

Modelling and Optimization for Adhesives

1. Introduction

Here, several data sets taken from the literature have been used in a study that develops models and uses these to produce optimum adhesive formulations. These data sets have also been looked at using data mining techniques (neurofuzzy logic) in a related case study.

Although the mechanism of adhesion remains in general poorly understood, adhesives fall broadly into a number of classes. One is thermoset adhesives, which form chemical crosslinks both within the adhesive itself and (possibly) with the substrate. The others are thermoplastic (hotmelt) adhesives, that are applied at elevated temperatures and that form a firm adhesive joint when the cool. Both have been investigated here.

Generally, adhesives need to have a reasonably low viscosity when they are applied (so that they can cover the substrate easily) but they need to be capable of forming a strong joint that resists both pulling apart and shear forces, so they must be able to develop considerable mechanical strength. Historically, optimizing their performance has involved much trial and error.

2. Crosslinked Adhesives (e.g. Epoxy Systems)

2.1 Introduction

The data used in this study are taken from page 693 of a book on response surface methods, by Myers and Montgomery (1). Details of the chemistry are not specified in their book, but it appears likely that it refers to an epoxy system in which an epoxy resin is mixed with one or more crosslinkers (for example, amine systems). The adhesive has been formulated for an aerospace application.

In this data set, there are 3 'mixture components' consisting of one resin, and two crosslinkers referred to as CXA and CXB. The amounts of these materials must add to 100%. There are also 2 process variables – temperature and percentage relative humidity (RH%). The property that is measured is the pulloff force needed to separate two substrates.

Myers and Montgomery give 34 different experiments, chosen using a D-optimal experimental design. Of course, it is not a pre-requisite for our modelling exercise that 'designed' data be used; however, this was what was available.

2.2 Models

Since the corresponding data mining study with **FormRules** showed that all the input variables were important, all were used in developing the neural network models reported here (generated using **INForm**).

Records 11, 23 and 34 were withheld in order to validate the model (selected using the Smart selection option) and the other 31 experiments were used in the 'training' set. One thing worth noting is that the first time Smart Selection was used, and different records were withheld for training, a relatively poor model was developed. This illustrates the importance of investigating different 'smart selections' especially when using a designed experiment, since it is possible that the design might become unbalanced.

A 4-node hidden layer network was used; this was the default suggested by **INForm**. The other parameters were left at their defaults, except the number of iterations ("epochs") was changed from 1000 to 2000. The model shows a training error of 0.0023 and a test error of 0.019 (less than 10 times the test error). The ANOVA statistics showed an R^2 value in excess of 0.98.

2.3 Optimization

Only one property is given in this data set, so there is no opportunity here to investigate the trade-offs in balancing different and conflicting properties. The aim in the current optimization was to get a pulloff force in excess of 80. (The maximum in the current data set was 82.)

The optimization was carried out with the constraint that Resin + CXA + CXB must sum to 1, since the data were obtained using an experimental design that imposed this constraint.

For the initial optimization, unsurprisingly the goals were achieved, with a temperature of 100 degrees (the maximum used in the experiment) and a humidity of 15% (the lowest value used in the experiment). Resin was 0.81, CXA was 0.1 (the maximum value from the experiments), and CXB was 0.09.

The second optimization considered the case where the temperature was set to be 60 degrees. With this constraint, it proved impossible to create an adhesive with pulloff force exceeding 70.25, within the given design space. The optimum property was achieved with Resin 0.84, CXA 0.1 (again at the maximum) and CXB 0.05, and RH at the minimum 15%.

A third optimization was performed, looking at a relative humidity of 50%. With no constraint on the temperature, the optimum joint strength (71.72) was obtained at 100 degrees, with amount of Resin being 0.72, CXA 0.1, and CXB 0.18. Looking at a fourth case, where RH was forced to be 50% and temperature was fixed at 60 degrees, the joint strength was reduced further, and the highest value (65.9) was achieved with Resin 0.85, CXA 0.07 and CXB 0.06.

The optimizations show that increased relative humidity adversely affects the joint strength, as does an increased temperature. The exact formulation can, if required, be tailored to these process conditions to try to produce a strong joint.

3. Hot Melt Co-polyester Adhesives

3.1 Introduction

Hot melt adhesives are generally thermoplastic polymers that are applied in the molten state, and which bond to the substrate to provide an adhesive joint. The melting point must not be too high, and the adhesive must have a degree of crystallinity at lower temperatures (in order to have mechanical strength). The adhesive must not be too viscous when applied, but must also not be too tacky once cooling has occurred.

A popular class of hot melt adhesives is made up of co-polyesters, in which various acids are reacted with an alcohol like 1,4-butanediol. Generally, copolyesters are expected to have lower melting points than homopolyesters. The formulator must assess which acids to use, and the relative amounts of each that give the best properties.

The data set used here is taken from UK Patent Specification 1,515,727, filed by scientists at Dynamit Nobel (now part of the Akzo Nobel group). In this work, a base of terephthalic acid was used, with one or two of 5 other acids added in varying amounts. These added acids were sebacic acid, isophthalic acid, adipic acid, azelaic acid, and dim. fatty acid (an aliphatic dibasic acid containing 36 carbon atoms).

Information was available for 37 different formulations, and the properties measured were the melting point, the glass transition temperature T_g , the damping decrement (to assess crystallinity) and the viscosity.

3.2 Models

The corresponding data mining study with **FormRules** showed that good simple models could be obtained for all the properties except the viscosity. The neural network models using **INForm** showed similar trends, with R^2 for the viscosity not exceeding 0.6. Changing the neural network training parameters (e.g. output transfer function, number of nodes in the hidden layer, backpropagation type) did not make any improvement; this is consistent with the **FormRules** suggestion that no suitable model could be found.

With the **INForm** default parameters, the R^2 values for the other properties are summarized in Table 1. In developing this model, a 3-node hidden layer network was used, and records 6, 20 and 22 were withheld for model validation. For the 3 models, the calculated 'test error'

was small (on the order of the training error) indicating that the models should be suitably predictive.

Property	ANOVA R ² value
Melting Point	0.993
Tg	0.964
Damping	0.969

Table 1. ANOVA statistics for neural network models

3.3 Optimization

The lower the value of the damping decrement, the higher the degree of crystallinity. For hotmelt adhesives, a reasonably high degree of crystallinity is preferred. Therefore, our optimization search was for a material with low melting point (less than 100 degrees) and low damping decrement (less than 0.5). Both of these properties were weighted highly (10, the highest allowed value) in setting up the fitness 'desirability function'. Tg will also relate to crystallinity, but was weighted as less important, at 5. The optimization was set up to request a Tg in excess of 25 degrees. Because the viscosity model was poor, our optimization involved searching for a low-viscosity material, but weighting this at only 1 (on a scale of 1 to 10). A constraint was set up, requiring that the amounts of all the materials had to sum to 100%.

Using these criteria, the best formulation that could be found had a melting point of 57 degrees, Tg -26, damping decrement 0.5 and viscosity 0.27, so that all of our objectives were achieved except the requirement on Tg. The formulation that gave these properties contained the following percentages:

Material	Amount (%)
Terephthalic acid	15.7
Isophthalic acid	2.6
Adipic acid	38.7
Dim. fatty acid	2.6
Azelaic acid	35.9
Sebacic acid	4.5

Adjusting these so that only adipic, azelaic and terephthalic acids were present (by fixing the amounts of the other acids at zero) then re-optimizing, gave a formulation with the amounts show below:

Material	Amount (%)
Terephthalic acid	15.7
Adipic acid	38.7
Azelaic acid	35.9

This formulation had melting point of 57 degrees, Tg of -36, damping decrement 0.4 and viscosity 0.23. Interestingly, the mix of adipic acid and azelaic acid with a relatively small amount of terephthalic acid was not a combination that had been tried in the initial experimentation.

Alternatively if a formulation is sought that does not contain adipic, azelaic or dim. fatty acid, then the formulation below has a melting point of 50 degrees, a Tg of -25 degrees, damping of 0.5 and viscosity of 1.05. Sebacic acid completely dominates this formulation.

Material	Amount (%)
Terephthalic acid	15.7
Isophthalic acid	28.2
Sebacic acid	52.2

All of these optimizations were performed in a few seconds, allowing a wide range of options to be explored quickly.

4. Polystyrene Hotmelt Adhesives

4.1 Introduction

The second hotmelt example refers to an adhesive used to bond polypropylene. In a typical formulation, oligo(propene) can be mixed with SEBS (hydrogenated polystyrene - block polybutadiene - block polystyrene) and a range of tackifiers.

A study has been published by Setz *et al* (3) on a formulation whose ingredients consisted of, among other things (whose amounts were held constant)

- IPP10k - an isotactic oligo(propene) with $M_n = 10,000$
- TPE – a hydrogenated polystyrene - block polybutadiene - block polystyrene thermoplastic elastomer, with $M_n = 83000$
- TPEm - like TPE, but with grafted maleic acid anhydride
- T1 - a hydrocarbon resin tackifier, with $M_n = 690$
- T2 - a straight mineral oil

The amounts of all the materials were required to sum to 100%. The properties measured by Setz *et al* included τ_B (the lap shear strength), $\Delta\tau_B$ and the viscosity η . 29 different experiments were available for the lap shear strength and $\Delta\tau_B$, with only 20 available for viscosity.

Setz *et al* analyzed the data with a statistical approach, finding that for the lap shear strength one model would not fit the data satisfactorily. They concluded that this was because the mode of failure was sometimes adhesive, and sometimes cohesive (when failure took place within the adhesive itself, rather than at the substrate-adhesive interface).

4.2 Model Development

A data mining exercise using **FormRules** showed that TPEm and T1 had the largest effect on $\Delta\tau_B$. No good model was found for either τ_B or viscosity in the data mining study.

In the present work, where multi-layer perceptron neural networks are used for the modeling, quite a bit of effort was needed to develop good models. It was necessary to change the backpropagation algorithm from the default RPROP to standard batch backpropagation, and to change the output transfer function from linear to asymmetric sigmoidal. It was also necessary to increase the number of epochs used for training from the default 1000 to 5000. 3 nodes were used in the hidden layer, and records 17 and 18 were withheld for validation.

At first sight good models are developed for τ_B , $\Delta\tau_B$ and viscosity, in that the ANOVA R^2 values are good - for the 3 models they were 0.938, 0.911 and 0.996 respectively. The high value for viscosity may indicate some over-fitting to the data. However, these R^2 values are not supported by good values of the f-ratio (which should be greater than 4) so the models may be unreliable. To check the predictions, scatter plots were produced, and a typical example is shown in Figure 1. These plots generally suggest that the models should be satisfactory.

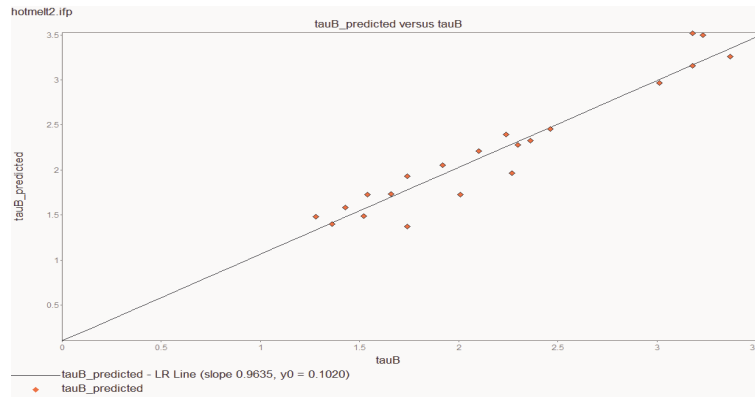


Figure 1. Scatter plot for lap shear strength, for training data set

The model for the lap shear strength, shown in Figure 2, illustrates one issue that was also highlighted by Setz *et al.* This is that there is a discontinuity in the data, which Setz *et al.* attribute to differences in the mode of failure. Of course, the shape of this plot depends on the values of the 'unspecified' variables.

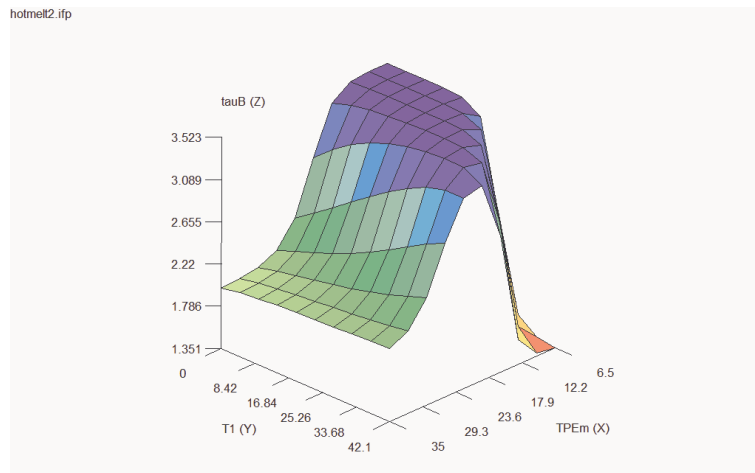


Figure 2. Effect of TPEm and T1 on the lap shear strength τ_B

One of the most interesting features of this study is that it has been possible to fit the data with a single model, rather than needing to invoke a two-model strategy as required by Setz *et al.*

4.3 Optimization

The optimization was constrained so that the total amount of all the ingredients added to 100%. In setting up the 'fitness function' it was assumed that lap shear strength should be in excess of 3.5 MPa, that viscosity should be less than 3 Pa s and that $\Delta\tau_B$ could take any value in its measured range. Lap shear strength was given a relative importance of 10 (on a 1 to 10 scale) with viscosity given a weighting of 8. The unimportant $\Delta\tau_B$ was weighted at just 1.

The genetic algorithm optimization gave a formulation consisting of:

T1	40.7
T2	5.6
iPP10k	22.0
TPEm	20.1
TPE	11.6

and predicted that this formulation would have a lap shear strength of 3.58, $\Delta\tau_B$ of 0.27, and viscosity of 2.4. This was not a formulation that was in the initial data set, so the optimization has found a genuinely new formulation.

5. Conclusions

This report has discussed 3 distinct adhesive formulations – a crosslinked thermoset, and two hotmelts that were formulated for different substrates. For the thermoset, where high quality data were available, it has been possible to develop a good model and to predict an optimum formulation that would have good joint strength.

For the thermoplastics (hotmelt adhesives) good models could in general be developed from the data, although for the polystyrene adhesive (in Section 4) quite a bit of adjustment of the training and neural network parameters was required. It was possible in these cases to look at the trade-offs between conflicting properties and to suggest various formulations that would meet specific end-use objectives. Each optimization typically took less than one minute on a 2.8GHz PC.

References

1. R H Myers and D C Montgomery, *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*, p 712, John Wiley & Sons, New York (2002)
2. Patent Specification 1 515 727 *Improvements in or relating to Copolyesters*
3. S Setz, M Semling and R Mülhaupt, Fuzzy set approach for fitting a continuous response surface in adhesion formulation, *Journal of Chemometrics*, **11** 403-418 (1997)