Modelling and Optimization of the Mechanical and other Material Properties of a Polymer Nanocomposite using Statistical Design of Experiments

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Abstract. Polymer compounds are complex systems that typically involve many additives that tend to interact with each other. The system is further complicated by the fact that the additives tend to have an effect on multiple material properties. Hence, the effect of a particular ingredient on a certain material property should not be quantified in isolation. For instance, an important consideration in evaluating the effectiveness of an ingredient is not only how it effects the property it was designed to effect but how it effects other properties, such as the mechanical properties of the compound, in the context of the proportions of the other ingredients. This can be achieved by using the principles of statistical design of experiments. In this investigation the mechanical properties of a polymer nanocomposite, a PVC compound including a Layered Double Hydroxide (LDH) nano-additive, are modelled using 2nd degree Scheffe polynomials. The proportions of all the ingredients (7 in total) are varied in a space filling experimental design. The mechanical properties of each formulation are tested using a tensile test on samples manufactured using injection molding. Injection molding is crucial because it produces homogenous test samples that give an accurate representation of the inherent mechanical properties of the material. The models are determined using k-fold cross validation. The mechanical property models, in conjunction with models of other important material properties, allow for an analysis of the effects and interactions of all of the ingredients. For instance, the analysis shows the negative effect that the LDH has on the elongation at break which needs to be taken into account when considering the positive effects it has on the thermal stability of the compound. Importantly the models can also be used to optimize the system.

INTRODUCTION

Polymer compounds typically require a number of additives to be practically and commercially viable. This results in a mixture system which is complex for three specific reasons. The first is that the additives tend to interact with each other and the polymer; there are many examples of synergisms and antagonisms between polymer additives. Secondly, the additives tend to affect multiple material properties of the compound. Finally due to the fact that a polymer compound is a mixture system it is impossible to make an independent change in the relative proportion of a single ingredient.

This means that it is important to evaluate the effectiveness of each ingredient in the context of the relative proportions of the other ingredients. It is also important when evaluating a certain ingredient to not only consider the property that a particular additive was designed to effect but also to consider how it effects other material properties such as, for instance, the mechanical properties of the compound.

This can be achieved using the principles of statistical design of experiments. The purpose of the investigation was to empirically model the mechanical and other important material properties of a polymer nanocomposite as a function of the relative proportions (mass fractions) of the ingredients using statistical experimental design. A secondary aim of the investigation was to enable the optimization of the polymer compound.

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In the investigation a flexible PVC compound including a Layered Double Hydroxide (LDH) nano-additive was used due to the significant number of additives typically required to make the compound practically and commercially viable and its consequent complexity. The basic mechanical properties were determined using a tensile test on injection molded tensile bars. In addition the thermal stability and fire retardancy properties were determined. The experimental design was done using JMP Statistical Software, the experiments were conducted in a laboratory environment and the data analysis was done using programs written in Python programming language using Jupyter (Kluyver 2016).

EXPERIMENTAL DESIGN

The aim of the statistical experimental design is to determine empirical models that can be used to describe the basic mechanical properties as well as the thermal stability and flame retardancy of the polymer nanocomposite as a function of the relative proportions of the ingredients which can be defined as the mass fractions of the ingredients.

Selection of Response Variables

The experimental methods used to determine the response variables are the tensile test for the mechanical properties, the torque rheometer for the thermal stability and the cone calorimeter for the fire retardancy. The tensile test is used because it covers the basic mechanical properties of the compound (Grellmann 2013). The torque rheometer is selected because it is the most realistic indicator of thermal stability during processing for the system (Wilkes 2005). Finally the cone calorimeter test is selected because it gives the most complete information concerning fire retardancy with the closest simulation of a real fire (Joseph 2016).

Choice of Factors and Ranges

The factors for the experiment (i.e. the variables) are the mass fractions of the 7 ingredients used in the polymer compound. The actual ingredients that are used (which are the PVC resin, thermal stabilizer, plasticizer, two types of fillers, fire retardant and LDH) are not varied. 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.

For the tensile test a sample preparation step is required where the tensile bars are injection molded. This is used so that a test sample that is as homogenous as possible is manufactured which represents the intrinsic mechanical properties of the material. This means that the compound must be injection moldable which limits the experimental space. Considering this a set of limits for the experimental space is proposed. 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 models meaningful by minimizing the effect of variance.

Choice of Experimental Design

Since the system is a mixture and the experimental space is constrained there are a number of options for the experimental design such as the extreme vertices, D-optimal and space filling designs (Smith 2005, Montgomery 2013). For this investigation the space filling design is used so that the experimental points are distributed evenly throughout the 6 dimensional experimental space. The number of experimental points that are used needs to be greater than the number of parameters of the model, but is limited by the time and resources available to execute the experiment. In this investigation enough experimental points will be used to fit a 2nd order Scheffe polynomial which has the form

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

where q is the number of factors in $\boldsymbol{x}$, y is the response and β are the model parameters. A Scheffe polynomial is essentially an ordinary polynomial which has been derived to take into account the mixture constraint (i.e. that all proportions must sum to 1). A special feature of the Scheffe polynomials is that the second order term β_{ij} is interpretable in that it quantifies interactions between ingredients i.e. synergism and antagonism (Scheffe 1958).

RESULTS AND DISCUSSION

Model Selection

For every response variable a Scheffe polynomial is required that can be used to predict it as a function of the design variables. To determine the 'best' Scheffe polynomial for each response variable requires that all possible variants of the Scheffe polynomial are tested using the data. The maximum number of terms in a 2^{nd} degree Scheffe polynomial where $q = 7$ is 28. 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 (Montgomery 2013)). If the model complexity is 2 the number of possible models increases to 21 and then to 56 for 3 terms etc., increasing exponentially with increasing model complexity. In total there are 2.35 million different possible models for the 2^{nd} degree Scheffe polynomial with $q = 7$.

To validate all the possible models the data from the experiments 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. 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 Scheffe model will all be 0 as well. All of the possible models are then scored using k-fold cross validation (a validation technique that is used to evaluate the predictive ability of a model (Hastie 2009)) with $k = 3$. The scoring results can be illustrated by plotting the highest score for each level of model complexity as is shown in **FIGURE 1**.

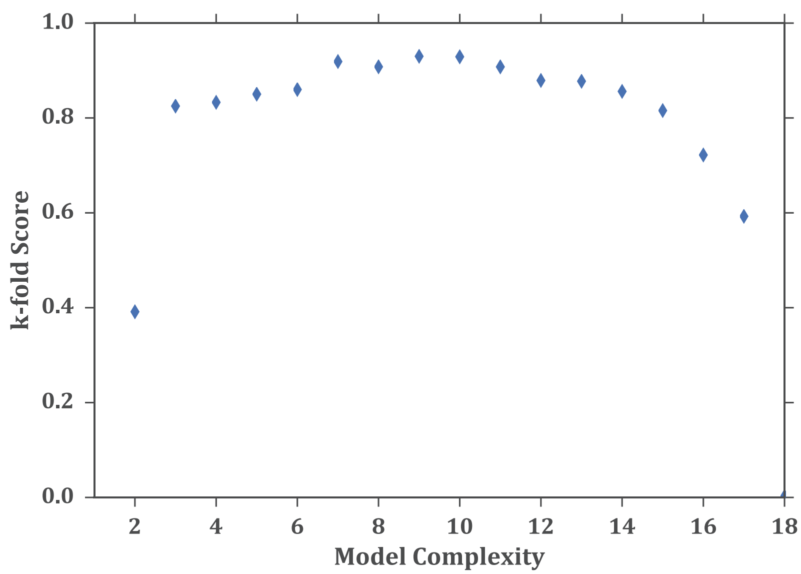

FIGURE 1. k-fold scores for the models fitted to the % elongation at break measured using a tensile test

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 1**. The score increases, plateaus and then eventually decreases due to overfitting. The model with the highest score is selected.

Model Analysis

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 analyzed using the *t*-statistic. This is demonstrated again using the % elongation at break measured using a tensile test. The *t*-values for the terms of the selected model are shown in **FIGURE 2**.

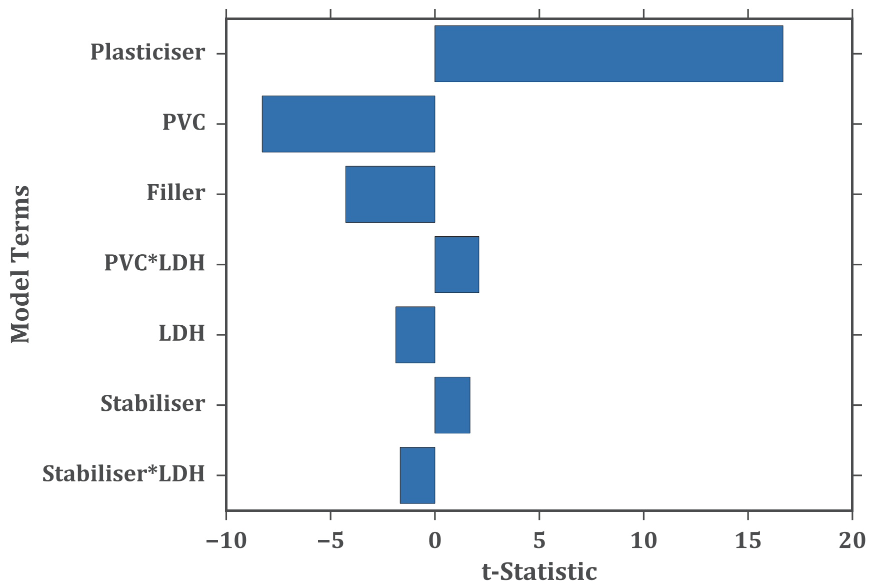

FIGURE 2. *t*-statistic for the model terms for % elongation at break measured using a tensile test

From **FIGURE 2** it is clear that the plasticizer and the polymer are very important when it comes to the elongation at break of the compound. It is also clear that the polymer and the LDH nano-additive interact synergistically whereas the thermal stabilizer and LDH have an antagonistic relationship. The analysis demonstrated above shows how statistical experimental design can be used to draw conclusions about the behavior of all the included design variables and their interaction with each other over the entire experimental space. 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 elongation at break the score for the selected model is 0.92 which is very high (the highest possible score being 1).

Sensitivity Analysis

It is clear from the analysis above that the overall effect of a particular ingredient on a particular response variable can be dependent on the mass fractions of the other ingredients, due to the interaction terms. To determine the overall effect of each ingredient a sensitivity analysis of the response variable at a certain formulation can be used which can be determined by calculating the partial derivatives. The values of the partial derivatives at a certain formulation show the effect of making a very small independant increase in the relevant ingredient. This is interpreted as the sensitivity of the model and is a very useful method to analyze the effects of the individual ingredients on the different response variables. An example of this is shown in **FIGURE 3**.

FIGURE 3 shows the negative effect that the LDH has on the elongation at break. It also shows the strong positive effect that the LDH has on the final thermal degradation time (measured using a torque rheometer) and the smoke reducing effect it has (measured using a cone calorimeter). The empirical models quantify the effects that the ingredients have on the material properties of the compound taking into account the relative proportions of the other ingredients. This means that, as is illustrated in **FIGURE 3**, the negative effect that LDH has on the elongation can be taken into account when evaluating the positive effects it has on other material properties.

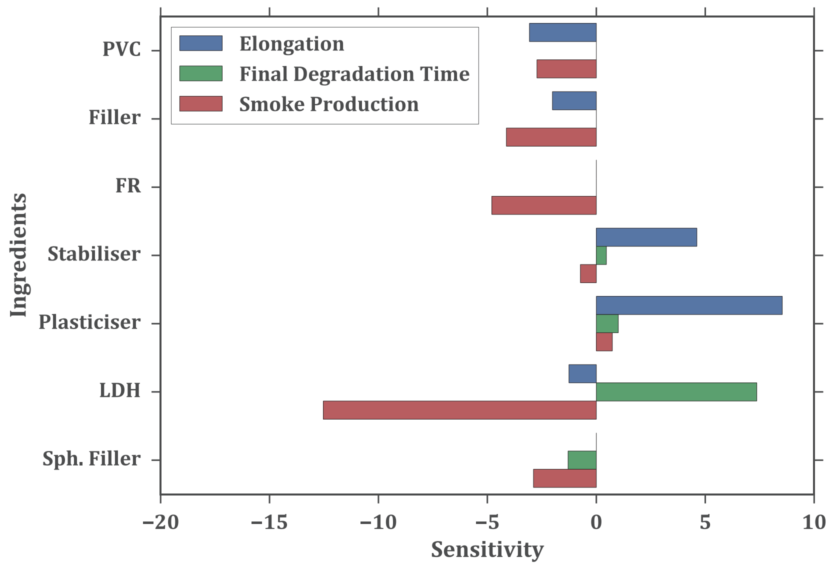

FIGURE 3. Model sensitivities at an example formulation for selected material properties

Finally it is important to mention that the mechanical and other material properties can be used to optimize the system. For instance the overall cost of the formulation can be minimized using a simple cost function as the objective function, where the cost of each ingredient is multiplied by its mass fraction, while using the material models as constraints. The material model constraints ensure that the desired material properties are achieved.

CONCLUSIONS

It can be concluded that the response variables describing the mechanical and other material properties as a function of the mass fractions of the polymer nanocomposite ingredients can be modelled effectively using 2^{nd} order Scheffe 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 2^{nd} order Scheffe polynomial are particularly useful in identifying synergistic and antagonistic relationships between ingredients. Sensitivity analysis can be used to determine the overall effect of an ingredient on a response variable at a given formulation. Finally it can be concluded that the empirical models can be used to optimize the system.

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