June 2008, Rev. I

EPOXY CRYSTALLIZATION

What is Epoxy Resin Crystallization?

It often comes as a surprise, but Epoxy Technology's suppliers have assured us that crystallization is an inconvenience rather than a problem. The ones who are most aware of it are the users of epoxy resin. Frequently, a jar, bottle, bucket or container looks cloudy, turbid, or even solid upon inspecting its contents. Crystallization by definition refers to a phase change from liquid resin to its solid format. It can be viewed similarly as water turning from liquid into ice, and vice versa. Crystallization of epoxy resins is completely reversible, like freeze/thaw cycles of ice and water. As water remains unchanged from repeated cycles, so do the original properties of epoxy resin.

Signs of crystallization

According to Epoxy Technology's suppliers, crystallization may appear in the form of cloudiness, free floating crystals, crystal masses, or as completely solidified mass. Since the crystals are higher density than the liquid resin, they sink to the bottom of the container. At the onset of crystallization, the clear resin begins to look foggy, cloudy, hazy, or turbid to milky white. The white sedimentation continues to build, pack and spread, typically from the bottom of the container to corresponding side-walls. This sandy like texture will eventually overcome the entire contents of the container. Once solidified, crystallized epoxy resin can be stored indefinitely in this state.

Why does crystallization occur?

Many plastic resins are super-cooled liquids, including Bisphenol A–type and F-type epoxy resins. They are supposed to be solid format at room temperature, but remain in liquid state below their freezing temperature, which is 42°C for Bisphenol A-type or 55°C for Bisphenol F–type epoxies. Liquids super cool because crystallization can be too slow of a process, or the seed crystals are not readily formed. In general, super cooled liquid resins have a natural tendency to crystallize at low(er) temperatures. Other factors such as extreme cold, fluctuation in ambient temperatures and thermal cycling, causes seed crystal growth and may induce materials to revert back to their natural, solid state.

Causes of crystallization

Crystallization can be difficult to predict and eliminate entirely. It happens randomly, without warning, and may affect parts of a given production batch (it is normal for a few containers from the same batch to show differing degrees of crystallization deposits). Understanding the factors that contribute towards crystallization, and how to deal with them, is the best way to keep this problem from becoming an annoyance. According to our suppliers, the tendency for liquid epoxy resins to become crystallized depends on the purity of the resin, the resin viscosity, additives, the moisture content and temperature history (extreme cold or thermal cycles).

- *High Purity*

Typically, high purity resins are more easily crystallized than impure resins. A narrow molecular weight distribution from Bisphenol A – type is indicative of the former, while broader MW distributions the latter. One model for high MW impurities is the addition of anti-freeze into water. It has the effect of lowering the melting temperature, thus making it harder to crystallize. The same can be said with adding higher MW oligomers or isomers into an epoxy resin formulation. Avoiding crystallization of resins due to their purity is more of Epoxy Technology's formulating challenge, and not for Epoxy Technology's customers. Rather, Epoxy Technology's customers should understand that crystallization of EPO-TEK® 301-2 part A is indication of its purity and homogeneity, and not viewed as a negative byproduct.

- *Low Viscosity*

In general, higher MW resins result in higher viscosity of the resin and are less prone to be crystallized. The rate of crystallization is faster in a lower viscosity resin. Lowering the temperature increases the viscosity of the resin, thus reducing molecular motion and the rate of crystallization. Storing "crystal seed free resin" at 0°C is one method to reduce the rate of crystallization, but this may not be the best idea for Epoxy Technology's customers. As explained above, 0°C might be enough of "extreme cold" or may be viewed as enough of a thermal cycle, to cause hidden seed crystals to propagate into a solid mass.

- *Additive – solid fillers*

Solid, inorganic fillers sometimes act as seeds for crystal growth. Precipitated calcium carbonate has been shown to increase the rate of crystallization (eg. ISO 4985, Plastics – Liquid Epoxy Resin – Determination of Tendency to Crystallize). Epoxy Technology has found other fillers like alumina and silica to have a similar effect. Even the scratch of a sidewall of a glass or metal container can be enough of a "filler" to promote seed crystal growth.

- *Temperature*

Epoxy Technology's understands from its suppliers that while cold temperatures do reduce the crystal formation/growth by slowing movement (increased viscosity), extreme cold accelerates crystal formation once seed crystals have formed.

- *Thermal Cycles*

Temperature cycles of as little as 20-30°C are the most common cause of crystallization. Once the material is warmed, molecular motion is enhanced allowing liquid epoxy to orient itself around "seed" crystals. Subsequent exposure of an "oriented" material to cold temperature will then accelerate crystal growth. Once started, the crystallization typically goes to completion resulting in a solid mass. The temperature fluctuations that occur between night and day start or enhance the crystal growth process.

Solutions

Crystallization of epoxy resins is typically an inconvenience and not a problem. Increasing the temperature of Bisphenol A – type epoxies above 50°C (throughout the container) for a few hours will re-melt the resin. For Bisphenol F – type epoxies, at least 70°C is required. Be certain all crystals (macro and micro) have melted away, and can no longer act as seeds, before cooling to 23°C. According to Epoxy Technology's suppliers, the storage temperature should not be any higher or longer than necessary as some color and/or viscosity build could develop. Carefully watch the container sides, the container bottom and the areas around the caps when inspecting for signs of crystallization that could nucleate additional crystal growth. If possible, it is recommended to clean the bottle caps and bottle neck with solvent (isopropanol or acetone) during each use, in order to prevent seeds from developing. The same applies for spigots, spouts, pumps, piping and valves. Controlling and monitoring shipping and storage temperatures is a good way to prevent crystallization from fluctuations in temperature. Good housekeeping is the best way to prevent crystallization.

Conclusions

Epoxy Technology's suppliers have assured us that crystallization is unpredictable and there are no fixed rules. Limiting temperature fluctuations, however, will reduce the tendency to crystallize. If crystallization does occur, simply warming the resin to melt the crystals is an easy way to deal with this common phenomenon.

Questions

Contact your nearest EPO-TEK® representative http://www.epotek.com/representatives.asp, or email us directly at techserv@epotek.com.