

Data Mining for Adhesives

1. Introduction

Adhesives can involve either chemical or physical bonds. Hotmelt adhesives, for example, typically work by heating up both the adhesive and substrate so that the adhesive penetrates into the top layers of the substrate, binding them together. Many other adhesives, though, rely on a chemical bond forming between the adhesive and substrate, and within the adhesive itself.

Not only the ingredient mix, but also process conditions (like temperature and relative humidity) can affect the adhesive bond. Typically, a useful measure of adhesive strength is the 'pulloff force'. Of course, the adhesive joint can fail in a number of modes: failure within the adhesive itself, failure between the substrate and adhesive, or failure within the substrate.

Here, several data sets taken from the literature have been examined to find the underlying relationships between the ingredients, processing conditions, and properties.

2. Crosslinked Adhesives (Epoxy Systems)

2.1 Introduction

The data used in this study are taken from page 693 of a book by Myers and Montgomery (1). Although details of the chemistry are not specified in their book, it appears that this is likely to be 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 need to 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 the **FormRules** data mining exercise that 'designed' data be used; however, this was what was available.

2.2 Model Development

The data were typed into a spreadsheet and imported into **FormRules**. The default parameters were used for training. This meant that the model selection criterion was Structural Risk Minimization. Based on the number of experiments available (34) the default C1 parameter was 0.868.

Using these parameters it was possible to develop a model with an ANOVA R^2 value in excess of 95%, reflecting the high quality of the data. Not surprisingly, the model involved all of the parameters, as Figure 1 shows.

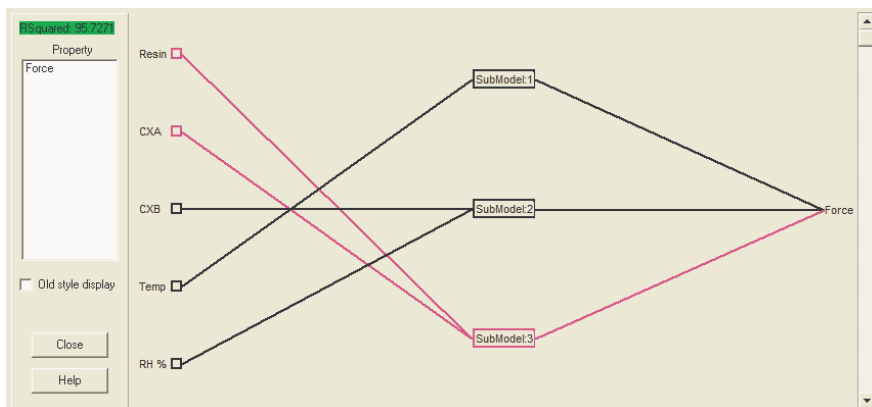


Figure 1. Graphical Representation of Model for Pulloff Force

Figure 1 shows that the data mining has discovered an interaction between the amount of resin and the amount of crosslinker A (CXA), and that these 2 inputs have the largest effect in determining the overall values for the model. (The largest components are shown in purple). There is an interaction between the relative humidity and the amount of CXB. The effect of temperature is independent of the other variables, as shown by the fact that it contributes to a separate submodel.

2.3 Rules

The main set of rules shows that

IF CXA is LOW AND Resin is LOW THEN Force is HIGH (1.00)
IF CXA is LOW AND Resin is HIGH THEN Force is LOW (1.00)
IF CXA is HIGH AND Resin is LOW THEN Force is HIGH (1.00)
IF CXA is HIGH AND Resin is HIGH THEN Force is LOW (1.00)

Closer examination of these rules shows that if the amount of resin is low, then the pulloff force is high, while if the amount of resin is high, the pulloff force is low. The amount of crosslinker A does not have a noticeable effect on these rules – certainly not to the accuracy that the ‘confidence levels’ are given.

Intuitively this rule seems logical – if there is more crosslinker, a stronger bond is developed. The related simulation studies using **DryAdd**, showing the effect of varying composition on crosslinking density, can help to elucidate this.

The second set of rules involves the crosslinker B and the relative humidity. Here, the rules are

IF RH % is LOW AND CXB is LOW THEN Force is HIGH (1.00)
IF RH % is LOW AND CXB is HIGH THEN Force is LOW (1.00)
IF RH % is HIGH AND CXB is LOW THEN Force is HIGH (0.94)
IF RH % is HIGH AND CXB is HIGH THEN Force is LOW (1.00)

Once again, it can be seen upon closer examination that if CXB is low, the pulloff force is high, while if CXB is high, then the pulloff force is low. Adding more of this crosslinker actually seems to weaken the bond. The relative humidity has only a minor effect, decreasing the pulloff force somewhat when RH% is high. However, clearly the effect of CXB is dominant.

The final rules show the temperature dependence. These are

IF Temp is LOW THEN Force is LOW (0.86)
IF Temp is HIGH THEN Force is HIGH (1.00)

Low cure temperatures will lead to low pulloff forces, i.e. weak joints. Again, intuitively this seems reasonable, since the crosslinks may not form unless the temperature is high enough to initiate reaction.

3. Hot Melt Co-polyester Adhesives

3.1 Introduction

Hot melt adhesives are generally thermoplastic polymers (as opposed to thermosets, discussed above) which 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 they must have a degree of crystallinity. They must not be too viscous when they are applied, but must also not be too tacky once they are cooled.

One class of hot melt adhesives that has proved popular is comprised 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

Using the default values – Structural Risk Minimization as the model selection criterion, with C1 value 0.87 - good models (with R^2 values in excess of 90%) could be found for all properties except viscosity. The model for viscosity could not be improved by changing the model selection criterion, indicating that there is insufficient cause-and-effect information within the data. It is possible that there is some other effect (for example, temperature) which is not controlled but which is affecting the viscosity. One of the most interesting things about this example is that despite the fact that the acids have been added only one or two at a time into the terephthalic acid, quite a lot of information can be extracted for most of the properties.

For the properties where good models could be obtained, useful information could be extracted. In particular:

- Melting point (MP) depended primarily on the amount of terephthalic and azelaic acids. The amount of isophthalic and sebacic acids also played a significant role, but neither dim. fatty acid nor adipic acid had a noticeable affect. The R^2 value for this model was in excess of 98%.
- T_g depended primarily on the amounts of terephthalic and isophthalic acids, with azelaic acid playing a minor role. R^2 exceeded 95%.
- As Figure 2 shows, damping depended on all the inputs except dim. fatty acid. For this model, R^2 was in excess of 98%.

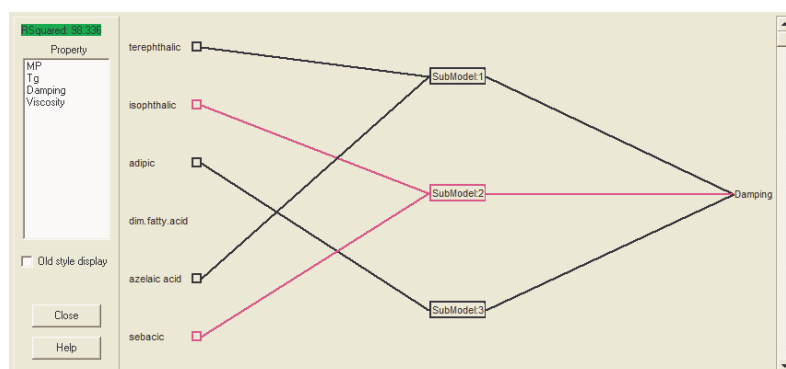


Figure 2. Graphical display of the inputs affecting Damping

3.3 Rules

The rules are quite complex – in some ways surprisingly so, given the amount of data available. For the melting point, the rules are

From the first submodel (which has the largest effect on the predicted values)

- IF terephthalic is LOW AND azelaic acid is LOW THEN MP is LOW (1.00)
- IF terephthalic is LOW AND azelaic acid is HIGH THEN MP is LOW (1.00)
- IF terephthalic is MID AND azelaic acid is LOW THEN MP is LOW (0.55)
- IF terephthalic is MID AND azelaic acid is HIGH THEN MP is LOW (1.00)
- IF terephthalic is HIGH AND azelaic acid is LOW THEN MP is HIGH (1.00)
- IF terephthalic is HIGH AND azelaic acid is HIGH THEN MP is HIGH (1.00)

Here, the terephthalic acid is having the largest effect in determining whether the melting point is high or low. The amount of azelaic acid plays a relatively minor role, but is most noticeable when the terephthalic acid is in the mid-range and the amount of azelaic acid is low. The plot in Figure 3 below, taken from the model, shows this graphically.

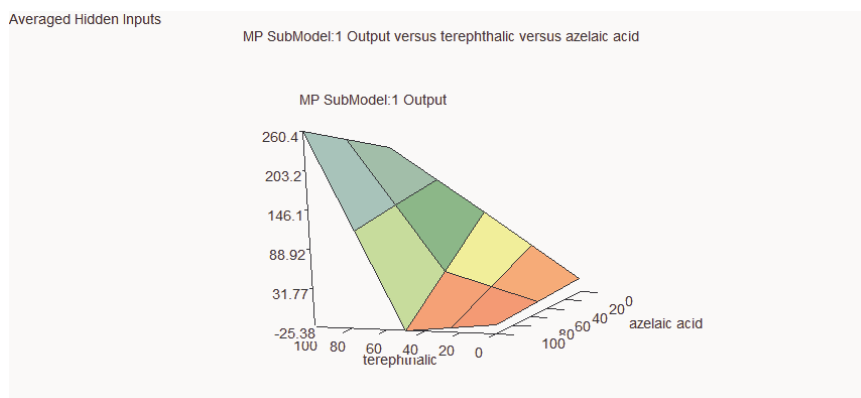


Figure 3. Submodel plot showing effect of amounts of terephthalic and azelaic acid on Melting Point

The second submodel contains the remaining rules for the melting point, which are as follows:

- IF isophthalic is LOW AND sebacic is LOW THEN MP is HIGH (0.62)
- IF isophthalic is LOW AND sebacic is HIGH THEN MP is HIGH (0.71)
- IF isophthalic is MID AND sebacic is LOW THEN MP is LOW (0.54)
- IF isophthalic is MID AND sebacic is HIGH THEN MP is LOW (1.00)
- IF isophthalic is HIGH AND sebacic is LOW THEN MP is HIGH (1.00)
- IF isophthalic is HIGH AND sebacic is HIGH THEN MP is LOW (1.00)

This can be displayed graphically, as shown in Figure 4.

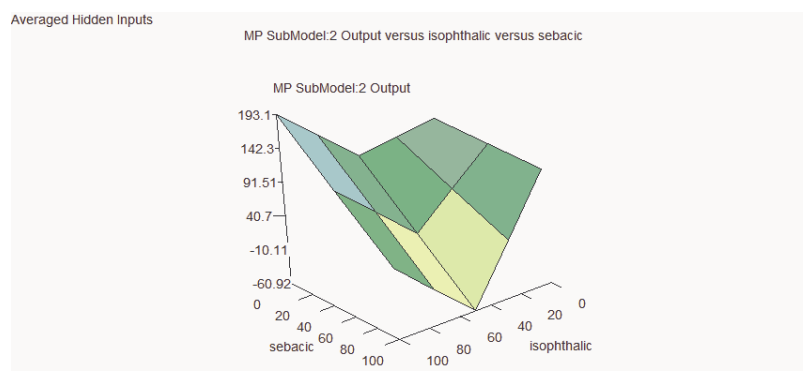


Figure 4. Effect of isophthalic and sebacic acids on melting point.

Note that intermediate concentrations of isophthalic acid lead to the lowest melting points.

The rules that determine the glass transition temperature are as follows. From the first submodel, the rules are:

- IF terephthalic is LOW AND isophthalic is LOW THEN Tg is LOW (1.00)
- IF terephthalic is LOW AND isophthalic is HIGH THEN Tg is LOW (0.69)
- IF terephthalic is MID AND isophthalic is LOW THEN Tg is LOW (1.00)
- IF terephthalic is MID AND isophthalic is HIGH THEN Tg is HIGH (1.00)
- IF terephthalic is HIGH AND isophthalic is LOW THEN Tg is HIGH (0.97)
- IF terephthalic is HIGH AND isophthalic is HIGH THEN Tg is HIGH (1.00)

Again, Tg is dominated by the amount of terephthalic acid, but there is some interaction with the amount of isophthalic acid. Increasing the amount of isophthalic acid leads to some increase in the glass transition temperature.

The second submodel involves the amount of azelaic acid, and the rules are:

IF azelaic acid is LOW THEN Tg is HIGH (1.00)
 IF azelaic acid is MID THEN Tg is HIGH (0.89)
 IF azelaic acid is HIGH THEN Tg is HIGH (1.00)

Again, the effect of the azelaic acid is small; intermediate amounts of this material tend to decrease the Tg, but low or high amounts give a high Tg.

Damping is the final property for which a good model was obtained. The lower the damping decrement, the higher the degree of crystallinity of the polymer. As discussed above, all the acids except dim. fatty acid contribute to this model. The rules that are extracted from the model are:

From the most important submodel (which, as the purple colour in the graphical display denotes, contains the highest positive and most negative contribution:

IF isophthalic is LOW AND sebacic is LOW THEN Damping is LOW (1.00)
 IF isophthalic is LOW AND sebacic is HIGH THEN Damping is LOW (1.00)
 IF isophthalic is HIGH AND sebacic is LOW THEN Damping is LOW (1.00)
 IF isophthalic is HIGH AND sebacic is HIGH THEN Damping is HIGH (1.00)
)

There is some interaction between isophthalic acid and sebacic acid. In particular, when the amount of isophthalic acid is high, then the amount of sebacic acid completely changes the damping properties, giving low values when the amount is low, and high values when it is high. This effect is not noticed when the amount of isophthalic acid is low, since in that cases the damping is low regardless of the amount of sebacic acid.

There are two other submodels, as the graphical display in Figure 2 showed. For one of these, the rules are:

IF terephthalic is LOW_1(5) AND azelaic acid is LOW THEN Damping is HIGH (1.00)
 IF terephthalic is LOW_1(5) AND azelaic acid is HIGH THEN Damping is LOW (1.00)
 IF terephthalic is MID_2(5) AND azelaic acid is LOW THEN Damping is HIGH (1.00)
 IF terephthalic is MID_2(5) AND azelaic acid is HIGH THEN Damping is HIGH (1.00)
 IF terephthalic is MID_3(5) AND azelaic acid is LOW THEN Damping is HIGH (1.00)
 IF terephthalic is MID_3(5) AND azelaic acid is HIGH THEN Damping is HIGH (1.00)
 IF terephthalic is MID_4(5) AND azelaic acid is LOW THEN Damping is LOW (0.88)
 IF terephthalic is MID_4(5) AND azelaic acid is HIGH THEN Damping is LOW (1.00)
 IF terephthalic is HIGH_5(5) AND azelaic acid is LOW THEN Damping is LOW (1.00)
 IF terephthalic is HIGH_5(5) AND azelaic acid is HIGH THEN Damping is LOW (1.00)

and

IF adipic is LOW THEN Damping is HIGH (1.00)
 IF adipic is MID THEN Damping is HIGH (1.00)
 IF adipic is HIGH THEN Damping is LOW (1.00)

The first set of rules shows an interaction between terephthalic and azelaic acid. The dependence on terephthalic acid is complex, as Figure 5 shows.

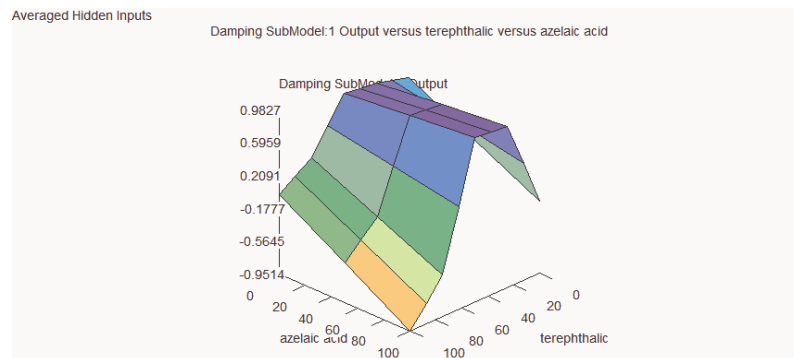


Figure 5. Effect of terephthalic and azelaic acids on Damping

Damping is at its maximum when the amount of terephthalic acid lies between about 25 to 55. Adding azelaic acid decreases the damping at high concentrations of terephthalic acid, but this effect is less marked when terephthalic acid is present in low amounts.

The final set of rules shows that at high concentrations of adipic acid, damping is low. Otherwise, it is high. There is no interaction found between amounts of adipic acid and any other ingredient.

As mentioned above, it is interesting that dim. fatty acid seems to have no effect on any of the properties – possibly because the data do not contain enough cause-and-effect information. Since the acids are mixed only one or two at a time into the base terephthalic acid, this is perhaps not surprising.

4. Polystyrene Hotmelt Adhesives

4.1 Introduction

This second hotmelt example refers to a different data set containing information on a hotmelt 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

- 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 total amount of the material was required to sum to 100%. The properties they measured 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 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).

4.2 Model Development

Neurofuzzy logic was used to 'mine' the data, using the **FormRules** package. For both τ_B and viscosity, suitable models could not be found, even by changing the model selection criterion and risking overtraining. This strongly suggests that either the data contain insufficient cause-and-effect information, or there is too much scatter in the measurements, for a model to be developed. Interestingly, a good model could be developed for $\Delta\tau_B$, and it is possible that some sort of 'cancellation of errors' means that this measurement is more reliable. The ANOVA statistics gave an R^2 value of 0.767 for this model, and although this is not excellent, it does indicate that some faith can be put in the model.

4.3 Rules for $\Delta\tau_B$

Because the models were so poor, the rules are not reported for the lap shear strength or for the viscosity. For $\Delta\tau_B$, the rules are as follows:

IF TPEm is LOW_1(4) AND T1 is LOW THEN delta_tauB is HIGH (0.57)
IF TPEm is LOW_1(4) AND T1 is HIGH THEN delta_tauB is HIGH (0.92)

IF TPEm is MID_2(4) AND T1 is LOW THEN delta_tauB is LOW (1.00)
 IF TPEm is MID_2(4) AND T1 is HIGH THEN delta_tauB is LOW (0.85)
 IF TPEm is MID_3(4) AND T1 is LOW THEN delta_tauB is LOW (0.88)
 IF TPEm is MID_3(4) AND T1 is HIGH THEN delta_tauB is HIGH (0.77)
 IF TPEm is HIGH_4(4) AND T1 is LOW THEN delta_tauB is LOW (0.86)
 IF TPEm is HIGH_4(4) AND T1 is HIGH THEN delta_tauB is LOW (0.99)

Therefore, only the tackifier and the maleic-acid-grafted triblock copolymer play a significant role for this property. The relationship is complex, as the plot in Figure 6 shows.

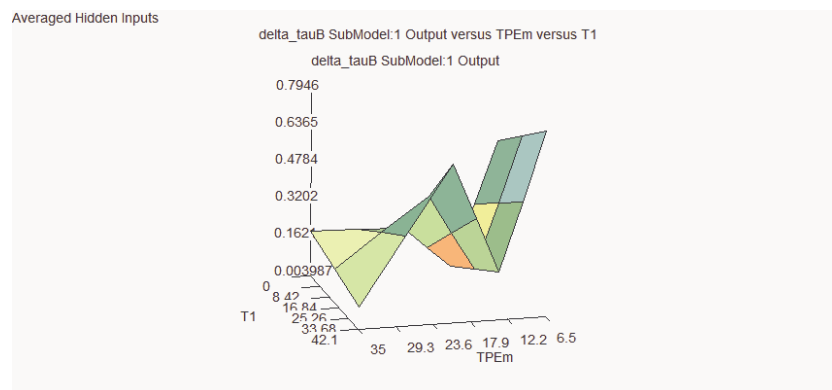


Figure 6. Effect of tackifier T1 and copolymer TPEm on $\Delta\tau_B$

From this data mining exercise, it appears that the data are insufficiently consistent for a realistic simple model to be developed. This is in substantial agreement with the conclusions reached by Setz *et al.* However, as the related study using conventional neural networks concludes, using more parameters in the model (as is done in the neural network study) allows the non-linearities to be fitted more accurately.

5. Conclusions

This report covers 3 distinct adhesive formulations – one crosslinked thermoset, and two hotmelts that were formulated for different substrates. For the first two cases, high quality data were available and good models and rules could be developed. In the third case, the data were less clear-cut, since the joint could fail either at the substrate-adhesive interface, or alternatively it could fail cohesively. In this last case, a good model could be developed for only one of the properties.

Where the data were of sufficient quality, the data mining exercise was valuable in highlighting the key relationships between the ingredients and/or processing conditions, and the measured properties. This was especially true in the case of the thermoset example, where the data had been obtained by doing careful experimentation that spanned the design space comprehensively.

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))