Crystallization-Resistant Epoxy Resins

Epoxy Resin Crystallization: An Overview

Crystallization is a frequent aggravation for those who work with epoxy resins. The signs are unmistakable: slightly cloudy resin, grainy sediment sinking to the bottom, or—worst of all—resin that has completely solidified. In most cases, careful warming will reverse the process. However, warming costs time and energy, and with certain epoxy resin systems and additives, warming isn't an option so the crystallized resin goes to waste.

Why does crystallization happen? Liquid epoxy resins (either based on DGEBPA[1] or DGEBPF[2]) are super-cooled liquids at room temperature. A super-cooled liquid is below its freezing point, yet not solid. Such liquids will crystallize in the presence of either a seed crystal or some other type of nucleus around which a crystal structure can form. Lacking any such nucleus, the liquid phase will be maintained down to the temperature at which dynamic arrest occurs.

[1] DGEBPA = diglycidyl ether of bisphenol-A (e.g., EPON Resin 828) [2] DGEBPF = diglycidyl ether of bisphenol-F (e.g., EPON Resin 862)

Crystallization-Resistant Epoxy Resins

Certain epoxy resin characteristics—such as molecular weight, viscosity, or the presence of additives or modifiers—affect their propensity to crystallize. Hexion Inc. (Hexion) supplies options for minimizing crystallization in many situations, as well as systems that have increased resistance to crystallization. (See Table 1.)

Table 1 : Attributes Affecting Epoxy Resin Crystallization

Product	Attribute	Remarks
Increase resistance to crystallization		
EPON Resin 830	High MW/high WPE (DGEBPA)	WPE >195
EPON Resin 862	DGEBPF	Nucleation resistant; exhibits slow growth after nucleation; avoid HELOXY Modifier 61
EPON Resin 863	DGEBPF	Improved crystallization resistance; viscosity 65 – 95 P (similar to EPON Resin 862); avoid HELOXY Modifier 61
EPON Resin 824	Specialty low viscosity epoxy resin	Viscosity 40 – 70 P; alternative to EPON Resin 862 (but chemical resistance may be lowered); adding HELOXY Modifiers might increase tendency to crystallize
HELOXY Modifier 62	Cresyl glycidyl ether	Aromatic glycidyl ether modifier that offers improved crystallization resistance vs. most other modifiers.
Decrease resistance to crystallization		
EPON Resins 825 and 826	Low MW/low WPE, high purity, BPA-based resins, presence of seed crystals	Crystallization has been observed with these resins; if seed crystals are present from earlier batch then this will accelerate crystallization
HELOXY Modifier 61	Lower viscosity from reactive diluents or modifiers such as butyl glycidyl ether, presence of seed crystals	Adding this modifier may increase the likelihood of crystallization; if seed crystals are present from earlier batch then this will accelerate crystallization

High Molecular Weight Resins to Reduce Crystal Formation

Higher molecular weight resins, such as EPON™ Resin 830, inhibit crystal formation. As the average molecular weight of an epoxy resin (weight per epoxide or WPE) increases, the percentage of higher molecular weight polymers and isomers increases. These isomers and higher molecular weight species reduce the tendency for crystal formation and growth. For this reason, DGEBPA and DGEBPF epoxy resins with WPE values higher than 195—such as EPON Resin 830—are typically considered to be crystallization-resistant.

Solutions to Reduce Crystallization When Low Viscosity is Desired

Lower viscosity, such as that induced by reactive diluents or modifiers, encourages crystal formation and growth because it enhances chain mobility and alignment into a crystal structure. Other additives, such as modifiers and wetting agents, can also affect the rate of crystal formation and growth. Generally, though, if seed crystals are excluded, crystallization will be rare.

For reduced crystallization where low viscosity is desirable, Hexion has developed EPON™ Resin 824 and blends of EPON™ Resins 828 and 862.

EPON Resin 824 is a DGEBPA resin chemically-modified to reduce viscosity to the EPON™ Resin 826 range (40 - 70 Poise). This resin has a greatly reduced tendency to crystallize and can be used in many applications where EPON Resin 826 is used. Furthermore, if EPON Resin 824 is modified with HELOXY Modifiers, crystallization resistance of the system may be affected.

Hexion also offers blends of EPON Resin 828 and EPON Resin 862. These materials show superior resistance to crystallization and have viscosities in the same range as EPON Resin 826 (65 – 95 P). Blends of EPON Resin 828 containing 40% to 80% wt of EPON Resin 862 generally remain crystal-free under laboratory and field conditions.

A Modifier to Decrease Crystallization in Low-Molecular-Weight Epoxy Resins

Crystallization of low molecular weight, high purity, BPA-based resins has been observed. Specifically with EPON™ Resins 825 and 826—DGEBPA crystals are formed. EPON Resin 828 is generally considered to be resistant to crystallization, although the use of certain viscosity modifiers also increases its crystallization tendencies as well. Modification of lower viscosity resin blends with butyl glycidyl ether (HELOXY™ Modifier 61) increases the likelihood of crystallization. Modification with cresyl glycidyl ether (HELOXY™ Modifier 62), on the other hand, can help low molecular weight resins resist crystallization.

Epoxy Resins That Decrease Crystallization by Resisting Nucleation

Hexion also offers two nucleation- resistant epoxy resin options—EPON Resin 862, and EPON™ Resin 863. Although EPON Resin 862 is capable of crystallization, it typically resists nucleation and exhibits slow growth after nucleation, resulting in a smaller amount or a small lower layer, slurry of crystals. For greater crystallization resistance, Hexion offers EPON Resin 863. Note, however, that if EPON Resins 862 or 863 are diluted with HELOXY Modifier 61, crystallization can occur more readily. Crystals of Bisphenol-F epoxy resins have a high melting point—80 - 85 °C—making reconstitution difficult.

Prevention of Epoxy Resin Crystallization: Storage Temperature

Proper storage temperatures can minimize epoxy resin crystallization. Within temperature ranges between the glass transition point (-10 to -20 °C / 14 to -4 °F) and the crystallization melting point (45 to 50 °C / 113 to 122 °F), crystallization of DGEBPA resins is possible. Therefore, to prevent crystallization, DGEBPA resins should be stored at temperatures above 50 °C (122 °F). However, temperatures no greater than necessary should be used, to prevent WPE changes during storage. Blends of DGEBPF resins with HELOXY™ Modifiers 8 and 61 show a greater tendency to crystallize and should not be stored below 25 °C. If aromatic modifiers are acceptable, blend epoxy resins with HELOXY Modifier 62 for improved crystallization resistance.

How to Remove Crystallization in Epoxy Resins

For DGEBPA resins that have crystallized:

Crystals of DGEBPA will melt in the range of 45 to 50 °C / 113 to 122 °F, so careful warming of crystallized epoxy resin can eliminate the crystals. Carefully heat the tank, drum or pail to 140 °F (60 °C) for at least one hour to melt any crystalline material. Ensure that all associated piping, pumps, etc. are heated similarly. This heating will eliminate any crystals from the system that could nucleate additional crystal growth. If heated storage of resins is possible, temperatures slightly greater than 122 °F (50 °C) should be maintained to prevent seed crystal formation.

For unmodified DGEBPF resins that have crystallized:

Heat the tank, drum, or pail to 180 - 190 °F (88 °C) for at least one hour to melt any crystalline material (CAUTION: Any other materials that have been added to the resin may be adversely affected by these temperatures; hazardous polymerization or decomposition may result). Ensure that all associated piping, pumps, etc. are heated similarly. This heating will remove any crystals from the system that could nucleate additional crystal growth. If the resin is stored heated, the lowest effective temperature should be used.

CAUTION Any materials or modification that might have been made to either the DGEBPA resin or the DGEBPF resin could be adversely affected by heating above room temperature. In the extreme case, hazardous polymerization or decomposition is possible (depending on the type and level of modification). Do not heat epoxy resins that have been modified or formulated unless you have consulted with the appropriate raw material supplier(s) to understand the potential effects of heat treatment on the raw material or blends of the raw material with the epoxy resin.

Hexion: Helping you make it in today's world.

Our global team produces the best in specialty chemicals and performance materials and provides the technical expertise to customize them to your exact needs. The result? Specific solutions, not generic products, leading to thousands of breakthroughs that improve bottom lines and enhance lives.

Reach our Global Customer Service network at:

U.S., Canada and Latin America
+1 888 443 9466 / +1 614 986 2497
E-mail: 4information@hexion.com

Europe, Middle East, Africa and India
+800 836 43581 / +40 212 534 754
E-mail: 4information.eu@hexion.com

China and Other Asia Pacific Countries
+800 820 0202 / +60 3 9206 1551
+60 3 9206 1543
E-mail: 4information.ap@hexion.com

Please refer to the literature code HXN-712 when contacting us.

HEXION™

World Headquarters
180 East Broad Street
Columbus, OH 43215-3799

HXN-712 01/15.