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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} **:**
C08K 7/02, C08L 63/00, 63/02, B32B 27/04, 27/38

A1

(11) International Publication Number: **WO 97/24398**

(43) International Publication Date: 10 July 1997 (10.07.97)

(21) International Application Number: PCT/US96/20585

(22) International Filing Date: 19 December 1996 (19.12.96)

(30) Priority Data:
08/579,509 27 December 1995 (27.12.95) US

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(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: EPOXY RESIN(S) WITH CURING AGENT AND TOUGHENER

(57) Abstract

An epoxy resin composition containing isomers of epoxy resins other than para- or 4,4'-isomers at levels of at least about 33 % by weight provides higher modulus matrices yielding composites with improved compression, tension and shear strengths. The epoxy resin contains at least about 33 % by weight of glycidyl amine group-containing epoxy resin(s) which are isomers other than para- or 4,4'-isomers and from 0-67 % by weight of aromatic epoxy resin(s). The epoxy resin is blended with a curing agent and a polymeric toughening agent.

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EPOXY RESIN(S) WITH CURING AGENT AND TOUGHENER

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to epoxy resin matrix formulations used to prepare prepregs and composites having improved mechanical properties.

Description of Related Art.

Composites comprising high strength filaments in a resin matrix are well known materials. In particular, the high specific strength and stiffness of carbon fiber-epoxy composites makes them suitable for use in weight-sensitive structural applications such as for aircraft components. Historically, these composites have demonstrated excellent tensile strength and modulus, but compression strengths have been a limiting factor in structure design, particularly under hot-wet conditions. Additionally, the trend in recent years toward increasing the damage tolerance of composites has at times come at the expense of hot-wet compression or open hole compression (OHC) strength. One goal in the development of new composite materials is to achieve a balance of properties: excellent toughness and tensile properties combined with excellent hot-wet compression and notched compression strength.

One way to improve the compression strength of a carbon fiber composite is to improve the modulus of the matrix material. Under a compressive load, the fiber will tend to buckle, and the buckling load will be increased if the matrix material surrounding the fiber is stiffer. A reference which discusses this concept is "The Effect of Matrix Modulus on Lamina Compression Strength" by Gene B.

Portelli, et al, Int. SAMPE Symp. Exhib. 1992, 37, 783-95. However, to achieve a balance of properties in the composite, the increase in stiffness of the matrix should not come at the expense of resin toughness or strain to failure.

There are a number of patent references which disclose curable epoxy resin compositions suitable for use in the manufacture of composites. For example, U.S. Patent 4,269,759 discloses resin compositions containing 3,3'-tetraglycidyldiaminodiphenylsulfone (3,3'-TGDDS) as a component of resin compositions yielding composites with improved mechanical properties. The object of the invention disclosed by this patent is twofold; to form an epoxy composition compatible with rubber, and to provide a composition having a highly crosslinked rubber network and a high initial Tg which is insensitive to moisture and the presence of rubber. The preferred resin composition comprises five ingredients: (3,3'-TGDDS, curing agent, rubber, catalyst, and free radical initiator), and carbon fiber composites of the resin composition are also disclosed.

U.S. Patent 4,783,506 discloses damage tolerant composites comprising high strength filaments dispersed in a tough epoxy phase comprising a crosslinked epoxy resin matrix which also contains dispersed, infusible rubber particles. The epoxy compound may comprise a polyepoxide having from 2 to about 4 epoxy groups per molecule such as diglycidyl ether of bisphenol A or resorcinol diglycidyl ether (1,3-bis-(2,3-epoxy propoxy) benzene).

U.S. Patent 4,959,438 discloses epoxy resin compositions yielding composites with $\geq$ 38 ksi CAI strength, and $\geq$ 150 ksi 0° compression strength at 180°F wet. The specified epoxy compositions contain: a bifunctional epoxy resin, a trifunctional epoxy resin, a phenolic compound, and a curative. The triglycidyl derivative of meta-aminophenol is mentioned as one example of a trifunctional epoxy which may be used in the disclosed compositions.

U.S. Patent 5,317,068 also discloses epoxy compositions having good composite mechanical properties along with good prepreg tack and drape. The compositions comprise: a tetrafunctional epoxy resin, a trifunctional epoxy resin, and a bisphenol-A epoxy resin having a number and weight average molecular weight to provide a particular range of M_w/M_n ratios. The trigycidyl derivative of meta-aminophenol is mentioned as one example of a trifunctional epoxy which may be used in the compositions.

JP-3021631 (91-A) abstract discloses epoxy resin compositions which contain the reaction product of an amine or amide with an epoxy. One of the ingredients used in making the epoxy includes a minor amount of the triglycidyl derivative of meta-amino phenol.

JP-94008341 (B-2) abstract discloses polyethersulfone-toughened epoxy compositions based on a mixture of epoxy resins which may include up to 30% by weight of triglycidyl meta-aminophenol.

JP-61250021 (86-A) and JP-61250022 (86-A) abstracts each disclose matrix epoxy resin compositions which may contain minor amounts of N,N,O-glycidylaminophenol as a component of a mixed epoxy system.

JP 58187422 (83-A) abstract discloses an epoxy resin composition containing a condensate of bisphenol A and epihalohydrin or bis(diglycidylaminophenol)methane or m-diglycidyl aminophenylglycidylether cured using a combination of dicyanamide and an N,N-dimethyl urea derivative.

However, none of the references discussed above appears to disclose cured composite materials which provide an improved balance of mechanical properties, i.e., excellent toughness and tensile properties combined with excellent hot-wet compression and notched compression strength.

SUMMARY OF THE INVENTION

The present invention provides for composite materials having an improved balance of mechanical properties prepared from a curable resin composition comprising a mixture of: a) an epoxy resin component comprising: (i) at least about 33% by weight of one or a mixture of aromatic epoxy resins which have glycidyl amine groups or a glycidyl amine group and a glycidyl ether group in the 1,2- or 1,3-position of an aromatic ring system or which have glycidyl amine or glycidyl ether groups in the 2,2', 2,3', 2,4', 3,3', or 3,4' positions of two aromatic rings joined by a direct link or a linking group; and (ii) from 0 to about 67% by weight of one or a mixture of aromatic epoxy resins having at least 2 epoxy groups per molecule and which differ from component a(i); b) a curing agent for said epoxy resin component; and c) a polymeric toughening agent selected from the group consisting of thermoplastic polymers, uncured rubbers, aromatic oligomers having functional groups reactive with said glycidyl ether or glycidyl amine groups, and mixtures thereof. In a more preferred embodiment, the composition also contains: d) from 0 to about 50 parts by weight of infusible particles dispersed in said composition, and e) from 0 to about 10 parts by weight of a cure accelerator.

In the preferred embodiment, component a(ii) is an aromatic epoxy containing glycidyl ether or glycidyl amine groups, or a combination of such groups, in the para positions of the aromatic ring system, or in 4,4' positions of a linked aromatic system, or in a monosubstituted aromatic ring, and is present in the composition at a level of at least about 5% by weight, based on the content of epoxy resin present in the composition.

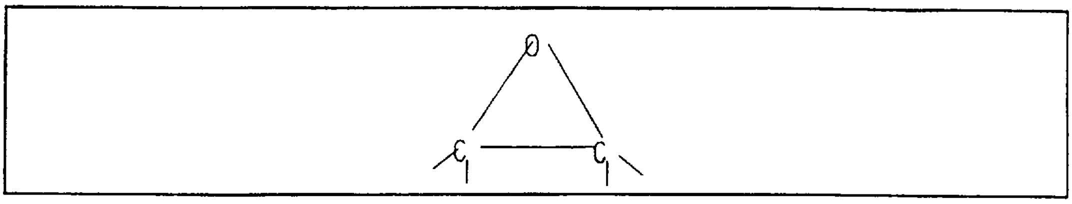
The invention also provides for prepreg compositions containing high strength carbon-based fibers and to cured composites prepared therefrom.

The matrix epoxy resin formulations of this invention contain isomers of epoxy resins other than or in addition to the conventional para- or 4,4'- isomers. The inclusion of these other isomers in the matrix resin formulation at levels of at least 33% by weight, based on epoxy resin content, leads to higher modulus matrices which then yield composites with improved compression, open hole compression, tension, and shear strengths compared to composites made with conventional epoxy resin isomers. The damage tolerance of the composites of this invention is the same or better than comparative state of the art composites.

DETAILED DESCRIPTION OF THE INVENTION

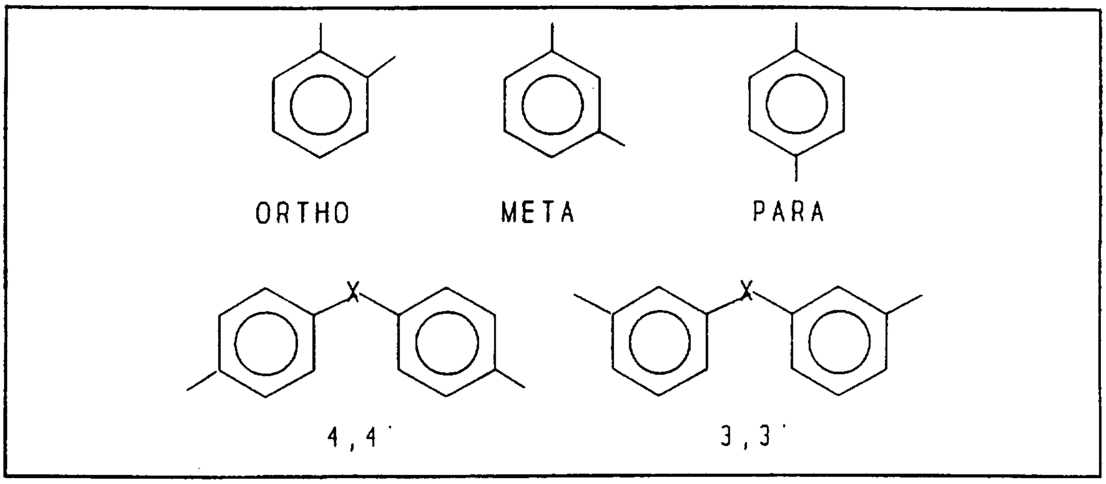
The epoxy resin compositions which are the subject of this invention comprise one or more epoxy resins; a reactive aromatic oligomer component or a thermoplastic polymer component, or a mixture thereof; and a curing agent. A cure accelerator may also be present. Optionally, infusible particles, which act to toughen the resulting composite, may be present in the resin composition. The epoxy resin composition may be in the form of a film for impregnating bands of high strength filaments, a mass of material that can be rendered molten by heat and spread on bands of high strength filaments, or a dissolution product which can impregnate high strength filaments in dipping operations.

The epoxy resins contain on average more than one epoxide group per molecule, and preferably average at least two epoxide groups per molecule. The term epoxide group as used herein refers to the simplest epoxide group which is the three membered ring:



The terms epoxy (or epoxide), 1,2-epoxy (or epoxide), vicinal epoxy (or epoxide), and oxirane ring are also art recognized names for this epoxide group.

Epoxy resins having between two and about four epoxide groups per molecule are particularly preferred in the resin compositions which are the subject of this invention. One type of epoxy resin used in the compositions which are the subject of this invention is derived from aromatic compounds, ie. compounds containing phenylene groups. Three orientations of the substituents on a phenylene ring are possible, and these are designated ortho- (o), meta- (m), and para- (p). For two phenylene groups joined by a linking group X, there are a number of possible isomers: 2,1', 2,3'; 2,4'; 3,3'; 3,4'; and 4,4'. Commercially available epoxy resins are typically para- or 4,4'- isomers. For example, the diglycidylether of bisphenol-A (DGEBA), a widely used epoxy resin available as Ciba-Geigy's Araldite GY 6010, Shell Chemical's Epon 828, or Dow Chemical's DER 332, is a



4,4' isomer. Tetraglycidylmethylenedianiline (TGMDA), available as Ciba-Geigy's Araldite MY 721, or Shell's 1077 is a 4,4' isomer. Triglycidyl-para-aminophenol, available as Ciba-Geigy's Araldite MY 0510, or as Shell's Epon 1075, is a para- isomer. Another type of aromatic epoxy resin is a monosubstituted aromatic compound which has two epoxide groups per molecule. An example of this type is diglycidyl aniline, available as GAN from Ajinomoto USA, Inc.

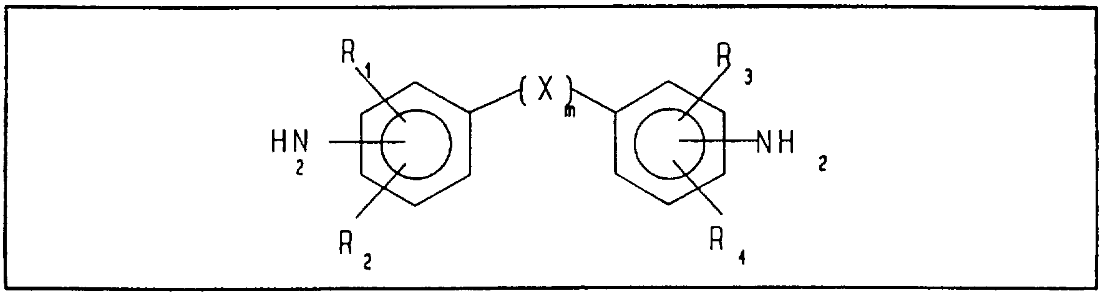
At least one of the epoxy resins in the compositions of this invention is an isomer other than para- or 4,4'-. These epoxy resins are referred to as "isomeric epoxies" for the purposes of this invention. Meta- or 3,3'- isomers are preferred. Triglycidyl-meta-aminophenol and tetra-glycidyl-3,3'-diaminodiphenylsulfone are preferred isomeric epoxies for inclusion in the subject compositions. Other examples of isomeric epoxies are tetraglycidyl-3,3'-methylenedianiline, tetraglycidyl-2,4'-methylenedianiline, tetraglycidyl-2'-methyl-2,4'-diaminodiphenylmethane, triglycidyl-ortho-aminophenol, diglycidyl-3,3'-dihydroxy-diphenylmethane, 2,2-bis[m-(2,3-epoxy-propoxy)phenyl]-propane, and the like.

One or more of the isomeric epoxy resins described above may comprise 100% of the epoxy content of the composition or these may be blended with up to 67% by weight of one or more of the conventional aromatic para-, 4,4'- or monosubstituted-epoxy resins as also described above. These resins generally contain glycidyl ether or glycidyl amine groups, or a combination of such groups, in the 1,4 position of a single aromatic ring structure or in the 4,4' position of two aromatic rings joined by a direct link or a linking group such as a methylene, isopropylidene or a sulfone group.

Examples of conventional epoxies of this type include triglycidyl-para-aminophenol, diglycidyl-bisphenol A, diglycidyl-bisphenol F, tetraglycidyl-4,4'-diaminodiphenylmethane, diglycidyl ether of 1,6-dihydroxynaphthalene, tetraglycidyl-bis(4-amino-3-ethylphenyl) methane and mixtures thereof.

Preferred epoxy resin compositions contain at least 33% by weight, more preferably at least about 45% by weight and most preferably at least about 50% by weight of the epoxy resin content of one or more of the isomeric epoxy resin components, with the balance of the epoxy content being one or more of the conventional para, 4,4', or monosubstituted epoxy resins. More preferred compositions contain from about 45 to 95% by weight of the isomeric epoxy resin component. In a preferred embodiment, isomeric epoxy resin component a(i) and the more conventional epoxy resin component a(ii) are present in respective weight ratios of from about 10:1 to about 1:2.

The curing agent present in the composition may be an amine hardener, more preferably an aromatic diamine having the structure:



where R_1, R_2, R_3, and R_4 are independently hydrogen, halogen, or an alkyl or alkoxy group with 1 to 12 carbon atoms, and X is O, S, SO_2, alkylene, alkylidene, and oxoalkylene, and m is 0 or 1, a phenylene diamine, or a heterocyclic diamine. Particularly preferred aromatic diamines are 3,3'- or 4,4'-diaminodiphenylsulfone. Other aromatic diamines include a methylenedianiline, such as 4,4'-methylenedianiline; a diaminodiphenylsulfide; a diaminodiphenylether; a diaminobenzophenone; benzidene; 4,4'-thiodianiline; meta-phenylenediamine; 2,6-diaminopyridine; 2,4-toluenediamine; 4,4'-[1,4-phenylene(1-methylethylidene)]bis(2,6-dimethylbenzenamine), eg. Shell's Epon HPT curing agent 1062-M; and dianisidine. Still other aromatic diamines such as the di(aminophenoxy)diphenyl ethers or sulfones can be employed if desired. Alicyclic amines such as menthane diamine may also be employed. In some cases, aliphatic amines such as secondary alkylamines which are normally fast reacting hardeners can be used alone or in combination with other amine hardeners provided the concentration and/or curing temperature are sufficiently low to permit control of the curing rate. Other fast reacting hardeners which can be employed as curing agents for making the epoxy resins of the invention are dicyandiamide (Dicy), borontrifluoride-amine complexes, imidazoles, polyamides, o-tolylbiguanide, and the like. Such catalytic hardeners may be used in conjunction with an amine.

The amine hardener is present in the composition in an amount sufficient to crosslink or cure the composition and preferably is present in an amount which provides from 0.3 to 1.5 equivalents and more preferably from 0.5 to 1.2 equivalents of active hydrogen atoms per one equivalent of epoxide groups in the composition.

The curing agent may also be anhydrides and dianhydrides such as carboxylic acid anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, nadicmethyl-anhydride, phthalic anhydride, maleic anhydride, polyazilicpolyanhydride, trimellitic anhydride, benzophenone tetracarboxylic dianhydride, and pyromellitic anhydride. The glycol adducts of these anhydrides may also be used as curatives.

Preferably, the curative is present in the composition at a level of from about 5 to about 100 parts by weight, more preferably from about 20 to 60 parts by weight curative per 100 parts by weight of the epoxy resin content of the composition.

The epoxy resin compositions may additionally include an accelerator to increase the rate of cure. Any of the accelerators known and used in the epoxy resin art may be employed in conventional amounts, including Lewis acid-amine complexes such as BF_3-monoethylamine, BF_3-triethanolamine, BF_3-piperidine, and BF_3-2-methylimidazole; amines such as imidazole, 1-methylimidazole, 2-methylimidazole, 2-ethyl-4-methylimidazole, N,N-dimethylbenzylamine, and other tertiary amines; acid salts of tertiary amines such as the p-toluene sulfonic acid salts of imidazoles or morpholine; salicylic acid salts of imidazoles or benzyldimethylamine, dicyandiamide, 1,1-dimethyl-3-phenyl urea or other substituted ureas such as monuron, diuron, or phenuron; substituted imidazoles, trifluoromethanesulfonic acid salts; carbamides such as toluene-2,4-bis-(N,N-dimethyl carbamide); guanidines such as di-ortho-tolyl guanidine, diphenyl guanidine, tetramethyl guanidine; hydroxyl-containing compounds such as bisphenols A, F, or S, catechol, dihydroxynapthalene, hydroquinone, tetrabromobisphenol A; and organophosphonium halides. The cure accelerators are typically used at a level of about 0 to 10 parts by weight per 100 parts of the epoxy resin content of the formulation, and are used at a preferred level of at least 1 part by weight up to 5 parts by weight when present in the formulation.

The composition also contains a polymeric toughening agent which includes thermoplastic polymers, rubber, aromatic oligomers having functional groups reactive with the glycidyl ether or glycidyl amine groups present in the epoxy component, or mixtures thereof.

The thermoplastic component may comprise engineering or performance grade thermoplastics. The thermoplastic component should be soluble in the epoxy resin component and will be present in a concentration dependent upon the thermoplastic selected and the particular end use envisioned. Examples of suitable thermoplastics are polyarylates, polyimides, polyamides, polyetherimides (PEI), polyamideimides, polyarylethers, phenoxy resins, polyarylsulfones, polyethersulfones, polyether-ketones, polyphenylene ethers and polycarbonates. Aromatic polymers are the preferred thermoplastics, particularly polyether sulfones.

Where the toughening agent is a rubber, it is generally added without a curative or crosslinking agent for the rubber elastomer so that highly cross linked, rigid networks are not formed. Suitable rubbers which may be used include natural rubber, polyisoprene, polybutadiene, copolymers of butadiene with styrene and/or acrylonitrile, copolymers of isobutylene with up to 10wt. % of isoprene or para-methylstyrene as well as halogenated versions thereof, polychloroprene, elastomeric copolymers of ethylene and propylene, elastomeric terpolymers of ethylene, propylene and a non-conjugated diene, such as ethylidene norbornene and like materials. Butadiene/acrylonitrile copolymers are especially preferred.

In the embodiments of this invention that employ a reactive aromatic oligomer component, such component contains functional groups which are reactive with the epoxy resin component and/or the amine hardener of the composition. In one preferred embodiment, the oligomer is epoxy-reactive (ie. it reacts with epoxide groups) and has at least 1.4 epoxy reactive groups per molecule. The reactive aromatic oligomer preferably contains divalent aromatic groups such as phenylene, diphenylene, or naphthalene groups linked by the same or different divalent non-aromatic linking groups. Exemplary linking groups are oxy (-O-); sulfonyl ($-SO_2-$); divalent sulfur (-S-); oxyalkylene (-OR-) or oxyalkyleneoxy (-ORO-) wherein R is a lower alkylene preferably with 1-3 carbon atoms; lower alkylene (-R-) or alkylidene ($-R(R_1)_y-$) wherein R and R_1 contain 1-3 carbon atoms and y is 1 or 2; ester groups such as $-(R_1)_xCOO(R_2)_y-$ wherein R_1 and R_2 are independently lower alkylene preferably with 1 to 3 carbon atoms and x and y are independently zero or 1; and oxyalkylene, ie. $R2_1(C{=}O)R2_2$ where R_1 and R_2 are independently lower alkylene or a valence bond. The aromatic units can be substituted with non-interfering substituents such as chlorine, lower alkyl, phenyl, etc. Generally, at least 25% of the total number of carbon atoms in the reactive aromatic oligomer will be in aromatic structures, and preferably at least about 50% of the total carbon atoms are in aromatic structures.

The reactive aromatic oligomers are preferably polyethers, polysulfones, polyetherketones, polyethersulfones, polythioethersulfones, polyetherimides, or polyimides and more preferably contain sulfone bridged diphenylene units or ketone bridged diphenylene units. Other types of units which can be present in these preferred oligomers are aromatic or cycloaliphatic units that are not bridged (eg. naphthalene) or are bridged by groups which are essentially nonpolar, examples of which are alkylidenes such as isopropylidene bridges. Particularly preferred reactive oligomers contain sulfone or bridged diphenylene units and bisphenol units, a portion of the latter units optionally being replaced by divalent sulfur (-S-) to provide a reactive oligomer of the formula:

$$NH_2R''\text{-}O\text{-}(R\text{-}R')_m\text{-}(R\text{-}S)_n\text{-}R\text{-}O\text{-}R''NH_2$$

wherein R" is 3-phenylene or 4-phenylene, R is the residuum of a dihalodiphenylsulfone such as 4,4'-dichlorodiphenylsulfone or a dihalodiphenylketone, R' is the residuum of a dihydroxy or a dithiol aromatic compound such as bisphenol A, dihydroxy benzene biphenol, and quinoline, O is divalent oxygen, S is divalent sulfur, and m plus n averages between 8 and 25 and m is preferably at least 2. Reactive aromatic oligomers such as those disclosed in EPA 88.120096.8, may also be employed. Such oligomers include oligomers which are the reaction product of p-bis-(4-isopropylidene-2,6-dimethylaniline)benzene and 3,3',4,4'-benzophenone-tetracarboxylic dianhydride; the reaction product of p-bis-(4-isopropylidene-2,6-dimethylaniline)benzene and trimellitic anhydride acid chloride; the reaction product of p-bis-(4-isopropylidene-2,6-dimethylaniline)benzene and isophthaloyl dichloride; the reaction product of 1,3-diaminobenzene and isophthaloyl dichloride and the reaction product of 3,3',4,4'-benzophenone-tetracarboxylic dianhydride and diethyldiaminotoluene. Other amine or carboxylic acid derivative terminated oligomers as contemplated by EPA 88.120096.8 may also be employed, including amine or carboxylic acid terminated polyimides, polyamides, or polyamideimides.

The reactive aromatic oligomers preferably have reactive groups that are terminal groups on the oligomer backbone. The preferred reactive groups of the reactive oligomer are primary amino ($-NH_2$), hydroxyl (-OH), carboxyl (-COOA), where A is hydrogen or an alkali metal), anhydride, thiol, secondary amine, and epoxide groups. Especially preferred are reactive aromatic oligomers having at least about 1.7 reactive groups per molecule, and having at least about 70% of the total number of reactive groups present as primary amine, secondary amine, hydroxyl, and/or epoxide groups.

The preferred reactive aromatic oligomers are made for example, by reacting a molar excess of a sulfone such as dichlorodiphenylsulfone with a dihydroxy aromatic compound or compounds such as bisphenol A or 2,7-napthalenediol so as to yield a chloro-terminated oligomer, and then reacting this chloro-terminated oligomer with an alkali metal salt of a hydroxy amine compound, such as para- or meta- aminophenol to provide the reactive groups on the ends of the oligomer. Suitable sulfones for this procedure are meta- and para-dichlorodiphenylsulfones. Among the suitable dihydroxy aromatic compounds for use in this procedure are bisphenol A, bisphenol F, naphthalene diols, and biphenyl diols. More detailed procedural steps appear in U.S. Patent 4,789,722, which is herein incorporated by reference. Other procedures for producing oligomers having reactive endgroups are disclosed in U.S. Patents 3,895,064 and 3,563,951, the latter patent using a procedure which involves forming nitro terminated oligomers and then reducing the nitro groups to amines.

The glass transition temperature of the reactive aromatic oligomers preferably ranges between 150 and 250°C. A more preferred range is between 160 and 220°C. The molecular weight (number average) of the reactive aromatic oligomer preferably ranges between 2,000 and 10,000. Preferably, the reactive aromatic oligomer has a polydispersity (M_w/M_n) of between about 2.0 and 4.0 where M_w is the weight average molecular weight, and M_n is the number average molecular weight.

Another type of reactive aromatic oligomer useful as a toughening agent can be made by reacting an aromatic epoxy resin with a dihydric phenol. The dihydric phenol and the epoxy are mixed, with a phenol to epoxide ratio of about 0.4/1, and heated at about 135°C for about four hours to yield oligomers having a number average molecular weight of about 2,000 and a weight average molecular weight of about 6,000. These oligomers contain hydroxyl and epoxy functional groups which are reactive with the epoxy resin component and/or the amine hardener component of the composition. Suitable aromatic epoxy resins for this reaction include diglycidyl-bisphenol A, diglycidyl-bisphenol F, triglycidyl-p-aminophenol, and the like.

Suitable dihydric phenols include bisphenol A, bisphenol F, bisphenol S, 9,9'-bis(4-hydroxyphenyl)fluorene, and the like.

The thermoplastic polymer, rubber, reactive oligomer or a mixture of these is present in the composition at a preferred level of from about 5 to about 70 parts by weight, more preferably from about 15 to 60 parts by weight per 100 parts by weight of the epoxy resin present in the composition.

The epoxy resin compositions may optionally contain infusible particles which may be elastomeric, inorganic, or a mixture of elastomeric and inorganic materials. The infusible particles have a median particle size (ie. half are larger and half are smaller) ranging between 5 and 75 microns. The infusible particles may take a variety of shapes including cylindrical, spherical, elongated, platelet, or irregular. The particles are infusible insofar as they resist deformation and dissolution during manufacture of the epoxy resin composition and prepregs thereof.

The elastomeric particles may either be formed during the resin mixing process by precipitation from a rubber solution added to the epoxy resin composition (in situ particles) or they may be preformed and then dispersed as a powder during the mixing of the epoxy resin composition (ex situ particles).

In situ elastomeric particles are formed from a crosslinkable rubber polymer preferably having functionality such as carboxyl groups. Carboxy functional butadiene acrylonitrile polymers are preferred. An example of this latter polymer is Nipol 1472, marketed by Zeon Chemicals USA, Inc. A catalyst may be employed to enhance rubber particle formation. An example of such a catalyst is an aryl phosphonium halide such as ethyltriphenylphosphonium iodide, available from Morton-Thiokol.

Suitable ex situ elastomeric particles include a variety of commercially available rubbers such as copolymers of butadiene or isoprene with acrylonitrile or vinyl aromatic monomers such as styrene or vinyltoluene, or terpolymers of a diene, a vinyl aromatic monomer and acrylonitrile. Other suitable rubbers include natural rubber, silicone rubber, diene or olefin rubbers, and acrylic rubbers. The rubber particles may be formed by cryogenic grinding of larger pieces of rubber to yield irregularly shaped particles in the desired range of particle sizes. The particles may also be formed by spray drying, coagulating, precipitation, or flash evaporation of solutions or suspensions of rubbers. The particles may be formed by dispersion or emulsion polymerization or any other method suitable for the formation of particles in this size range. These rubber solutions or suspensions may be formed in the presence of a reinforcing filler.

The ex situ elastomeric particles preferably contain functionality which improves the adhesion between the particle and the epoxy matrix resin. For example, the elastomer may contain carboxyl groups which either react so as to chemically bond with the matrix or simply improve the compatibility of the particles with the resin due to their polar nature. Adhesion to the matrix can also be improved by swelling of the particles with the resin composition.

Examples of suitable commercially available ex situ elastomeric particles are Nipol 5078 from Zeon Chemicals USA Inc., a carboxy-functional acrylonitrile-butadiene copolymer, and Proteus 5025 from B.F. Goodrich, a carboxy-functional acrylonitrile-butadiene-styrene copolymer.

Suitable inorganic particles may be glass, ceramic, or other inorganic material. The particles are preferably spherical to minimize resin viscosity. They may be hollow or solid. Their composition may be soda lime glass, sodium borosilicate glass, aluminosilicate, fly ash, perlite, mica, ceramic, and the like. The inorganic particles are preferably coated with a coupling agent to improve compatibility or adhesion between the particle and the epoxy resin matrix. Suitable coupling agents may be silanes, such as 3-(glycidoxy)propyltrimethoxysilane or 3-aminopropyltriethoxysilane; titanates; zirconates; or the like. These inorganic particles are widely available commercially.

The infusible particles may be present in the composition at a level from 0 to about 50 parts by weight per 100 parts by weight of epoxy resin. Preferably the particles, when present, are present at a preferred level of from about 5 to 30 parts by weight per 100 parts by weight of epoxy resin.

Compositions containing polymeric toughening agents and infusible particles of the type disclosed herein are more particularly described in U.S. Patents 4,656,207; 4,783,506 and EPO 486,044, the complete disclosures of which are incorporated herein by reference.

Other ingredients such as catalysts, antioxidants, processing aids, and the like may be included in the epoxy resin compositions in minor amounts.

Table A below provides the general and preferred ranges, as parts by weight, for the epoxy resin component, the thermoplastic polymer, rubber or reactive aromatic oligomer, hardener, cure accelerator, and infusible particles present in the thermosetting epoxy resin compositions of this invention.

Table A

	General	More Preferred
Isomeric Epoxy Resin	33-100	45-95
Conventional Epoxy Resin	0-67	5-55
Thermoplastic, rubber or Reactive Aromatic Oligomer	5-70 phe*	15-60 phe
Hardener (Curing Agent)	5-100 phe	20-60 phe
Cure Accelerator	0-10 phe	1-5 phe
Infusible Particles	0-50 phe	5-30 phe

* phe - per hundred parts by weight of epoxy resin.

The epoxy resin compositions are mixed using conventional procedures. Typically, the epoxy resins are charged to a suitable container, heated to 80-150°C and preferably to 60-130°C (depending on the particular formulation) while stirring. If a thermoplastic polymer or reactive aromatic oligomer is a component of the resin composition, it is dispersed, and the mixture is stirred until the polymer or oligomer dissolves. Alternatively, the polymer or oligomer can be in the form of a fine powder that dissolves upon cure.

If the epoxy resin composition contains in situ rubber particles, a solution containing 10 to 20% of a rubber polymer dissolved in 90 to 80% of a low boiling solvent is added after the thermoplastic or reactive aromatic oligomer has been added to the epoxy resins. The solvent is then distilled from the mixture while stirring. More detail on the in situ rubber particle formation process may be found in the above referenced U.S. Patent 4,783,506.

If the epoxy resin composition contains ex situ rubber particles, they may be dispersed in the resin or reserved for application to the prepreg in some other way, for example, as described below. The ex situ particles may be dispersed in the resin before or after the thermoplastic or oligomer is dissolved. Typically, the particles are dispersed before the curing agent is added, although they may be added later.

The curing agent is dispersed at a suitable temperature depending on its composition, followed optionally by a cure accelerator.

The epoxy resin composition is used to impregnate high strength filaments or fibers comprised of carbon or graphite, glass, aromatic polyamides (such as Kevlar from DuPont), boron, and the like to make prepreg. Composites containing from about 30 to 70% and preferably from about 40 to 70% of these fibers based on the total volume of the composite are preferred in making composite structures.

This invention has particular applicability to composites which are made from materials commonly referred to as "prepregs". Prepregs comprise resin and high strength filaments which are previously in the form of filamentary bundles (often called "rovings" or "tows") comprising a multitude the filaments before the manufacture of the prepreg, which is typically in the form of a flat sheet. Each tow of carbon fiber, for example, typically bundles between about 500 and 20,000 filaments. A plurality of filamentary bundles are aligned or woven together in making prepreg in sheet form. Alternatively, the prepreg may be in the form of a single bundle of filaments impregnated with resin. This latter prepreg form finds use in processes such as filament winding, fiber placement, and pultrusion.

The preferred high strength filaments are carbon or graphite fiber filaments made, for example, by carbonizing polyacrylonitrile, rayon, or pitch. Examples of preferred high strength filaments are AS4, IM6, IM7, and IM8 carbon fiber marketed by Hercules Incorporated.

The prepregs of this invention are made by combining the epoxy resin compositions and high strength filaments using conventional techniques. For example, the epoxy resin composition can be made into a film on a sheet of release paper in a film process. Film carried by upper and lower release papers is pressed into bands or sheets of high strength filaments in making prepreg by this process. Alternatively, a "hot bead" process may be used wherein the epoxy resin composition is rendered molten and pressed into the bands or sheets of high strength filaments. Still another route is by dissolving the epoxy resin composition in a solvent, passing the high strength filaments through a bath containing the solvent, and then driving off the solvent to provide the prepreg.

In all of the aforementioned techniques of making prepreg, the optional infusible particles are trapped or filtered by the filament tows or bundles, thereby providing a prepreg that has these particles on its surface rather than between the filaments in the bundles or tows of filaments. Alternative methods for affixing ex situ infusible particles to the surface of the prepreg include sprinkling, spreading, or spraying the dry particles onto the tacky surface of the prepreg. In another method, a film containing a portion of the matrix resin and the infusible particles is applied to the surface of a prepreg already impregnated with the remainder of the resin. The infusible particles dispersed in a portion of the matrix resin can also be coated onto the surface of a prepreg containing the remainder of the resin.

Other methods of preparing prepreg known to those skilled in the art may also be followed in the practice of this invention.

The prepregs are simply laid on one another and then cured in making the composites of this invention. Composite test panels as outlined in Table B were layed up and cured.

Test panels were typically cured 2-4 hours at 350°F in an autoclave. Cure times for particular composites are specified in the Examples. The appropriate tests were then carried out to determine the mechanical properties of the composites of this invention. The reported test data for 0° tension, 0° compression, and open hole compression have been normalized to 60% fiber volume.

Table B

Test	Layup	Number of Plies	Specimen Size, LXW, (in)
Compression After Impact Str (CAI)	$(+45/0/-45/90)_{4S}$	32	6X4
Open Hole Compression Str (OHC)	$(+45/0/-45/90)_{2S}$	16	12X1.5
0° Compression Str	Unidirectional	8	2.5X0.5
0° Tension Str, Mod	Unidirectional	8	9X0.5
0° Short Beam Shear Str (SBS)	Unidirectional	16	1X0.25

A number of epoxy resin compositions were made with various isomeric epoxies. The epoxy resin compositions were then used to make prepregs containing carbon fiber in the form of a plurality of tows each comprising a multitude of filaments. The prepregs were layed up and cured in the manner described above.

The following Examples illustrate practice of this invention and are not intended as a limitation thereof. All parts and percentages in the Examples are parts and percentages by weight.

Table C identifies the composition of all the commercially available ingredients used in the formulations described in the Examples.

Table C

Tradename or Abbreviation	Composition
RD92-119	triglycidyl-meta-aminophenol from Ciba-Geigy
MY 0510, HPT 1076	triglycidyl-para-aminophenol from Ciba-Geigy (0510) or Shell (1076)
PY 306 and LY 9703	diglycidyl-bisphenol F from Ciba-Geigy
Nipol 1472	carboxy functional butadiene-acrylonitrile rubber from Zeon Chemicals
3,3'DDS	3,3'-diaminodiphenylsulfone from Ciba-Geigy
4,4'DDS	4,4'-diaminodiphenylsulfone from Ciba-Geigy
RD92-405	tetraglycidyl-3,3'-diaminodiphenylsulfone from Ciba-Geigy
MY 721	tetraglycidyl-4,4'-diaminodiphenylmethane from Ciba-Geigy
Epiclon 4032	diglycidyl ether of 1,6-dihydroxynapthalene from Dainippon Ink & Chemicals Inc.
MY 722	tetraglycidyl-bis(4-amino-3-ethylphenyl)methane from Ciba Geigy
RD92-451	tetraglycidyl-2'-methyl-2,4'-diaminodiphenylmethane from Ciba-Geigy
GAN	diglycidyl aniline from Ajinomoto USA, Inc.
Victrex 5003P	polyethersulfone polymer from ICI

Table D describes the test methods employed to obtain resin and composite mechanical property data in the Examples.

TABLE D

TEST TYPE	TEST DESCRIPTION
Cured resin dynamic storage modulus (E')	Dynamic Mechanical Analysis (DMA) Resonant mode Heating rate: 10°C/min
Conditioning of wet test samples	Cured resin DMA, Short beam shear strength: 48 hour boil 0° and Open hole compression strength: 2 week water soak @ 160°F
Compression after impact (CAI)	SACMA SRM 2R-94
0° Compressive strength	SACMA SRM 1R-94 (except 0° rather than 0/90° specimen was used) (modified) ASTM D695
0° Tensile Properties	ASTM D3039
Short Beam Shear Strength	ASTM D2344
Open Hole Compression Strength	SACMA 3R-94

Examples

Example 1

RD92-119 (200 g) and PY 306 (120 g) were warmed to 70°C in a one quart can and hydroxy-terminated polyethersulfone oligomer (208 g) was added slowly. The mixture was heated to 128°C and held for 2.5 hours to dissolve the oligomer. The mixture was cooled to 71°C and 214 g of a solution of Nipol 1472 rubber in methylethyl ketone (MEK) (15% solids) was added. The mixture was heated to remove the MEK, and the resin mixture was held at 125°C for 30 minutes. The mix was cooled to 110°C and PY 306 (80 g) was added. This composition was designated "Part A".

Part A (1788 g) was heated to 90°C and 3,3'DDS (525 g) was added. This resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg tape having a fiber areal weight of 149 g/m^2 and a resin content of 34%. This prepreg was layed up into composite test panels. The results of the composite mechanical tests are shown in Table 1 along with the results from comparative Example A. Inspection of Table 1 shows that the composite properties of the Example 1 resin, which contains the meta- isomer of triglycidylaminophenol, are superior to the Example A resin, which contains the para-isomer of triglycidylaminophenol.

Comparative Example A

MY 0510 (167 g), LY 9703 (33.4 g), hydroxy-terminated polyethersulfone oligomer (173.8g), and MEK (139.5 g) were charged to a 1 liter flask, heated to 60°C, and held for 2 hours to dissolve the oligomer. 177.3 g of a 15% solids solution of Nipol 1472 in MEK was added. The mixture was stirred and the MEK was distilled from the mixture while gradually increasing the temperature to 105°C. More LY 9703 (133.6 g) was added after the MEK was removed, and then the 3,3'DDS curative (163.7 g) was added to the resin mixture. The resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg tape having a fiber areal weight of 144 g/m^2 and a resin content of 34%. The prepreg was layed up into composite test panels. The results of the composite mechanical tests are shown in Table 1 along with the results from Example 1.

Table 1

	Example 1	Example A
Cured resin E'@ RT dry, ksi	523	474
Cured resin E'@ 180°F wet, ksi	439	370
Composite Properties		
CAI, ksi	54.5	49.9
0° Compressive Str, ksi	277	229
0° Comp Str, 180°F wet, ksi	215	201
0° Tensile Str, ksi	419	397
0° Tensile Mod, msi	23.1	23.4
Elongation, %	1.70	1.59
Short Beam Shear Str, ksi	16.1	14.6
SBS Str, 180°F wet, ksi	10.6	9.4

Example 2

RD92-405 (403 g) and diglycidyl aniline (202 g) were placed in a 1 quart can and heated to 80°C. Victrex 5003P (215 g) was added slowly and the temperature was increased to 125°C and held for 5.5 hours to dissolve the polymer. Additional RD92-405 (538 g) was added to the mixture and blended. The mix was cooled to 108°C and 3,3'DDS (457 g) was added. The resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg tape having a fiber areal weight of 146 g/m^2 and a resin content of 36%. The prepreg was layed up into composite test panels. The results of the composite mechanical tests are shown in Table 2 along with the results from comparative Example B. Inspection of Table 2 shows that the compressive , open hole compressive, and shear strengths of the Example 2 resin, which contains meta- epoxy and 3,3'- epoxy isomers, are superior to those of the Example B resin, which contains para- and 4,4'- epoxy isomers. The CAI strength and tensile strength of the Example 2 composite are the same as the Example B composite.

Comparative Example B

MY 0510 (900 g) and MY 721 (900 g) were mixed in a 1 gallon can and heated to 60°C. Victrex 5003P (540 g) was added slowly and the mixture was heated to 125°C and held for 3 hours. The mixture was cooled to 95°C and 3,3'DDS (770 g) and 4,4'DDS (86 g) were added. The resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg tape having a fiber areal weight of 146 g/m^2 and a resin content of 35%. The prepreg was layed up into composite test panels. The results of the composite mechanical tests are shown in Table 2 along with the results from comparative Example B.

Table 2

	Example 2	Example B
Cured resin E'@ RT dry, ksi	758	665
Cured resin E'@ 250°F wet, ksi	550	479
Composite Properties		
CAI, ksi	31	31
0° Compressive Str, ksi	338	307
0° Comp Str, 250°F wet, ksi	237	159
0° Tensile Str, ksi	385	385
0° Tensile Mod, msi	24.4	22.5
Elongation, %	1.47	1.57
Short Beam Shear Str, ksi	21.9	18.7
SBS Str, 250°F wet, ksi	12.5	9.8
OHC Str, ksi	52.7	49.7
OHC Str, 250°F wet,ksi	40.8	36.9

Example 3

RD92-119 (750 g) and PY 306 (750 g) were placed in a 1 gallon can and heated to 74°C. Hydroxy-terminated polyethersulfone oligomer (900 g) was added slowly and the temperature was increased to 125°C and held for 3 hours to dissolve the oligomer. The mix was cooled to 95°C and 3,3'DDS (705 g) was added. The resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg tape having a fiber areal weight of 144 g/m^2 and a resin content of 35.6%. The prepreg was layed up into composite test panels. The results of the composite mechanical tests are shown in Table 3 along with the results from comparative Example C. Inspection of Table

3 shows that the compressive, open hole compressive, shear, and CAI strengths of the composite from the Example 3 resin, which contains the meta- isomer of triglycidylaminophenol, are superior to the Example C resin, which contains the para- isomer of triglycidylaminophenol. The tensile properties of the Example 3 composite are the same as the Example C composite.

Comparative Example C

MY 0510 (750 g) and PY 306 (750 g) were mixed in a 1 gallon can and heated to 75°C. Hydroxy-terminated polyethersulfone oligomer (990 g) was added slowly and the temperature was increased to 125°C and held for 5 hours to dissolve the oligomer. The mix was cooled to 95°C and 3,3'DDS (735 g) was added. The resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg tape having a fiber areal weight of 145 g/m^2 and a resin content of 36%. The prepreg was layed up into composite test panels. The results of the composite mechanical tests are shown in Table 3 along with the results from Example 3.

Table 3

	Example 3	Example C
Cured resin E'@ RT Dry, ksi	608	553
Cured resin E'@ 180°F wet, ksi	496	465
Composite Properties		
CAI, ksi	41.8	40
0° Tensile Strength, ksi	411	409
0° Tensile Modulus, msi	23.9	23.4
Elongation, %	1.62	1.61
RT Dry 0° Compressive Strength, ksi	300	239
180°F Wet 0° Compressive Strength, ksi	197	183
RT Dry SBS Strength, ksi	19.2	17.3
180°F Wet SBS Strength, ksi	12.5	9.9
OHC Strength, ksi	47.4	44.8

Example 4

RD92-119 (284 g), RD92-451 (284 g), MY 722 (142 g), Epiclon 4032 (142 g), and diglycidylaniline (73 g) were mixed in a 1 gallon can and heated to 80°C. Victrex 5003P (209 g) was dispersed and the temperature was increased to 125°C and held for 7 hours to dissolve the polymer. The mix was cooled to 100°C and 3,3'DDS (357 g) was added. The resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg tape having a fiber areal weight of 144 g/m^2 and a resin content of 34%. The prepreg was layed up into composite test panels. The following composite mechanical properties were measured: CAI strength: 34.6 ksi; OHC strength: 49.0 ksi; 250°F wet OHC strength: 35.4 ksi; SBS strength: 19.0 ksi; 250°F wet SBS strength: 9.8 ksi.

Example 5

HPT 1076 (225 g) and PY 306 (45 g) were warmed to 80°C in a one quart can and hydroxy-terminated polyethersulfone oligomer (235 g) was added slowly. The mixture was heated to 128°C and held for 2.5 hours to dissolve the oligomer. The mixture was cooled to 75°C and 295 g of a solution of Nipol 1472 rubber in methylethyl ketone (MEK) (15% solids) was added. The mixture was heated to remove the MEK, and the resin mixture was held at 125°C for 30 minutes. The mix was cooled to 100°C and RD92-405 (550 g) was added and blended in. 3,3'DDS (340 g) was added after the mix was cooled to 85°C. This resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg tape having a fiber areal weight of 146 g/m^2 and a resin content of 35%. This prepreg was layed up into composite test panels. The following composite mechanical properties were measured: CAI strength: 34.2 ksi; OHC strength: 51.6 ksi; 250°F wet OHC strength: 36.0 ksi; SBS strength: 18.6 ksi; 250°F wet SBS strength: 10.3 ksi; 0° compressive strength: 322 ksi; 250°F wet 0° compressive strength: 209 ksi.

Example 6

RD92-119 (900 g), Epiclon 4032 (720 g), and MY 721 (180 g) were placed in a 1 gallon can and heated to 65°C. Hydroxy-terminated polyethersulfone oligomer (936 g) was added slowly and the temperature was increased to 125°C and held for 5.5 hours to dissolve the oligomer. The mix was cooled to 95°C and 4,4'DDS (792 g) was added. The resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg tape having a fiber areal weight of 190 g/m^2 and a resin content of 35.3%. The prepreg was layed up into composite test panels. The following composite mechanical properties were measured: CAI strength: 37.0 ksi; OHC strength: 50.3 ksi; 180°F wet

OHC strength: 39.0 ksi; 0° tensile strength: 412 ksi; 0° tensile modulus: 23.6 msi; 0° compressive strength: 312 ksi; 180°F wet 0° compressive strength: 212 ksi.

Example 7

RD92-119 (183.48 g) was heated to 60°C and combined with dicyandiamide (8.26 g) and diuron, which is 3-(3,4 dichlorophenyl-1,1-dimethyl urea (8.26 g). A resin casting was made and cured at 200°F 1 hour and 250°F for 2 hours. As a control, MY 0510 (229.36 g) was heated to 60°C and combined with dicyandiamide (10.32 g) and diuron (10.32 g). A neat resin casting was made and cured in the same way as the RD92-119 casting. Dynamic mechanical analysis yielded these results:

	RD92-119/dicy	MY0510/dicy
E'@ 80°C, ksi	734	578
E'@ 80°C wet, ksi	543	455

A higher dynamic storage modulus (E') is correlated with improved composite compressive and shear strengths. The RD92-119 casting containing the triglycidyl-m-aminophenol epoxy resin exhibited improved performance compared to the MY 0510 casting containing the triglycidyl-p-aminophenol epoxy resin.

Example 8

RD92-405 (1345.5 g) and PY 306 (736 g) were placed in a 1 gallon can and heated to 80°C. Victrex 5003P (391 g) was dispersed, and the temperature was increased to 125°C and held for 6 hours and 40 minutes to dissolve the polymer. The mix was cooled to 95°C, and 3,3'DDS (754.4 g) was added. The resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg having a fiber, a real weight of 143 g/m^2 and a resin content of 36%.

The prepreg was layed up into composite test panels. The following composite mechanical properties were measured: CAl strength: 38.3 ksi; 180°F wet OHC strength: 40.7 ksi: 250°F wet OHC strength: 35.1 ksi; SBS strength: 21.0 ksi; 180°F wet SBS strength: 13.9 ksi; 250°F wet SBS strength: 11.2 ksi; 0° compressive strength: 321 ksi; 180°F wet 0° compressive strength: 261 ksi; 250°F wet 0° compressive strength: 202 ksi; 0° tensile strength: 395 ksi; 0° tensile modulus: 23.2 msi, 0° tensile elongation: 1.62%.

Example 9

RD92-405 (1750 g) and diglycidylaniline (250 g) were mixed in a 1 gallon can and heated to 75°C. Hydroxy-terminted polyethersulfone oligomer (525 g) was dispersed, and the temperature was increased to 105°C and held for 7 hours and 40minutes to dissolve the oligomer. The mix was cooled to 95°C, and 3,3'DDS (800 g) was added. The resin was filmed onto release paper, and combined with IM7 carbon fibers to yield unidirectional prepreg having a fiber areal weight of 190 g/m^2 and a resin content of 36%. The prepreg was layed up into composite test panels. The following composite mechanical properties was measured: CAl strength: 28.4 ksi; OHC strength: 55.6 ksi; 180°F wet OHC strength: 45.7 ksi: 250°F wet OHC strength: 40.5 ksi; SBS strength: 22.9 ksi; 250°F wet SBS strength: 12.5 ksi; 0° compressive strength: 274 ksi; 250°F wet 0° compressive strength: 231 ksi; 0° tensile strength; 423 ksi; 0° tensile modulus: 23.6 msi; 0° tensile elongation: 1.68%.

The cured compositions and prepregs made in accordance with this invention can be used in any structural application where high strength and lightweight performance is desired. These include aircraft structural components such as jet or rocket engine housings, (nacelles); airplane stabilizer, rudder, aileron and flap structures; wing and fuselage structural components; wing, fuselage and rocket skins and like applications.

What is claimed is:

1. A curable resin composition comprising a mixture of:

a) an epoxy resin component comprising:
   (i) at least about 33% by weight of one or a mixture of aromatic epoxy resins which have glycidyl amine groups or a glycidyl amine group and a glycidyl ether group in the 1,2- or 1,3-position of an aromatic ring system or which have glycidyl amine or glycidyl ether groups in the 2,2', 2,3', 2,4', 3,3' or 3,4' positions of two aromatic rings joined by a direct link or a linking group; and
   (ii) from 0 to about 67% by weight of one or a mixture of aromatic epoxy resins having at least 2 epoxy groups per molecule and which differ from component a(i);
b) a curing agent for said epoxy resin component; and
c) a polymeric toughening agent selected from the group consisting of thermoplastic polymers, uncured rubbers, aromatic oligomers having functional groups reactive with said glycidyl ether or glycidyl amine groups, and mixtures thereof;

2. The composition of claim 1 wherein said curing agent is present in said composition at a level of from about 5 to about 100 parts by weight per 100 parts by weight of said epoxy resin component.

3. The composition of claim 2 wherein said polymeric toughening agent is present in said composition at a level of from about 5 to about 70 parts by weight per 100 parts by weight of said epoxy resin component.

4. The composition of claim 1 further containing:

d) from 0 to about 50 parts by weight of infusible particles dispersed in said composition per 100 parts by weight of said epoxy resin component.

5. The composition of claim 1 further containing:

e) from 0 to about 10 parts by weight of a cure accelerator per 100 parts by weight of said epoxy resin component.

6. The composition of claim 1 wherein said epoxy component a(i) contains a glycidyl amine and a glycidyl ether group in the 1,3-positions of an aromatic ring system or in the 3,3' or 2,4' positions of two aromatic rings joined by a direct link or a linking group.

7. The composition of claim 1 wherein said epoxy component a(i) contains a glycidyl ether group in the 3,3' or 2,4' positions of two aromatic rings joined by a direct link or a linking group.

8. The composition of claim 1 wherein said polymeric toughening agent component (c) is present in said composition at a level of from about 5 to about 70 parts by weight per 100 parts by weight of said epoxy resin component.

9. The composition of claim 8 wherein component (c) is selected from the group consisting of polyarylates, polyimides, polyamides, polyetherimides, polyamide-imides,

polyarylethers, phenoxy resins, polyarylsulfones, polyethersulfones, polyetherketones, polyphenylene ethers, and polycarbonates.

10. The composition of claim 9 wherein component (c) comprises a terminally functional polyether sulfone oligomer.

11. The composition of claim 10 wherein said oligomer is selected from the group consisting of hydroxy-terminated polyether sulfone oligomers and amine-terminated polyethersulfone oligomers.

12. The composition of claim 9 wherein component (c) comprises a polyethersulfone thermoplastic polymer.

13. The composition of claim 4 containing at least about 1 part by weight of component (d) comprising infusible elastomeric particles.

14. The composition of claim 1 wherein said epoxy resin component comprises at least about 5% by weight of component a(ii).

15. The composition of claim 14 wherein component a(i) is triglycidyl-meta-aminophenol.

16. The composition of claim 14 wherein component a(i) is tetraglycidyl-3,3'-diaminodiphenylsulfone.

17. The composition of claim 14 wherein component a(i) is triglycidyl-meta-aminophenol.

18. The composition of claim 14 wherein component a(i) is tetraglycidyl-3,3'-diaminodiphenylsulfone.

19. The composition of claim 14 wherein component (c) comprises a terminally functional polyether sulfone oligomer present at a level of at least about 5 parts by weight per 100 parts by weight of said epoxy resin.

20. The composition of claim 19 wherein said oligomer is selected from the group consisting of hydroxy-terminated polyether sulfone oligomers and amine-terminated polyether-sulfone oligomers.

21. The composition of claim 14 wherein component (c) comprises a polyethersulfone thermoplastic polymer present at a level of at least about 5 parts by weight per 100 parts by weight of said epoxy resin.

22. The composition of claim 14 containing at least about 1 part by weight of component (d) infusible particles.

23. The composition of claim 22 wherein said infusible particles comprise elastomeric particles present at a level of about 5 to 30 parts by weight.

24. The composition of claim 14 wherein epoxy resin components a(i) and a(ii) are present in respective weight ratios of from about 10:1 to about 1:2.

25. The composition of claim 14 wherein said epoxy resin comprises at least about 45% by weight of component a(i).

26. The composition of claim 25 wherein said epoxy resin comprises at least about 50% by weight of component a(i).

27. The composition of claim 1 containing from about 20 to 60 parts by weight of said curing agent.

28. The composition of claim 27 wherein said curing agent comprises a diamine.

29. The composition of claim 28 wherein said diamine is 3,3'-diaminodiphenylsulfone.

30. The composition of claim 28 wherein said diamine is 4,4'-diaminodiphenylsulfone.

31. The composition of claim 14 wherein said epoxy component a(ii) contains glycidyl ether or glycidyl amine groups in the 1,4-position of an aromatic ring system or in the 4,4'-position of two aromatic rings joined by a direct link or a linking group.

32. The composition of claim 14 wherein said epoxy component a(ii) is selected from the group consisting of triglycidyl-para-aminophenol, diglycidyl-bisphenol F, diglycidyl-bisphenol A, tetraglycidyl-4,4'-diaminodiphenylmethane, diglycidyl ether of 1,6-dihydroxynaphthalene, tetraglycidyl-bis(4-amino-3-ethylphenyl)methane, diglycidyl aniline and mixtures thereof.

33. The composition of claim 14 wherein said epoxy component a(i) is selected from the group consisting of triglycidyl-metaaminophenol, tetraglycidyl-3,3'-diaminodiphenylsulfone, tetraglycidyl-3,3'-methylenedianiline, tetraglycidyl-2,4'-methylenedianiline, tetraglycidyl-2'-methyl-2,4'-diaminodiphenylmethane, triglycidyl-ortho-aminophenol, diglycidyl-3,3'-dihydroxydiphenylmethane, 2,2-bis[m-(2,3-epoxy-propoxy)phenyl]-propane and mixtures thereof.

34. A curable resin composition comprising a mixture of:

a) 100 parts by weight of an epoxy resin component comprising:

(i) at least about 33% by weight of one or a mixture of aromatic epoxy resins which have glycidyl amine groups or a glycidyl amine group and a glycidyl ether group in the 1,2 or 1,3 positions of an aromatic ring system or which have glycidyl amine or glycidyl ether groups in the 2,2', 2,3', 2,4', 3,3', or 3,4' positions of two aromatic rings joined by a direct link or a linking group; and

(ii) from about 5 to about 67% by weight of one or a mixture of epoxy resins containing one or a combination of glycidyl amine groups and glycidyl ether groups in the 1,4 position of an aromatic ring system or in the 4,4' position of two aromatic rings joined by a direct link or a linking group;

b) from about 5 to about 100 parts by weight of a curing agent for said epoxy resin component;

c) from about 5 to about 70 parts by weight of a polymeric toughening agent selected from the group consisting of thermoplastic polymers, uncured rubbers, aromatic oligomers having functional groups reactive with said glycidal ether or glycidal amine groups, and mixtures thereof;

d) from 0 to about 50 parts by weight of infusible particles; and

e) from 0 to about 10 parts by weight of a cure accelerator.

35. The composition of claim 34 wherein said epoxy component a(i) contains a glycidyl amine and a glycidyl ether group in the 1,3-positions of an aromatic ring system or in the 3,3' or 2,4' positions of two aromatic rings joined by a direct link or a linking group.

36. The composition of claim 34 wherein said epoxy component a(i) contains a glycidyl ether group in the 3,3' or 2,4' positions of two aromatic rings joined by a direct link or a linking group.

37. The composition of claim 34 wherein component (c) is selected from the group consisting of polyarylates, polyimides, polyamides, polyetherimides, polyamide-imides, polyarylethers, phenoxy resins, polyarylsulfones, polyethersulfones, polyetherketones, polyphenylene ethers, and polycarbonates.

38. The composition of claim 37 wherein component (c) comprises a terminally functional polyether sulfone oligomer.

39. The composition of claim 38 wherein said oligomer is selected from the group consisting of hydroxy-terminated polyether sulfone oligomers and amine-terminated polyether-sulfone oligomers.

40. The composition of claim 37 wherein component (c) comprises a polyethersulfone thermoplastic polymer.

41. The composition of claim 34 containing at least about 1 part by weight of component (d) comprising infusible elastomeric particles.

42. The composition of claim 34 wherein component a(i) is triglycidyl-meta-aminophenol.

43. The composition of claim 34 wherein component a(i) is tetraglycidyl-3,3'-diaminodiphenylsulfone.

44. The composition of claim 34 wherein component a(i) is triglycidyl-meta-aminophenol.

45. The composition of claim 34 wherein component a(i) is tetraglycidyl-3,3'-diaminodiphenylsulfone.

46. The composition of claim 34 wherein component (c) comprises a terminally functional polyether sulfone oligomer.

47. The composition of claim 46 wherein said oligomer is selected from the group consisting of hydroxy-terminated polyether sulfone oligomers and amine-terminated polyether-sulfone oligomers.

48. The composition of claim 34 wherein component (c) comprises a polyethersulfone thermoplastic polymer.

49. The composition of claim 34 containing at least about 1 part by weight of component (d) infusible particles.

50. The composition of claim 49 wherein said infusible particles comprise elastomeric particles present at a level of about 5 to 30 parts by weight.

51. The composition of claim 34 wherein epoxy resin components a(i) and a(ii) are present in respective weight ratios of from about 10:1 to about 1:2.

52. The composition of claim 34 wherein said epoxy resin comprises at least about 45% by weight of component a(i).

53. The composition of claim 52 wherein said epoxy resin comprises at least about 50% by weight of component a(i).

54. The composition of claim 34 containing from about 20 to 60 parts by weight of said curing agent.

55. The composition of claim 54 wherein said curing agent comprises a diamine.

56. The composition of claim 55 wherein said diamine is 3,3'-diaminodiphenylsulfone.

57. The composition of claim 55 wherein said diamine is 4,4'-diaminodiphenylsulfone.

58. The composition of claim 34 wherein said epoxy component a(ii) is selected from the group consisting of triglycidyl-para-aminophenol, diglycidyl-bisphenol F, diglycidyl-bisphenol A, tetraglycidyl-4,4'-diaminodiphenylmethane, diglycidyl ether of 1,6-dihydroxynaphthalene, tetraglycidyl-bis(4-amino-3-ethylphenyl)methane, diglycidyl aniline and mixtures thereof.

59. The composition of claim 34 wherein said epoxy component a(i) is selected from the group consisting of triglycidyl-meta-aminophenol, tetraglycidyl-3,3'-diaminodiphenylsulfone, tetraglycidyl-3,3'-methylenedianiline, tetraglycidyl-2,4'-methylenedianiline, tetraglycidyl-2'-methyl-2,4'-diaminodiphenylmethane, triglycidyl-ortho-aminophenol, diglycidyl-3,3'-dihydroxydiphenylmethane, 2,2-

bis[m-(2,3-epoxy-propoxy)phenyl]-propane and mixtures thereof.

60. A thermoset resinous composition prepared by curing the composition of claim 1.

61. A thermoset resinous composition prepared by curing the composition of claim 14.

62. A thermoset resinous composition prepared by curing the composition of claim 34.

63. A prepreg used for the manufacture of damage tolerance structural composites comprising high strength fibrous material impregnated with the resin composition of claim 1.

64. A prepreg used for the manufacture of damage tolerance structural composites comprising high strength fibrous material impregnated with the resin composition of claim 14.

65. A prepreg used for the manufacture of damage tolerance structural composites comprising high strength fibrous material impregnated with the resin composition of claim 34.

66. The prepreg of claim 63 wherein said high strength fibers are carbon fibers.

67. The prepreg of claim 64 wherein said high strength fibers are carbon fibers.

68. The prepreg of claim 65 wherein said high strength fibers are carbon fibers.

69. The prepreg of claim 63 wherein from about 30 to about 70 volume percent of said prepreg comprise said high strength fibers.

70. The prepreg of claim 64 wherein from about 30 to about 70 volume percent of said prepreg comprise said high strength fibers.

71. The prepreg of claim 65 wherein from about 30 to about 70 volume percent of said prepreg comprise said high strength fibers.

72. A thermoset composite prepared by curing the prepreg of claim 63.

73. A thermoset composite prepared by curing the prepreg of claim 64.

74. A thermoset composite prepared by curing the prepreg of claim 65.

75. The thermoset composite of claim 72 wherein said high strength fibers are carbon fibers.

76. The thermoset composite of claim 73 wherein said high strength fibers are carbon fibers.

77. The thermoset composite of claim 74 wherein said high strength fibers are carbon fibers.

78. The thermoset composite of claim 72 wherein from about 30 to about 70 volume percent of said composite comprises said high strength fibers.

79. The thermoset composite of claim 73 wherein from about 30 to about 70 volume percent of said composite comprises said high strength fibers.

80. The thermoset composite of claim 74 wherein from about 30 to about 70 volume percent of said composite comprises said high strength fibers.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20585

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :CO8K 7/02; CO8L 63/00, 63/02; B32B 27/04, 27/38
US CL :428/413, 417; 523/427, 428, 429, 466, 468; 525/423, 438, 463, 526
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/413, 417; 523/427, 428, 429, 466, 468; 525/423, 438, 463, 526

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, JPOABS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,179,139 A (SUGIMORI et al.) 12 January 1993, column 4, lines 34-43 and 49-54 and column 6, Table 2, Example 8.	1-80
A	JP 94-008341 B2 (TORAY INDUSTRIES INC.) 02 FEBRUARY 1994, abstract.	1-80
A	US 4,959,438 A (TADA et al.) 25 September 1990, column 3, lines 14-16; column 4, lines 53-54 and columns 7-8, Examples 8 and 9.	1-80
A	US 4,783,506 A (GAWIN) 08 November 1988, column 3, lines 32-33 and 40-42; column 4, lines 24 and 56-60 and column 6, line 17.	1-80

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 11 MARCH 1997	Date of mailing of the international search report 04 APR 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ROBERT SELLERS JaB for Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20585

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,447,785 A (KISHI et al.) 05 September 1995, column 4, lines 67-68; column 5, lines 19-24 and columns 17-18, Example 1.	1-80

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20585

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1.

1) The epoxy resin a) in the presence or absence of the aromatic epoxy resin (ii).

2) The curing agents b) such as 3.3'-diaminodiphenylsulfone and 4,4'-diaminodiphenylsulfone.

3) The polymeric toughening agents c) such as polyarylates, polyimides, polyamides, polyetherimides, polyamide-imides, polyarylethers, phenoxy resins, polyarylsulfones, polyethersulfones, polyetherketones, polyphenylene ethers, polycarbonates, hydroxy-terminated polyethersulfones and amine-terminated polyethersulfones.

The claims are deemed to correspond to the species listed above in the following manner:

1) Claims 34-62.

2) Claims 29, 30, 56 and 57.

3) Claims 9, 11, 12, 37, 39 and 40.

The following claims are generic: 1-28, 31-33 and 63-80.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons:

1) The presence of the aromatic epoxy resin (ii) yields a distinct cured product from the composition without it based on the additional epoxy functionality reacted with the curing agent.

2) The curing agents embrace species such as aromatic diamines, dicyandiamide, boron trifluoride-amine complexes, imidazoles, polyamides, o-tolylbiguanides and (di)anhydrides (Specification, page 8, line 25 to page 9, line 32) which do not share a common structure and lead to diverse reactions with the epoxy resin(s).

3) The polymeric toughening agents do not possess a common structure and therefore confer different reactivities and physical properties to the composition.