

Modelling Crosslinked Systems: Polyesters with a Melamine Formaldehyde Crosslinker

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 groups.

The present example discusses hexamethoxymethylolmelamine (HMMM), a commercial crosslinker which is generally available. It is straightforward to see how the same reactions would apply to hexamethoxymelamine – where the reactions in the present report give off methanol, those for hexamethoxymelamine would result in the loss of a water molecule.

Set-up for Materials and Reactions

Figure 1 shows a simple set-up in which HMMM is mixed with a polyester (assumed to have molecular weight 1000 and average functionality of 3OH groups). Of course, a more complicated mixture could have been set up, but this illustrates the key concepts of this crosslinked system. Generally, the ratio of methoxy groups to hydroxyl groups can be varied to try to control the properties of the finished system. (See the paper by Tusar et al, reference 1.)

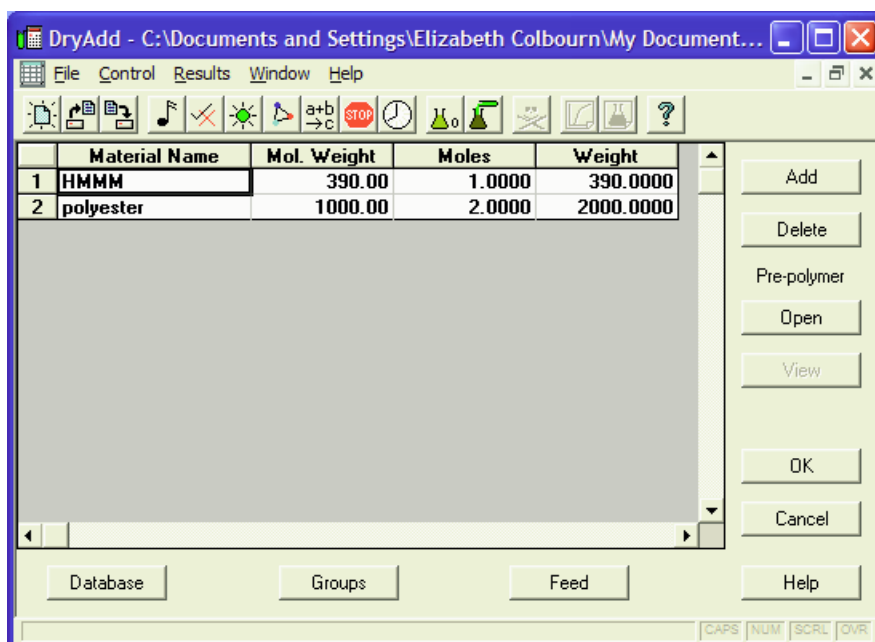


Figure 1. Materials set-up for HMMM-crosslinked polyester system

For this particular stoichiometry, there are an equal number of methoxy and hydroxyl groups (6 per molecule on HMMM, 3 per molecule on the polyester, with twice as many polyester molecules as HMMM molecules). Later on in this study, the stoichiometry was varied.

As Figure 2 shows, in this study the simplest reaction scheme has been assumed. Methoxy groups on the HMMM molecule react with OH groups on the polymer (generally via acid catalysis) to give ether bonds and a loss of CH₃OH. The loss of methanol is reflected in the Loss/Gain column of the reaction scheme, since each methanol molecule has a molecular weight of 32.

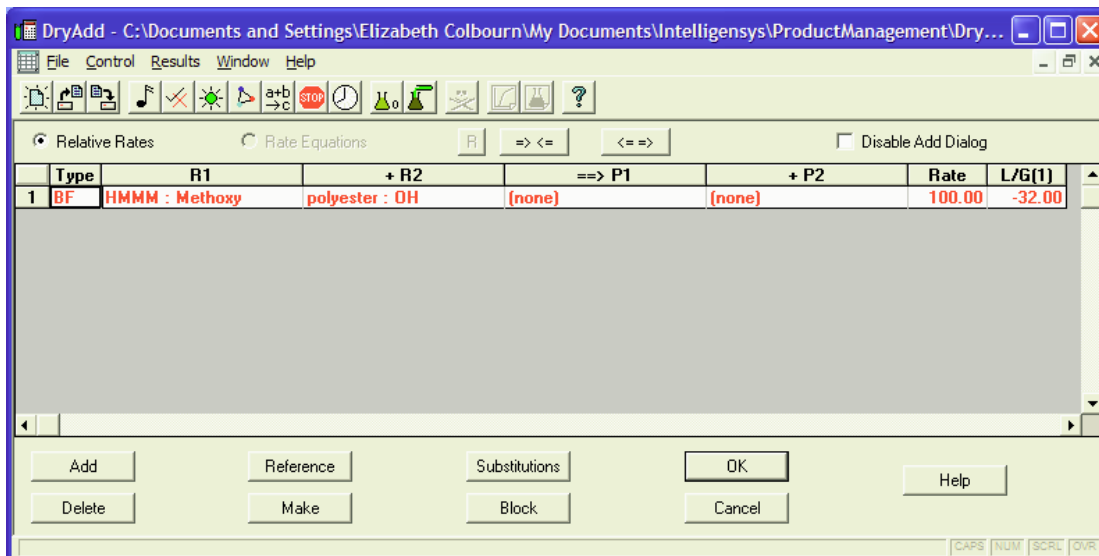


Figure 2. Reaction scheme showing reaction of methoxy group with hydroxyl

Simulation of Crosslinking Process

50,000 molecules were used in the Monte Carlo simulation. The conversion was monitored as a function of the number of hydroxyl groups.

Figure 3 shows the size of the largest group and also the number of secondary cycles. (Secondary cycles contribute to the elasticity of the crosslinked system.) This figure shows that gelation occurs at just over 40% conversion.

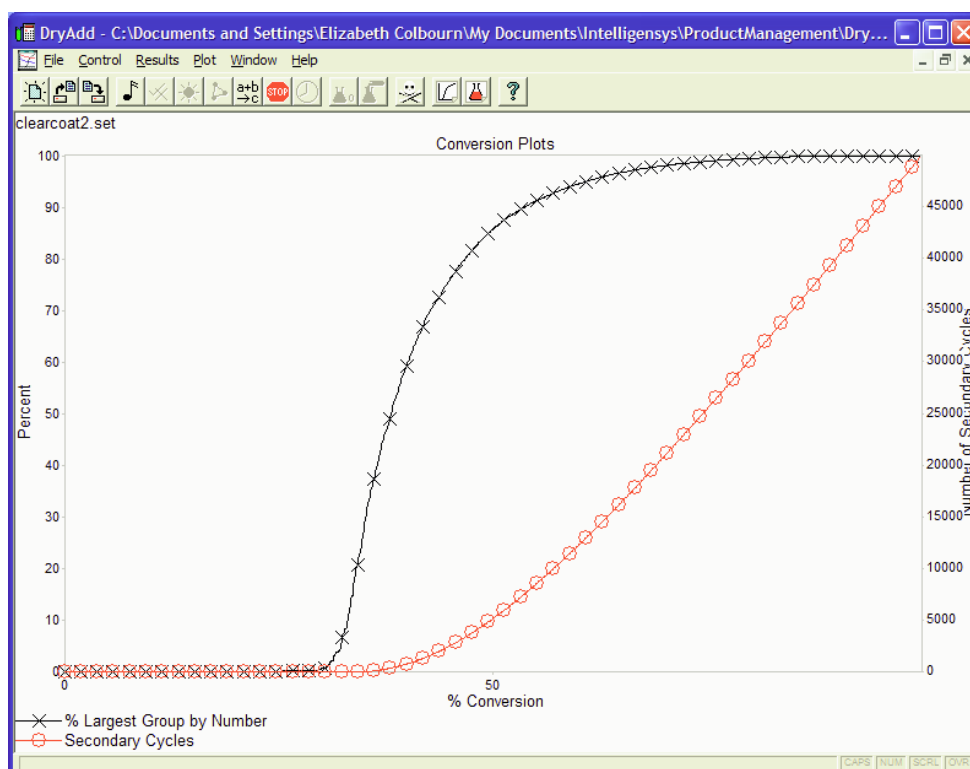


Figure 3. Gelation in 1:1 stoichiometric system

Tusar *et al* (1) have varied the ratio of hydroxy:methoxy from 1:0.5 to 1:1.5. These 2 extremes were also investigated here, by changing the molar ratio of HMMM to polyester from 1:1 (above) to 0.5 to 2.0 (in one instance, giving hydroxyl to methoxy ratio of 1 to 0.5), and (in the second instance) to 1.5 moles of HMMM to 2 moles of polyester (giving a

hydroxyl:methoxy ratio of 1:1.5). Note that the total number of moles is irrelevant for the simulation; it is the ratio of the amounts of the two materials that is the important factor.

Figure 4 shows the gel plot for the first case, where there are twice as many hydroxyl groups as methoxy groups. A key point to note here is that the number of secondary cycles at the end of the reaction is significantly smaller than in the first (stoichiometric) case. Gelation occurs at just under 25% conversion, where the conversion is measured with respect to the OH groups.

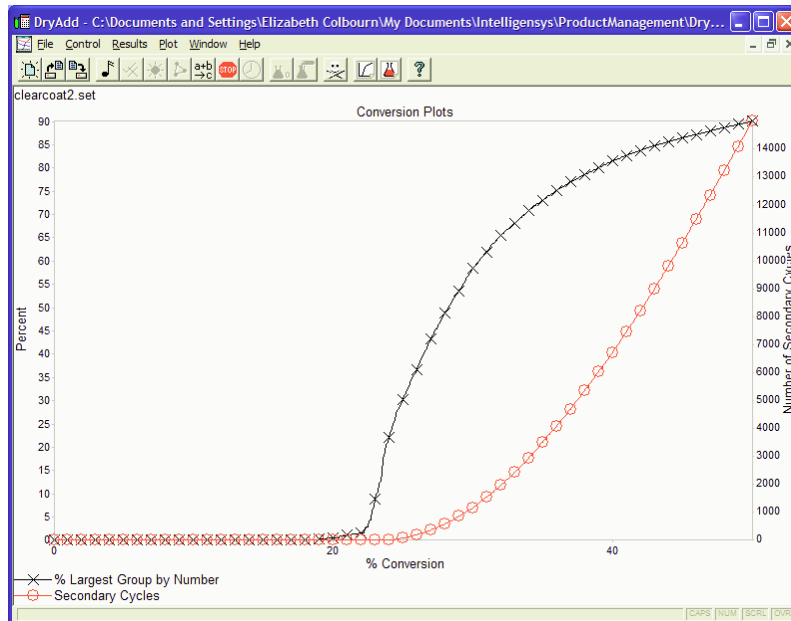


Figure 4. Gel plot for case where there are twice as many OH groups as methoxy groups

The final case has 1.5 methoxy groups for each hydroxyl group, achieved for our trial by using a quantity of 1.5 moles of crosslinker to 2 moles of polyester. The gel plot is shown in Figure 5 for this case. Gelation occurs at just above 45% conversion.

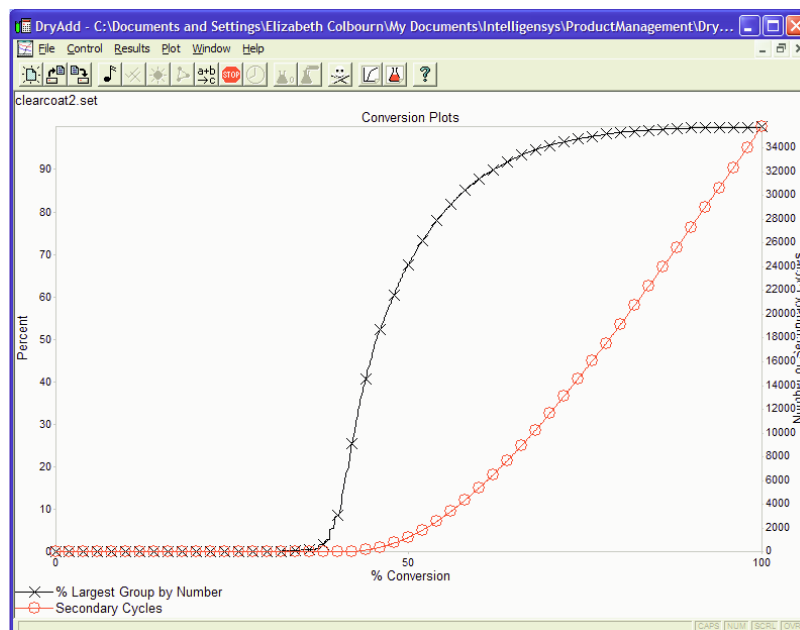


Figure 5. Gel plot for case where the hydroxyl:methoxy ratio is 1:1.5

The Network Analysis capability within **DryAdd** (which is based on a graph theoretic analysis of the network) shows the variation in some of the key parameters for the 3 cases. These are summarized in Table 1.

	Stoichiometric mix	OH:Methoxy 1:0.5	OH:Methoxy 1:1.5
Crosslink density	0.00136	0.0006822	0.00105
EEC as % of gel	100%	59%	99.6%
Mc (gel)	366.4	1235	409.1
Mc (EEC)	366.4	734.5	407.4

Table 1. Results from graph theoretic analysis of crosslinked network

Within Table 1, Mc is the average molecular weight between entanglements in the gel. EEC refers to the Elastically Effective Component of the gel. Standard texts on rubber elasticity describe these concepts in more detail.

The simulations also show whether any material is left unused at the end of the simulation. For the second case, where the number of OH groups is twice the number of methoxy groups on the crosslinker, over 10% of the polyester chains are unreacted. This might be expected to affect the weatherability of the cured system.

Conclusions

Generally, the hardness of a material relates to its glass transition temperature T_g, which in turn relates to how tightly the material is crosslinked. The above study shows that the greatest degree of crosslinking can be expected for a stoichiometric mixture of the crosslinker and polyester resin. Increasing the hydroxyl functionality results in a significantly less crosslinked system; increasing the crosslinker functionality makes relatively little change.

It has been possible to model this system with a simple reaction scheme; more complex reactions could be added if required. It has not been possible to make a direct comparison with the work of Tusar *et al* (1) since they did not give sufficient details for their polyester (in particular, molecular weight and functionality) that its composition could be input accurately into **DryAdd**.

References

1. 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)