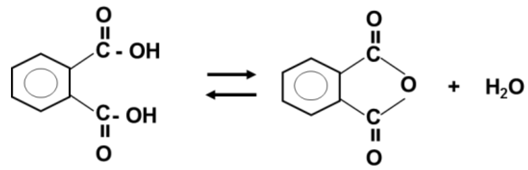
ANHYDRIDE CURED-EPOXY MATRICES

Introduction/Background

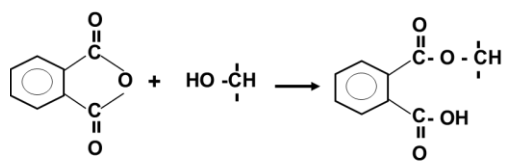
Epoxy resins can be cured with a variety of compounds called curing agents which are also known as curatives, hardeners, or converters. One of themost widely used classes/types of curing agents for epoxy resins is anhydrides. These acid anhydride curing agents are derived from the elimination of water from diacids as shown below. This is a reversible reaction. Therefore, anhydride curing agents must be adequately protected from moisture since they will revert to the diacid.



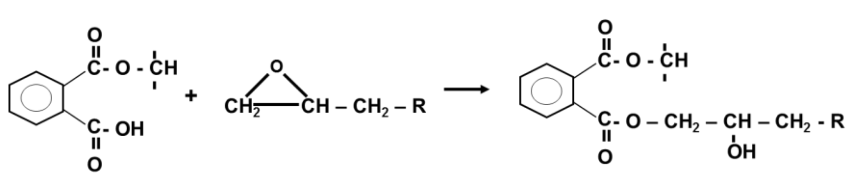
Phthalic Acid Phthalic Anhydride

If diacid is present, it will increase the reactivity with epoxy resin and may affect cured properties. As with amine cured epoxy resins, anhydride cured epoxy resins produce a heteropolymer consisting of epoxy molecules linked together through the reactive sites of the anhydride curing agent. The majority of anhydrides used for curing epoxy resin matrices are liquids but solid dianhydrides also find limited use as curing agents in fiber reinforced composite applications. The reactivity of most liquid anhydride curing agents with epoxy resins is very slow without the addition of a catalyst, even at high temperature. Different from amine curing agents, the reaction mechanism of anhydrides with epoxies is complex and subject to many competing reactions. Some of the variables affecting the reaction mechanism include, the gel time and temperature, post-cure time and temperature, type and concentration of accelerator, hydroxyl concentration present, ratio of anhydride to epoxy (A/E ratio), amount of free acid, and type of epoxy resin. While there are many possible reactions with epoxy resins, the 3 major reactions are shown below using phthalic anhydride as an example.

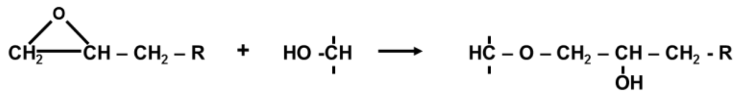
Secondary alcohols from the epoxy backbone or other alcohols (aliphatic) react with the anhydride forming a monoester.



The corresponding carboxylic acid can then react with an epoxy group forming a diester.



A competing reaction is epoxy groups reacting with a secondary alcohol forming an (β-hydroxy) ether linkage.



The secondary alcohol may be a product of esterification or on the backbone of the epoxy. If the equivalents of anhydride used to cure the epoxy is less than one, the tendency for etherification increases. In relation to the catalyst type, acid catalysts tend to promote more etherification than basic catalysts. The cure cycle also has a significant effect on the reaction mechanism. It is possible that systems gelled at lower temperatures may have more etherifcation, where higher temperature holds predominantly result in esterification. Ether linkages have much better thermal stability as compared to ester linkages. While the cure cycle and gelation temperature may not noticeably influence the thermal or chemical stability of API's formulated anhydride cured epoxy resin systems to a great extent, it may be worth experimenting with the cure cycle with this in mind. In general, the first two reactions shown above are the dominant reactions occurring in anhydride cured epoxy resin systems, with etherification occurring to a much lesser extent.

The anhydride curing agent(s) along with selection of the epoxy type, backbone, and functionality dictate the physical and mechanical properties of the matrices. Depending on the formulation, a wide range of characteristics can be designed ranging from crystal clear (i.e. water white) matrices, having high UV stability, to thermally stable, high glass transition temperature systems. It is these characteristics, UV and thermal stability, along with lower cure exotherm, and lower cure shrinkage, that set these materials apart from amine cured epoxy matrices. Another advantageous feature of anhydride cured epoxy systems is the high mix ratio of anhydride (Part B) to epoxy resin (Part A). This dramatically lowers the viscosity of the mixed resin system which is beneficial to many composite processes. In some cases, the anhydride component (Part B) may be greater than the epoxy component (Part A). Therefore, special attention is required when mixing these resins if most of the users experience has been with two part amine systems, which almost always require lower amine (Part B) ratios. A further advantage, however, is that if the mix ratio is off a little for the anhydride, the cured properties will not be as affected as with amine cured matrices.

While anhydride cured epoxy systems offer many benefits when compared to amine cured epoxies, there are some notable drawbacks that limit utilization in many applications. In an uncured state, anhydrides react almost instantaneously with water, which limit their use in processes that have extended open time to humidity. Further complicating the use of anhydride cured epoxy systems is that the reaction mechanisms are influenced by the cure cycle and they have no cure end-point. Different from amine cured epoxy systems, anhydride cured epoxy systems continue to react at the cure temperature and may never become theoretically vitrified. Probably the greatest drawbacks of cured anhydride cured epoxy matrices is the ester linkages, which are susceptible to hydrolysis given the conditions of high humidity or water in combination with high temperature. If the matrix is exposed to high temperature in the presence of water (pressure), the matrix can dissolve and can revert back to a liquid in as little as 24-48 hours.

Acid anhydrides are used in many fiber reinforced composite processes including filament winding, pultrusion, VARTM, and RTM. Due to their moisture sensitivity, the use of anhydrides is limited in prepreg systems. If anhydrides are used as curing agents in epoxy prepregs, solid powdered dianhydrides are most common. The use of poly-films on both sides of the material is usually necessary so that it is not contaminated by moisture. Most commonly, two part epoxy (Part A) and anhydride (Part B) resin systems are used for manufacturing advanced fiber reinforced composites. In applications such as filament winding, the time to over wrap the adjacent layer should be minimized if manufacturing is performed in a humid environment. Furthermore, if resin baths are used (e.g. infusion or pultrusion), especially having large surface area to volume, it is best to use the mixed product as fast as possible, adding more as needed. Covering the mixed product to protect from a humid environment is also good practice. In normal manufacturing environments having controlled temperature and humidity, these issues will not be of concern. In all cases, containers of the anhydride curing agent (Part B) must be adequately sealed from the atmosphere during storage and after use. Also, moisture can cause some anhydride curing agents to crystallize and can cold temperatures. It is always best to discuss proper storage conditions with API if not familiar with these types of curing agents.

Shown below is a summary of some of the main advantages and disadvantages of anhydride cured epoxy systems. Please read all material safety data sheets (MSDS) before using the product.

ADVANTAGES

- Long pot-life
- Low cost
- Low viscosity
- Excellent wetting and adhesion
- Excellent thermal stability
- Low cure shrinkage
- Low exotherm

DISADVANTAGES

- Reaction (uncured) with water
- Moderate stiffness and strength
- Process dependent cure mechanisms and properties - no cure end point
- Hydrolysis of cured matrices
- Never used as matrix for structural commercial airplane/aerospace composites - no data base

Comments & Questions: Please call 707 747 6738 or email at service@poleramic.com

This information is for educational purposes only. API does not take any responsibility for actions made by any party by or from the utilization of information contained in this document.