder will continue to rise and the PVC may undergo thermal degradation. It is also important to note that there is an upper limit to the amount of plasticiser that can be absorbed by the PVC (depending on the grade of PVC). If high speed mixing was done correctly a well distributed dry powder is formed (Wilkes, et al., 2005).

The next step is to disperse the agglomerated additives throughout the PVC matrix. The PVC itself also needs to be dispersed due to the fact that it exists as agglomerates of smaller primary PVC particles in its powdered form. The dispersion is achieved through melting the PVC and applying elongational (as opposed to shear) work to the PVC melt. This second compounding step can be done in the same step as forming the final part or as a separate compounding step. Compounding equipment used for this step includes batch internal mixers (Banbury), continuous internal mixers, single screw compounders, reciprocating single screw compounders (Buss Kneader) and co- and counter-rotating twin screw compounders (Wilkes, et al., 2005).
2.1.3.2 Final Part Fabrication

As mentioned, processing of PVC is not possible without additives. However, the formulation of PVC compounds can be manipulated to enable a number of different processing methods for final part fabrication. The main processing methods in use are blow moulding, calendaring, sheet extrusion, profile extrusion, wire and cable extrusion, thermoforming and injection moulding (Wilkes, et al., 2005).

The main difficulty with processing PVC is its inherent thermal instability and the autocatalytic nature of the thermal degradation process. The rapid nature in which the degradation reaction can occur, once initiated, and the resulting crosslinking of the polymer chains can lead to catastrophic failure during processing. This, however, can be avoided by sufficiently stabilising the PVC compound and designing PVC processing equipment accordingly. General processing practices which lower the risk of PVC degrading during processing, to a point where the final part is compromised, include: decreasing residence time and avoiding stagnation zones where PVC compound can accumulate and initiate degradation (Wilkes, et al., 2005).

2.1.4 Testing Methods

2.1.4.1 Thermal Stability

Determining the thermal stability of a PVC compound is a crucial part of evaluating its suitability for processing. A number of methods to test the thermal stability of PVC compounds have been developed over the years using different mechanisms and principles of the degradation process. The methods can be broadly classified into those that measure static thermal stability and those that measure dynamic stability. The main methods used to determine the thermal stability of PVC are
torque rheometer testing (dynamic), HCl evolution testing (generally static) and oven stability testing (static) (Wilkes, et al., 2005) (Wypych, 2008).

2.1.4.1.1 Torque Rheometer

The torque rheometer is the single best piece of laboratory equipment to measure the dynamic thermal stability of PVC (Wilkes, et al., 2005). A torque rheometer is essentially a batch mixer where the torque applied to the rotors, at constant rotational speed, and the temperature of the polymer melt as a function of time are measured (Ari, 2010). A schematic diagram of the mixing chamber of a torque rheometer is shown in Figure 3

![Figure 3: Mixing chamber of a torque rheometer (Wilkes, et al., 2005)](image)

To determine the dynamic thermal stability of a PVC compound, the compound is introduced into the mixing chamber which is heated to a set temperature. After the initial melting of the PVC the torque measurement will stabilise at a certain resting torque until the PVC starts to degrade thermally. The thermal degradation causes crosslinking of the polymer chains which leads to an increase in the torque required to maintain the rotational speed of the rotors. The thermal stability time is defined as the time from when the PVC has melted to the point where thermal...
degradation has started (Wilkes, et al., 2005). A typical torque curve is shown in Figure 4.

![Torque Curve Diagram](image)

Figure 4: Typical torque curve measured using a torque rheometer for a flexible grade PVC (ASTM, 2002)

Besides giving information about the dynamic thermal stability of a PVC compound, the torque curve also gives information on the viscosity and general flow behaviour of the PVC. The combination of all this information makes the torque rheometer an excellent instrument for gaining insight into the processing behaviour of PVC compounds (Ari, 2010).

2.1.4.1.2 Thermomat

A Thermomat (also called a Rancimat) is used to measure the evolution of HCl from PVC as it is heated isothermally. The HCl released during heating is a product of the thermal degradation reaction (as discussed in section 2.1.1.1.). Therefore, a measurement of the HCl evolution is effectively a measurement of the thermal degradation of the PVC compound. A Thermomat works by isothermally heating a small amount of PVC in a sample holder. The gases that evolve from the PVC are swept to a separate container, holding distilled water, with nitrogen. The
conductivity of the water is measured as a function of time. The conductivity and the HCl content are directly proportional (Wypych, 2008).

As is the case with the torque curve produced by the torque rheometer, some work is required to obtain a quantitative measure of the thermal stability (in this case static thermal stability) from the conductivity curve. A simple method to obtain a thermal stability time from the conductivity curve is to define a conductivity value such that the stability time is the time it takes the conductivity to exceed the defined value. Figure 5 demonstrates this principle for conductivity curves from an investigation into the stabilisation of PVC with LDHs (Labuschagne, et al., 2015).

![Figure 5: Conductivity curves for PVC stabilised with different LDHs (Labuschagne, et al., 2006)](image)

It is clear from Figure 5 that the abovementioned method is flawed due to the fact that the stability time is effectively based on a single data point where the threshold conductivity is exceeded. A method is required that uses all of the available data points to determine the stability time so that the global shape of the conductivity curve is taken into account. This can be achieved by fitting the following model to the conductivity curve.
\[
\sigma(t) = \sigma_{\text{min}} + mt + \beta F(t)
\]  

(1)

where \(\sigma_{\text{min}}\) is the conductivity offset at time \(t = 0\), \(m\) is the slope of the initial part of the curve compensating for any linear signal drift in the measurement, \(\beta\) is a proportionality constant and \(F(t)\) is a response function which represents the shape of the conductivity curve over the entire time span of the data. It has been shown that the empirical function

\[
F(t) = \ln \left[ 1 + \left( \frac{t}{\tau} \right)^\theta \right]
\]

(2)

describes the data well. The thermal stability time can then be calculated from the fitted curve using equations 1 and 2. One way to do this is to define the point of the onset of degradation as the intercept between the time axis and the tangent line to the inflection point of \(F(t)\). This is shown in Figure 6.

![Figure 6: Method to determine onset of degradation for conductivity curve (Focke, et al., 2016)](image)

The intercept point can be calculated from the fitted parameters, \(\tau\) and \(\theta\), of \(F(t)\) using the following equation
\[ t_{\text{int}} = \tau (\theta - 1)^{\frac{1}{\theta}} \left[ 1 - \frac{\ln(\theta)}{(\theta - 1)} \right] \]  

(3)

The time taken to reach the onset of degradation (which is effectively \( t_{\text{int}} \)) is then defined as the thermal stability (Focke, et al., 2016).

2.1.4.1.3 Colour

It is well documented that during thermal degradation the colour of PVC changes. This has been linked with the number and length of polyene sequences formed in the PVC matrix as a result of the degradation reaction (Wilkes, et al., 2005). The colour stability of PVC is typically measured using different oven aging techniques. Traditionally the colour of different samples was visually inspected using reference samples. A more modern method uses scans or images of the PVC samples. The colour of the image or scan is captured numerically using the CIE tristimulus values. The CIE tristimulus values are then expressed as a yellowing index (\( YI \)) using the following equation.

\[ YI = 100 \frac{1.28X - 1.06Z}{Y} \]  

(4)

where \( X, Y \) and \( Z \) are the CIE tristimulus values. Generally, as the PVC becomes more degraded \( YI \) will increase. This technique allows for a more scientific and repeatable comparison of the colours of different PVC samples (Wypych, 2008).

2.1.4.2 Fire Retardancy

Testing the fire retardancy of materials is difficult due to the complexity and poor reproducibility of fires. As a result of this several different techniques are used to study the fire retardancy of materials. The different techniques focus on describing different aspects of the combustion process such as: the ease of ignition, flame
propagation, heat release and smoke production. The different techniques are broadly classified into small, medium and large scale tests. Small scale tests, as the name suggests, involve the combustion of very small amounts of material with as little as 5 mg required for Micro Cone Calorimeter (MCC) tests. Medium scale tests are generally more comprehensive such as Cone Calorimetry, but require more material and are generally more complex. Large-scale tests, such as room and corridor experiments, are the closest to simulating real fire conditions, but are expensive and difficult to control (Joseph, et al., 2016).

2.1.4.2.1 Limited Oxygen Index

The Limited Oxygen Index (LOI) test is a relatively simplistic flame retardancy test. A polymer sample in the form of a small plaque, rod or thin film is fixed into place so that it stands up vertically in a glass cylinder. A mixture of oxygen and nitrogen is fed through the glass tube at a controlled ratio. After approximately 30 s of allowing the gas to flow, the top of the polymer sample is ignited using a torch. The LOI value is defined as the oxygen concentration, in the oxygen/nitrogen mixture, which sustains candle like combustion of the sample such that 5 cm of the sample burns in 3 min (Joseph, et al., 2016).

It is important, however, to understand the limitations of LOI. The LOI test is not a good indicator of the performance of a material in a real fire situation due to the low heat and artificially high oxygen environments. Hence on its own LOI is not sufficient to capture the full mechanism of a flame retardant. It is generally accepted that LOI is effectively a measure of the ease of extinction of a material, which is only one part of the full range of properties involved in fire retardancy (Wilkes, et al., 2005).

In spite of this it is still the most widely used flame retardancy laboratory test due to its convenience and good reproducibility. It is a useful tool for highlighting
and/or ranking the flammability of materials. It is used successfully in industry as a screening and quality control tool (Joseph, et al., 2016) (Laoutid, et al., 2009). For PVC, as with other materials, it is still required in many specifications and can be used as an incomplete indicator of the effectiveness of fire retarding additives during research and development (Wilkes, et al., 2005).

2.1.4.2.2 Cone Calorimeter

Cone Calorimetry is a medium scale fire retardancy test that is the method of choice for evaluating the behaviour of a material in a real fire scenario without having to do large-scale testing. A schematic diagram of a Cone Calorimeter is shown in Figure 7.

Figure 7: Schematic diagram of a Cone Calorimeter (Laoutid, et al., 2009)

In Cone Calorimetry a sample (generally 100 by 100 by 3 mm in size) is secured in a sample holder situated on a load cell. The purpose of the load cell is to measure
mass loss during combustion. A cone shaped electrical heater that is designed to uniformly irradiate the sample with a constant heat flux is used to heat the sample. The heating causes the sample to degrade and release volatile flammable species. The released gases are ignited by an electric spark situated above the sample (upon sustained combustion the spark igniter is removed). The combustion gases are captured by an exhaust duct system consisting of a fan and hood. The gas flow, oxygen, carbon monoxide and carbon dioxide concentrations and the smoke density are measured in the exhaust duct system.

A number of important fire parameters can be calculated from the Cone Calorimeter results including: time to ignition, mass loss rate, heat release rates (typically the peak heat release rate is analysed), total heat released and smoke production. The heat release rate in particular, is considered to be one of the most important parameters used to determine how a material will contribute to the growth of a fire. The heat release rate is calculated from the measurements described above using the oxygen consumption principle. The oxygen consumption principle linearly correlates the amount of heat produced during the combustion of organic materials to the amount of oxygen consumed (Joseph, et al., 2016) (Laoutid, et al., 2009).

2.1.4.2.3 Micro Cone Calorimeter

The MCC (also referred to as a Pyrolysis Combustion Flow Calorimeter) has recently been shown to be a valuable small scale test. MCC can be used to screen the flammability of materials quickly while requiring only a few milligrams of material per test. As the name suggests MCC works using the same principle, namely the oxygen consumption principle, as the Cone Calorimeter. In the test the polymer sample is heated at a constant rate in an inert atmosphere of nitrogen until it undergoes pyrolysis. The pyrolysate is then combusted in an excess of oxygen and the oxygen consumption is measured. The heat release rate is then
calculated and, similarly to the Cone Calorimeter, the peak heat release rate and total heat release rate are used for analysis. For the MCC the temperature at peak heat release rate is also used (Joseph, et al., 2016).

2.1.4.3 Mechanical Properties

The tensile test is considered to be the fundamental test for the mechanical testing of polymers. This is in spite of the fact that in practice pure tensile loading is not common. The conventional tensile test requires that certain conditions with regard to the method of testing and the sample are adhered to. The loading, applied through a constant cross-head speed, must be without impact, increasing slowly and steadily until fracture of the specimen occurs. The aim is to generate a uniaxial loading and stress state in the sample at a sufficient distance from the top and bottom clamp. In terms of the testing sample it is important that the polymer material is homogenous and isotropic. There should also be no geometric imperfections such as notches or lumps.

To characterise the tensile properties of a polymer there are generally two tests that are performed at two different cross-head speeds. The first test is to determine the elastic modulus \( E \) where a cross-head speed of \( v_T = 1 \text{ mm/min} \) is used. \( E \) is calculated according to Hooke’s Law using the secant method shown in Figure 8.

The second test is to determine the remaining tensile properties such as the strength and deformation. For polymers it is most commonly performed at \( v_T = 50 \text{ mm/min} \). Typical stress-strain curves for various types of polymers are shown in Figure 9. The parameters typically derived from the curves to analyse the tensile properties are the maximum tensile strength, the tensile strength at break and the elongation at break.
Figure 8: Secant method to determine $E$ (Grellmann & Seidler, 2013)

Figure 9: Typical stress-strain curves for polymers from brittle (a) to completely elastomeric (e) materials (Grellmann & Seidler, 2013)
Besides the tensile test, there are a number of other more specialised tests such as the impact test, the notched tensile test or bending tests which test other more specific mechanical properties (Grellmann & Seidler, 2013).

### 2.1.5 Environmental Concerns

The use of PVC and the PVC industry in general has had to face and still faces a number of environmental issues. The main issues are the vinyl chloride monomer (VCM), which is toxic and possibly carcinogenic, the use of toxic or otherwise dangerous additives and the possibility of dioxin formation during PVC waste incineration. The VCM issue has been largely addressed through technologies that drastically reduce VCM emissions and residues in VCM manufacturing and PVC polymerisation plants (Wilkes, et al., 2005).

The use of toxic or dangerous additives refers mainly to the use of phthalate plasticisers, which can be endocrine disruptors in certain forms, and to the use of lead and cadmium based stabilisers, which are both toxic heavy metals. In terms of the plasticisers, the shorter chain length phthalates such as diethylhexyl phthalate (DEHP) have been largely replaced by longer chain length phthalates such as DINP and diisodecyl phthalate (DIDP). Studies have shown that DINP and DIDP are not endocrine disruptors and that PVC products containing DINP or DIDP are unlikely to pose a risk to adults or infants. The advantage of using longer chain phthalates is that they are more permanent due to a significantly lower migration rate and are less soluble in water. The use of lead and cadmium in the stabilisation of PVC is avoided by using so called heavy metal free stabilisers such as calcium and zinc stearates, zeolites and LDHs.

In terms of the formation of dioxins, this has been shown to be caused mainly through the use of inefficient incinerator designs and that it is not a function of the amount of PVC fed to the incinerator. In spite of these findings, it is still important
to reduce the amount of waste produced by the use of PVC (as is true for all plastics) which will eventually need to be disposed of and usually ends up in landfill sites. Two methods to do this are to increase the amount of PVC which is recycled and to use PVC for applications requiring a longer service life, for which it is well suited in any case (Attenberger, et al., 2011) (Wilkes, et al., 2005).

2.1.6 Comments on the Economics of PVC

PVC is defined as a commodity plastic together with other plastics such as PE and PP. Consequently, most of the applications, especially those that are produced in bulk such as PVC pipes, window profiles and cables, are also commodities (Wilkes, et al., 2005). 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 realised by even a small reduction in production costs (Towler & Sinnott, 2013).

2.2 Layered Double Hydroxides

LDHs are clay like materials that have a wide range of chemical compositions. The general structure of an LDH involves cationic layers with, a crystalline structure, that are connected with anions intercalated in between the cationic layers to maintain the electro neutrality of the complete structure. This is expressed with the generalised chemical formula \([M^{II}_{1-x}M^{III}_x(OH)_2][X^{q-x/q}_nH_2O]\) where \([M^{II}_{1-x}M^{III}_x(OH)_2]\) represents the cationic layer and \([X^{q-x/q}_nH_2O]\) represents the intercalated anionic layer composition. The formula is frequently written in a shortened form as \([M^{II}-M^{III}-X]\). LDH particles tend to be plate-like with a fairly regular hexagonal shape (Forano, et al., 2006).

As has already been mentioned in section 2.1.1.1, LDHs act as a secondary stabiliser when incorporated into PVC. In addition to this it has been shown that
LDHs can act as a fire retardant. The proposed fire retarding mechanisms for LDH are the release of CO₂ and water during combustion, acting in a similar mechanism as inorganic hydroxide fire retardants such as ATH (see section 2.1.1.3), and the formation of insulating char layer as a result of the decomposition of the LDH which produces various metal oxides (Wang & Zhang, 2004).

LDHs can be synthesised in a number of ways, with the most common method being the co-precipitation method (Forano, et al., 2006). The main disadvantage of the co-precipitation method is that it produces a sodium rich effluent. Recently a new method called the dissolution precipitation method has been developed. The main advantage of this method is that it produces almost no effluent (Labuschagne, et al., 2006).

2.3 Fly Ash as a Spherical Filler

Fly ash 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 (van der Merwe, et al., 2014). One application for fly ash is as a cheap functional filler for polymeric materials. Examples of polymers where fly ash has been used as a filler are high density polyethylene (HDPE), polyethylene terephthalate (PET), PP and polyurethane (PU) (Wypych, 2016). The morphology of fly ash particles is shown in Figure 10.

Figure 10: SEM micrographs of fly ash particles (van der Merwe, et al., 2014)
2.4 Statistical Design of Experiments

Statistical Design of Experiments (DoE) is a scientific approach to the process of planning an experiment. The aim of DoE is to facilitate the analysis of the experimental data with predetermined statistical methods so that valid and objective conclusions can be made. Typically the aim is also to produce an empirical model that describes the relationship of the input variables to the response variable. These empirical models can be used to perform system analysis and optimisation, if the experiments are designed correctly. The DoE process can be summarised in the following steps (Montgomery, 2013):

1. **Defining the problem.** There are a number of reasons why experiments are conducted and it is important to understand what the broader objective of the experiment is during planning. Some examples of the broader reasons for conducting an experiment are: characterisation, optimisation and/or confirmation.

2. **Selection of the response variable or variables.** Here the most important thing is that the variables that are selected provide useful information about the system. It is also important here to make sure that the practical aspects of obtaining the response data are understood and taken into account.

3. **Choice of factors and ranges.** There are usually many factors that influence a system, which can be broadly classified into nuisance and potential design factors. It is also important to determine the range of the factors, or in other words the region or experimental space of interest.

4. **Choice of experimental design.** This involves choosing the number of experimental points (or runs) that will be used and how those points will be distributed in the experimental space. The experimental design is determined strongly by the shape of the empirical model that will be used to analyse the data and by the choices made in steps 1 to 3. Note that experiments typically require resources and therefore the number of
experimental runs that can be performed may be limited due to financial or
time constraints. Another aspect of defining the experimental design is
choosing the order in which the experiments are performed. An important
principal here (which is often overlooked) is randomisation i.e. the
experimental runs should be performed in a random order. Randomisation
is essential because one of the underlying assumptions of statistical
methods is that observations and errors are independently distributed
random variables.

5. *Performing the experiment.* It is vital to execute the planned experiment
correctly. Errors in the execution will make it difficult to make meaningful
conclusion, regardless of how well the experiment is designed.

6. *Statistical analysis of the data*

7. *Conclusions and recommendations*

### 2.4.1 Mixtures

Mixture experiments are experiments where the factors are the components or
ingredients of a mixture. This means that the values or levels of the factors are not
independent and consequently classical designs, such as the factorial design,
cannot be used. The inter-dependence of the mixture factors is enforced by the
logical constraint on a mixture given as

\[ \sum_{i=1}^{q} x_i = 1 \]  \hspace{1cm} (5)

where

\[ 0 \leq x_i \leq 1 \hspace{0.5cm} i = 1, 2, \ldots, q \]  \hspace{1cm} (6)
The $x$ values are the proportions of each of the components in the mixture and $q$ is the number of components. The effect of the mixture constraint on the experimental space for $q = 3$ is shown in Figure 11.

![Diagram](image)

**Figure 11: Constrained factor space for mixtures with $q = 3$ (Montgomery, 2013)**

The cube in Figure 11 is an example of the experimental space for independent factors with the limits coded to be between 0 and 1. The plane dissecting the cube, visible as a triangle in the figure, is the mixture space where equation 5 is satisfied. This plane is the familiar ternary diagram when represented in two dimensions (Montgomery, 2013). In general, the experimental space for a mixture is a regular simplex with $(p - 1)$ dimensions, so for $q = 4$, for instance, it is a tetrahedron (Scheffe, 1958).

Besides having an effect on the experimental space, the mixture constraint also needs to be taken into account when describing a mixture response variable using an empirical model. The models used to empirically model mixture behaviour are called Scheffé polynomials. The simplest Scheffé polynomial where the degree $n = 1$ has the following form
\[ y = \sum_{1 \leq i \leq q} \beta_i x_i \]  

(7)

where \( q \) is the number of factors in \( x \), \( y \) is the response and \( \beta \) are the model parameters. If \( n = 2 \)

\[ y = \sum_{1 \leq i \leq q} \beta_i x_i + \sum_{1 \leq i < j \leq q} \beta_{ij} x_i x_j \]  

(8)

and if \( n = 3 \)

\[ y = \sum_{1 \leq i \leq q} \beta_i x_i + \sum_{1 \leq i < j \leq q} \beta_{ij} x_i x_j + \sum_{1 \leq i < j \leq q} \gamma_{ij} x_i x_j (x_i - x_j) \]  

\[ + \sum_{1 \leq i < j < k \leq q} \beta_{ijk} x_i x_j x_k \]  

(9)

The total number of model parameters is given by the formula

\[ \binom{n + q - 1}{n} \]  

(10)

increasing significantly as \( n \) and \( q \) are increased. A fourth form of the Scheffé polynomial, referred to as the special cubic, can also be used where equation 9 is used but the three-way interaction term \( \sum_{1 \leq i < j < k \leq q} \beta_{ijk} x_i x_j x_k \) is neglected. The terms in the Scheffé polynomials are relatively simple to interpret, particularly for equations 7 and 8. The parameter \( \beta_i \) in all the models represents the expected response for the pure component, where \( x_i = 1 \). It can also be interpreted as the linear effect of that component on the mixture response. All the other parameters, besides \( \beta_i \), represent non-linear effects. The parameter \( \beta_{ij} \) is the simplest out of these to interpret representing synergistic or antagonistic interactions between
two components. Note that an intercept and squared or cubic terms are not included in the Scheffé polynomials (Scheffe, 1958) (Montgomery, 2013).

The simplest experimental designs for mixtures are the simplex designs. Simplex designs for $q = 3$ with Scheffé polynomials with different degrees $n$ are shown in Figure 12

![Simplex designs for Scheffé polynomials with $n = 1$, 2 and 3](image)

Figure 12: Simplex designs for Scheffé polynomials with $n = 1$, 2 and 3 (Montgomery, 2013)

Unfortunately as soon as there are constraints on the levels of the factors the experimental space is no longer a simplex but an irregular polyhedron (with the exception of the case where there are only lower bounds on each factor).

Experimental designs for constrained mixtures are less intuitive and require an algorithm for the positioning of the experimental points. Examples of experimental designs used for constrained mixtures are D-optimal designs, extreme vertices designs and space filling designs. In a D-optimal design the experimental points are distributed using optimisation such that the model parameters of the chosen model can be predicted as accurately as possible. For instance, a D-optimal design for a third degree Scheffé polynomial with no constraints on the factors would look almost the same as the simplex design in Figure 12. In an extreme vertex design an experimental point is placed in each
vertex of the constraints. This is relatively simple when there are not many factors and constraints but becomes significantly more complex as the number of factors and constraints increases; and therefore is generated using an algorithm. In a space filling design a set number of experimental points are distributed throughout the design space so that the distance between each point and its closest neighbour is maximised. This can be cast as a minimax optimisation problem and solved accordingly (Lundsted, et al., 1998) (Montgomery, 2013) (SAS Institute Inc., 2015). The extreme vertex and space filling designs for a constrained mixture space are shown schematically in Figure 13.

![Extreme Vertex Design and Space Filling Design](image)

**Figure 13: Schematic diagram of extreme vertex and space filling designs**

### 2.5 Model Selection and K-fold Cross-Validation

A general principle in statistical learning is that the predictive ability of a model is a function of the model complexity and that that function exhibits a maximum. This principle is illustrated in Figure 14. The eventual increase in the prediction error (red line) is a result of overfitting on the test data. Note that in Figure 14 the training set (blue line) refers to the data used to fit the model and the test set (red line) refers to an independent data set that is not used in fitting the data. Note also that the model complexity is effectively the number of model terms included in the model.
Naturally to determine the appropriate model for a particular data set, taking into account the above principle, a method to quantify the predictive ability of a model is required. This is typically referred to as model validation. The method used in the example above to quantify the predictive ability with an independent training and testing set is the most basic model validation method. The disadvantage of this simplistic validation technique for real data is that the results can depend on the choice of how the data points are divided amongst the training and testing set.

A solution to this problem is to use $k$-fold cross-validation. In $k$-fold cross-validation the data set is divided into $k$ roughly equally sized smaller data sets or ‘folds’. The model is trained using $k-1$ folds and validated against the remaining fold. This is repeated $k$ times with the mean prediction error typically reported (Hastie, et al., 2009).

Figure 14: Behaviour of test sample (red curve) and training sample error (blue curve) as model complexity is increased for a 100 simulated training sets with 50 experimental points each (Hastie, et al., 2009)
3 Optimisation

3.1 Problem Statement

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

3.2 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 are varied. The actual ingredients that are used are not varied. The ingredients that are used for the PVC compound are shown in Table 1

<table>
<thead>
<tr>
<th>Description</th>
<th>Trade Name</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>flexible grade PVC resin</td>
<td>PVC Resin S7106</td>
<td>Sasol</td>
</tr>
<tr>
<td>Stearic acid coated CaCO₃</td>
<td>Kulucoate 2</td>
<td>Idwala</td>
</tr>
<tr>
<td>ATH and Sb₂O₃ one-pack</td>
<td>Flamex 0</td>
<td>Associated Additives</td>
</tr>
<tr>
<td>Ca/Zn Stabiliser</td>
<td>Naftosafe® PKN65119</td>
<td>Associated Additives</td>
</tr>
<tr>
<td>DINP</td>
<td>DINP</td>
<td>Isegen South Africa</td>
</tr>
<tr>
<td>Ca-Al-CO₃ LDH</td>
<td>N/A</td>
<td>Engelbrecht &amp; Mentz</td>
</tr>
<tr>
<td>Fly ash (spherical)</td>
<td>Plasfill®.5</td>
<td>Ash Resources</td>
</tr>
</tbody>
</table>

The PVC resin, Ca/Zn stabiliser, DINP and fire retardant (FR) were selected so that achieving the desired properties required for an underground mine cable insulation or protective sheath is possible. The calcium/zinc (Ca/Zn) stabiliser, which consists of a mixture of Ca and Zn stearate, is included as a primary thermal stabiliser. This is necessary due to the fact that the only other thermal stabiliser, namely the LDH, only acts as a secondary stabiliser and so in theory cannot stabilise PVC in isolation. The DINP is included because plasticisation is necessary.
The FR, which is the ATH and Sb$_2$O$_3$ based one-pack, is added due to the stringent fire retardancy requirements for underground mine cables and due to the fact that DINP is included which is known to decrease the natural flame retardancy of PVC. The stearic acid coated CaCO$_3$ is not strictly necessary for achieving the desired material properties but is added as a filler due to its low cost. All of these five ingredients discussed above are also selected because they are the industry standard used for flexible PVC compounds in South Africa.

The final two ingredients, namely the Ca-Al-CO$_3$ LDH and the fly ash, are not industry standard. The Ca-Al-CO$_3$ LDH is produced using the novel dissolution precipitation method and is included as both a secondary stabiliser and as a fire retardant. The fly ash is added as a spherical filler. It is hypothesised that the spherical filler will synergistically interact with the platelet like particles in a ball bearing effect. It has also been successfully used as a cost reducing filler in other polymers.

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

### 3.3 Identification of the Objective Function

The objective function is given by

$$f = \sum_{i=1}^{7} c_i x_i$$  \hspace{1cm} (11)

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.

3.4 Identification of Constraints

The first constraints are the logical constraints required because the system is a mixture (see section 2.4.1) which are

\[
\sum_{i=1}^{7} x_i = 1 \quad (12)
\]

\[
0 \leq x_i \leq 1 \quad i = 1, 2, \ldots, 7 \quad (13)
\]

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 when formulating any PVC compound. 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. 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. This is due to the nature of optimisation and can in this case be confirmed by a basic understanding of the system. The FR, which is expensive, is included in the system because it is necessary due to the highly flammable DINP which is in turn necessary to provide flexibility to the PVC compound. If the flexibility of the final compound is not constrained it is logical that the amount of DINP used will be as little as possible so that the expensive FR
is not necessary, leading to a compound with very low flexibility. 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 as

\[ p = g(x) \]  \hspace{1cm} (14)

where \( p \) is some value describing the property and \( g \) is a function of the design variable \( x \). The constraints for each \( g \) are then defined as

\[ g(x) \geq p_{\text{lim}} \]  \hspace{1cm} (15)

if the desired values for \( p \) are high or

\[ g(x) \leq p_{\text{lim}} \]  \hspace{1cm} (16)

if the desired values are low. The \( p_{\text{lim}} \) value is the desired minimum or maximum requirement for each \( p \).

The functions required for \( g \) 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 optimise the system. Statistical design of experiments is used to develop the models.
4 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 (i.e. the mass fractions of the selected ingredients) as described in the previous section.

4.1 Selection of the Response Variables

The experimental methods that are selected are shown in Table 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Experimental Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Stability</td>
<td>Torque Rheometer</td>
</tr>
<tr>
<td></td>
<td>Thermomat</td>
</tr>
<tr>
<td></td>
<td>Colour</td>
</tr>
<tr>
<td>Fire Retardancy</td>
<td>Cone Calorimetry</td>
</tr>
<tr>
<td></td>
<td>MCC</td>
</tr>
<tr>
<td></td>
<td>LOI</td>
</tr>
<tr>
<td>Mechanical</td>
<td>Tensile Test</td>
</tr>
</tbody>
</table>

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. 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. A colour 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. The colour 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 MCC test is also done even though it gives less information and is not a good simulation of real fire behaviour, 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 LOI test which gives the least information but is used because it is still often a requirement for the specification of products and compounds.

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.

### 4.2 Choice of Factors and Ranges

The factors for the experiment are the same as the design variables for the optimisation defined in section 3.2. 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 is achieved using a laboratory twin-screw extruder (more detail will be given in section 4.4). The twin-screw extruder can only process material
that falls within 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. The problem is that it is quite possible to irreparably damage the extruder if a PVC formulation is compounded which either requires too much torque from the motor or degrades completely during extrusion which will corrode the screw and barrel and put extreme strain on the motor. It is also not possible to simply stop the extruder during compounding if the operator observes that the motor is under strain because the barrel temperature will decrease very slowly and the PVC will degrade, even if it is stabilised. The only real solution is to try and flush the PVC from the extruder using PE or a similar compound but even that will only work if the PVC does not degrade beyond a certain point. Since the degradation is autocatalytic the PVC can degrade 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.

Due to the fact that the limits of the experimental space cannot be determined using the extruder without the risk of damaging it, a set of preliminary limits were proposed. The proposed limits are

\[ 0.2 \leq x_{PVC} \leq 0.955 \]  \hspace{1cm} (17)
\[ 0.04 \leq x_{DINP} \leq 0.5 \]  \hspace{1cm} (18)
\[ 0.005 \leq x_{stab} \leq 0.1 \]  \hspace{1cm} (19)
\[ 0 \leq x_{fill} \leq 0.7 \]  \hspace{1cm} (20)
\[ 0 \leq x_{LDH} \leq 0.7 \]  \hspace{1cm} (21)
\[ 0 \leq x_{FR} \leq 0.7 \]  \hspace{1cm} (22)
\[ x_{fill} + x_{LDH} + x_{FR} \leq 0.7 \]  \hspace{1cm} (23)
Note that at this stage the spherical filler had not been included in the selection of materials. The combination of constraints creates a constrained design space in six dimensions which has 77 vertices. The vertices can be found using an extreme vertices design generated using JMP® statistical software (SAS Institute Inc., 2015). 8 of the 77 vertices were selected where the number of active constraints is as low as possible. The formulations are given in Table 3.

Table 3: Selected extreme vertices (active constraints are in bold)

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVC</th>
<th>Filler</th>
<th>FR</th>
<th>Stabiliser</th>
<th>DINP</th>
<th>LDH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.725</td>
<td>0</td>
<td>0</td>
<td>0.005</td>
<td>0.27</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.63</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.27</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.9075</td>
<td>0</td>
<td>0</td>
<td>0.0525</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.4475</td>
<td>0</td>
<td>0</td>
<td>0.0525</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.255</td>
<td>0</td>
<td>0</td>
<td>0.005</td>
<td>0.04</td>
<td>0.7</td>
</tr>
<tr>
<td>6</td>
<td>0.255</td>
<td>0.7</td>
<td>0</td>
<td>0.005</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0.255</td>
<td>0</td>
<td>0.7</td>
<td>0.005</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0.955</td>
<td>0</td>
<td>0</td>
<td>0.005</td>
<td>0.04</td>
<td>0</td>
</tr>
</tbody>
</table>

The 8 formulations were tested using a torque rheometer with a block temperature of 200 °C and a rotor speed of 50 rpm. The samples were prepared by mixing the relevant powders in a kitchen mixer to obtain a dry powder. A high speed mixer was not used because it requires at least 2 kg of the sample which means a large amount of material would be wasted since only 72 g are required to do a torque rheometer run. Using a kitchen mixer is not ideal because the bearings in the mixing head tend to overheat, before the PVC powder mixture reaches the required temperature to absorb the liquid DINP, and had to be cooled intermittently so that a dry powder could be achieved. This was possible for all of the samples except sample 4 where there was the biggest ratio of DINP to PVC and consequently the PVC could not absorb all of the DINP.

The torque rheometer curves were analysed visually by examining the gelling time, thermal stability time and resting torque. All of the torque curves except the curve for sample 2 showed that the relevant formulations are not likely to be
processable using the twin-screw extruder. Samples 1, 5, 6, 7 and 8 all exhibit very short thermal stability times below 8 min, samples 3, 5, 6, 7 and 8 all have high resting torques starting at 15 N·m and going as high as 25 N·m and samples 6 and 7 exhibit long gelling times especially sample 6 which has a gelling time of just under 20 min. It is clear that the constraints given by equations 17 -23 are not stringent enough. The problems with the formulations above are clearer if they are expressed using the traditional unit used for PVC formulations which is grams per hundred grams of resin (phr) shown in Table 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVC</th>
<th>Filler</th>
<th>FR</th>
<th>Stabiliser</th>
<th>DNP</th>
<th>LDH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0.7</td>
<td>37.2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>15.9</td>
<td>42.9</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>5.8</td>
<td>4.4</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>11.7</td>
<td>111.7</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
<td>15.7</td>
<td>274.5</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>274.5</td>
<td>0</td>
<td>2.0</td>
<td>15.7</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>274.5</td>
<td>0</td>
<td>2.0</td>
<td>15.7</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>4.2</td>
<td>0</td>
</tr>
</tbody>
</table>

Inorganic filler loading of 275 phr and plasticiser loading of 112 phr is significantly higher than found in any commercial flexible PVC compounds. On the other hand stabiliser loadings below 2 phr and plasticiser loadings as low as 4.2 phr are very low. Many commercial and patented formulations can be found in the reference work by Wypych (2009).

Based on the above observations a new set of limits is proposed which are expressed in phr. This means that the limits are effectively based on the mass fraction of the PVC. The new limits are shown in Table 5.
Table 5: Limits for experimental space

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Limit (phr)</th>
<th>Lower</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td></td>
<td>0.4*</td>
<td>-</td>
</tr>
<tr>
<td>Filler</td>
<td></td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>FR</td>
<td></td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Stabiliser</td>
<td></td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>DINP</td>
<td></td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>LDH</td>
<td></td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>Spherical Filler</td>
<td></td>
<td>-</td>
<td>20</td>
</tr>
</tbody>
</table>

*Expressed as mass fraction i.e not phr

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 (which is now included) all limit the overall inorganic particulate loading. Lower limits are not necessary because inorganic particulate fillers will always have an adverse effect on the processing properties. The lower limit on the stabiliser ensures that the system is always sufficiently stabilised to be extruded. The lower limit on the DINP ensures that there is always sufficient lubrication for the extrusions (in rigid formulations where no DINP is used a lubricant is typically necessary), whereas the upper limit ensures that the DINP does not approach the absorption limit of the PVC. The exact upper limits for the FR, stabiliser 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 was not part of the formulations tested using the torque rheometer, and is relatively untested as an additive for PVC. The above limits can be expressed in terms of the design variables in the following inequalities:

\[ 0.4 \leq x_{PVC} \] \hspace{1cm} (24)
\[ x_{fill} \leq 0.7x_{PVC} \] \hspace{1cm} (25)
\[ x_{FR} \leq 0.2x_{PVC} \] \hspace{1cm} (26)
\[ 0.02x_{PVC} \leq x_{stab} \leq 0.1x_{PVC} \quad (27) \]
\[ 0.2x_{PVC} \leq x_{DINP} \leq 0.7x_{PVC} \quad (28) \]
\[ x_{LDH} \leq 0.15x_{PVC} \quad (29) \]
\[ x_{sp.h.fill} \leq 0.2x_{PVC} \quad (30) \]

### 4.3 Choice of Experimental Design

Since the system is a mixture and the experimental space is constrained there are three options for the experimental design, namely the extreme vertices, D-optimal and space filling designs. For the experimental space given in the previous section there are 360 extreme vertices. A subset of the 360 vertices can be determined using the same principal that is used for the space filling design. The problem with the extreme vertices design, in this case, is that all of the experimental points lie on the boundaries of the experimental space. The same is true for the D-optimal design. 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 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 empirical model, but is limited by the time and resources available to execute the experiment. Scheffé polynomials will be used to model the response variables because it is a mixture system. The number of parameters for Scheffé polynomials with different degrees, for \( q = 7 \), are shown in Table 6.
Table 6: Number of parameters for Scheffé polynomials where \( q = 7 \)

<table>
<thead>
<tr>
<th>( n )</th>
<th>No. of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
</tr>
<tr>
<td>3*</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>84</td>
</tr>
</tbody>
</table>

*Special cubic

Taking into account the full process required to perform the experiments (discussed in detail in the following section) and the time and material available it is decided that enough experimental points will be used to fit a special cubic Scheffé polynomial. It is also good practice to use a few additional experimental points than the number of model parameters so that the variance can be estimated. Therefore, 4 additional points will be used. The space filling design with 53 points in random order is generated using JMP® statistical software (SAS Institute Inc., 2015). Each experimental point, or in other words each formulation, is identified by a sample number from 1 to 53.

4.4 Performing the Experiments

Each experimental point represents a different PVC formulation which needs to be compounded. Note that the various experimental methods used to test the compounds differ in terms of availability, time required and resources required. This means that it is in some cases not possible to test all of the 53 compounds, however this only means that a random subset of the original space filling design is used and the degree of the Scheffé polynomial may need to be reduced.

4.4.1 Compound Preparation

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. At least 2 kg of material is required for effective mixing to take place, due to the size of the mixing chamber and the height of the blades above the bottom of the chamber. A rough calculation on the amount of compound required per sample for all of the different planned experiments, and taking into account inevitable material losses during compounding, showed that 2 kg was more than enough. The required mass of each of the ingredients (calculated by multiplying the relevant mass fraction by 2 kg) for a given sample was added to the mixing chamber. The mixing was started on the low speed setting for 10 s after which the mixing was switched to high speed. After 2 min the mixing was stopped so that the mixing chamber could be opened and the mixture examined. If the mixture was a dry free flowing powder (showing that all the DINP had been absorbed) the mixture was removed from the mixing chamber and the chamber was cleaned using a vacuum cleaner. If the mixture was not a dry powder mixing was started again, on the high speed setting, for an additional 2 min. This process was repeated until a dry mixture was formed. In general 4 min of mixing was sufficient except for a few formulations with a high DINP content which required 6 min.

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. The extruder has four thermostatically controlled heating stages. The feeding stage temperature was set at 150 °C, the two intermediate stages were set at 160 °C and 170 °C and the die temperature was set at 180 °C. The compounding was done in daily batches. At the beginning of each day PE was used to purge the barrel of any material remaining from the previous day. On the first day of compounding the PE was run until the extrudate was clear. The dry powder samples were then run continuously throughout the day. The extruder speed was set to approximately 130 rpm and the feed rate was adjusted for each sample (which had different powder flow characteristics) so that there was no build-up of material at the feeding zone. The crossover point between samples was marked by using a very
small amount of orange dye poured into the feeding zone. The amount of extrudate discarded during crossover was treated liberally since there was little risk of having too little extruded compound for the experiments, and it was important that contaminating a sample with another sample was avoided. After cooling in a water bath the extrudate was pelletized using a chipper. Finally the pelletized compound was dried in an oven at 60 °C for approximately 24 h to remove any excess water from the water bath.

4.4.2 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 IPython (Perez & Granger, 2007). The stability time is defined as the time from the first point that the torque is less than 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 15 as an example.
Figure 15: Torque rheometer curve for sample 1 showing the stability time and final degradation time.

4.4.3 Thermomat

The Thermomat tests were done according to ISO 182-3 using a Metrohm 895 Professional PVC Thermomat. 0.5 g of PVC compound cut into pieces no bigger than 2 mm by 2mm was used. The Thermomat temperature used was 200 °C, the nitrogen flow was 7 l·h⁻¹ and 60 mL of distilled water was used.

The stability time is defined by equation 3 repeated here for convenience

\[ t_{int} = \tau (\theta - 1) \theta \left[ 1 - \frac{\ln(\theta)}{(\theta - 1)} \right] \]  

(3)

where the parameters \( \tau \) and \( \theta \) are found by fitting the model given by equations 1 and 2, which can be written as

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

(31)

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

4.4.4 Colour

The pressed sheets required for the Cone Calorimetry measurements (described in the following section) were also used to determine the colour 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 colour 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 with a colour rendering index of 93%.

The resultant images were analysed using a program written in Python programming language. The program converts the image into red, green and blue (RGB) colour values. The RGB values are then converted to CIE tristimulus values which is possible due to the fact that the white balance of the images is known and standard D65 illuminants were used. The CIE tristimulus values are then expressed as \(YI\) values. 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 (Wright, 2016).
4.4.5 Cone Calorimetry

The Cone Calorimetry measurements were conducted according to ISO 5660-1:2015. The samples were prepared by pressing the pellets 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.

At the start of each day the Cone Calorimeter was calibrated. Unfortunately during calibration the C-factor (which is a calibration constant for the orifice flow meter) was not within the prescribed range of 0.04 to 0.046. It was however constant enough, not varying by more than 0.002 on successive testing days. The C-factor values for the 3 days of testing were 0.03692, 0.03584 and 0.0378 all within a range of 0.00196. The C-factor issue means that the calculated heat release rates are not absolute values, but they are comparable between the samples in this study. If a direct comparison with heat release rates from literature are required in a future study the heat release rates can be converted by testing a standard sample on the Cone Calorimeter. The following values were calculated by the Cone Calorimeter software for each sample: the peak heat release rate (pHRR) in kW/m², the total heat released (tHR) in MJ/m², the total smoke production (tSP) in m², 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/m². The MAHRE value is used as a measure of the risk of a fire spreading to other objects in a fire situation.

4.4.6 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 (t) and temperature (T) at the pHRR and the tHR for each peak was determined using a program written in Python programming language.
4.4.7 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 3mm by 3mm by 100 mm rods which were then used for the LOI measurement. The LOI value was determined by changing the O$_2$ concentration of the O$_2$/N$_2$ mixture until at least three samples burnt so that the 50 mm mark was reached in 3 min ± 5 s.

4.4.8 Tensile Test

Unlike for the Colour, 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 moulding. A Boy® 22 A injection moulding machine fitted with a specialised screw and barrel specifically designed for injection moulding PVC was used.

The specialised 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 moulding 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 moulded in order of decreasing stability, i.e. the compounds with the least risk were injection moulded first. Ordering the compounds in terms of thermal stability is in conflict with the randomisation principle (see section 2.4) but is deemed necessary due to the high cost of the injection moulding machine and specialised screw.

The pelletized PVC for each of the selected samples was dried under vacuum for 6 h at 60 °C before injection moulding. 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 mould for the standard 1BA tensile bar was used and the mould temperature was set at 30 °C. For each sample the injection moulding machine was run, discarding all the tensile bars produced, until the process stabilised. 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 can happen outside the testing zone which means the results are invalid, and measurements are usually done at least in triplicate with the mean reported.

The tensile testing was done according to ISO 527-2 using a Zwick tensile tester. A cross-head speed of 1 mm-min⁻¹ was used to determine the $E$ modulus and a speed of 50 mm-min⁻¹ was used to determine elongation and tensile strength at break. A minimum of three repeat measurements (i.e. three tensile bars) were used per sample with the mean values reported.
5 Results and Discussion

5.1 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 a 2nd order Scheffé polynomial with \( q = 7 \) there are 28 model terms that can be used to construct a model; 7 first order terms and 21 interaction terms. 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). 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. This effect for the full range of model complexities is shown in Figure 16.

In total there are 2.35 million different possible models for the 2nd degree Scheffé polynomial with \( q = 7 \). For a special cubic Scheffé polynomial with 49 model terms the number of possible models would be significantly larger due to the combinatorial effects at work. This is one of the reasons why only the 2nd order Scheffé polynomial and not the special cubic is used for this study. The other reasons are:

- To validate the model part of the data must be withheld which means there is not enough data to effectively validate a model with 49 terms. This was not considered in the experimental design
- The data set is not complete (see section 4.4) which means that for the effected response variables there is not enough data in any case
• The additional model terms in the special cubic do not make the model more interpretable
• The results using only the 2nd order Scheffé (which will still be discussed in detail) show a good prediction for many of the response variables without requiring the additional model flexibility

Figure 16: Number of possible models for 2nd order Scheffé polynomial with different model complexities for \( q = 7 \)

To validate all the possible models for a 2nd degree Scheffé polynomial the data from the experiments described in sections 4.4.2 to 4.4.8 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 normalised to be between -1 and 1 using the following transformation

\[
y^* = 2 \left( \frac{y - y_{\text{min}}}{y_{\text{max}} - y_{\text{min}}} \right) - 1
\]

\( (32) \)
where $y^*$ is the scaled response value and $y_{\text{max}}$ and $y_{\text{min}}$ 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 full data set is referred to as the matrix $Y$ and each column representing a certain response variable as the vector $y$.

The design variables can be expressed in a similar way with each row representing a sample number and each column representing a design variable given by the matrix $D$

$$D = \begin{bmatrix}
X_{1,PVC} & X_{1,fill} & \cdots & X_{1,sp,h,fill} \\
\vdots & \vdots & \ddots & \vdots \\
X_{53,PVC} & X_{53,fill} & \cdots & X_{53,sp,h,fill}
\end{bmatrix}$$  \hspace{1cm} (33)

The interaction terms for the 2nd order Scheffé polynomial can be included as additional columns to form the matrix $X$

$$X = \begin{bmatrix}
X_{1,PVC} & \cdots & X_{1,sp,h,fill} & X_{1,PVC}X_{1,fill} & \cdots & X_{1,LDH}X_{1,sp,h,fill} \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
X_{53,PVC} & \cdots & X_{53,sp,h,fill} & X_{53,PVC}X_{53,fill} & \cdots & X_{53,LDH}X_{53,sp,h,fill}
\end{bmatrix}$$  \hspace{1cm} (34)

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

$$y = X\beta + \epsilon$$  \hspace{1cm} (35)
where $\beta$ is a column vector of the model parameters and $\epsilon$ represents the measurement error for each sample. Estimates of the model parameters, referred to as $\hat{\beta}$, can then be determined using ordinary least squares which gives the equation

$$\hat{\beta} = (X^T X)^{-1} X^T y$$

(36)

Note that an ordinary least squares algorithm is used to find $\hat{\beta}$ that does not actually use equation 36. 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 $y$ that row is excluded for $X$ and $y$.

Therefore for each response variable, $y$ and $X$ are constructed based on all the samples for which there is data. 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 with $k = 3$. The score is determined by calculating the $R^2$ value on the data that is withheld for each iteration and averaging the three scores. To minimise any effects on the score resultant from the order in which the experiments were conducted, the order of the samples is randomised 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 17 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 17. 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 favoured due to the fact that models with lower complexity with close to the maximum possible score are more likely to indicate the true behaviour 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. This is illustrated for the example above in Figure 18.
5.2 Model Analysis

5.2.1 Statistical Significance of Model Terms

Each of the specific models that are selected contain information about the relationship between the design variables and the response variable. The statistical significance of each term can be analysed 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 19.

![Figure 19: 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%](image)

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 19 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 stabilising 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 of Figure 19 shows that the DINP itself has a negative effect on the long term stability but also synergises (although less strongly) with the spherical filler and the primary stabiliser. The spherical filler and LDH also show a negative effect in isolation however there is some evidence of synergism between them. Interestingly there is relatively strong evidence of antagonism between the LDH and primary stabiliser. This is contrary to what is reported in literature for LDHs in general which are specifically mentioned as synergists to primary stabilisers.

The analysis demonstrated above shows how the use of statistical experimental design can be used to draw conclusions about the behaviour of all the included design variables and their interaction with each other over the entire experimental space. To make the same observations using the favoured 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. 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.
5.2.2 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 interaction terms. To determine the overall effect of each ingredient 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

\[
\begin{align*}
y^* &= -6.5x_{stab} - 4.6x_{DINP} - 12.3x_{LDH} - 8.6x_{sph,fill} \\
&+ 60.5x_{stab}x_{DINP} - 206x_{stab}x_{LDH} \\
&+ 114.9x_{DINP}x_{LDH} + 39.6x_{DINP}x_{sph,fill} \\
&+ 50x_{LDH}x_{sph,fill}
\end{align*}
\]

has the following partial derivatives

\[
\begin{align*}
\frac{\partial y^*}{\partial x_{PVC}} &= \frac{\partial y^*}{\partial x_{fill}} = \frac{\partial y^*}{\partial x_{FR}} = 0 \\
\frac{\partial y^*}{\partial x_{stab}} &= -6.5 + 60.5x_{DINP} - 206x_{LDH} \\
\frac{\partial y^*}{\partial x_{DINP}} &= -4.6 + 60.5x_{stab} + 114.9x_{LDH} + 39.6x_{sph,fill} \\
\frac{\partial y^*}{\partial x_{LDH}} &= -12.3 - 206x_{stab} + 114.9x_{DINP} + 50x_{sph,fill} \\
\frac{\partial y^*}{\partial x_{sph,fill}} &= -8.6 + 39.6x_{DINP} + 50x_{LDH}
\end{align*}
\]

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 analyse 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 (Wypych, 2009) which is shown in Table 7

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass Fraction (%)</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>46.3</td>
<td>100</td>
</tr>
<tr>
<td>Filler</td>
<td>16.2</td>
<td>35</td>
</tr>
<tr>
<td>FR</td>
<td>4.6</td>
<td>10</td>
</tr>
<tr>
<td>Stabiliser</td>
<td>1.4</td>
<td>3</td>
</tr>
<tr>
<td>DINP</td>
<td>23.1</td>
<td>50</td>
</tr>
<tr>
<td>LDH</td>
<td>1.4</td>
<td>3</td>
</tr>
<tr>
<td>Spherical Filler</td>
<td>6.9</td>
<td>15</td>
</tr>
</tbody>
</table>

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 20.

Figure 20: Thermal stability sensitivities at the example formulation
Note that the sensitivities for the final degradation time shown in Figure 20 are calculated using equations 37 to 42. The strong influence of the primary and secondary stabilisers on the thermal stability in general is clear. The primary stabiliser, however, clearly 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 also interesting to note that an increase in the stabiliser for the example formulation leads to an increase in long term stability in spite of the antagonism between the LDH and the stabiliser. This shows why sensitivity analysis is necessary, giving insight into the model behaviour which is not necessarily clear from the statistical analysis of the model parameters.

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 i.e. due to the fact that all the design variables must sum to 1. Consider the sensitivity analysis of the final degradation time shown in Figure 20. The final degradation time is not sensitive to 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. In effect changing the phr of one ingredient will always change the mass fractions for all of the ingredients in the formulation. This is illustrated in Figure 21 where the effect of a 1 phr increase for each of the ingredients on the scaled response variables for Figure 20 is shown.

Figure 21: Change in y* for thermal stability induced by a 1 phr increase for each ingredient

Figure 21 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 analysed. 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 20.

It is also important to note that Figure 20 and Figure 21 are quite similar, especially when it comes to the most significant ingredients for the thermal stability which are the primary stabiliser 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 minimising the necessary change in any particular other ingredient. In other words it is a way of absorbing the required change in the other ingredients by spreading it out over all of the ingredients.

The sensitivities for the fire retardancy and mechanical properties at the example formulation (shown in Figure 22 and Figure 23) can be similarly analysed. From Figure 22 the importance of the FR to the pHRR and MAHRE measurements is clear (take note that low pHRR, MAHRE and tSP values are desired). In particular the pHRR is shown to be significantly more sensitive to the FR than to any of the other ingredients. 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. The 0 sensitivity values for pHRR and MAHRE indicate that the corresponding
models do not include the LDH design variable $x_{LDH}$. Based on this evidence the LDH can only be classified as a smoke suppressant and not as a true fire retardant.

Figure 22: Fire retardancy sensitivities at the example formulation

Figure 23: Mechanical property sensitivities at the example formulation
The interpretation of the elongation and tensile strength sensitivities shown in Figure 23 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 probable adverse effects on the elongation at break of the material. The interpretation of the sensitivities for $E$ is not as straightforward 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). For instance if a small increase in the mass fraction of DINP in the example formulation is made and the mass fraction of Filler is decreased accordingly so that the mixture constraint is maintained, $E$ will decrease (i.e. the compound will become more flexible). In this case it is easier to see the effect of increasing or decreasing a certain ingredient by examining the change in the response variable introduced by increasing the phr of that ingredient as was done for Figure 21. This is shown in Figure 24.

It is clear that the actual change in the response variable $E$ introduced by an increase of 1 phr in each ingredient (Figure 24) looks quite different to the sensitivities of $E$ (Figure 23). This demonstrates how the sensitivities need to be considered together for a real change in the formulation. For elongation and tensile strength, the two figures are quite similar due to the fact that the differences in the ingredient sensitivities are more pronounced.
Figure 24: Change in $y^*$ for mechanical properties induced by a 1 phr change for each ingredient

5.3 Optimisation

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

5.3.1 Optimum Solution

The optimisation can be summarised as follows: minimise

$$f = \sum_{i=1}^{7} c_i x_i$$  \hspace{1cm} (11)
subject to

\[ \sum_{i=1}^{7} x_i = 1 \]  
\[ 0 \leq x_i \leq 1 \quad i = 1, 2, \ldots, 7 \]  
\[ g(x) \geq p_{lim} \]  
\[ g(x) \leq p_{lim} \]  
\[ 0.4 \leq x_{PVC} \]  
\[ x_{fill} \leq 0.7x_{PVC} \]  
\[ x_{FR} \leq 0.2x_{PVC} \]  
\[ 0.02x_{PVC} \leq x_{stab} \leq 0.1x_{PVC} \]  
\[ 0.2x_{PVC} \leq x_{DINP} \leq 0.7x_{PVC} \]  
\[ x_{LDH} \leq 0.15x_{PVC} \]  
\[ x_{sph. fill} \leq 0.2x_{PVC} \]  

The details for equations 11 to 16 are found in section 3. Equations 24 to 30, 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 \( c \) 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 to give a realistic demonstration of the optimisation. 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 8.

The limits on the properties are also estimated, taking into account the requirements for underground mine cables outlined in section 2.1.2.1. 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 variable is shown in Table 9.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Cost (R/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>15</td>
</tr>
<tr>
<td>Filler</td>
<td>8</td>
</tr>
<tr>
<td>FR</td>
<td>48</td>
</tr>
<tr>
<td>Stabiliser</td>
<td>45</td>
</tr>
<tr>
<td>DINP</td>
<td>30</td>
</tr>
<tr>
<td>LDH</td>
<td>40</td>
</tr>
<tr>
<td>Spherical Filler</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 9: Property limits for optimisation including the range of measured values and $k$-fold scores

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Response Variable</th>
<th>Max</th>
<th>Min</th>
<th>$p_{\text{lim}}$</th>
<th>$k$-fold Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torque Rheometer</td>
<td>Stability Time (min)</td>
<td>141.4</td>
<td>8.5</td>
<td>$\geq 25$</td>
<td>0.58</td>
</tr>
<tr>
<td>Cone Calorimeter</td>
<td>Final Degradation Time (min)</td>
<td>346.9</td>
<td>12.6</td>
<td>$\geq 80$</td>
<td>0.57</td>
</tr>
<tr>
<td>Cone Calorimeter</td>
<td>MARHE (kW/m$^2$)</td>
<td>179.2</td>
<td>12.1</td>
<td>$\leq 85$</td>
<td>0.89</td>
</tr>
<tr>
<td>Cone Calorimeter</td>
<td>pHRR (kW/m$^2$)</td>
<td>242.8</td>
<td>60.0</td>
<td>$\leq 125$</td>
<td>0.7</td>
</tr>
<tr>
<td>Tensile Test</td>
<td>$E$ (MPa)</td>
<td>1917.7</td>
<td>23.6</td>
<td>$\leq 300$</td>
<td>0.86</td>
</tr>
<tr>
<td>Tensile Test</td>
<td>Elongation at Break (%)</td>
<td>114.8</td>
<td>9.8</td>
<td>$\geq 50$</td>
<td>0.92</td>
</tr>
<tr>
<td>Tensile Test</td>
<td>Tensile Strength at Break (MPa)</td>
<td>29.5</td>
<td>10.6</td>
<td>$\geq 18$</td>
<td>0.92</td>
</tr>
</tbody>
</table>

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 optimisation 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 (the highest possible score being 1), which means significantly lower safety factors are required.

The optimum solution is found using a constrained non-linear optimisation algorithm called Sequential Least Squares Quadratic Programming (SLSQP). Multiple starts are used, with randomly generated $x_0$ values for each start, to increase the chance of finding the global optimum. The optimum solution for the settings shown in Table 8 and Table 9 is shown in Table 10. All the response variable values are shown in Table 11 with the response variables which are included in the constraints and the values which are constrained in bold.

### Table 10: Example optimum formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass Fraction (%)</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>53.19</td>
<td>100.0</td>
</tr>
<tr>
<td>Filler</td>
<td>3.34</td>
<td>6.3</td>
</tr>
<tr>
<td>FR</td>
<td>10.04</td>
<td>18.9</td>
</tr>
<tr>
<td>Stabiliser</td>
<td>1.06</td>
<td>2.0</td>
</tr>
<tr>
<td>DINP</td>
<td>18.99</td>
<td>35.7</td>
</tr>
<tr>
<td>LDH</td>
<td>2.73</td>
<td>5.1</td>
</tr>
<tr>
<td>Spherical Filler</td>
<td>10.64</td>
<td>20.0</td>
</tr>
</tbody>
</table>

**Objective Function (R/kg)**: 20.65

### Table 11: Response variable values at the example optimum solution

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Response Variable</th>
<th>Max</th>
<th>Min</th>
<th>Value</th>
<th>$k$-fold Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torque Rheometer</td>
<td>Stability Time (min)</td>
<td>141.4</td>
<td>8.5</td>
<td>32.2</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>Final Degradation Time (min)</td>
<td>346.9</td>
<td>12.6</td>
<td><strong>80.0</strong></td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>Resting Torque (N·m)</td>
<td>8.7</td>
<td>-1.9</td>
<td>3.9</td>
<td>0.61</td>
</tr>
<tr>
<td>Thermomat</td>
<td>Stability Time (min)</td>
<td>451.4</td>
<td>0.0</td>
<td>50.6</td>
<td>0.41</td>
</tr>
<tr>
<td>Colour</td>
<td>YI</td>
<td>140.8</td>
<td>-4.9</td>
<td>44.7</td>
<td>0.63</td>
</tr>
<tr>
<td>Cone Calorimeter</td>
<td>MARHE (kW/m²)</td>
<td>179.2</td>
<td>12.1</td>
<td><strong>85.0</strong></td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>pHRR (kW/m²)</td>
<td>242.8</td>
<td>60.0</td>
<td><strong>125.0</strong></td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>t to pHRR (s)</td>
<td>460.0</td>
<td>25.0</td>
<td>132.1</td>
<td>0.65</td>
</tr>
</tbody>
</table>
Table 11 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 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

\[ x_{sph\ fill} \leq 0.2x_{PVC} \]  
\[ 0.02x_{PVC} \leq x_{stab} \]

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. This will be further discussed in the following section.
5.3.2 Parametric Analysis

Parametric analysis involves determining the influence of changes in the input settings on the optimal solution. It can be used to analyse the system as a whole. Fortunately for this system the optimisation is very simple requiring no more than a few seconds to find a solution. This makes it possible to perform very detailed parametric analyses. A number of example analyses are used to demonstrate how they can be performed and how useful they are. The examples are also used to highlight some interesting aspects of the system.

5.3.2.1 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 optimisation 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 8 and Table 9 (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 25 and Figure 26.

Figure 26 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. Initially there is no change in any of the values which shows that the final degradation time constraint is not active here. Evidently the other constraints result in a final degradation time of greater than 30 min. At some point between 30 and 40 min the constraint becomes active and the mass fractions, as well as the objective function value shown in Figure 25, start to change.
Figure 25: Parametric analysis for minimum final degradation time showing objective function value

Figure 26: Parametric analysis for minimum final degradation time showing formulation
Closer inspection reveals that initially, after the constraint has become active, the final degradation time is increased by increasing the primary stabiliser. This is shown more clearly in Figure 27.

![Graph showing parametric analysis for minimum final degradation time (30 – 50 min) showing selected ingredient mass fractions](image)

Figure 27: Parametric analysis for minimum final degradation time (30 – 50 min) showing selected ingredient mass fractions

After the initial increase of the primary stabiliser, the amount of LDH is increased while the primary stabiliser increases only slightly. Then between 42.5 and 45 min the amount of primary stabiliser suddenly drops and starts to decrease. Complex behaviour such as this can only be revealed by taking into account the entire system.

Note also that the constraints from the experimental design are active at different points of the parametric analysis. The upper limit on the spherical filler seems to be active regardless of the minimum final degradation time. This is evident by the fact that it changes proportionally to the change in the PVC. If the constraints on
the original design are not applied extrapolation of the response variable models is allowed. This is shown in Figure 28.

Extrapolation decreases the confidence in the predicted values. Extrapolating purely empirical models is always questionable even if steps are taken to avoid overfitting. However the extrapolation can still be used to make useful observations about the system behaviour. For instance it is clear that the experimental space for future investigations needs to be expanded to include higher mass fractions of spherical filler. In fact the extrapolation indicates that it may be possible and economically beneficial to completely replace the traditional CaCO$_3$ filler with the spherical fly ash filler. This warrants further investigation. Note that since the constraints are relaxed the objective function will either decrease or remain the same. In this case it is decreased.
It is important to note that the changes in the formulation can be far more drastic and unexpected than those shown in Figure 26. For instance, if the spherical filler, for some reason, is more expensive than the CaCO₃ filler the parametric analysis of the minimum final degradation time shows interesting results, where it is clear that the optimisation can yield very different formulations with even a small change in the input settings. This is illustrated in Figure 29 where a spherical filler cost of 14 R/kg is used.

Figure 29: Parametric analysis for final degradation time, where the cost of spherical filler is 14 R/kg, showing formulation (the PVC and FR mass fractions are not shown because they change very little)

5.3.2.2 Change in Cost of Ingredient

The costs for the ingredients used in the objective function can also be changed. A parametric analysis where the costs are varied can be very useful in a commercial setting. To demonstrate this a parametric analysis where the cost of the LDH is
changed will be analysed. The parametric analysis is shown in Figure 30 and Figure 31.

Figure 30: Parametric analysis of LDH cost showing the objective value

Figure 31: Parametric analysis of LDH cost showing ingredient mass fractions
For a PVC formulator or cable manufacturer an analysis of the following type can be used to determine the impact of a change in the cost of the LDH on the production cost and optimum formulation. For a manufacturer of the LDH the parametric analysis can be used, for instance, as a tool to determine the appropriate selling price of the LDH.

Consider for example the hypothetical situation where a manufacturer of the LDH is negotiating a contract to supply LDH to a compounder, who needs to manufacture a set mass of PVC compound using the ingredients used in this study. In this case the total profit depends on both the profit margin on the LDH and on how much LDH the compounder uses. This can be expressed by multiplying the profit margin of the LDH by the mass fraction of the LDH used in the optimum formulation to determine the profit per kg required by the supplier. This is shown, using a hypothetical production cost of 10 R/kg for the LDH, in Figure 32.

![Figure 32: Parametric analysis on LDH cost showing hypothetical profit](image-url)
Figure 32 shows that for this example it is possible to sell the LDH at 15 R/kg or 25 R/kg and make the same amount of profit. This is due to the fact that there is a point where the amount of LDH included in the optimum formulation is drastically reduced. From Figure 30 it is clear that the overall cost of the PVC compound is significantly lower at 15 R/kg than 25 R/kg. In the hypothetical example the LDH manufacturer can present the compounder with a much more attractive offer at 15 R/kg than 25 R/kg while making the same amount of profit. The sudden decrease in the amount of LDH included in the formulation (and the other associated changes in the formulation) can be attributed to the point where the LDH becomes more expensive than the PVC resin, which has a cost of 15 R/kg. This shows the importance of the ingredient costs relative to each other.

Even though the above example is crude (in particular using an unrealistically low cost of production for the LDH) it demonstrates how parametric analysis can be used to make important decisions, taking into account the entire system behaviour. 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 simpler. It is also important to note that in a commercial setting the exact values used for the input settings are important. It is recommended that accurate values for the ingredient costs and required response variable settings for flexible PVC underground mine cable insulation are researched. It is further recommended that parametric analyses are conducted that address specific industry relevant questions.

5.3.2.3 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 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 long term thermal stability (final degradation time) is no longer satisfactory. The optimisation 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 12 and Table 13.

Table 12: Optimum formulation with constraining Thermomat rather than Torque Rheometer Measurements

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass Fraction (%)</th>
<th>Case 0</th>
<th>Case 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td></td>
<td>53.19</td>
<td>52.07</td>
</tr>
<tr>
<td>Filler</td>
<td></td>
<td>3.34</td>
<td>6.76</td>
</tr>
<tr>
<td>FR</td>
<td></td>
<td>10.04</td>
<td>10.19</td>
</tr>
<tr>
<td>Stabiliser</td>
<td></td>
<td>1.06</td>
<td>1.56</td>
</tr>
<tr>
<td>DINP</td>
<td></td>
<td>18.99</td>
<td>19.01</td>
</tr>
<tr>
<td>LDH</td>
<td></td>
<td>2.73</td>
<td>0</td>
</tr>
<tr>
<td>Spherical Filler</td>
<td></td>
<td>10.64</td>
<td>10.41</td>
</tr>
<tr>
<td>Objective Function (R/kg)</td>
<td></td>
<td>20.65</td>
<td>19.96</td>
</tr>
</tbody>
</table>

Table 13: Response variable values for thermal stability

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Response Variable</th>
<th>Value</th>
<th>k-fold Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torque Rheometer</td>
<td>Stability Time (min)</td>
<td>32.2</td>
<td>19.2</td>
</tr>
<tr>
<td></td>
<td>Final Degradation Time (min)</td>
<td>80.0</td>
<td>27.07</td>
</tr>
<tr>
<td></td>
<td>Resting Torque (N·m)</td>
<td>3.9</td>
<td>4.2</td>
</tr>
<tr>
<td>Thermomat Colour</td>
<td>Stability Time (min)</td>
<td>50.6</td>
<td>55.0</td>
</tr>
<tr>
<td></td>
<td>YI</td>
<td>44.7</td>
<td>10.2</td>
</tr>
</tbody>
</table>

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 stabilising 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 report, but is recommended for future work due to the fact that the data set is well suited to such an investigation.

5.4 Implementation

All of the calculations and analyses described in sections 5.1 to 5.3 were done using code written in Python programming language using IPython Interactive Computing (Perez & Granger, 2007). The model validation was done using scikit-learn (Pedregosa, et al., 2011) and the model statistics were calculated using Statsmodels (Seabold & Perktold, 2010). The optimisation of the system was done using SciPy (Millman & Aivazis, 2011). All the code is available online at https://github.com/reinhardfechter/FlexPVCModel.

5.5 Labour and Time Savings

The usefulness of the models, determined using statistical experimental design, 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 the time required for the Torque Rheometer, Cone Calorimeter and Tensile Tests. The Torque Rheometer tests took approximately 90 min with an additional 30 min of cleaning required per run. This makes it possible to do about 4 runs in a normal 8 h working day. The Cone Calorimeter tests require calibration for every day of testing which takes approximately 3 h. The remaining time in the day can be used to do ± 15 runs considering that another hour is required to shut down the machine. The samples also need to be pressed into sheets before doing Cone Calorimetry, ± 15 samples can be pressed in a day. For the tensile testing ± 7 samples can be tested in a day (each sample is tested in triplicate). Additionally the samples for the tensile testing are prepared using injection moulding where ± 8 samples, with 15 tensile bars each, could be processed in a day. The compound for all of the samples was prepared using high speed mixing, where 20 batches a day could be processed, and compounding using a twin screw extruder, where 12 samples could be compounded in a day including heat up and cool down times. From the above information the approximate total time required to obtain the Torque Rheometer, Cone Calorimeter and Tensile Test data used for this investigation can be calculated as shown in Table 14.

Table 14: Number of days required to obtain Torque Rheometer, Cone Calorimeter and Tensile Test data

<table>
<thead>
<tr>
<th>Process/Equipment</th>
<th>No. Samples</th>
<th>No. Samples/Day</th>
<th>No. Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Speed Mixing</td>
<td>53</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Compounding</td>
<td>53</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>Torque Rheometer</td>
<td>46</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>Pressing</td>
<td>40</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>Cone Calorimeter</td>
<td>40</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>Injection Moulding</td>
<td>27</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Tensile Test</td>
<td>27</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td></td>
<td><strong>34</strong></td>
</tr>
</tbody>
</table>
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 test 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 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. If the formulator is prudent a formulation with a thermal stability that is slightly higher than the requirement is selected. 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, again with 5 additional formulations measured in triplicate. 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 summarised in Table 15 including a calculation of the approximate amount of time required.
Table 15: Number of experiments and amount of time required for example of next-best-guess approach using one-factor-at-a-time experiments

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>High Speed Mixing</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>8</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>Compounding</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>Torque Rheometer</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>54</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>Pressing</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>54</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>Cone Calorimeter</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>54</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>Injection Moulding</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>54</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Tensile Test</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>54</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>41</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At this point in the hypothetical example more time has already been spent than what is shown in Table 14 (i.e. what was approximately required in this investigation for the measurements used in the example). 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 optimisation 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 labour and time to get to an optimum solution.
6 Conclusions and Recommendations

6.1 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. The DINP itself is shown to have a negative effect and additional weaker synergistic effects with the spherical filler and primary stabiliser. The spherical filler and LDH similarly show a negative effect in isolation however there is evidence that supports the hypothesis that they are synergists. Finally it is interesting to note that there is relatively strong evidence of antagonism between the LDH and primary stabiliser 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 favoured in the literature on LDH as a PVC additive. It is recommended that a detailed statistical analysis of all the response models is conducted and that previously unreported interactions and effects, including those described above are investigated further.
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, based on an existing commercial cable 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 stabiliser and the LDH. It also shows how the primary stabiliser has a stronger influence on short term stability while the LDH has a stronger influence on long term stability. The sensitivity analysis shows that an increase in the stabiliser for the example formulation leads to an increase in long term stability in spite of the antagonism between the LDH and the stabiliser. This demonstrates how sensitivity analysis gives insight into the model behaviour which is not necessarily clear from the statistical analysis of the model parameters.

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.

It is important, however, to understand that the independent change in the amount of an ingredient, shown by the sensitivity analysis, is not possible for a mixture due
to the mixture constraint. When making a real change to the mass fraction of a certain ingredient the mass fraction of at least one other ingredient must also change to maintain the mixture constraint. Therefore, for a real change in the formulation, the sensitivities of at least two ingredients need to be taken into account.

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 why, for instance, a change in the phr of the FR in the example formulation, will have an effect on the thermal stability even though, according to the sensitivity analysis, the FR itself has no effect. 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. If, however, 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 minimising the necessary change in any particular other ingredient.

6.2 Optimisation

It can also be concluded that the models make it possible to minimise 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 analyse 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 analysis shows that initially there is no change in the formulation because the final degradation time constraint is not active. Then at 40 min the constraint becomes active, indicated by a change in the formulation. Initially the final degradation time is increased by increasing the amount of primary stabiliser. Then the LDH is introduced and increased steadily while the primary stabiliser is still increased but to a lesser degree. At some point between 42.5 and 45 min the amount of primary stabiliser suddenly drops and starts to decrease. Complex behaviour such as this can only be revealed by taking into account the entire system.

It is also noted that the constraints from the experimental design are active at certain points of the parametric analysis. Repeating the parametric analysis described above without the experimental space constraints, i.e. allowing the models to extrapolate, indicates that it may be possible and economically beneficial to completely replace the traditional CaCO₃ filler with the spherical fly ash filler. It is recommended that an expanded experimental space allowing for higher mass fractions of spherical filler is investigated.

A similar parametric analysis is conducted where the cost of the LDH is varied. The analysis shows how the formulation changes drastically, in particular decreasing the amount of LDH used, when the LDH cost becomes larger than the resin cost. It is shown using a hypothetical situation that a quantitative description of such
behaviour can be used to make informed commercial decisions, which take into account the complex behaviour of the system in question. To make conclusions that are more directly relevant to industry it is recommended that the exact input settings for the optimisation are researched. It is then recommended that parametric analyses are designed that answer specific questions relevant to the industry.

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 stabilising effects of LDH. The different measurement techniques for fire retardancy can be similarly investigated. It is recommended that a detailed investigation comparing the different measuring techniques is conducted using the data collected for this investigation.

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 labour savings. This is due to the efficiency with which statistical experimental design uses experimental data.
7 Future Work

Some recommendations for future work, based directly on the conclusions, have already been made in the previous section. Additional recommendations for future work based on the broader outcomes of this investigation are discussed here.

The analysis of the data as it is presented in this report (i.e. by using optimisation) has been implemented using code written in Python programming language. This means that in its current state the analysis of the data, and hence the data itself, is inaccessible to anyone that is unfamiliar with how to manipulate or run code written in Python programming language (or does not have the time to figure out how the code works).

To make the analysis of the data accessible and usable, for anyone with a basic understanding of the system under study and the analysis methods used, requires an interface. For example, a simple interface could be designed that allows a user to change the mass fractions of the 7 ingredients and observe the resultant material properties, which are calculated in the background using the empirical models. This will allow a user to ‘play around’ with different formulations and observe how the material properties change. It is important to note however that a mechanism is required that makes sure that the mixture constraint is maintained. One way to do this is to allow the user to make changes in the phr of the various additives which can then be converted to mass fractions by the program. This is also a more familiar unit for anyone who has worked with PVC formulations and/or research before.

Additionally the interface would allow the user to enter the costs of each ingredient, select which material properties should be constrained and what the value of the limits should be. The user would then be able to press a button which performs the optimisation and displays the optimum formulation, the material
properties of the formulation and the objective function value (unless no optimum solution could be found in which case an appropriate error message should be displayed). This basic idea can be modified further depending on specific user requirements. Examples of this would be to make comparisons between different formulations easier or to allow the user to conduct parametric analyses such as those shown in section 5.3.2.

All the recommendations for future work made up until this point (except the recommendation to expand the experimental space to include more spherical filler) do not require any additional physical experiments. However, with the current data set, it is only possible to find an optimum formulation, or make definitive conclusions about the behaviour of the mixture, within the experimental space. For the recommendation to investigate higher mass fractions of spherical filler the experimental space can be expanded by simply conducting some additional experiments using the same 7 ingredients used in this investigation. If, however, a researcher or formulator is interested in investigating one or more new ingredients there will be new terms in the Scheffé models, which need to be taking into account.

For instance say a formulator is interested in the same system that was investigated here, except that a different LDH is to be investigated. For this new investigation only enough experiments are required to determine the additional model terms, which include the linear term for the new LDH and the interaction terms of the new LDH with the 6 other ingredients (i.e. the PVC, filler, FR, DINP, stabiliser and spherical filler, assuming that a 2nd order Scheffé polynomial is used). The other terms that do not involve the new LDH have already been determined in this investigation and do not need to be determined again. If the same validation strategy is used, i.e. using $k$-fold cross validation with $k = 3$, 11 additional experimental points (formulations) are required for the 7 new model terms. The number of experimental points can be calculated using the equation
\[ N_e = \left\lfloor N \frac{k}{k - 1} \right\rfloor \quad (43) \]

where \( N \) is the number of terms and \( N_e \) is the number of experimental points. The new data that is collected and the data from this investigation can then be combined into a single data set which can be analysed using effectively the same methods used in this investigation.

If a PVC compound that contains none of the ingredients that were used in this investigation is of interest a new separate data set needs to be generated. This can be done by following the same procedure which is outlined in this report. In fact the method that is used in this investigation can be generalised to optimise the proportions of the ingredients of any mixture.
8 References


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