



Virantage® PESU Epoxy Tougheners for Prepreg Manufacturing

Virantage® polyethersulfone (PESU) is an amorphous, high-temperature thermoplastic that offers excellent thermal and hydrolytic stability. PESU micropowders are used as an additive to improve the toughness and damage tolerance of epoxy composite systems used for applications requiring high strength and low weight. These high-performance tougheners are widely used in prepreg production for latest-generation commercial aircraft, military aircraft, automotive and other advanced transportation systems.

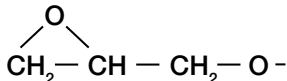
This document discusses PESU's chemical compatibility in epoxy composite systems as well as formulation techniques used to optimize PESU's effectiveness as a toughening agent for prepreg manufacturing for aerospace applications.

The Basics of Epoxy Resins

Epoxy resins are a class of materials that are characterized by the presence of epoxide functional groups. A typical example is bisphenol A epoxy (Figure 1), commonly referred to as a diglycidyl ether of bisphenol A (DGEBA). Glycidyl ether refers to the epoxide functionality at the ends of the bisphenol A backbone (Figure 2).

The epoxide group can react with either another epoxide on an adjacent polymer chain (homopolymerization) or with a co-reactant curative or hardener. Typical classifications of curatives include polyfunctional amines, acid anhydrides, phenols, alcohols, and thiols.

Figure 2: Glycidyl ether functionality



Cross-linking that occurs during the curing reaction connects random polymer chains in the epoxy resin, resulting in a thermoset or infusible material that exhibits superior mechanical, thermal, and chemical resistance properties. The various stages of the curing reaction will be discussed in greater detail below.

Multi-functional Epoxies and Hardeners

High-performance structural composites for the aerospace industry typically use multi-functional epoxy resins in combination with aromatic amine hardeners to achieve the desired combination of mechanical, thermal, and environmental properties. Typical multi-functional epoxies include triglycidyl ether of amino phenol (TGAP) and tetraglycidyl ether of diamino diphenyl methane (TGDDM), which are shown in Figure 3. Typical aromatic amine hardeners are isomers of diamino diphenyl sulfone (DADPS), which is shown in Figure 4.

Figure 1: Bisphenol A epoxy resin

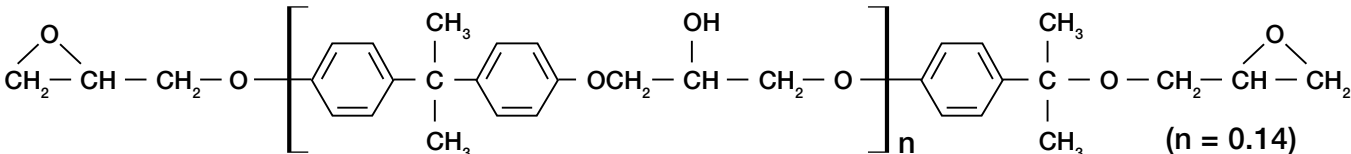


Figure 3: Multi-functional epoxy resins

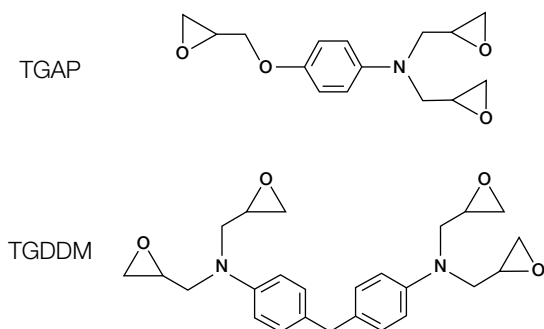
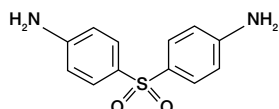


Figure 4: Diamino diphenyl sulfone (DADPS)



Stoichiometry and Mixing Issues

The epoxy-to-hardener mix ratio (stoichiometry) can be adjusted from the theoretical 1:1 ratio of amine hydrogens in the hardener to epoxide groups in the epoxy to optimize processing characteristics such as viscosity and shelf life, while retaining the desired cured properties.

Since the amine-epoxide reaction is exothermic, precise control of the mixing conditions to avoid localized hot spots is extremely important. The goal is to provide sufficient heat and agitation in order to achieve a homogeneous mixture of epoxy and hardener, while minimizing the progression of the curing reaction. The minimally reacted epoxy-hardener system is referred to as a B-stage resin, which is discussed later in this document.

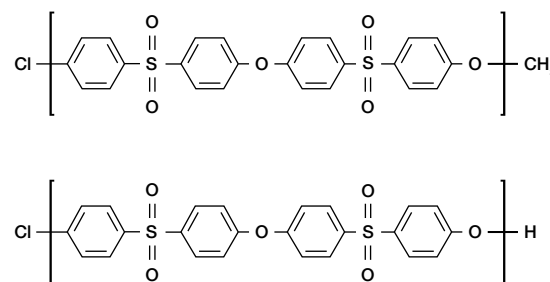
Toughened Epoxy Resin

To achieve the desired combination of mechanical, thermal, and environmental properties required in high-performance composites, the epoxy-hardener system must be further modified to overcome the inherent brittleness of the epoxy-hardener system. A variety of toughening additives have been developed that include butyl-nitrile rubbers or thermoplastic resins.

PESU is a thermoplastic resin that is one of the most effective toughening additives commercially available. It provides excellent resistance to heat and moisture, while maintaining the desired mechanical properties of the resin formulation.

PESU resin is produced both as a non-functionalized and a hydroxyl-functionalized resin (Figure 5), and both of them can be used as toughening additives.

Figure 5: Non-functionalized PESU and OH-functionalized PESU



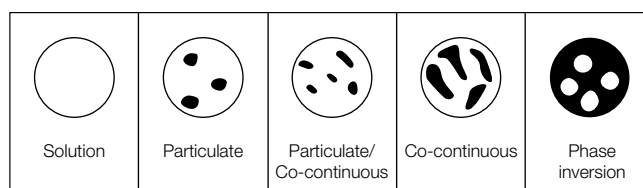
Adding PESU to the A-stage epoxy resin-hardener formulation (unreacted system) should result in the complete dissolution of the PESU into the formulation. Failure to fully dissolve the PESU toughener will result in a defective cast resin film and ultimately a poor quality prepreg part.

Dissolution of the PESU additive is greatly facilitated by preparing the PESU with a controlled, small particle size distribution. The maximum recommended PESU particle size is about 150 microns. A maximum dissolution temperature of 120 °C is recommended.

Toughened Epoxy Morphology

As the resin formulation proceeds through the B-stage condition (described below) to its ultimate C-stage or fully-cured condition, PESU's solubility in the thermoset matrix decreases. This results in a fully-cured system having a complex, sea-island morphology (Figure 6) with PESU islands surrounded by a sea of the thermoset epoxy formulation.

Figure 6: Illustration of epoxy-hardener-PESU morphology development



This particular morphology effectively toughens the resin formulation due to the uniform distribution of the PESU islands and their strong adherence to the surrounding thermoset matrix. The continuous morphology has been found to produce the optimal combination of toughening and mechanical performance. The PESU islands serve to blunt the propagation of cracks that would otherwise result in a brittle failure of the composite. Although the precise mechanism of this toughening effect has not been rigorously established, the utility of the PESU toughener has been demonstrated repeatedly in a range of high-performance composite applications for over 25 years.

Formulators must manage the conflicting desires of extending the working life of the resin formulation (so-called pot life) versus achieving a fully-cured C-stage as quickly as possible. Precise control of the stoichiometry, mixing conditions, and cast film storage is required as well as careful selection of prepreg and composite process conditions to optimize the conflicting pot-life and full-cure desires.

Mixing Hardware

There are several considerations when selecting the appropriate mixing equipment and operating conditions. Mixing equipment that provides vacuum capability with anchor agitation or planetary agitation is best suited to accomplish the needed dispersion of hardener and toughener in the epoxy resin formulation. Heating the liquid epoxy resin prior to and during dissolution improves the rate of dissolution of the hardener and toughener additives as well. As previously noted, precise control of mixing temperatures, uniform agitation, and a metered rate for adding components are essential to producing high-quality epoxy formulations for prepreg production.

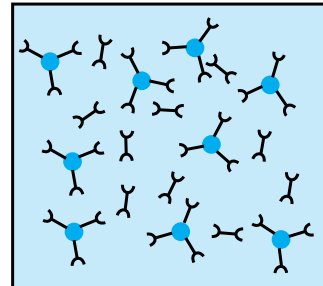
Once the mixing and dissolution of the hardener and toughening additives have been completed, the highly reactive resin mixture should be processed immediately into a cast film and chilled to -18°C to preserve its pot life for subsequent prepreg production; other chilling options are noted later in this document.

Prepreg Production with Toughened Epoxy Resin and Reinforcing Fibers

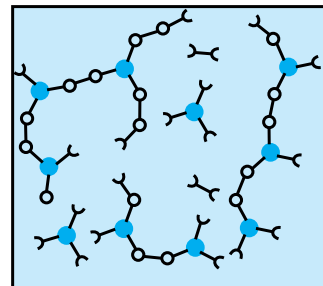
As epoxy resin formulations are prepared for prepreg manufacturing, the curing reaction is conducted in a series of stages to effectively combine the epoxy resin matrix with the prepreg reinforcement, which is typically carbon, glass, or aramid fibers. These stages are referred to as A-stage, B-stage, and C-stage. Figure 7 illustrates the development of the curing reaction as the epoxy-hardener system progresses from an uncured A-stage to a partially-cured, but still fusible B-stage, and fully-cured C-stage (thermoset condition).

The so-called gel point occurs when the curing reaction is approximately 60% complete, and it represents the condition when the polymer system can no longer be melted. If the prepreg reaches this point prior to being assembled into a cured composite, it will have lost its ability to be adhered to in successive laminate layers, and it is usually scrapped.

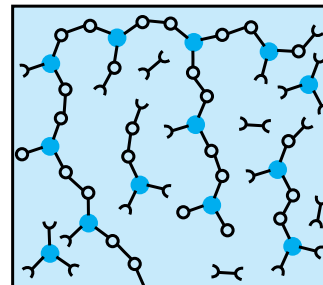
Figure 7: Curing stages



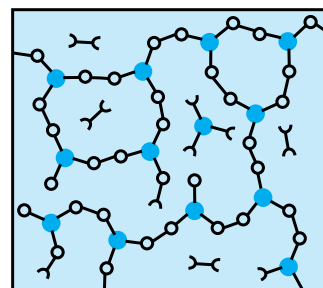
A-stage epoxy resin
(uncured)



B-stage epoxy resin
(partially-cured, but
still fusible)



Epoxy resin becomes
infusible (gel point)
around 60% cure



C-stage epoxy resin
(fully-cured, infusible)

Figure 8: Typical hot-melt resin film production

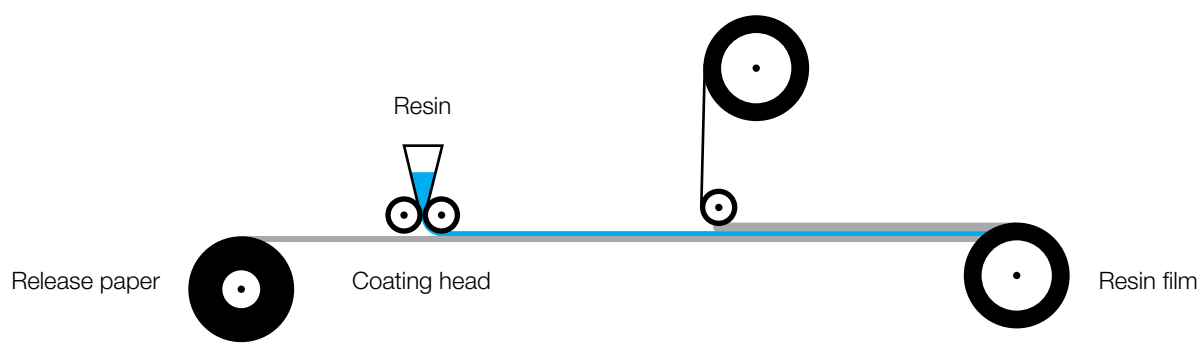
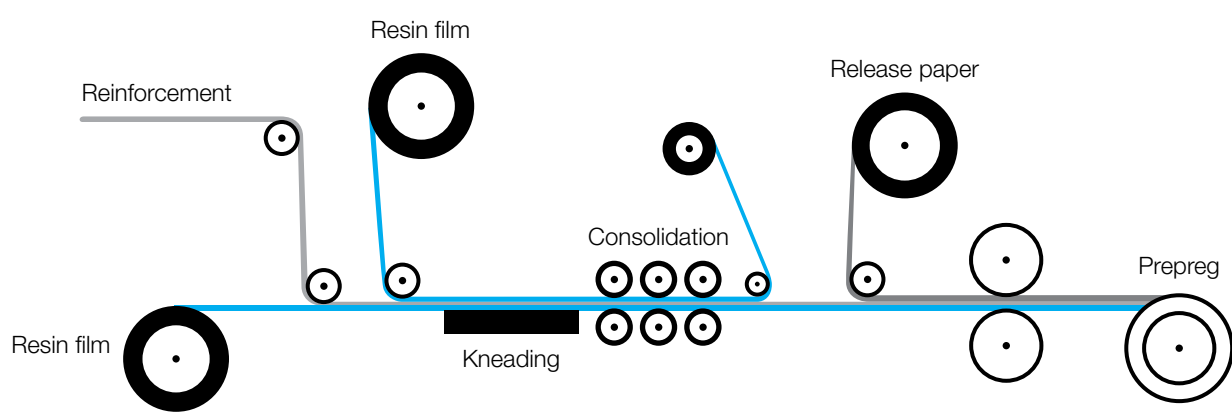


Figure 9: Typical hot-melt prepreg tape production



Hot-melt Prepreg Processes

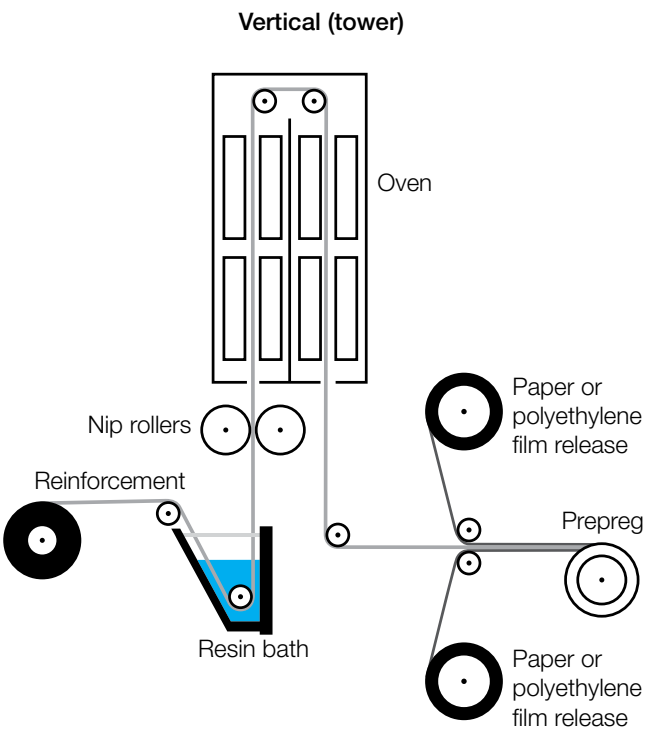
In a prepreg operation, the epoxy resin formulation can be processed using either a hot-melt prepreg process (Figures 8 and 9) or a solution prepreg process (Figure 10). In the hot-melt prepreg process, the A-stage resin formulation is melted and cast onto release paper as a thin film. This melting and casting operation advances the formulation into the B-stage cure. To preserve as much shelf life as possible, typically the cast film is immediately chilled to -18 °C to minimize further curing reaction in the cast film. The film may then be stored for a finite period.

In a subsequent operation, after the resin film is warmed to ambient conditions, it is combined with a web of reinforcement fibers to produce a sandwich, which results in the impregnation of the B-stage epoxy formulation into the web of reinforcement fibers. Impregnation is accomplished by passing the sandwich of B-stage resin film and web of reinforcement fibers through a series of heated compaction rolls that cause the resin to melt and wet out the reinforcement web. This melting operation causes the B-stage resin to continue to cure, requiring the prepreg sandwich to be immediately chilled upon completion of the impregnation to delay advancement of the curing reaction.

Next, the cooled prepreg tape is covered with release paper, collected as a roll, packaged, and immediately placed in a -18 °C freezer to halt the curing reaction. Freezer storage at this temperature typically allows

a shelf life of about six months. However, if the prepreg is allowed to remain at ambient conditions, the curing reaction will proceed to beyond the gel point within a few days. As a result, the prepreg tape loses its tackiness, becoming stiff and unusable for composite laminate production.

Figure 10: Typical solution prepreg tape production



Solution Prepreg Processes

In the solution prepreg process, the A-stage resin formulation is dissolved into a solvent system to produce a high-percentage solids solution. The web of reinforcement fibers is then drawn through the resin formulation solution and into a drying/curing oven. In the oven, the solvent is evaporated and the reinforcement web-resin formulation sandwich is advanced into a B-stage condition. The sandwich is allowed to cool to ambient conditions to delay completion of the curing reaction. Next, the cooled prepreg tape is covered with release paper, collected on a roll, packaged, and immediately placed in a -18°C freezer for the same reasons previously discussed for the hot-melt prepreg process.

Safety Considerations

The epoxy-hardener reaction is highly exothermic, and a substantial amount of heat is generated when formulating large quantities of epoxy resin. Continuous monitoring and careful temperature control of the mixing operation is essential in order to prevent a runaway exothermic reaction.

Even at ambient conditions, the rate of the epoxy-hardener reaction is fast. Formulations should be stored at -18 °C at all times in order to minimize the progression of the curing reaction.

Proper protective equipment must be worn when working with epoxy-hardener systems as contact can produce contact dermatitis if not handled properly in a well-ventilated workspace. Always ensure that epoxy formulations are handled and stored under recommended conditions. See the respective safety data sheets (SDS) for more information.

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