

Modelling the Formation of a Melamine Formaldehyde Resin

Introduction

Melamine formaldehyde resins are more resistant both to heat and chemical staining than urea-formaldehyde systems, and in cross-linked form provide a useful thermoset plastic. Unlike phenol-formaldehyde systems, they are colourless. They find use in textile finishes, surface coatings, and moulding materials.

Initial reaction between the monomers (usually at temperatures in excess of 80C, in aqueous solution and a slightly alkaline environment) give methylolamines. With M:F ratios of 1:2 to 1:3, dimethylolmelamine is formed. Decreasing the M:F ratio to 1:8 will give hexamethylolmelamines, in which all of the NH₂ groups are converted to methylol. These are often used as crosslinkers in reactions with other resins, like acrylates or polyesters – a separate application note is available to discuss this.

In MF resins, in a possible second stage of the reaction, crosslinks can be formed by methylol-methylol reactions to produce ether links (with consequent loss of water) or by methylol-amine condensations that produce methylene bridges (again with loss of water). These reactions are usually facilitated by heat, and, in the case of ether links, an acidic environment. This second stage is employed, for example, in the formation of Melmac and related materials.

Set-up for Materials and Reactions

Figure 1 shows the materials setup for the melamine-formaldehyde resin, with 1 mole of melamine and 3 of formaldehyde.

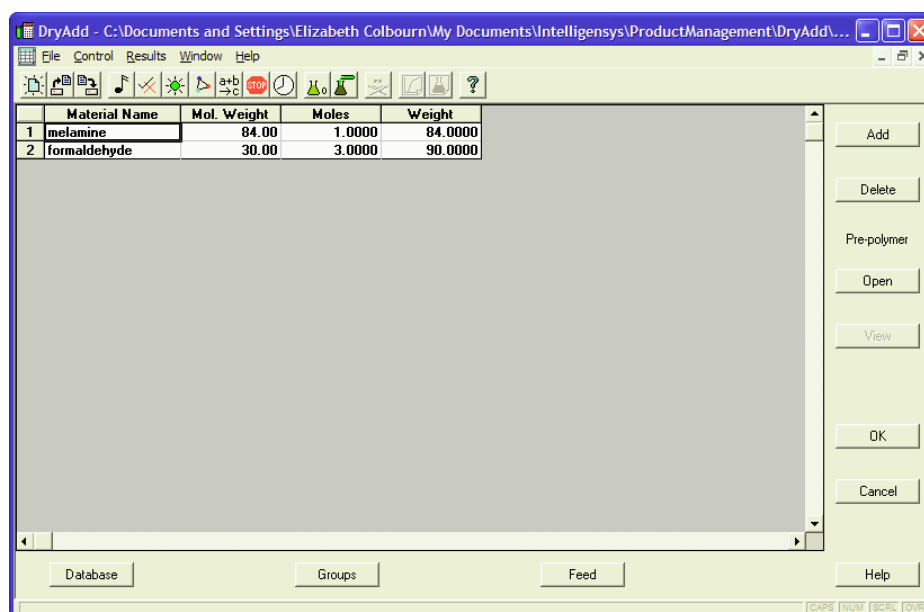


Figure 1. DryAdd's Materials Workscreen

An initial population of 100,000 monomers was assumed for the simulation. Figure 2 shows the functional groups for the melamine, with 3 NH₂ groups present. The NH₂ group has been identified as a primary aliphatic amine with no beta hydroxyl. The additional group type on the melamine is a 'phantom group' i.e. a functional group that is not present at the start of the reaction, but which is formed during the reaction process. Table 1 shows the additional groups that have been set up for the two materials (urea and formaldehyde). Note that the Group Code is optional – this does not need to be set within **DryAdd**, although it can help when the 'automatic reaction setting' feature is used.

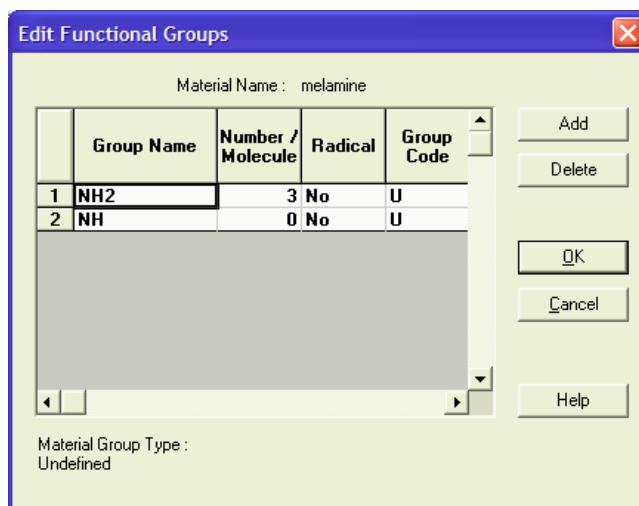


Figure 2. The functional groups on the melamine molecules

| Material | Group Name | Number per molecule | Group code |
|--------------|--------------|---------------------|--|
| Melamine | NH2 | 3 | Amine-Aliphatic-Primary-No beta hydroxyl |
| Melamine | NH | 0 | Amine-Aliphatic-Secondary-Beta hydroxyl |
| Formaldehyde | Formaldehyde | 1 | Miscellaneous |
| Formaldehyde | CH2OH | 0 | Miscellaneous |

Table 1. The functional groups for the materials, including 'phantom' groups

Figure 3 shows the reaction scheme, which is similar to that for urea formaldehyde. Reactions that produce products that do not react with other groups are considered to have product (*none*). This reaction scheme includes the second-stage reactions, in which the methylol groups condense.

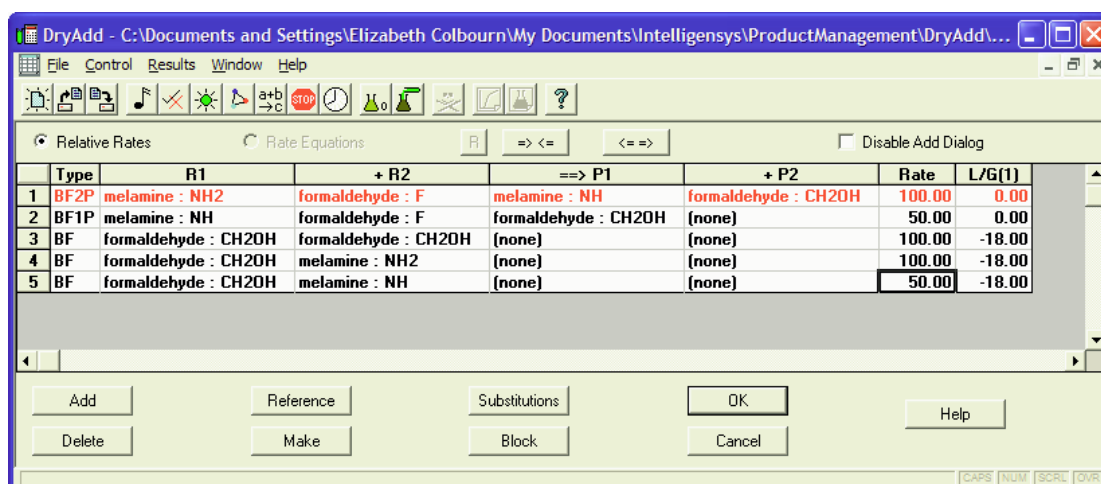


Figure 3. The reaction scheme for the initial phase of melamine-formaldehyde chemistry

The 'Rate' column contains relative reaction rates for the various reactions. (Within **DryAdd**, it is also possible to use absolute rates, if these are available.) It is possible to start the reaction assuming that only the first two reactions (of melamine with the formaldehyde groups) will take place, by setting the other rates to 0. The rates can be changed later in the

simulation, to 'switch on' these reactions. Here, we have assumed that, because of steric hindrance, the NH groups (which by definition are next to an initially-formed methylol group) are only half as reactive as the NH₂ groups.

The 'L/G' column contains information on the loss or gain of molecular weight in the reaction. The value of -18 in the final three reactions shows that in these cases, one molecule of water (molecular weight 18) will be lost when the reaction takes place.

DryAdd has the ability to model substitution effects, for instance if the reaction rate of a particular site is affected by the number of sites that have already reacted on the molecule. It can also take account of increasing molecular weight build-up on diffusion of molecules, which can slow subsequent reactions. However, neither of these effects has been taken into account in the present study except through, as discussed above, the relative rates of the various reactions.

DryAdd also provides the ability to 'block' reactions of molecules above a specific size. So, for the first phase reaction, it is possible to block the reactions of molecules greater than size 3, since tetramethylol species are known not to be formed. This 'block' feature has not been used here, however.

Running the Simulation: Cross-linked system

For the case of Melamine:Formaldehyde ratio of 1:3, the plots of the largest group and the number of secondary cycles vs. conversion are given in Figure 4. The onset of gelation is generally associated with a rapid rise in the molecular weight of the largest group, or with the rapid increase in the number of secondary cycles. Figure 4 shows that, for this M:F ratio, gelation occurs at about 58% conversion.

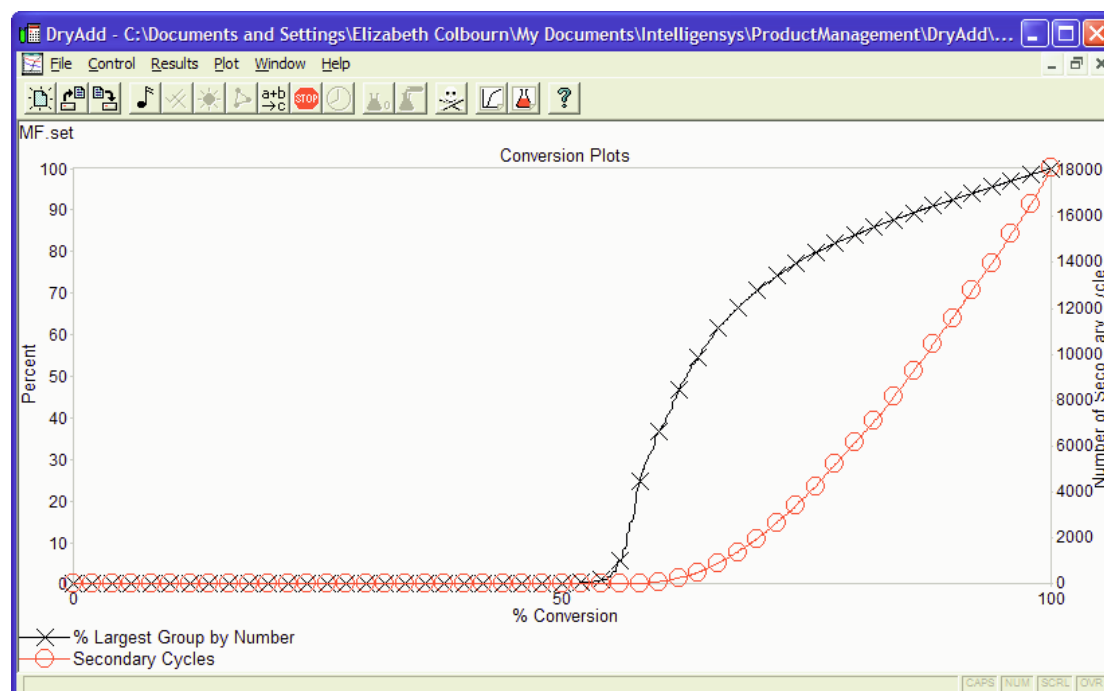


Figure 4. Onset of gelation for M:F ratio of 1:3. Conversion is measured with respect to the number of formaldehyde groups

When the amount of formaldehyde is decreased, so that the M:F ratio is 1:2, gelation is slightly delayed to about 65% conversion of formaldehyde groups, as shown in Figure 5.

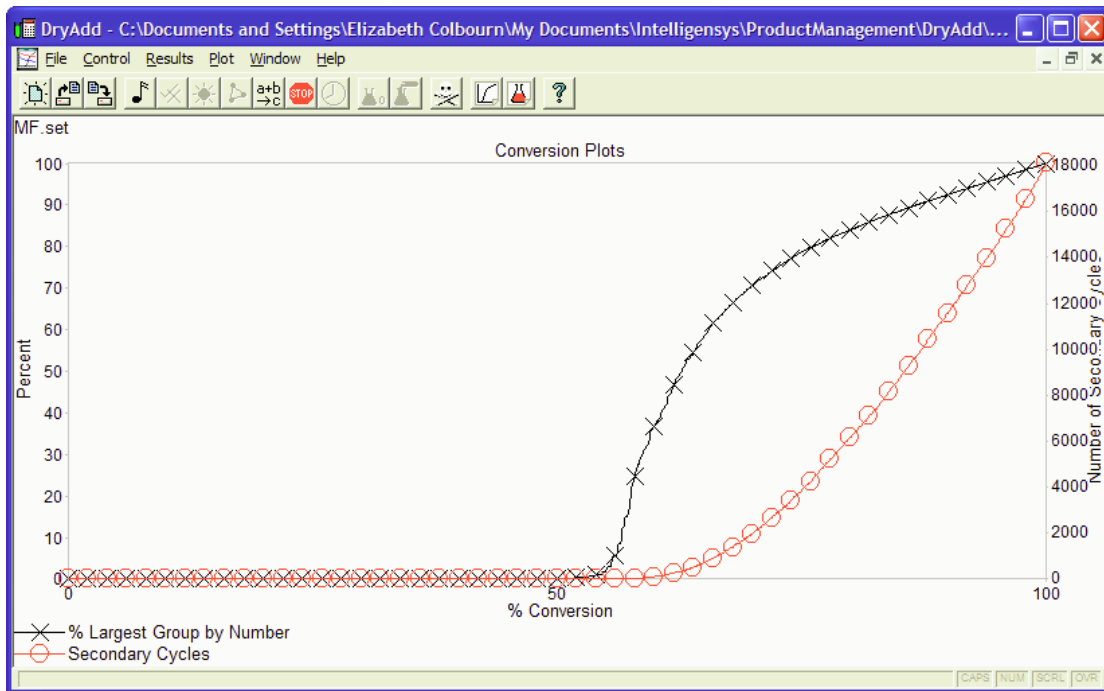


Figure 5. Onset of gelation for M:F ratio of 1:2. Gelation is delayed as the formaldehyde amount is reduced.

When the M:F ratio is 1:8, i.e. at the other end of the generally accepted 'commercial' range, then gelation is much earlier (at just below 40% conversion) as Figure 6 shows.

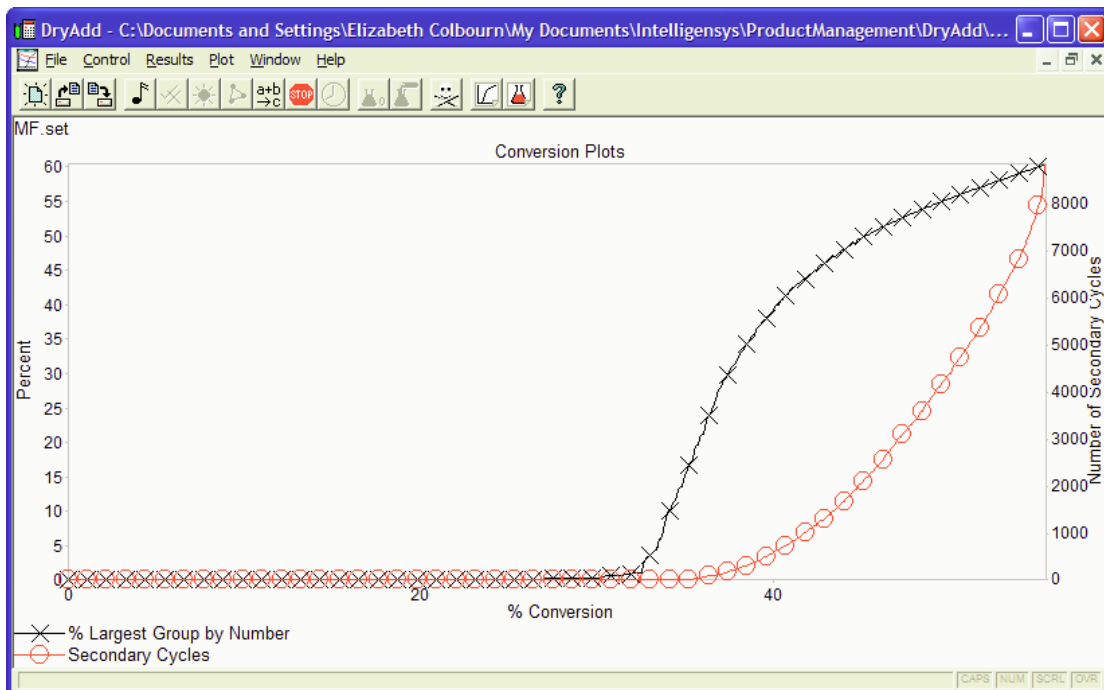


Figure 6. Onset of gelation for M:F ratio of 1:8. Gelation occurs below 40% conversion.

In this last case, there is an excess of formaldehyde, with 44.5% remaining unreacted. There are no further amine or methylol groups that are capable of reaction.

The network can be analyzed in all 3 cases, and the results are presented in Table 1. In all cases, all of the polymerized material is in the elastically effective component of the gel.

| | M:F 1:2 | M:F 1:3 | M:F 1:8 |
|-------------------|----------------|----------------|----------------|
| M_c in EEC | 66.67 | 53.16 | 60.7 |
| Crosslink density | 0.007185 | 0.01112 | 0.0105 |
| Tightness | 0.794 | 0.98 | 1 |

Table 1. Results of network analysis for 3 different M:F compositions

Conclusions

It has been possible to set up a reaction scheme to model the creation of melamine-formaldehyde crosslinkers, which can be used in subsequent formulations. An example is given in a related case study, on automotive clearcoats.

It has also been possible to model a system in which the melamine-formaldehyde crosslinker is self-reacted to give a hard resin. Varying the stoichiometry makes some difference to the crosslink density, and hence to the ultimate hardness of the finished product.