



SOLVAY
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Selection and Processing Guide

Virantage® PESU Tougheners

High-performance composites are used in demanding structural applications that require sustained stiffness and high specific strength when exposed to high temperatures and aggressive environments. Typical application areas include aerospace, military aircraft, automotive, and wind power generation.

Thermoset epoxies such as bisphenol-A diglycidyl ether (DGEBA), triglycidyl-p-aminophenol (TGAP) and tetraglycidyl diamino diphenylmethane (TGDDM) offer strength, stiffness, chemical resistance, high glass transition temperature and hot-wet performance. However, these desirable properties are often achieved at the expense of toughness, which can lead to low damage tolerance in carbon fiber reinforced epoxy composites.

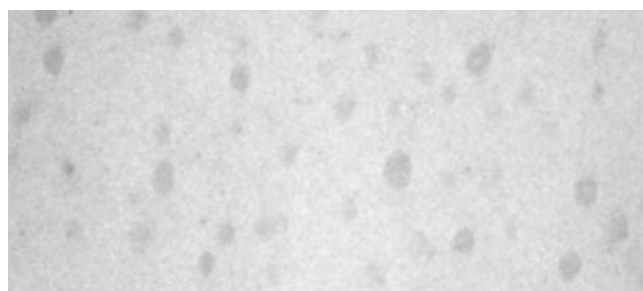
High-temperature thermoplastics such as Virantage® polyethersulfone (PESU) improve the toughness of epoxy systems while retaining high modulus, high temperature capability, hot-wet performance and resistance to aggressive environments.

Toughening Mechanisms

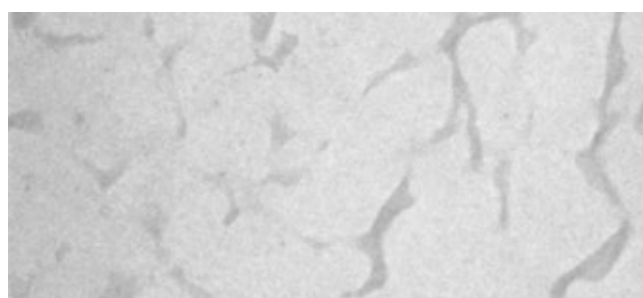
Although controversy exists in scientific literature concerning the exact mechanisms associated with the improvement of fracture toughness of epoxies with high-performance thermoplastics, a few points are widely accepted. When reactive PESU (r-PESU) is used to toughen epoxy systems, a phase-separated morphology

within the resin matrix occurs. This multi-phase morphology (Figure 1) is necessary to achieve improved toughness. A co-continuous morphology is believed to be the most effective.^{1,2}

Figure 1: Micrographs of two-phase morphology in a PESU/TGAP epoxy system



Discrete two-phase morphology using 10 % r-PESU



Co-continuous two-phase morphology using 15 % r-PESU

Table 1: Typical properties of Virantage® PESU tougheners

Virantage® Grade	Molecular Weights by GPC [g/mole x 1,000]	Solution Viscosity 25 % in DMAc at 40 °C [cP]	OH End Groups [micro-equiv/g]	Residual Solvent [%]
VW-10200 RP	45	600	68	0.3
VW-10300 P	55	700	Not applicable	0.5
VW-10700 RP	22	80	159	0.3
VW-30500 RP	14	30	400 ⁽¹⁾	0.5

⁽¹⁾End groups for VW-30500RP are amine (NH₂), not hydroxyl (OH)

Figure 2: Fracture toughness as a function of molecular weight

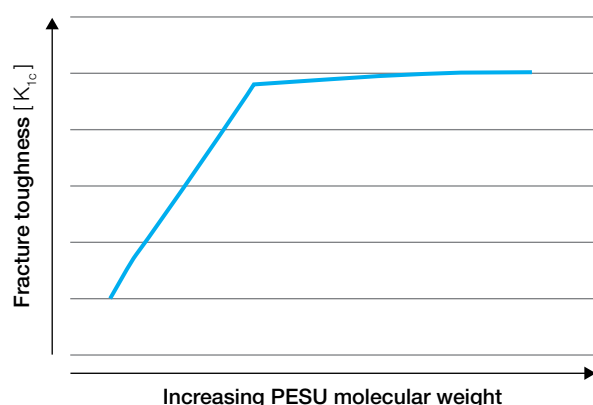
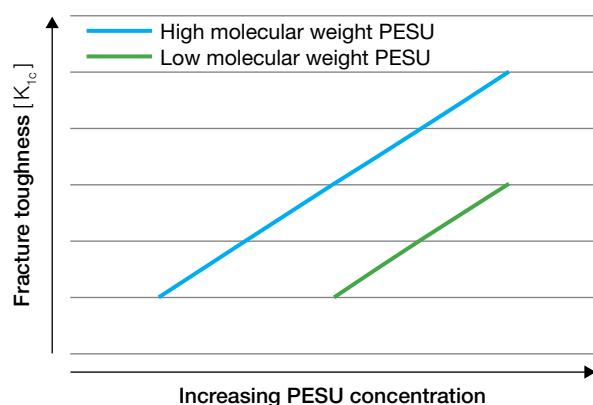


Figure 3: Effect of concentration on fracture toughness



The toughening efficacy of PESU depends on concentration, molecular weight and difference in molecular weight between PESU and the epoxy.^{3,4}

Typical relationships between molecular weight, concentration and toughness are shown in Figures 2 and 3. The epoxy fracture toughness (K_{IC}) can be increased by a factor of 2 to 3 by adding 10 % – 30 % PESU to the resin matrix, according to a number of literature citations.

A co-continuous phase occurs at a loading level of 15 % – 20 % depending on the system and the molecular weight of the additive. Higher molecular weight PESU forms a robust second phase and then a co-continuous phase at lower loading levels than low molecular weight PESU. Low molecular weight products are often used to offer toughening with minimal impact on the epoxy system viscosity.

Product Selection

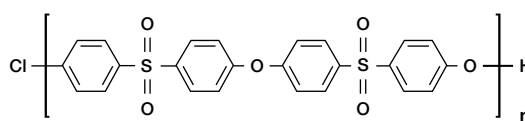
Building on over 40 years of experience developing and manufacturing sulfone polymers, Solvay has introduced a family of PESU, sulfone-based epoxy tougheners that are marketed under the Virantage® trade name. Available in reactive and non-reactive grades, these powdered materials offer a number of key performance attributes and enhanced processability:

- High modulus at elevated temperatures
- High glass transition temperature of 220 °C (428 °F)
- High toughness and ductility (> 50 % break elongation)
- Thermal stability and retention of properties after long-term exposure
- Outstanding hydrolytic stability
- Broad chemical resistance
- Reactive functionality

Virantage® VW-10200 RP

A hydroxy-functionalized PESU with a weight average molecular weight of 45,000 g/mole. The basic structure of this high molecular weight product is shown in Figure 4.

Figure 4: Repeating unit structure of hydroxy-functionalized r-PESU



Virantage® VW-10300 P

A non-reactive PESU for use where reactive functionality is not desired.

Virantage® VW-10700 RP

Based on the same chemistry as VW-10200 RP but is approximately half the molecular weight with 3 to 4 times higher level of hydroxy-functionality.

Virantage® DAMS VW-30500 RP

A low molecular weight macromeric sulfone polymer grade based on the backbone of polysulfone. The structure is shown in Figure 5.

Figure 5: Repeating unit structure of Di Amino Macromer of Sulfone (DAMS)

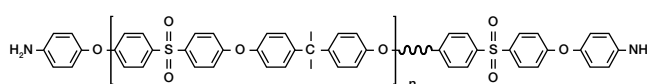


Table 2: Particle size distribution

Virantage® Grade	Typical Particle Size D90 [μm]
VW-10200 RP	500
VW-10200 RFP	65
VW-10200 RSFP	38
VW-10700 RP	500
VW-10700 RFP	75
VW-10700 RSFP	45

Virantage® PESU tougheners can be micronized down to 45 microns in diameter. Micronizing facilitates efficient dissolution of the polymers into the epoxy resin. Since the surface area increases by the square of the change in radius as the particle size is reduced, significant reductions in dissolution time can be realized by reducing the particle size of the r-PESU. VW-10200 RP and VW-10700 RP are offered in reactive fine particle (RFP) and reactive super fine particle (RSFP) grades for even faster dissolution.

In addition to Virantage® products, Solvay offers a number of other chemistries for use as tougheners for high-performance composites: Torlon® polyamide-imide (PAI), KetaSpire® polyetheretherketone (PEEK), Radel® polyphenylsulfone (PPSU), and Udel® polysulfone (PSU). Please visit our website or contact your Solvay Specialty Polymers representative for additional information.

Rheology

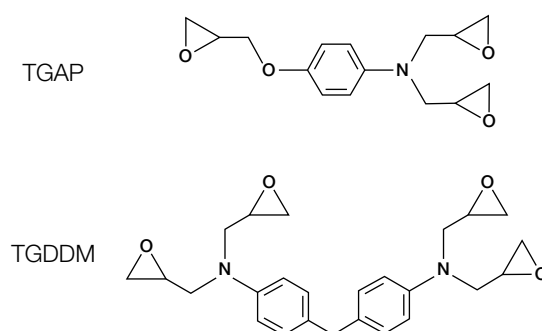
Adding high molecular weight sulfone polymer increases the viscosity of an epoxy solution. The change in viscosity may require some modifications to the subsequent composite preparation processes. This effect is most relevant to resin transfer molding (RTM) systems where low viscosity is critical.

The change in viscosity depends on the concentration and molecular weight of the additive. Lower molecular weight VW-10700 RP epoxy solutions are substantially lower in viscosity than the comparable solids content solutions of VW-10200 RP. VW-30500 RP aminated macromer of sulfone gives epoxy solutions that are even lower in viscosity than the VW-10700 RP systems. The lower solution viscosities of the VW-10700 RP and VW-30500 RP systems provide enhanced processability for both conventional pre-preg and alternative resin infusion and resin transfer molding operations.

It is not possible to anticipate the effects of all the potential formulation permutations containing epoxies, tougheners and other fillers. Therefore, basic guidelines based on commercial systems are provided.

Virantage® PESU tougheners are used in a variety of difunctional and multifunctional epoxy resins. Structures of the two most common epoxy resins are shown in Figure 6. Typical properties are provided in Table 3.

Solution viscosity measurements for each of these epoxies show the effect that the addition of Virantage® r-PESU has on viscosity. Viscosity measurements were taken at 60 °C (140 °F) and 75 °C (167 °F) using a VT-550 viscometer at a shear rate of 30 sec⁻¹ with a MV-DIN spindle/cup.

Figure 6: Structures of TGAP and TGDDM epoxy resins**Table 3:** Typical properties of TGAP and TGDDM neat epoxy resins⁵

Property	TGAP	TGDDM
Equivalents of epoxy/gram	96	115
Viscosity		
cP	710 (at 25 °C)	4,835 (at 50 °C)
Pa-sec	0.71 (at 25 °C)	4,835 (at 25 °C)

Figures 7 and 8 illustrate the effect of increasing sulfone polymer content with the TGAP epoxy at 60 °C (140 °F) and 75 °C (167 °F). Figures 9 and 10 show the effect of increasing sulfone polymer content with the TGDDM epoxy.

The viscosity of a given system can also be altered significantly by changes in temperature. The effect of temperature on viscosity measured using dynamic mechanical analysis with a parallel plate configuration for a TGAP/4, 4' DDS (4, 4'-diaminodiphenylsulfone) system containing almost 20 % of VW-10200 r-PESU is shown in Figure 11.

As with any epoxy system, increasing the temperature will also increase the reactivity and will subsequently reduce the gel time. The two effects must be considered simultaneously when choosing process temperatures.

Figure 7: Viscosities of Virantage®/TGAP at 60 °C (140 °F)

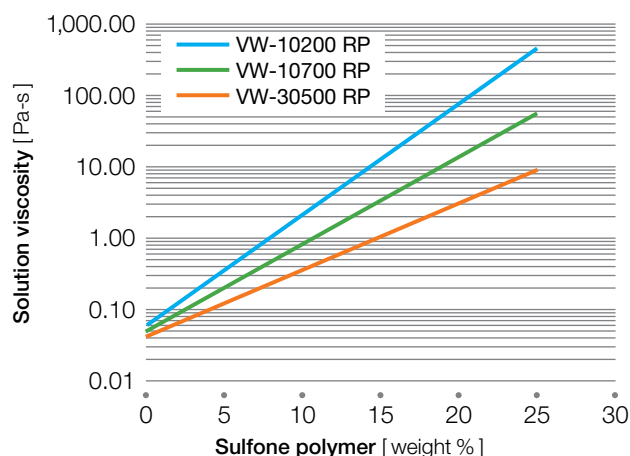


Figure 8: Viscosities of Virantage®/TGAP at 75 °C (167 °F)

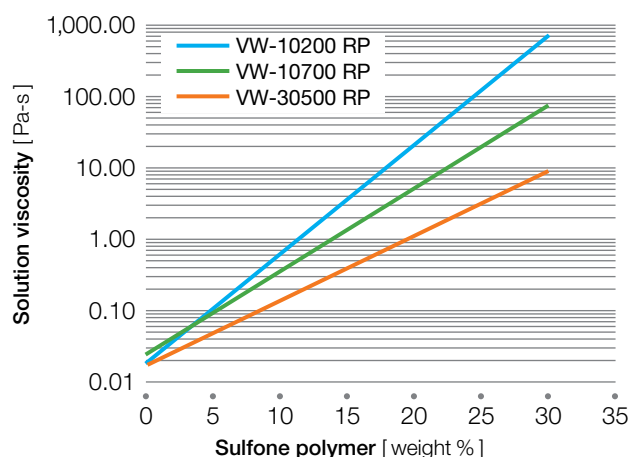


Figure 9: Viscosities of Virantage®/TGDDM at 60 °C (140 °F)

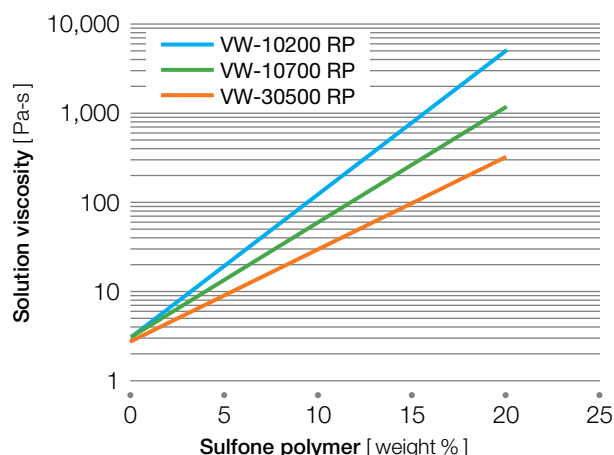


Figure 10: Viscosities of Virantage®/TGDDM at 75 °C (167 °F)

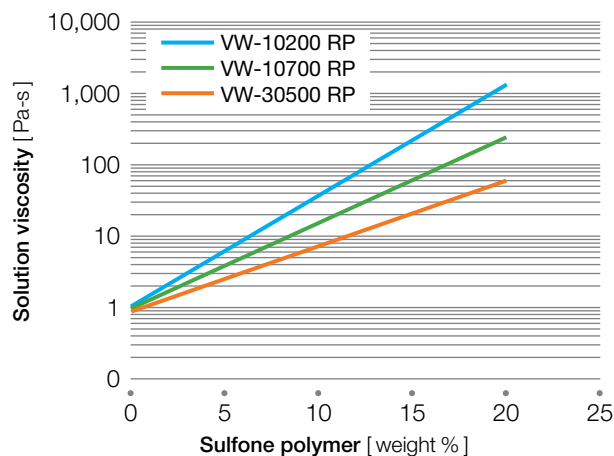
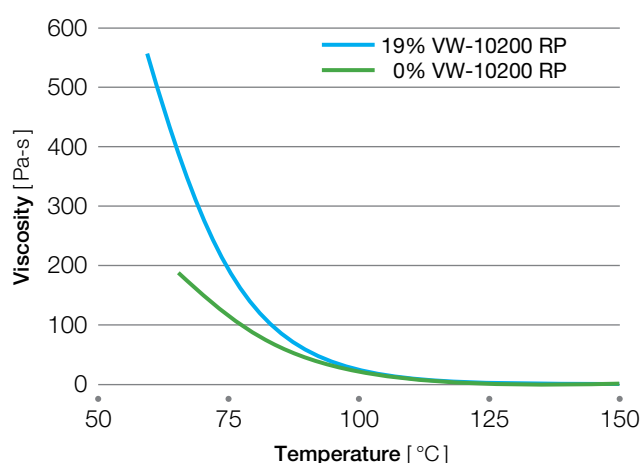


Figure 11: Effect of temperature on viscosity of uncured TGAP/4, 4' DDS system containing VW-10200 RP⁽¹⁾



⁽¹⁾ Viscosities may vary from those shown in other figures due to the addition of 4, 4' DDS, low levels of curing, and test method.

Processing

Storage and Handling

Virantage® products are stable at room temperature and should be stored in a closed container. When preparing epoxy systems using Virantage® PESU tougheners, refer to the epoxy manufacturer's product guidelines for storage and stability information.

Precautions should be taken when handling fine powders in order to prevent dust explosions. Please refer to the material safety data sheet for each product for exact handling and personal protective equipment requirements.

Drying

PESU and other sulfone polymers can absorb small amounts of water and retain up to 2 % moisture at equilibrium. Although they are hydrolytically stable, it is best to dry them prior to processing to remove casual surface moisture. Processing wet resin can result in additional bubble formation during processing.

Virantage® r-PESU products can be dried in any number of commercial powder dryers; the most simple is a circulating hot air oven. Recommended drying times are either 4 hours at 150 °C (300 °F), or 5 hours at 135 °C (275 °F).

Drier inlet air temperature must be high enough to maintain a polymer temperature of at least 135 °C (275 °F), and the dew point of the inlet air should be -40 °C (-40 °F). An air-tight oven equipped with a dehumidifying unit in which the air is recirculated over a drying bed is recommended as the most uniform and efficient drying method.

Air filtration in desiccated dryers is recommended to maintain product cleanliness. It is suitable to leave product in a dryer overnight. Dried resin should be placed in sealed containers to maintain dryness.⁶ After drying, return the polymer to the temperature at which it will be used to avoid creating hot spots in the epoxy system during mixing.

Mixing

This document cannot address the wide variety of formulations that may be prepared with the broad range of commercially available epoxy/hardener systems as well as other additives, catalysts and diluents available. Please refer to product literature for each product to be used in a composition for appropriate guidelines. Basic guidelines are given below.

Virantage® PESU tougheners can be added to a variety of commercial epoxy systems via several different methods. PESU can be directly dissolved in a liquid epoxy system followed by the addition of curing agent. It can also be dissolved in a number of solvents and then mixed with epoxy/hardener systems. PESU may also be adducted with an epoxy using a catalyst followed by the addition of hardener.

Equipment

Commercial mixers used in epoxy processing and food service are recommended as they can offer closed systems with vacuum, good temperature control and excellent mixing capability. Mixers that offer anchor agitation or planetary agitation are recommended. Commercial mixers that offer multiple mixing mechanisms are effective for diverse needs such as dispersion of additives.

Heating

Heating liquid epoxy systems prior to dissolution enhances the rate of dissolution of soluble additives such as PESU. The most efficient heating can be done using a jacketed mixer with temperature capabilities of 100 °C to 130 °C (212 °F to 266 °F). Higher temperatures can be achieved through the use of oil heaters as water-based heaters are limited. Special care should be taken to avoid hot spots during the heating process with slow and consistent stirring.

Charging

If possible, slowly add the PESU powder to the epoxy. Adding powder too quickly will lead to the formation of agglomerates that take longer to dissolve. It can also lead to fouling of equipment and difficulty in ensuring that all of the powder is well mixed. Rapid dumping of large quantities of powder into a liquid epoxy is not recommended.

Dissolution

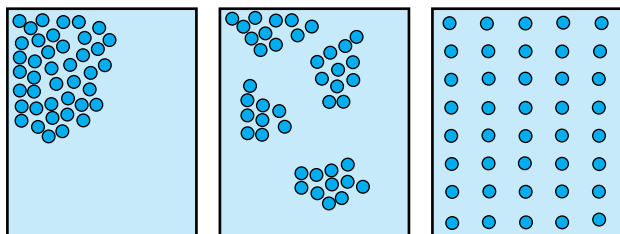
Higher molecular weight polymers take longer to dissolve and result in a higher viscosity solution. Efficient dissolution is ultimately achieved by maximizing the surface area of exposure between the epoxy and toughener. This can be done by reducing the particle size through the use of fine powders, reducing entrained air that can coalesce at the interface between solid particles and the liquid through the use of vacuum, and by optimizing distribution within the mixer. The geometry of the stirring mechanism, agitation rate and temperature will affect the dissolution time.

In order for the addition of PESU to epoxy systems to be effective, excellent distribution is essential. Distribution is more desirable than dispersion, but both mechanisms are often employed in the mixing of epoxy systems, particularly those with inorganic fillers.

Distribution and dispersion are very different mechanisms. Distribution is the act of spreading out "solute" in "solvent", and in mixing, this means to divide continuously until the concentration of an additive is consistent throughout the mixture. Dispersion is the act of breaking up agglomerated substances, and in mixing, this is often done with high shear.

Figure 12: Mechanisms of distribution and dispersion

Distribution in a mixture



Dispersion of additives

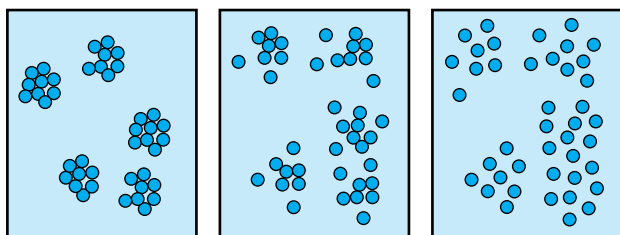


Figure 12 shows the difference between distribution and dispersion. Focus should be placed on efficient distribution. The high shear required for dispersion can result in localized heating which in turn can create hot spots and uncontrolled reactions in epoxy systems.

CAUTION: Extreme caution should be taken when working with epoxy systems to minimize excessive heat. Overheating and generation of hot spots due to shear can cause un-controllable exothermic reactions. When large batches are mixed, refer to specific product literature for temperature limits.

Some epoxy manufacturers also recommend that accelerators should not be used to prevent hot spots if batches are prepared without any dilution by fillers, additives, or solvents.

Solvents

Virantage® PESU is soluble in a number of commercial epoxy systems. In some cases, it is desirable to dissolve PESU, epoxies and other additives in a solvent for viscosity reduction and easier additive incorporation. Suitable solvents for PESU/epoxy blends are shown below:

- N-Methyl Pyrrolidone (NMP)
- N,N Dimethylformamide (DMF)
- N,N Dimethylacetamide (DMAC)
- Acetone*
- Methylene Chloride*

**Acetone and methylene chloride offer limited solubility when dissolving PESU by itself.*

CAUTION: When working with solvents adequate ventilation and appropriate personal protective equipment are required to minimize exposure and risk of fire or explosion. Refer to the manufacturer provided material safety data sheets for handling instructions.

Adducting

Virantage® PESU can be used to create an adduct with epoxy using a catalyst such as triphenyl phosphine at extremely low concentrations.

Degassing

Some applications require that epoxy systems be free of gas or solvents prior to application. Degassing can be conducted in-situ using a closed mixer with vacuum or by degassing after mixing. The temperature should be chosen to allow mobility for any entrained air or solvents and to minimize crosslinking or curing. Degassing should be done in a gentle fashion. Pulling a vacuum too quickly will cause an entire mass of mixture to swell instead of releasing bubbles. This behavior will be even more prominent in higher viscosity mixtures.

Curing

Follow the epoxy manufacturer's recommendations on cure times and temperatures for the specific system in use. Gentle temperature ramps are recommended to prevent the formation of hot spots or runaway reactions.

Although the morphology of toughened epoxy systems depends on concentration and molecular weight of the toughener, it is also highly dependent on the curing kinetics. A multi-phase morphology is necessary for improved toughness, and a co-continuous morphology is believed to offer the most effective toughness.^{1,2} Curing at high temperatures increases the reaction rate and can result in a finely dispersed PESU phase. Curing at lower temperatures allows for the formation of larger domains or co-continuous morphology. Both of these formations will improve the toughening efficacy.

Curing kinetics can be modified by changes in temperature. Accelerators can also be used to reduce cure time. Post curing at 200 °C (392 °F) is often also carried out to complete morphology development which can alter glass transition temperature, modulus and fracture toughness.

Cleaning

Refer to epoxy product data sheets for specific cleaning and disposal recommendations. Many epoxies can be cleaned up with organic solvents such as acetone, methylene chloride and methyl ethyl ketone. Although PESU is not hazardous, most commonly used solvents are hazardous. Toxicology and flammability requirements of such products should be reviewed prior to handling and disposal.

References

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- ² "Cure and Physical Properties of Thermoplastic Modified Epoxy Resins Based on Polyethersulfone" A.J. MacKinnon, S.D. Jenkins, P.T. McGrail, R. A. Pethrick. *Journal of Applied Polymer Science*, Vol. 58, 2345-2355 (1995)
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- ⁵ Araldite® MY 510 and MY 720 Product Datasheets
- ⁶ Udel® Polysulfone and Veradel® Polyethersulfone Design Guides

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