

Characteristics of Bis F and Phenol Novolac Epoxy Resins

Compositional differences and their effect on Performance

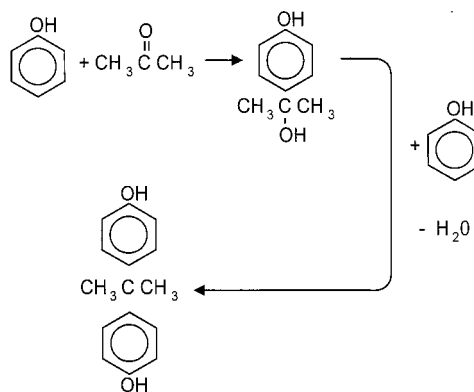
John Cech, General Manager CVC Specialty Chemicals, Inc

Both phenol novolac epoxy resins (EPN) and Bis phenol F epoxy resins (BFDGE) are produced from a phenol formaldehyde phenolic resin. Bis phenol A Epoxy resin (LER) is made from a phenol acetone phenolic resin. These starting phenolic resins are reacted with epichlorohydrin to produce the final epoxy resin. The stoichiometry used in the production of the phenolic resin will influence the functionality of the phenolic resin and consequently the epoxy resin made from it.

Production of the phenolic involves a classic addition/condensation reaction. The initial reaction is an addition reaction of the ketone/aldehyde to phenol. These are ortho and para directed on the aromatic ring.

The addition reaction results in the formation of an alkanol phenol. Because of steric hindrance, the reaction is over 96% directed to the para position when acetone is the reactant. This intermediate is isopropanol phenol. With formaldehyde the resultant addition product is methanol phenol. Both alkanol phenols are unstable and will condense with additional phenol to form the phenolic terminated resin. This sequence for Bis Phenol A is shown below:

BISPHENOL A SYNTHESIS

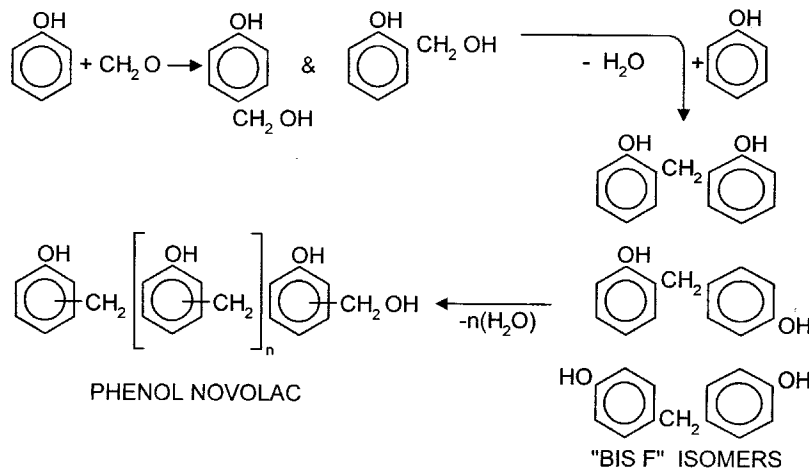


Because of steric hindrance the condensation product of isopropanol phenol is over 96% 4,4' isopropylidene biphenol– a 2 functional phenolic resin. In theory additional reactions can occur in the available ortho positions, but steric hindrance prevents this reaction with acetone.

Phenol formaldehyde reactions on the other hand are not as sterically hindered. With control of reaction condition, catalyst selection, as much as 20-30% of the formaldehyde reaction can occur at the ortho position. Included are multiple reactions of formaldehyde to a single phenol molecule. Like phenol/acetone reactions the resultant methylolated resin will condense. The condensation with phenol of methylol phenol creates Bis phenol F a 2 functional phenolic analogous to Bis phenol A. This condensation will result in a mixture of o,o, o,p, and p,p isomers. The resultant phenolic displays the classic triplet peak for Bis F epoxy resin when measured by HLPC or GC.

In addition to condensation of methylol phenol with phenol these condensations can also occur with methylol phenol and with di and tri methylolated phenol. The resultant phenolic is consequently multifunctional and shown below:

NOVOLAC SYNTHESIS



As expected, reaction conditions, catalyst, addition rates and reactant ratios influence both the concentration of di and multifunctional phenolic formation, and the distribution of the isomer ratios. The resultant resin will have an average functionality that is based on the weighted average of these components, but it is safe to say that unless purification is involved all resins are a mixture of each fraction. In other words all Bis F phenolics have some multifunctional component and all phenol novolacs have a Bis F component. Bis Phenol A on the other hand can only be 2 functional for all practical purposes.

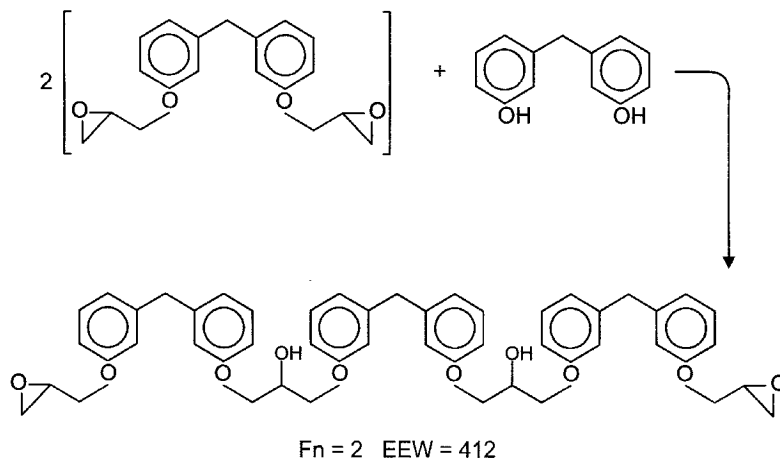
Before conversion to the epoxy resin, excess phenol is distilled from the resin. At this stage the functionality of the phenol novolac is set. Reaction with epichlorohydrin will not change this functionality, but simply react off all the available phenol OH groups, in the formation of the resultant epoxy.

Reactions with epichlorohydrin involve use of an excess of epichlorohydrin and are conducted under alkali conditions. The intermediate formed in this reaction is the chlorohydrin of the phenolic resin.

The chlorohydrin will ring close in the presence of an acid scavenger to form the resulting epoxy resin and salt. The salt is removed and the excess epichlorohydrin is distilled in the finishing of the final resin. Excess epichlorohydrin is used to maximize the reaction of the phenolic with epichlorohydrin. During the reaction between epichlorohydrin and the phenolic resin while in the presence of an acid scavenger, ring closing can and will occur. This means that as the epi is reacting with the phenolic, the epoxy resin is being formed through ring closure. This resin in the presence of unreacted phenolic will compete with epi for reactions. The epoxy resin phenolic reaction is the basis of advancement or polymerization of the forming resin.

Advancement reactions increase the molecular weight of epoxy resins, but do not change their functionality. In other words, epoxy terminated resins are still epoxy functional and retain the functionality of the starting phenolic resin. Their epoxy equivalent weight (EEW) is increased by the increase in molecular weight. These advancement components are generally referred to by the number of repeating units ($n > 0$). This is shown below:

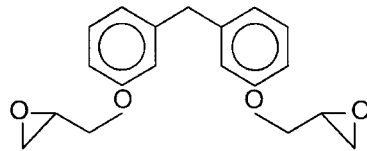
ADVANCEMENT



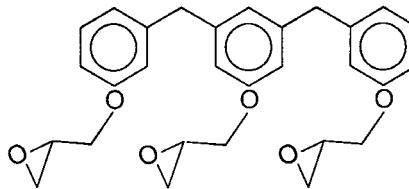
The advancement of the epoxy resin increases its viscosity as well. For LER this increase results in the various grades sold commercially. In the table below the three common grades are shown:

Grade	Viscosity Range	% n > 0	Typical EEW
Standard	12,000 – 13,000	8-9	190
Low Viscosity	9,500 – 10,500	3-4	182
Distilled	4,500 – 6,000	1	176

Bis F and EPN resins also contain advancement resins and like LER these components raise the viscosity and EEW of the epoxy resin. But unlike Bis A resins, they also have multifunctional components. While they also raise the viscosity, they do not raise the EEW. This is shown below:



Fn = 2 EEW = 156



Fn = 3 EEW = 158

This more complex blend of advancement and multifunctionality in Bis F and EPN resins often leads to confusion over the actual composition as it relates to the performance expectation of the resin. In the table below are the major resins supplied by CVC comparing the average functionality, viscosity and EEW of each:

Grade	Typical Viscosity	Functionality	EEW
EPALLOY 8220	2300	2.05	166
EPALLOY 8225	3800	2.05	173
EPALLOY 8230	4000	2.15	168
EPALLOY 8240	7100	2.35	170
EPALLOY 8250	22000	2.6	171
EPALLOY 8330	23000 *	3.6	173
EPALLOY 8350	40000 *	3.6	179

* Measured at 52°C

Note in comparing 8220 and 8225, that functionalities are the same, but the viscosities and EEW are different. Each starts with the same phenolic resin, but by varying the reaction conditions and formulation used, 8225 has a higher advancement component. The same conditions apply when comparing 8330 and 8350. This can be seen by HPLC analysis and is shown in the table below.

Product	Area weight %		
	Fn = 2	Fn = 3	Fn > 3 and advancement
EPALLOY 8220	77.1%	13.3%	9.5%
EPALLOY 8225	78.5	10.3	11.2
EPALLOY 8230	67.9	17.5	14.6
EPALLOY 8240	61.0	19.7	19.3
EPALLOY 8250	45.8	22.8	31.5
EPALLOY 8330	23.3	16.5	60.2

Failure to understand this difference can result in selection of the wrong resin with too high a viscosity and/or the use of the incorrect stoichiometry with the curing agent selected. Since most of the interest in these resins is to process systems that maximize thermal or chemical resistance, it is generally desirable to use the highest functionality at a given viscosity. In other words, minimize the advancement and maximize the functionality at any viscosity.

As a rule of thumb, the lower the EEW at a given viscosity the higher the functionality and lower the advancement. EPALLOY 8225 and 8230 are good examples of this. In the table below a comparison of the Tg of all the standard commercial CVC Epoxy Novolacs are shown for illustration.

Product	Functionality	Tg
EPALLOY 8220	2.05	129
EPALLOY 8225	2.05	129
EPALLOY 8230	2.15	131
EPALLOY 8240	2.35	145
EPALLOY 8250	2.60	160
EPALLOY 8330	3.60	198

Samples cured with PACM at 100°C for 1 hr followed by a 200°C post cure for 4 hours

In conclusion, use of epoxy phenol novolacs including Bis F can greatly enhance the performance of corrosion resistant coatings and high temperature composites. In selecting resins for these applications it is important to understand the influence of functionality, advancement and their relationship on viscosity and EEW in formulating systems. Failure to do so can result in selecting a resin that will fail because it is inadequately cured or exhibits a viscosity that is too high. Proper selection of the resin and matching the correct curing agent stoichiometry will guarantee optimal performance.