



Epoxy Crystallisation

Introduction

Liquid DGEBCA (Diglycidylether of Bis-phenol-A) epoxy resins and the liquid DGEBCF (Diglycidylether of Bis-phenol-F) epoxy resins are supercooled liquids at room temperature. That is, they are solids at room temperatures but normally remain liquid below their solidification temperature. Technically the solidification / melting point of DGEBCA is 45-50C and DGEBCF is 80-85C. They supercool because the crystallisation process is slow at ordinary temperatures and they do not readily form the seed crystals that are required for solidification to occur. As one increases the average molecular weight, higher molecular weight species and isomers increase. These isomers and higher molecular weight species reduce the tendency for crystal formation and growth.

Crystallisation shows up as cloudiness, free floating crystals, crystal masses, or as a completely solidified mass. It is the same process that causes honey to crystallise at home. The crystallisation phenomenon is possible in all epoxy resin and hardeners. It is the phase change of a material from a liquid to a solid crystalline state. The main ingredient of most epoxy resins is a solid material at room temperature. Exposure to extreme cold, temperature cycles and other factors may induce crystal growth and revert the materials back to their natural solid state. Crystallisation is difficult to predict or eliminate entirely. It happens without warning and may only affect part of a given lot of material. While it may be only an inconvenience with two components systems, it can cause major problems with one components. Understanding the factors believed to influence crystallisation and the methods of dealing with it can turn this problem into merely an annoyance.

Causes

Epoxy crystallisation occurs similarly to other crystal growth. High purity, low viscosity, impurities, extreme cold, and temperature cycles all increase the probability of occurrence. Usually the presence of a “seed” initiates the crystallisation process. Here are some of the factors that contribute to the crystallisation process in epoxy resin.

High Purity

A high purity resin has been stripped of all chemical by-products and contaminants and falls within a given range of molecular weights. The presence of by-products and a wide range of molecular weights serves to broaden the temperature transition range between liquid and solid. High purity resins have a narrow temperature range during which they transform from liquid to solid. An analogy is pure water which transforms from liquid to crystalline solid (freezes) at 0°C.



Yet with the addition of another chemical “table salt”, the water freezes at much lower temperatures. The closer a high purity resin gets to the point where it changes from a liquid to a glassy crystalline solid state the greater the chance minute crystals will start to form. These crystals act as seeds and in combination with other factors can rapidly change the liquid to a solid.

Low Viscosity

Low viscosity resins are very low in molecular weight and short chained. The lower the viscosity the easier the liquid epoxy can move and orient itself around seed crystals. High molecular weight, high viscosity materials are longer chained and less prone to crystallise. Storing a “seed” free liquid at low (0°C) temperatures will slow molecular motion and impede crystal formation and growth. Diluents and modifiers generally increase the rate of crystal formation and growth, however there are significant differences on the tendency to crystallise between diluents. Other additives, such as pigments, fillers and wetting agents, can also affect the rate of crystal formation and growth. Generally, if one prevents the introduction of seed crystals into a resin handling system, crystallisation will be a rare event unless one is handling high purity resins.

Impurities

Impurities, usually minute particulate matter, can often act as “seeds” in unfilled systems, initiating the formation of resin crystals which then continue to propagate. Fillers rarely initiate crystallisation due to their large size and high content, actually they often act to inhibit crystallisation.

Extreme Cold

While cold does impede growth by slowing movement, extreme cold (-40°C) accelerates crystal formation once seed crystals have formed and if low enough can cause complete crystallisation by itself.

Temperature Cycles

Temperature cycles as little as 20-30°C can create a vicious circle that is the most common cause of crystallisation. 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 crystallisation typically goes to completion resulting in a solid mass. The temperature fluctuations that occur between daytime and nighttime temperatures can initiate and/or accelerate the crystal growth process. These can occur during transit, while sitting on a loading dock or the production floor.

Solutions

Crystallisation in base resins and two component formulations is a major inconvenience but not an insurmountable problem. Heating these materials several hours at 50-60°C easily reverses the phenomenon. All the crystals must be completely melted as any microscopic unmelted crystals will act as “seeds” and cause the crystallisation to return in days. Along with the gentle heating the material should also be stirred and the container sides and bottom scrapped to assure all crystals have been melted and the heat is being evenly distributed. If crystals reappear, merely apply heat and remelt. One component systems should not be heated as product damage or curing may occur. Controlling and monitoring shipping and storage conditions is critical for minimising temperature fluctuations. Good housekeeping is another factor as container spouts, spigots and closures must be kept free of resin buildup to prevent crystal formation here as well. While epoxy compounders and end users have heightened their awareness to crystallisation it still remains very difficult to accurately predict or eliminate. If crystallisation remains a recurrent problem, products less prone to crystallise may have to be evaluated as alternatives.