Optimizing Automotive Clearcoats

1. Introduction

A number of studies have been reported in the literature on automotive clearcoats. Generally clearcoats are the finishing topcoat on automobiles, added to improve appearance. The aim is to have a high gloss finish that resists scratching. Clearcoats initially used a significant amount of solvent, but with environmental pressure to reduce VOCs the driver is now towards higher solids formulations.

For most clearcoats, a resin (typically an acrylic or a polyester) is mixed with a crosslinker (typically a melamine formaldehyde). Varying the resin:crosslinker ratio will affect the properties. Selecting different resins can also have a significant effect – as indeed can different crosslinkers.

Below, we describe 3 studies using different datasets that have been reported in the literature.

2. Structure-Property Relationships in Acrylic Clearcoat Binders

2.1 Introduction

In a paper published in 1990, Kruithof and van den Haak (1) looked at the effect of incorporating various specialist monomers. It is generally understood that increased solubility of the high-solids coatings arises by using monomers with bulky branched groups, or linear flexible bulky groups. However, these generally decrease T_g (and hence hardness) of the finished clearcoat. Using rigid bulky groups is expected to increase hardness.

Kruithor and van den Haak looked at 4 monomers

- t-butyl acrylate (TBA)
- isobornyl acrylate (IBOA)
- 4-t-butyl cyclohexyl methacrylate (TBCMA)
- 3,3,5-trimethyl cyclohexyl methacrylate (TMCMA)

The melamine-formaldehyde crosslinker chosen in all cases was Setamine US141. In a statistically designed experiment (not required for **INForm**, but needed in their response surface treatment) they varied the amount of monomer, the amount of crosslinker, and the film thickness. (Thicker films are expected to be harder.) The central composite design they used included 6 repeats of the centroid, and required 20 experiments for each monomer. The properties measured were the solids content (w/w after 2 hours at 120^{o}C) and the Knoop hardness. (Knoop hardness is measured by dropping a diamond-shaped weight on the coated surface, and measuring the depth and width of the indentation.)

2.2 Model Development

The data were put into **INForm** so that neural network models could be developed, and 10% of the data was withheld to validate the model. The other 80 records were used for training. The network used a 4-node hidden layer with asymmetric transfer functions. RPROP, **INForm's** default backpropagation algorithm, was used.

As expected from the **FormRules** study on the same data, it was not easy to develop a good model for the Solids Content. No set of parameters could be found that gave a model with an ANOVA R^2 value in excess of 0.69 for Solids Content. For Knoop Hardness, however, a good model was found (R^2 0.80). This confirms the **FormRules** conclusion: it is likely that some other factor, not measured in these experiments, is affecting Solids Content.

2.3 Optimization

The aim of optimization is to produce a formulation that gives a finish with high Knoop hardness and high solids content. A number of possible formulations have been examined here.

Study 1
For this study, we assumed that Knoop hardness was the most important property (weighted at 10) while Solids Content was also important (but weighted at 8). The optimizer searched for a formulation that had maximum hardness in excess of 9.9 (compared to the maximum measured value of 9.97) and solids content in excess of 53.5% (compared to the maximum measured value of 53.8%). The best formulation was

Monomer	TMCMA
Monomer %	17.79
MF%	37.11
Thickness μm	34.44

and this gave a Solids Content of 52.38% and Knoop hardness of 9.06. Therefore, it did not quite achieve our objectives. Our optimization confirms the results of Kruithof and van den Haak, who found that TMCMA had a significant beneficial effect both on hardness and on solids content.

Study 2
The response surfaces shown by Kruithof and van den Haak further show that for TMCMA, Knoop hardness is at its maximum when MF% is also at a maximum (45%). They do not definitively state what the film thickness was for these response surfaces, but in the text they imply that it is 40 μm. When the same constraint is used within **INForm** (film thickness of 40 μm) then the optimum formulation is found to be

Monomer	TMCMA
Monomer %	20.0
MF%	45.0
Thickness μm	40.0 (fixed)

giving a Knoop hardness of 8.99 and a solids content of 52.32. MF% has risen siginificantly from 37.5% (at thickness 34) to 45%, and in fact now lies at the maximum value used in the initial experimental design. Therefore, the somewhat thinner film is better. However, controlling film thickness, as Kruithof and van den Haak note, can be difficult.

2.3 Discussion
INForm has highlighted that Monomer 4 (TMCMA) is the best for giving high solids content and high Knoop hardness. This is consistent with the findings in the published work. Because **INForm** allows objectives to be set for multiple objectives, and because the models are not restricted to be linear, **INForm** has found a more accurate optimum from that obtained by examining the response surfaces. As discussed previously though (and as found in the associated data mining study using **FormRules**) the data for Solids Content does not adequately cover the cause-and-effect relationships so the model is relatively poor. This does not appear to have been highlighted by the statistical report.

The predicted optimum formulation is a new one, with better hardness, for the same solids content, as the experimentally measured points used in developing the models.

3. Crosslinking in Polyester Clearcoats

3.1 Introduction
Another dataset was published by Tusar *et al* (2) in *Surface Coatings International* in 1995. This used a polyester binder, with hexamethyoxymethyl melamine (HMMM) as the crosslinker. A full factorial 3-level design was done varying 3 inputs: ratio of the polyester to HMMM, the concentration of the catalyst and the curing temperature. They did not specify the exact nature of the polyester or the catalyst. Six properties were measured; these were hardness, elasticity, MIKB (methyl isobutyl ketone) wet-rub test, direct impact resistance, indirect impact resistance, and adhesion. However, only results for hardness were given in their paper, so that is the sole property that is discussed here.

In the paper, they report results for several repetitions, and these show a fair amount of scatter in the data. They have developed models using both statistics and neural networks; because of the statistical treatment, they limited the study to 3 input variables.

3.2 Model Development

The disadvantage of using a statistical design when using a neural network is that some of the data points need to be withheld for validation of the network. Tusar *et al* say that they did 15 additional experiments that could be used for validation, but they did not report the results in their paper. Here, 2 data records (10% of the original 26 given in their paper) were withheld for validation. The default neural network had 2 nodes in the hidden layer, with an asymmetric sigmoid transfer function for the hidden layer and a linear transfer function for the output layer. However, this gave fairly poor models (ANOVA R2 value only about 0.5) so some parameter changes were made. Our final preferred network had a 3-node hidden layer, used the standard backpropagation algorithm (rather than RPROP) and used asymmetric sigmoidal transfer functions for both the hidden and output nodes.

Even so, because of the scatter in the data, the best models that could be developed only had an ANOVA R^2 value on the order of 0.7. This is barely high enough to guarantee trustworthy models. Changing the transfer function for the output layer to an asymmetric sigmoid, and using all the data in the training set (keeping none back for validation) still gave R^2 of only 0.62 – a clear indication that the quality of the data is affecting the quality of the models. Either the scatter in the data is too great, or else there are important inputs that have not been controlled and measured.

As a final check, **INForm** was used with a 9-node hidden layer (which Tusar *et al* reported as the best in their study, which dealt with more properties). Some over-training can be expected, since there are many adjustable parameters for this model. Indeed that is observed, with a very high R^2 but poor predictivity. Consequently our subsequent studies were undertaken using the 3-node hidden layer network described above.

3.3 Optimization

Because only 3 input variables (factors) have been used, 3D plots can be used to show some of the key relationships. In particular, Figures 1-3 show the variation in hardness as a function of HMMM% and catalyst% for the 3 different cure temperatures 120, 150 and 180.

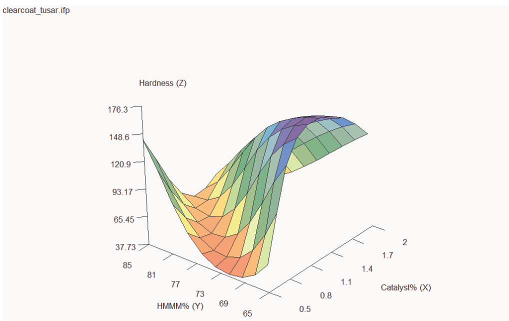

Figure 1. Hardness at Cure Temperature of 120°C

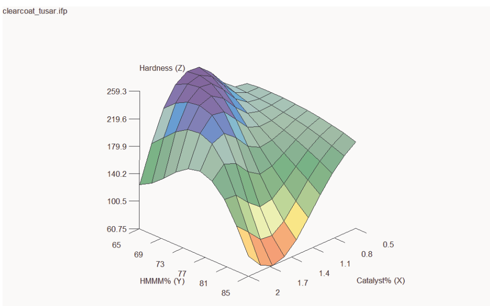

Figure 2. Hardness at Cure Temperature of 150°C

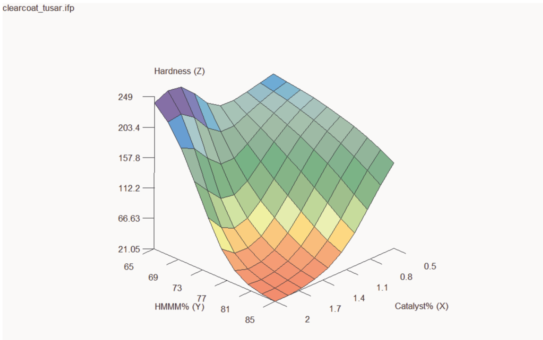

Figure 3. Hardness at Cure Temperature of 180°C

Clearly the hardness is a function of temperature as well as of HMMM% and catalyst%. This makes it difficult, if not impossible, to optimize reliably using the response surface approach. Consequently, in this study genetic algorithms were applied, in conjunction with the neural network model, to perform the optimization. The optimization was set up to look for formulations that produced hardness values in excess of 290, since the maximum value observed in the experimental training set was 291 (although it is worth noting that this was for a formulation which, when repeated, gave a hardness of only 51.5, and for which the neural network predicted a value of 181.). The optimum formulation calculated by **INForm** had a predicted hardness of 274.5, and consisted of 65% HMMM (at the lowest end of the range), 1.5% catalyst and a cure temperature of 160°C.

4. A Clearcoat Mixture Design

4.1 Introduction

This example uses data published by Myers and Montgomery (3) and involves a mixture design in which 3 components are varied, with the total amounts required to sum to 100%. The input variables (factors) are

- Monomer % (varies between 5% and 20%)
- Crosslinker % (varies between 25% and 40%)
- Resin % (varies between 55% to 70%, as required to make the total 100%)
- Monomer Supplier (one out of a choice of 2)
- Crosslinker Supplier (one out of a choice of 3)

The last two are ‘categories’ so these can be described as ‘categorical values’. Montgomery and Myers (3) describe how the experimental design was carried out. The study required 38 different experiments, and two properties (Knoop hardness and solids content) were measured.

4.2 Model Development

Here the neural network capabilities of **INForm** were used to develop models for the two properties. 3 data records (10% of the data) were withheld for validating the model. **INForm’s** default architecture for this case (5 inputs, 35 training records) is a 4-node hidden layer network. RPROP (the default) was used as the backpropagation algorithm, and the transfer functions were asymmetric sigmoid for the hidden layer and linear for the output layer. (Again these are the **INForm** default values.)

Good models were developed for both properties, with ANOVA R^2 values of 0.96 for Knoop hardness and 0.89 for Solids Content. This reflects the high quality of the data, which enabled the neural network to ‘learn’ good cause-and-effect models.

4.3 Optimization

The optimization was set up to request a hardness in excess of 14.5 (since the maximum in the training data was 15) and solids content in excess of 51.9. (The maximum in the training data was 52 for this property.) The Monomer Supplier and Crosslinker Suppler were required to take integer values, mapped to the corresponding categories. A further constraint was added, requiring that the amount of monomer, crosslinker and resin added to 100%.

The optimum formulation had a predicted hardness of 14 and a solids content of 51.36. This was produced with a mixture of 10.5% monomer, 30.5% crosslinker, and 59% resin. The monomer supplier was M2 and the crosslinker supplier was X1. These last 2 agree with the value determined by the statistical study, and could in fact by found relatively easily by a graphical examination of the data.

The response surface study (using statistical treatments) requested a hardness greater than 10 and a solids content greater than 50%. The response surfaces suggested that the monomer concentration should be 11.28%, crosslinker concentration 28.4%, and resin concentration (60.32%) as resin. This is broadly similar to the formulation obtained by **INForm**. However, **INForm** makes it much easier to look at the trade-offs, by weighting different properties according to their importance to a particular customer.

Using the above formulation in **INForm**, the hardness is predicted to be 12.2 while the solids content is predicted as 52.36. These are well within specification. The contour plot shown in Figure 4 shows that as long as crosslinker % is less than 31% and monomer concentration is less than 15%, a formulation that is in specification (hardness greater than 10) should be possible.

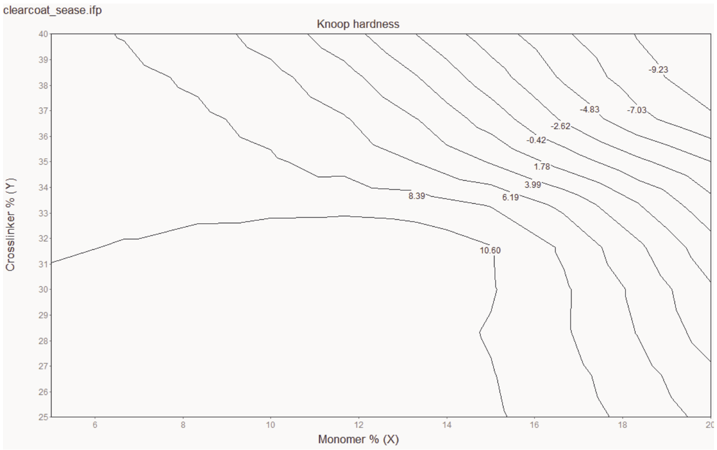

Figure 4. Knoop hardness as a function of monomer and crosslinker concentrations

However, it may be difficult to achieve the required solids content for these values. The genetic algorithms in **INForm's** optimizer therefore provide a more reliable and powerful way of finding the optimum formulation.

Conclusions

Neural networks have been used for modelling 3 different automotive clearcoat formulations. One of the key points to arise is that of assessment of the models. For some of the published papers, no model assessment has been given in the literature, and an examination here (together with the associated FormRules study) indicates that the data are not of high enough quality to develop really good models.

The neural networks were especially useful in capturing non-linear relationships, and examination of the 3D plots indicates that, in general, non-linearity is observed in these complex formulations.

Once good models were developed, it was straightforward to find optimum formulations to meet desired properties. In both the studies where Knoop hardness had to be obtained at the same time as high solids content, the optimization pointed the way to achieving these (generally conflicting) objectives.

References

1. K J H Kruithof and H J W van den Haak, A study of structure-properties relationships in automotive clearcoat binders by statistically designed experiments, *J Coatings Technology* 62 47-52 (1990)
2. L Tusar, M Tusar and N Leskovsek, A comparative study of polynomial and neural network modelling for the optimization of clear coat formulations, *Surface Coatings International* 427-434 (1995)
3. 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)