Epoxy Crystallization & Prevention Recommendations

Anyone that has regularly utilized liquid epoxy resins has most likely experienced crystallization issues. Crystallization issues appear as a cloudiness, free floating crystals, or crystal masses in the liquid resin, or as a completely solidified mass. This is not surprising considering that the normal thermodynamically stable condition of standard bisphenol A and bisphenol F liquid epoxy resins is a crystalline solid at room temperature. For example, standard bisphenol A liquid epoxy resins with an EEW of approximately 188 and an “n” value of 0.12 (as typically supplied by all major manufacturers), has a melting point of approximately 42 C (107.6 °F). Standard bisphenol F liquid epoxy resin has a melting point of 55 C (131 °F). At room temperature they are supercooled liquids, but the crystallization rate at room temperature (25 C or 77 °F) is very slow. The tendency for crystallization is also unpredictable, and can happen in days, weeks, months or even years. It can also affect portions of any single production Lot, with certain drums crystallizing and others remaining as liquid. However, crystallization can be limited or even eliminated, by selecting the right resin, utilizing some simple formulating techniques, ensuring proper storage conditions, and limiting foreign contamination.

Bisphenol A and bisphenol F liquid epoxy resins are produced and sold by many manufacturers. The products offered include standard grades, low viscosity grades, low hydrolyzable chloride grades, and many different modified grades. Some of these grades are much more susceptible to crystallization than others. Having a basic understanding of the chemistry involved with manufacturing the resins is important for understanding the differences in liquid epoxy resin grades that are offered by manufacturers. The idealized bisphenol A epoxy resin reaction is as follows:

This idealized reaction (as pictured above) shows us that when “n” approaches zero, you end up with a simple difunctional bisphenol A epoxy molecule (as pictured below) with a molecular weight of 340 and an EEW of 170, and a low viscosity of <5,000 centipoise at 25 C.
The same reaction example applies to bisphenol F liquid epoxy, with the bisphenol A reactant replaced with bisphenol F, and the resulting bisphenol F epoxy resin as follows:

Chemically pure resins have all the same molecules, low EEW and low viscosity. The lower viscosity allows them to move more freely and the consistent chemical structure (same molecules) allow them to line up more easily. This results in a much higher tendency to crystallize.

No manufacturer makes these “chemically pure” bisphenol A and bisphenol F liquid epoxy resins. However, they do make versions that are close to chemically pure, and these are the lower viscosity versions of the standard grades. These lower viscosity “more chemically pure” resins do have a higher tendency to crystallize.

The typical manufacturing processes utilized by resin manufacturers today (i.e. the fusion or taffy processes), produce liquid epoxy resins with a larger molecular weight distribution (lower to higher molecular weight molecules) and several side reaction by-products. The broader molecular weight distribution and the by-products increase viscosity and add variety to the molecules. The higher viscosity does not allow the molecules to move as freely as in a chemically pure resin, and the variety of molecules do not line up as easily to form crystalline solids. Thus, standard liquid epoxy resins produced by almost all manufactures have at least some “built-in” resistance to crystallization. The by-products produced in a typical standard liquid epoxy resin production process include the following:

These by-products not only impact the viscosity and reduce the tendency for crystallization of standard liquid epoxy resins, they also impact the reaction rate of the resin and the hydrolyzable chloride content.
The hydroxyl and chlorine containing by-products act as accelerators for epoxy amine reactions, so controlling their concentration in the supplied resin, is important to consistent reactivity (and most manufacturers do this quite well). The chlorohydrin by-products also add to the hydrolyzable chloride content of the resin. Therefore, low hydrolyzable chloride resins can be slower to react and the reduced “impurities” may increase crystallization. You should be careful to ensure that any move from a standard liquid epoxy resin grade to a lower viscosity and/or lower hydrolyzable chloride content grade does not result in reactivity changes or increased crystallization issues.

Knowing that variety in molecules (reduction of chemical purity) will decrease the chances of crystallization, allows one to formulate to achieve this result. For example, blending standard bisphenol A liquid epoxy resin with standard bisphenol F liquid epoxy resin, will significantly decrease the tendency for the blend to crystallize. It typically takes at least a 5-10% addition of bisphenol F liquid epoxy resin to bisphenol A liquid epoxy resin (and vise versa), to have a significant impact on crystallization resistance.

Using higher molecular weight/higher EEW resins, and/or adding them to lower EEW resins, also adds molecular variety to the mix and makes it harder for molecules to line up and crystallize. “It is believed that the higher-molecular-weight oligomers in the higher-EEW resins act to disrupt the crystal structures and prevent crystallization.”

One may conclude that adding reactive diluents to standard liquid epoxy resins (adding molecular variety and reducing chemical purity) would reduce tendency for crystallization. This is true for reactive diluents such as o-cresyl glycidyl ether and/or other aromatic diluents, as well as highly branched molecules like neodecanoic acid glycidyl ester. However, liner low viscosity reactive diluents such as C12-C14 aliphatic glycidyl ether (i.e. Epoxide 8, Heloxy 8, etc.) will actually increase the tendency for crystallization. The reason some reactive diluents help and others can hurt, has to do with the two mechanisms at play. Lowering the viscosity allows molecules to move more freely and line up, resulting in crystallization. If the reactive diluent is liner it will not produce as much interference (steric hindrance) as aromatic or highly branched reactive diluents, and thus, will not prevent crystallization.

Besides viscosity and molecular variety, storage conditions (temperature) and limiting particulate contaminates (dust or other contaminates), will also have a major impact on crystallization. Cold temperatures (reduced viscosity) can reduce the crystal formation/growth by slowing molecular movement, but resins with contaminates or seed crystals present, will accelerate crystal formation under colder temperatures. The contaminants act as seed sites for crystallization growth. Therefore, limiting particulate contamination and/or seed crystals is important to limiting crystallization.

Particulate contamination can come from a dirty environment in manufacturing, or poor handling practices (i.e. open containers, dust, dirt, unclean equipment, etc.) and containers, container spouts, spigots and closures with resin build-up. Particulate contamination can also come from certain filler additives. Fillers rarely initiate crystallization due to their large particle size and high addition levels. However, certain types of fillers, such as precipitated fillers (like precipitated calcium carbonate) have been known to initiate/accelerate crystallization. This fact is actually utilized in some test methods for measuring crystallization resistance (i.e. ISO 4895 “Plastics - Liquid epoxy resins - Determination of tendency to crystallize”).
Temperature cycling can have a big impact on crystallization. Temperature cycles of as little as 20 to 30°C are the most common cause of crystallization. When the resin is warmer, molecular movement is enhanced, which allows molecules to line up and begin crystallization (crystal seed formation). When crystal seeds formed at warmer temperatures are then exposed to colder temperatures the crystallization process will actually accelerate. Not only can temperature cycling be encountered during storage, but it also occurs when crystallized/solidified epoxy resin is heated (melted) back to its liquid state (especially if the resin is removed from the heat source prematurely). When re-melting standard bisphenol A liquid epoxy resin in a 55 gallon drum, it should be exposed to 50°C for at least 4-5 hours. When re-melting standard bisphenol F liquid epoxy resin in a 55 gallon drum, it should be exposed to 70°C for at least 4-5 hours. Before allowing the material to cool down, ensure that all solids/crystals have melted by checking the container sides, bottom and the areas around lid, bung or other transfer ports for crystallized material (including cloudy liquid areas) to ensure no seed crystals are remaining. Storing resin at a consistent room temperature of > 25°C and limiting contamination of resins will help prevent crystallization.

Although crystallization of bisphenol A and bisphenol F liquid epoxy resins can be unpredictable, eliminating exposure to extreme cold, broad temperature fluctuations, contaminants, and increasing the variety of molecules (reducing chemical purity) through some of the resin/diluent choices and formulating techniques listed above will help you limit crystallization issues.

TRiiSO has a full line of epoxy resins, reactive diluents, curatives, accelerators, and dispersants, rheology modifiers, flame retardants, anti-oxidants, and UV inhibitors/stabilizers to meet your application cure & performance requirements. Just ask your local TRiiSO technical sales representative for more information.

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References:
