

Simulating Cross-linking in Epoxy Resins

1. Introduction

Epoxy resins are used in a wide range of applications, from aerospace to marine. They are also (as Araldite and other products) popular household adhesives. They can be obtained in a wide range of formulations, but many are two-pack adhesives in which a curing agent is added to an epoxy resin to start the cure process.

Curing is often carried out using systems like amines, which ring-open the epoxide; however, attacking the ring using radicals or by Lewis acids or bases is also possible. Some of these are discussed in detail below.

2. Cure by Primary Amines

A textbook example is taken from the work of Cheng and Chiu (1). Here, DDS (bis 4-aminophenyl sulphone) is the amine curing agent, and it is mixed with an epoxy system consisting of DGEBA (diglycidyl ether bisphenol A, molecular weight 340) and a DGEBA-based epoxide (molecular weight 624) with a single hydroxyl sidechain. The workscreen showing the set-up of the materials is given in Figure 1; here, equimolar amounts of epoxide and amine groups have been assumed.

	Material Name	Mol. Weight	Moles	Weight
1	DGEBA	340.00	0.9700	329.8000
2	DDS	248.00	0.5000	124.0000
3	DGEBA-deriv	624.00	0.0300	18.7200

Figure 1. Materials Workscreen for Epoxy (DGEBA) cured with Primary Amine (DDS)

When epoxy ring opens, two new groups are created: a hydroxyl group, and a secondary amine group. The **DryAdd** simulation allows these to be set up as 'phantom' groups which are not present at the start, but which are created during the reaction. The reaction scheme is shown in Figure 2.

Type	R1	+ R2	==> P1	+ P2	Rate	L/G(1)
1	BF2P * : epoxide	DDS : amine1	* : hydroxyl	DDS : amine2	100.00	0.00
2	BF1P * : epoxide	DDS : amine2	* : hydroxyl	(none)	40.00	0.00
3	BF1P * : epoxide	* : hydroxyl	* : hydroxyl	(none)	10.00	0.00
4	BF1P * : epoxide	DGEBA-deriv : hydroxy2	* : hydroxyl	(none)	10.00	0.00

Figure 2. Reaction Scheme for Primary Amine interacting with Epoxide

Here, the BF2P refers to a bond-formation reaction leading to two new products – the hydroxyl group on the epoxide and a secondary amine on the DDS. (The * denotes that the group can be on any of the starting materials – in particular, the DGEBA and its derivative.) The BF1P reactions lead to only one new product – in particular, when a hydroxyl group reacts with the epoxide group, then a new hydroxyl group is created. Relative rates are taken from the paper by Chen and Chiu (1), and show that the fastest reaction occurs between the primary amine and the epoxy group. The reaction of the secondary amine with the epoxide ring is only 40% as fast. (Of course, this may depend crucially on the reaction temperature that is used.)

A population size of 100,000 monomers was assumed, and conversion is taken to be with respect to the number of epoxide groups.

When the simulation is run, and the largest group (by weight) and the number of secondary cycles are plotted, the graph obtained is shown in Figure 3.

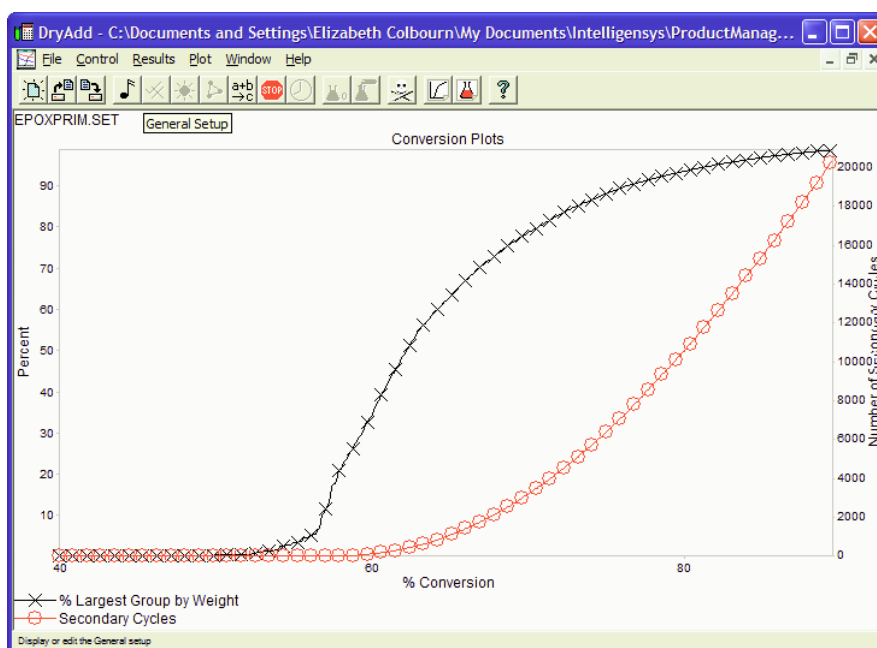


Figure 3. Gel point for DDS-DGEBA system

The gel point is generally taken as the point at which the number of secondary cycles starts to rise rapidly, which coincides with the point at which the largest group (defined in **DryAdd** as the gel) is growing at its fastest. The simulation was stopped when 90% of the epoxide groups had been reacted. At that point, the Network Analysis showed that the Elastically Effective Component (EEC) formed 84% of the gel (largest molecule), and that M_c (the average molecular weight between entanglements) was 500.6 in the whole system, and 425.3 in the EEC.

Changing the relative amounts of DGEBA and DGEBA-derivative from 0.97 and 0.03 respectively to 0.9 and 0.1 respectively does not change the gel point or the shape of the curve shown in Figure 3. However, it does make some change to the average molecular weight between entanglements, to 519.8 in the whole system, and 441.9 in the EEC. This is expected, since the DGEBA-derivative has a higher molecular weight.

However, changing the amount of epoxide-containing material relative to the amount of crosslinker does have a significant effect. Of course, this can be important when creating a formulation that is easy to use e.g. for do-it-yourself applications carried out at home by non-experts. To see what happens when you have 1.5 times as many amine groups as epoxide groups, the materials workscreen was set as in Figure 4.

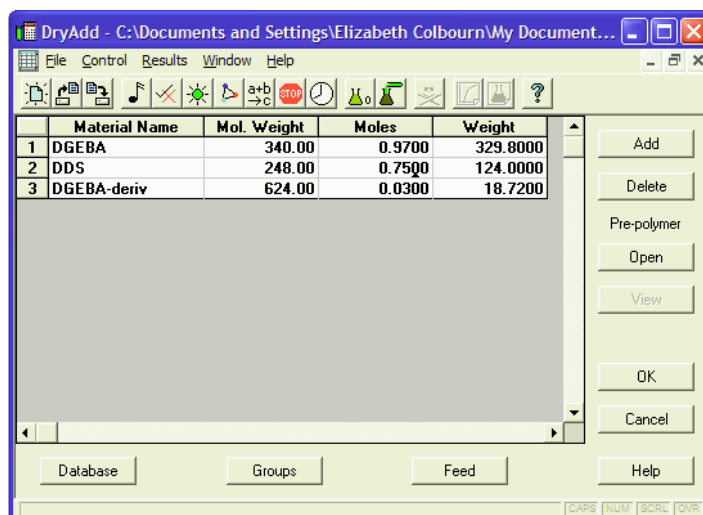


Figure 4. Materials screen when there are 1.5 moles of amine for each mole of epoxide groups

In this case, as Figure 5 shows, gelation is delayed to 75% conversion, and the number of secondary cycles is decreased (from about 20,000 in the equimolar case, to 14,000 here).

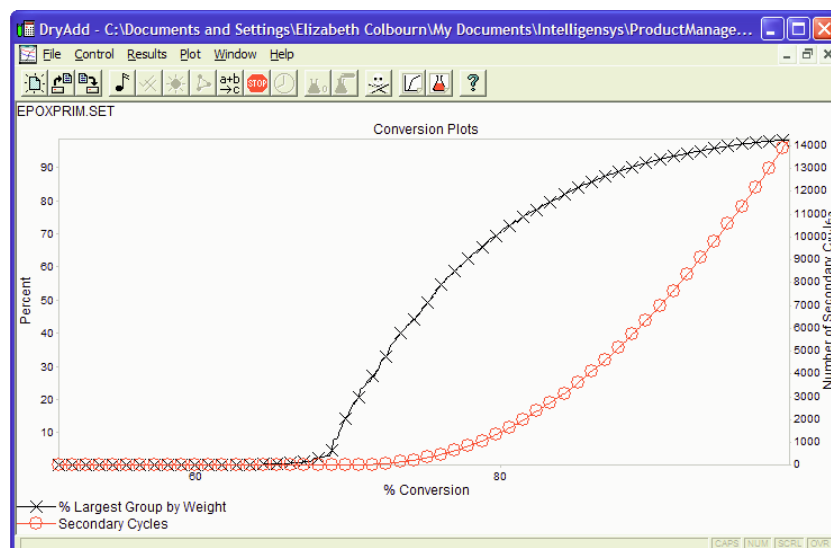


Figure 5. Onset of gelation is delayed when the amount of DDS is increased

The Network Analysis shows that M_c is increased to 569 in the EEC, and 674.3 in the full system. Therefore, the adhesive will be expected to be somewhat weaker and softer.

With two moles of amine for each mole of epoxy groups, gelation is delayed until 85% conversion. In the extreme case where there are 3 moles of amine for each mole of epoxide, then gelation simply does not occur. Therefore if the user naively thinks that adding more crosslinker will give better performance, they will be sadly disappointed.

3. Crosslinking using Tertiary Amines

Tertiary amines can act as catalysts for the epoxide ring-opening. The tertiary amine attacks the ring, leaving an O^- -like species. This goes on to attack more rings, giving a highly crosslinked system with many ether linkages.

A typical example is the reaction of diethyl amino propylene (DEAP) with the difunctional epoxy DGEBA. DEAP is set up with one group, called *initiator*. A reaction is set up, in which

initiator attacks the epoxy group. There are two epoxy groups on DGEBA, and we also set up a phantom group *Oxygen Ion* which is formed in the reaction. In subsequent reactions, the Oxygen Ion group can react with more epoxide groups, forming new *Oxygen Ion* groups.

The Reactions workscreen is shown in Figure 6. Here, it is assumed that the reaction with the *initiator* group is only 1/10 as fast as that when the resulting O⁻ group reacts with further epoxide rings. Only a relatively small amount of initiator is needed, to get the reaction started. After that, it proceeds autocatalytically. The degree of crosslinking, and the gel point, depend on how much tertiary amine (initiator) is present at the outset. If there is a lot, gelation is delayed.

Type	R1	+ R2	==> P1	+ P2	Rate	I
1	BF1P DGEBA : epoxy	DEAP : initiator	DGEBA : Oxygen ion	(none)	10.00	
2	BF1P DGEBA : epoxy	DGEBA : Oxygen ion	DGEBA : Oxygen ion	(none)	100.00	

Figure 6. Reactions workscreen for epoxy crosslinking with tertiary amine initiator

Figure 7 shows the gel plot when there is 1 mole of initiator (DEAP) for 100 moles of DGEBA. Gelation occurs relatively quickly, at just over 20% conversion of the epoxy groups. (This is the point where the number of secondary cycles starts to increase beyond a very few.)

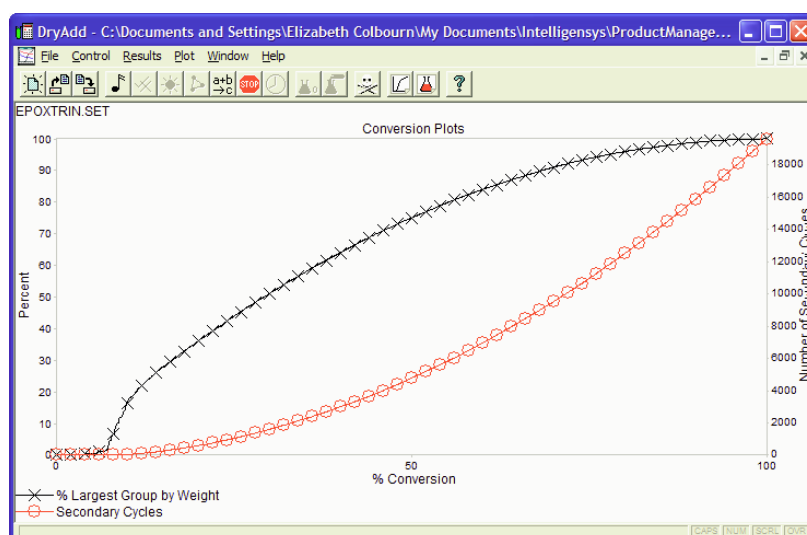


Figure 7. Gel point plot for DEAP reacting with DGEBA

The network analysis shows that all of the material has gone into the elastically effective component of the gel, and that the average molecular weight between entanglements is 171.7.

Increasing the amount of DEAP so that there are 5 moles of DEAP to 100 of DGEBA, Mc increases only fairly slightly, to 174.6 in the EEC and 177.5 in the entire system. The EEC forms 98% of the gel.

Increasingly DEAP to 10 moles of DEAP to 100 of DGEBA leads to a further increase in Mc, to 184 in the whole system. However, compared to the cure by primary amines, discussed in Section 2, the cure by tertiary amines is relatively insensitive to the amount of primary amine used, within reasonable bounds.

4. Other Systems

Mixed systems can be set up, in which both primary and tertiary amines are present. This is done by using a combination of the materials and reactions discussed in the previous two examples.

Initiation by free radical catalysts proceeds in a similar way to that using tertiary amines. However, in this case the initial reaction is the formation of a free radical (rather than the O⁻ group) and the reaction is propagated by the attack of this free radical upon other epoxide rings. The reaction scheme, however, is similar to that for tertiary amines, with the simple substitution of a radical group for the O⁻.

5. Validation

DryAdd has been validated for epoxy systems by Hädicke and Stutz (2), working at BASF. They have compared **DryAdd** results with those obtained using the statistical approach of Macosko and Miller. Their results conclude: "In general, the results of both methods are consistent; the simulation revealed some uncertainties only in the vicinity of the gel point. Since the statistical theories have been validated experimentally, it may be concluded that the simulation can successfully be used for the treatment of real, highly complicated multicomponent systems, which for practical purposes are intractable by statistical theories."

References

(1) K-C Cheng and W-Y Chiu, *Macromolecules* **27** 3406-3414 (1994)

(2) E Hädicke and H Stutz, Comparison of the structure of step-growth networks obtained Monte Carlo simulation and branching theory, *J Applied Polym Sci* **85** 929-935 (2002)