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(54) **Multi-electrolyte treatment of carbon fibres to modify shear resistance.**

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DescriptionFIELD OF THE INVENTION

5 This invention relates to a process for electrolytically treating the surface of carbon fibers to improve mechanical properties, particularly when the fibers are combined with a resin matrix to form a composite. The invention further relates to the improved carbon fibers per se and to composites comprising the improved fibers in a bis-maleimide matrix resin.

BACKGROUND OF THE INVENTION

Electrolytic treatments of carbon fibers to improve adhesion between the fibers and a matrix resin when forming composite materials are known. Strength properties and their permanence in composite materials, particularly in an adverse environment, depend on the interfacial bonding of the composite, that is on the strength of the bonding between the carbon fiber and the resin matrix. Thus the development of various processes to increase interfacial bonding has been a prime goal of composites research, as evidenced by the prior art.

U.S. patent 3,671,411 to Ray et al discloses subjecting a carbon or graphite fiber to an electrolytic reaction in an aqueous electrolyte whereby negative ions are attracted to the surface of the fiber acting as anode, thereby modifying the fiber surface. The patentees state that subsequent bonding to plastics and resins is improved to such an extent that the shear strengths are increased in many cases to more than double the values obtained without this particular pretreatment with little or no loss in tensile strength.

U.S. patent 4,401,533 to Saito et al. discloses electrolytically surface treating carbon fibers in an aqueous solution of a sulfuric acid salt while passing a current through the fiber at a specified range of current density, a specified range for the product of current density, voltage, and processing time, and while continuously moving the carbon fiber as an anode in the aqueous electrolytic solution. The patentees state that their method produces carbon fibers having good adhesive properties to resins and high tensile strength and heat-oxidation resistance.

U.S. patent 3,832,297 to Paul, Jr. discloses an electrolytic process for surface treating graphite fibers wherein the improvement resides in using organic and inorganic ammonium compounds dissolved in water which compounds will decompose substantially completely to gaseous products on heating at temperatures below about 250°C. Illustrative ammonium compounds are stated to include ammonium hydroxide, ammonium carbonate, ammonium bicarbonate, ammonium carbamate, ammonium benzoate, ammonium dithionate, ammonium hydrosulfide, ammonium sulfite, ammonium thiosulfate, and ammonium tartrate.

No prior art known to the inventors discloses an electrolytic treatment of carbon fibers in a particular sequence of electrolytic baths. The present invention employs sequential electrolytic treatments which provide carbon fibers useful in making composites having excellent mechanical properties, for example, edge delamination strength (EDS). EDS is a measure of toughness in carbon fiber composites which indicates the tendency of a composite to crack around rivet holes, the test for which is well known to the art.

SUMMARY OF THE INVENTION

This invention provides a method of surface treating carbon fibers to improve the mechanical properties of composites comprising said fibers reinforcing a bis-maleimide matrix resin, comprising the steps of:

- a) moving said fiber, as anode, through a first aqueous electrolytic bath containing an oxygen acid, followed by
- b) moving said fiber, as anode, through a second aqueous electrolytic bath containing an aqueous solution of an ammonium compound, said bath having a pH of at least about 8, wherein step b) is conducted at 0,5 to 5 mA/cm².

The term "carbon fiber" as used herein is intended to be generic to both carbon and graphite fibers and includes fibers prepared by heating fibrous polymeric materials such as polyacrylonitrile, polyvinyl alcohol, pitch, natural and regenerated cellulose and the like to carbonizing or graphitizing temperatures. Generally the fibers, which are composed of individual filaments too thin to have any practical mechanical ruggedness, are conveniently treated in multi-filament bundles well known in the art as tows. Other physical arrangements of fibers such as woven or non-woven mats are also possible.

The electrolytes which may be used in the first aqueous electrolytic bath (herein also referred to as "oxygen bath") include any electrolyte which electrolytically generates oxygen at the surface of the anode,

i.e. the carbon fiber being treated, whereby oxygen functionalities are generated on the fiber surface. Preferred are mineral acids and bases such as aqueous solutions of phosphoric acid, nitric acid, sulfuric acid, and alkali metal hydroxides including sodium and potassium hydroxide, and the like. Also preferred are neutral salts (i.e. which, when dissolved in water, yield a pH between about 4 and about 8) such as sodium sulfate, lithium sulfate, sodium perchlorate, and sodium tetrafluoroborate. For practical applications concentrations of electrolyte generally in the range of 0.05 to 20 weight percent, preferably in the range of 1 to 10 weight percent, are preferred.

In the second electrolytic bath (herein also referred to as an "ammonium bath") any ammonium salt which dissolves in water to yield a pH of at least about 8 may be employed. Preferred are ammonium hydroxide and ammonium bicarbonate. The ammonium compound is believed to improve composite properties through modifying the carbon fiber surface with -NH_2 functionalities. The concentration of ammonium salt can be any desired concentration sufficient to impart -NH_2 functionality to the carbon fiber surface such that mechanical properties in the composite are improved as measured, for example, by edge delamination strength. Generally such concentration will fall in a range of about 0.02 Molar (M) to about 5M, preferably about 0.05M to about 3M.

An auxiliary electrolyte such as any of the neutral salts or alkali metal hydroxides noted as suitable for use in the oxygen bath may be used to increase conductivity in the ammonium bath. Generally the concentration of such auxiliary electrolytes will range between about 0.01M and about 0.5M.

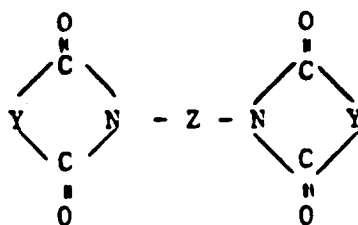
The voltage is not narrowly critical and can be adjusted generally to give a current density between about 0.5 and 5 milliamperes per square centimeter (mA/cm^2) of fiber surface area. Generally, the voltages employed in each bath will range between about 5 and 80 volts.

Bath temperatures are not narrowly critical and will generally be in the range of about 5°C to 50°C , the prevailing ambient (room) temperature or below being most preferably employed.

Voltage, current density, and residence time can be advantageously manipulated to expose the fiber to a total charge of from about 4 to 100 coulombs/gm, preferably about 7 to about 20 coulombs/gm. Using the general ranges of current density and voltage noted above, residence times between about 0.05 and about 1 minute are generally sufficient to achieve exposure to a charge within these ranges. Depending on practical bath lengths through which the tows are fed, usually a length between about 1 (0.305 m) and about 15 feet (4.572 m), line speeds of up to about 40 ft/min. (12.192 m/min) are entirely feasible.

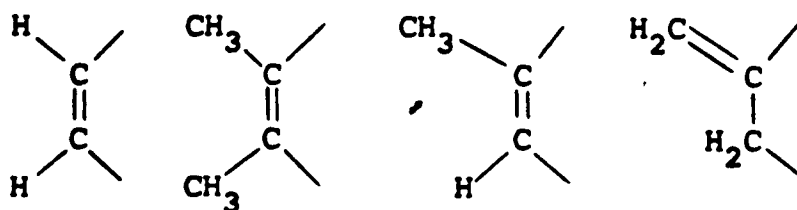
The present invention provides increased mechanical properties in thermosetting resin composites beyond that which can be ascribed to either of the baths alone or to their additive contributions. This result is surprising since electrolytically treating carbon fibers in the reverse bath sequence to that stipulated in the claims results in no improvement or, sometimes, even less improvement than that which results from using an oxygen bath alone.

Thermosetting bis-maleimide resins suitable for use in this invention are widely known in the art and, generally, are made by reacting a N,N' -bis-maleimide with a reactive comonomer capable of being copolymerized therewith. The general formula for suitable bis-maleimides includes those compounds of the formula

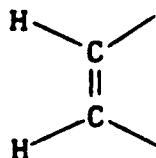


wherein

Y represents a divalent radical of at least 2 carbon atoms, preferably 2 to 6 carbon atoms, containing a carbon-carbon double bond. Y may, for example, be of the formula



10 The preferred structure for Y is



Y may, for example, be derived from acids or anhydrides such as maleic, citraconic, tetrahydrophthalic, and the like.

Z is a divalent radical which can be the residuum of a diamine containing at least 2 carbon atoms and generally not more than about 20 carbon atoms. "Residuum", of course, refers to that portion of a diamine exclusive of the two amino groups. Z can, for example, be

alkylene of 2 to 20 carbons atoms;

cycloalkylene of 5 or 6 carbon atoms;

heterocyclic of 4 or 5 carbon atoms and at least one nitrogen, sulfur, or oxygen atom in the heterocyclic ring; or

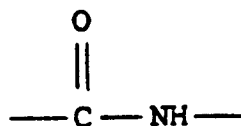
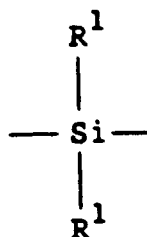
at least two mono-or dicarbocyclic aromatic or cycloalkylene groups which are linked to each other by a direct carbon-to-carbon bond or through a divalent linking group such as

—O—,

—S—,

alkylene of 1 to 3 carbon atoms, or a group of the formula

—P(O)R¹—:



in which R¹, which is alkyl of 1 to 5 carbon atoms, need not be the same within those groups containing more than one R¹.

Suitable N,N'-bis-maleimides include

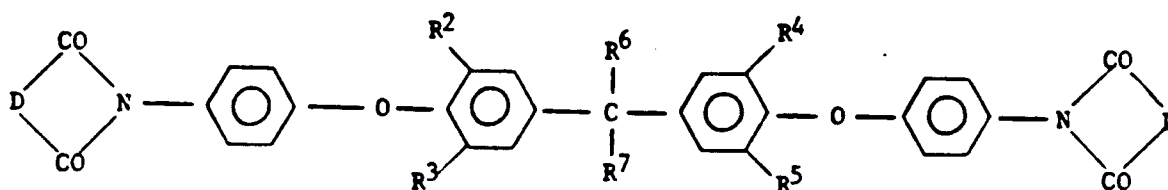
1,2-bismaleimido ethane,

1,6-bismaleimido hexane,

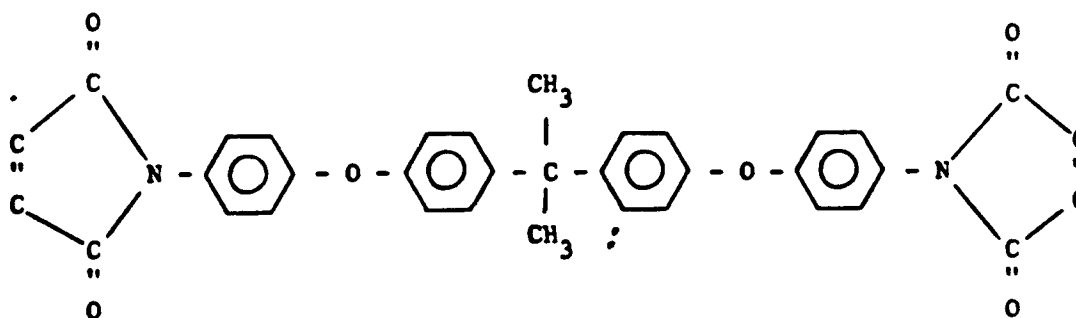
1,12-bismaleimido dodecane,
 1,6-bismaleimido -(2,2,4-trimethyl) hexane,
 1,3-bismaleimido benzene,
 1,4-bismaleimido benzene,
 5 4,4'-bismaleimido diphenyl methane,
 2,4-bismaleimido toluene,
 2,6-bismaleimido toluene,
 3,3'-bismaleimido diphenyl sulfone,
 4,4'-bismaleimido diphenyl sulfone,
 10 4,4'-bismaleimido diphenyl ether,
 4,4'-bismaleimido dicyclohexyl methane,
 4,4'-bismaleimido diphenyl cyclohexane,
 4,4'-bismaleimido diphenyl sulfide,
 N,N'-m-xylylene bismaleimide,
 15 N,N'-p-xylylene bismaleimide,
 N,N'-m-phenylene bis-citraconimide,
 N,N'-4,4'- diphenylene methane bis-citraconimide,

mixtures thereof, and the like. The above compounds are disclosed, for example, in U.S. patents 4,211,861 to Stenzenberger and 4,351,932 to Street et al. Other N,N'-bismaleimides and their preparation are disclosed in U.S. patents 3,562,223, 3,627,780 and 3,839,358, and 4,269,966.

Also suitable for use herein are ether bis-maleimides having the formula



wherein R², R³, R⁴ and R⁵ are independently hydrogen, lower alkyl having 1 to 6 carbon atoms, lower alkoxy having 1 to 6 carbon atoms, chlorine or bromine; R⁶ and R⁷ are independently hydrogen, methyl, ethyl, trifluoromethyl, or trichloromethyl; and D is an ethylenically unsaturated divalent group containing 2 to 24 carbon atoms. Particularly preferred is the following ether bis-maleimide



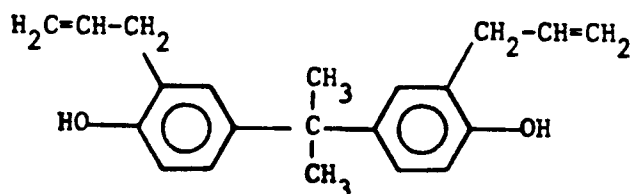
which can be made by reacting 2,2-bis [4-(4-aminophenoxy)phenyl] propane with maleic anhydride in acetone. These ether bis-maleimides, including the preferred compound, and their preparation are disclosed in U.S. patent 4,460,783 to Nishikawa et al.

Preferred bis-maleimides include

- (a) 4,4'-bismaleimido diphenyl methane,
- (b) 1,6-bismaleimido-(2,2,4-trimethyl)hexane,
- (c) eutectic mixtures of (a) and (b) with 2,4-bismaleimido toluene.

Any of the bis-maleimides disclosed in commonly assigned copending application Serial No. 564,400 filed December 22, 1983, which is herein incorporated by reference, may also be used in this invention.

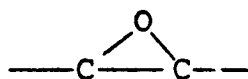
The liquid coreactants suitable for use in this invention for reacting with bis-maleimides to make bis-maleimide resins include 0,0'-diallylbisphenol A which has the structure



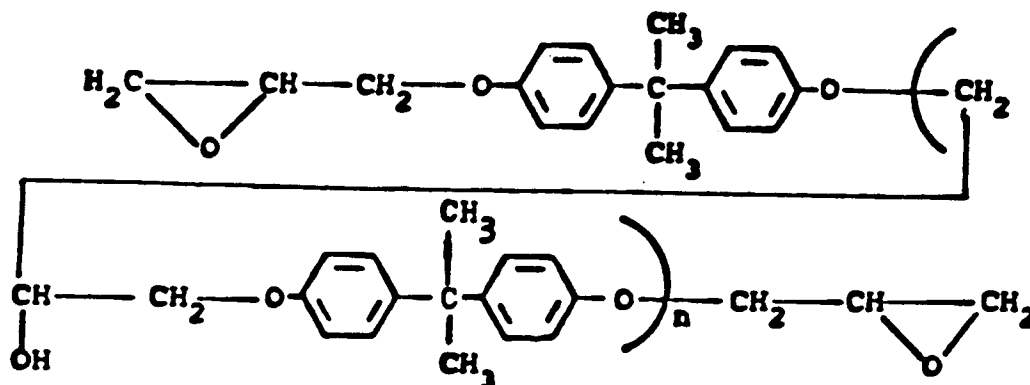
N-vinyl-2-pyrrolidinone, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, triallyl isocyanurate, diallyl phthalate, triallyl trimellitate, divinyl benzene, dicyclopentadienyl dienyl acrylate, dicyclopentadienyl oxyethyl acrylate, vinyl cyclohexene monoepoxide, 1,4-butanediol divinyl ether, 1,4-dihydroxy-2-butene, styrene, alpha methyl styrene, chlorostyrene, p-phenyl styrene, t-butyl styrene, phenyl vinyl ether, unsaturated polyesters, vinyl ester resins, and the like.

Preferred liquid coreactants include 0,0'-diallylbisphenol A, N-vinyl-2-pyrrolidone, triallyl isocyanurate, divinyl benzene, and ethylene glycol dimethacrylate.

Other liquid coreactants include epoxy resins containing one or more epoxy groups having the following formula:



The epoxy groups can be terminal epoxy groups or internal epoxy groups. The epoxides are of two general types: polyglycidyl compounds or products derived from epoxidation of dienes or polyenes. Polyglycidyl compounds contain a plurality of 1,2-epoxide groups derived from the reaction of a polyfunctional active hydrogen containing compound with an excess of an epihalohydrin under basic conditions. When the active hydrogen compound is a polyhydric alcohol or phenol, the resulting epoxide resin contains glycidyl ether groups. A preferred group of polyglycidyl compounds are made via condensation reactions with 2,2-bis(4-hydroxyphenyl)propane, also known as bisphenol A, and have structures such as I:



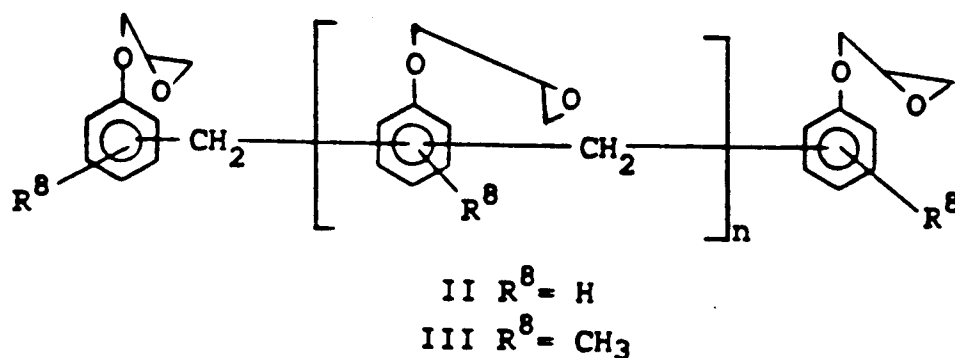
I

where n has a value from about 0 to about 15. These epoxides are bisphenol-A epoxy resins. They are available commercially under the trade names such as "Epon 828," "Epon 1001", and "Epon 1009" from

Shell Chemical Co., and as "DER 331", and "DER 334" from Dow Chemical Co. The most preferred bisphenol A epoxy resins have an "n" value between 0 and 10.

Polyepoxides which are polyglycidyl ethers of 4,4'-dihydroxydiphenyl methane, 4,4'-dihydroxydiphenyl sulfone, 4,4'-biphenol, 4,4'-dihydroxydiphenyl sulfide, phenolphthalein, resorcinol, 4,2'-biphenol, or tris(4-hydroxyphenyl) methane and the like, are useful in this invention. In addition, EPON 1031 (a tetraglycidyl derivative of 1,1,2,2-tetrakis(hydroxyphenyl)ethane from Shell Chemical Company), and Apogen 101, (a methylolated bisphenol A resin from Schaefer Chemical Co.) may also be used. Halogenated polyglycidyl compounds such as D.E.R. 542 (a brominated bisphenol A epoxy resin from Dow Chemical Company) are also useful. Other suitable epoxy resins include polyepoxides prepared from polyols such as pentaerythritol, glycerol, butanediol or trimethylolpropane and an epihalohydrin.

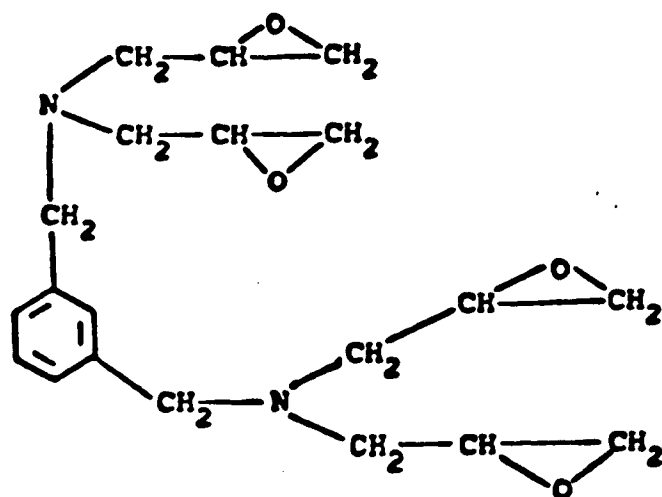
Polyglycidyl derivatives of phenol-formaldehyde novolaks such as II where $n = 0.1$ to 8 and cresol-formaldehyde novolaks such as III where $n = 0.1$ to 8 are also usable.



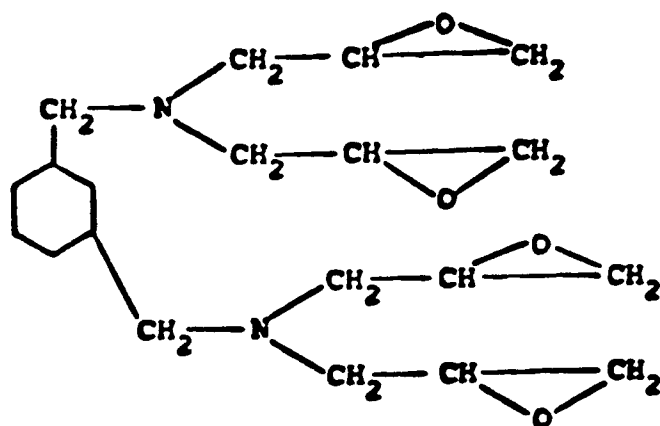
The former are commercially available as D.E.N. 431, D.E.N. 438, and D.E.N. 485 from Dow Chemical Company. The latter are available as, for example, ECN 1235, ECN 1273, and ECN 1299 (obtained from Ciba Geigy Corporation, Ardsley, NY). Other epoxidized novolaks such as SU-8 (obtained from Celanese Polymer Specialties Company, Louisville, KY) are also suitable.

Other polyfunctional active hydrogen compounds besides phenols and alcohols may be used to prepare the polyglycidyl adducts useful as reactive comonomers in this invention. They include amines, aminoalcohols and polycarboxylic acids.

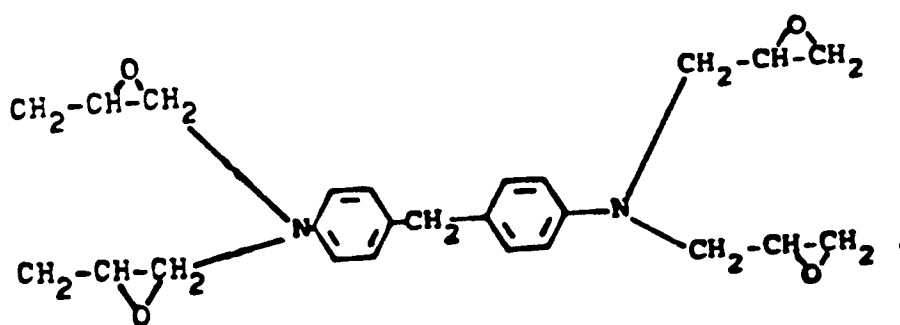
Adducts derived from amines include N,N-diglycidyl aniline, N,N-diglycidyl toluidine, N,N,N',N'-tetraglycidylxylylene diamine, (i.e., IV) N,N,N',N'-tetraglycidyl-bis (methylamino) cyclohexane (i.e. V) , N,N,N',N' tetraglycidyl-4,4'-diaminodiphenyl methane, (i.e. VI) N,N,N',N'-tetraglycidyl 3,3'-diaminodiphenyl sulfone, and N,N'-dimethyl-N,N'-diglycidyl-4,4'-diaminodiphenyl methane. Commercially available resins of this type include Glyamine 135 and Glyamine 125 (obtained from F.I.C. Corporation, San Francisco, CA.), Araldite MY-720 (obtained from Ciba Geigy Corporation) and PGA-X and PGA-C (obtained from The Sherwin-Williams Co., Chicago, Illinois).



IV



V



VI

Suitable polyglycidyl adducts derived from amino alcohols include O,N,N-triglycidyl-4-aminophenol, available as Araldite 0500 or Araldite 0510 (obtained from Ciba Geigy Corporation) and O,N,N-triglycidyl-3-aminophenol (available as Glyamine 115 from F.I.C. Corporation).

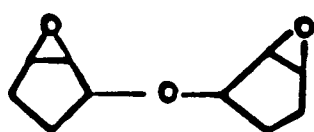
Also suitable for use as reactive comonomers are the glycidyl esters of carboxylic acids. Such glycidyl esters include, for example, diglycidyl phthalate, diglycidyl terephthalate, diglycidyl isophthalate, and

diglycidyl adipate. There may also be used polyepoxides such as triglycidyl cyanurates and isocyanurates, N,N-diglycidyl oxamides, N,N'-diglycidyl derivatives of hydantoins such as "XB 2793" (obtained from Ciba Geigy Corporation), diglycidyl esters of cycloaliphatic dicarboxylic acids, and polyglycidyl thioethers of polythiols.

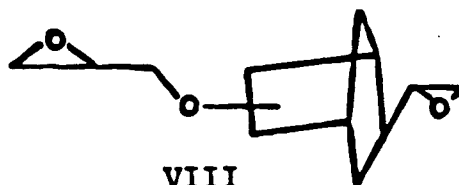
Other reactive epoxy-containing materials are copolymers of acrylic acid esters of glycidol such as glycidyl acrylate and glycidyl methacrylate with one or more copolymerizable vinyl compounds. Examples of such copolymers are 1:1 styrene-glycidyl methacrylate, 1:1 methyl methacrylate-glycidyl acrylate and 62.5:24:13.5 methyl methacrylate:ethyl acrylate:glycidyl methacrylate.

Silicone resins containing epoxy functionality, e.g., 2,4,6,8,10-pentakis [3-(2,3-epoxypropoxy)propyl]-2,4,6,8,10-pentamethylcyclotrisiloxane and the diglycidyl ether of 1,3-bis-(3-hydroxypropyl)-tetramethyldisiloxane) are also usable.

The second group of epoxy resins is prepared by epoxidation of dienes or polyenes. Resins of this type include bis(2,3-epoxycyclopentyl) ether, VII,



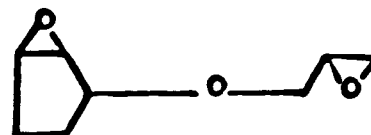
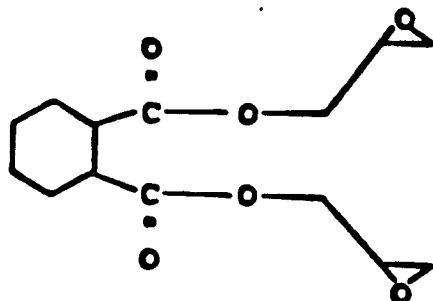
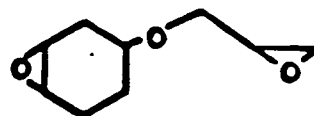
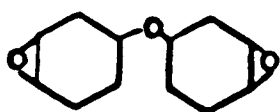
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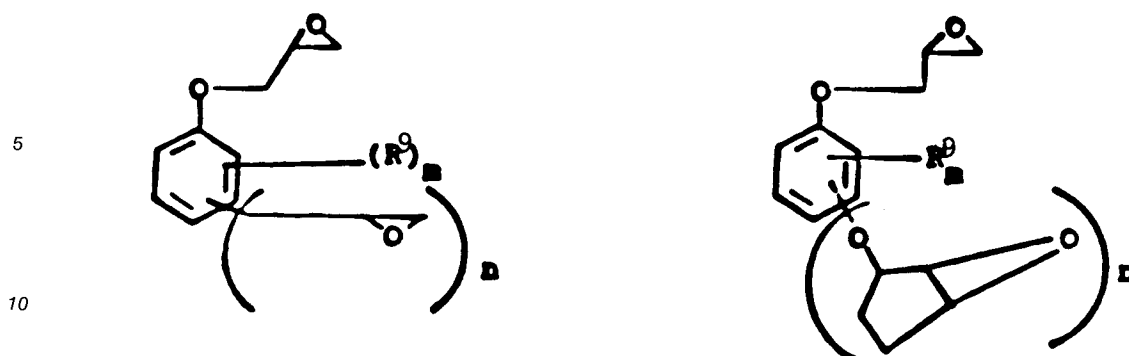
VIII

reaction products of VII with ethylene glycol which are described in U.S. Patent 3,398,102, 5(6)-glycidyl-2-(1,2-epoxyethyl)bicyclo[2.2.1] heptane, VIII, and dicyclopentadiene diepoxide. Commercial examples of these epoxides include vinylcyclohexene dioxide, e.g., "ERL-4206" (obtained from Union Carbide Corp.), 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate, e.g., "ERL-4221" (obtained from Union Carbide Corp.), 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexane carboxylate, e.g., "ERL-4201" (obtained from Union Carbide Corp.), bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, e.g., "ERL-4289" (obtained from Union Carbide Corp.), dipentene dioxide, e.g., "ERL-4269" (obtained from Union Carbide Corp.) 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexanemetadioxane, e.g., "ERL-4234" (obtained from Union Carbide Corp.) and epoxidized poly-butadiene, e.g., "Oxiron 2001" (obtained from FMC Corp.)

Other suitable reactive cycloaliphatic epoxides include those described in U.S. Patents 2,750,395; 2,890,194; and 3,318,822 which are incorporated herein by reference, and the following:



Other suitable epoxides include:



where n is 1 to 4, m is (5-n), and R⁹ is H, halogen or C₁ to C₄ alkyl.

The preferred epoxy resins are bis(2,3-epoxycyclopentyl)ether,

N,N,N',N'-tetraglycidyl xylenediamine,

N,N,N',N'- tetraglycidyl methylene dianiline,

O,N,N-triglycidyl-4-aminophenol, and

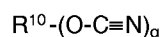
O,N,N-triglycidyl-3-aminophenol.

If epoxy resins are used, it may be desirable to add an aromatic diamine to the formulation. The diamine should have a low level of reactivity with the epoxy resin and the bis-maleimide at room temperature. Suitable polyamine hardeners for use in epoxy resin systems include 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, 3,4'-diaminobenzophenone, m-phenylene diamine, 4,4'-methylene dianiline, diethylene triamine, and the like. A stoichiometry of 0.3 to 2.0, preferably 0.5 to 1.5 equivalents of -NH per equivalent of 1,2-epoxide group can be used.

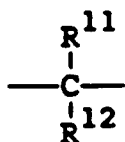
The epoxy resin system may additionally contain an accelerator to increase the rate of cure of the epoxy plus amine reaction. Accelerators which may be used herein include Lewis acid; amine complexes such as BF₃.monoethylamine, BF₃.piperidine, BF₃.2-methylimidazole; amines, such as imidazole and its derivatives such as 4-ethyl-2-methylimidazole, 1-methylimidazole, 2-methylimidazole; N,N-dimethylbenzylamine; acid salts of tertiary amines, such as the p-toluene sulfonic acid:imidazole complex, salts of trifluoro methane sulfonic acid, such as FC-520 (obtained from 3M Company), organophosphonium halides and dicyandiamide. If used, the accelerator may be from 1 to 6 percent by weight of the epoxy component.

The thermosetting resins may also contain compounds with one or more cyanate ester groups.

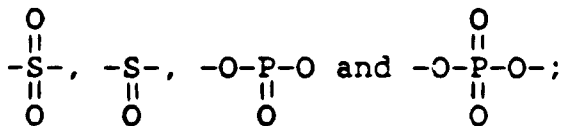
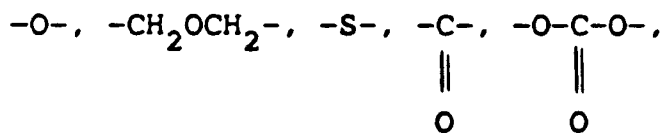
By cyanate ester is meant a compound having at least one cyanate group in its molecule. The cyanate ester is represented by the formula



wherein R¹⁰ is a residue derived from an aromatic hydrocarbon selected from the group consisting of benzene, biphenyl and naphthalene, or a residue derived from a compound in which at least two benzene rings are bonded to each other by a bridging member selected from the group consisting of



wherein R¹¹ and R¹² are the same or different and each represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms,



15 said aromatic residue R¹⁰ may be optionally substituted by a substituent selected from the group consisting of alkyl groups containing 1 to 4 carbon atoms, alkoxy groups containing 1 to 4 carbon atoms, chlorine and bromine; q is an integer of 1 to 5, and the cyanate group is always directly bonded to the aromatic nucleus.

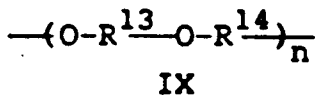
Examples of the cyanate ester include cyanatobenzene, dicyanatobenzene;

1,3,5-tricyanatobenzene;
20 1,3-, 1,4-, 1,6-, 1,8-, 2,6- or
2,7-dicyanatophthalene;
1,3,6-tricyanatophthalene;
4,4'-dicyanobiphenyl; bis(4-cyanatophenyl)methane;
2,2-bis(4-cyanatophenyl)propane;
25 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane;
2,2-bis(3,5-dibromo-4-dicyanatophenyl)propane;
bis(4-cyanatophenyl)ether;
bis(4-cyanatophenyl)thioether;
bis(4-cyanatophenyl)sulfone;
30 bis(4-cyanatophenyl)phosphite;
bis(4-cyanatophenyl)phosphate;
bis(3-chloro-4-cyanatophenyl)methane; cyanated novolak derived from novolak cyanated disphenol type
polycarbonate oligomer derived from bisphenol type polycarbonate oligomer and mixtures thereof.

Mixtures of bis-maleimides, epoxy resin systems, and compounds with one or more cyanate ester groups may be employed in this invention. Preferred mixtures are (i) bis-maleimide resin/epoxy resin system mixtures (ii) epoxy resins/cyanate ester compounds. and (iii) bis-maleimide resins/cyanate ester compounds.

The composites of this invention may optionally contain a small amount of a thermoplastic polymer. These materials have beneficial effects on the viscosity and film strength characteristics of the bismaleimide/reactive comonomer mixture.

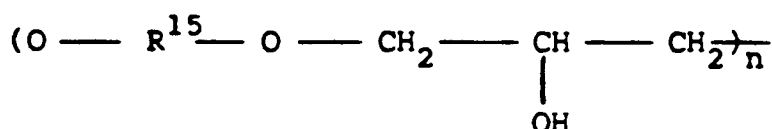
The thermoplastic polymers used in this invention include polyarylethers of formula IX which are described in U.S. Patents 4,108,837 and 4,175,175.



wherein R¹³ is a residuum of a dihydric phenol such as bisphenol A, hydroquinone, resorcinol, 4,4-biphenol, 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenyl sulfide, 4,4'-dihydroxy-3',3',5,5'-tetramethyldiphenyl sulfone and the like. R¹⁴ is a residuum of a benzenoid compound susceptible to nucleophilic aromatic substitution reactions such as 4,4'-dichlorodiphenyl sulfone, 4,4'-difluorobenzophenone, and the like. The average value of n is from about 8 to about 120.

Other suitable polyarylethers are described in U.S. Patent 3,332,209.

55 Also suitable are polyhydroxyethers of the formula:



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where R¹⁵ is a cycloaliphatic or aromatic divalent hydrocarbon radical and the average value of n is between about 8 and about 300; and polycarbonates such as those based on bisphenol A, tetramethyl bisphenol A, 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxy-3,3',5,5'-tetramethyl- diphenyl sulfone, 10 hydroquinone, resorcinol, 4,4'-dihydroxy-3,3',5,5'-tetramethyl diphenyl sulfide, 4,4'-biphenol, 4,4'-dihydroxydiphenyl sulfide, phenolphthalein, 2,2,4,4-tetramethyl-1,3-cyclobutane diol, and the like. Other suitable thermoplastics include poly (ε-caprolactone); polybutadiene; polybutadiene/acrylonitrile copolymers, including those optionally containing amine, carboxyl, hydroxy, or -SH groups; polyesters, such as poly(butylene terephthalate); poly(ethylene terephthalate); polyetherimides such as the Ultem resins (obtained from the 15 General Electric Company); acrylonitrile/ butadiene/styrene copolymers, polyamides such as nylon 6, nylon 6,6, nylon 6,12, and Trogamid T (obtained from Dynamit Nobel Corporation); poly(amide imides) such as Torlon poly(amide imide) (obtained from Amoco Chemical Corporation, Naperville, IL); polyolefins, polyethylene oxide; poly(butyl methacrylate); impact-modified polystyrene; sulfonated polyethylene; polyarylates such as those derived from bisphenol A and isophthalic and terephthalic acid; poly(2,6- dimethyl phenylene 20 oxide); polyvinyl chloride and its copolymers; polyacetals; polyphenylene sulfide and the like.

Poly(vinyl acetate) and copolymers of vinyl acetate with other vinyl and acrylic monomers can also be used. Thermoplastics such as low profile additives, for example, LP-40A, may also be used.

The bismaleimide thermosetting resin composition should contain between about 1 and about 99 weight percent, preferably 20-98 percent of bismaleimide; 1 to about 60 weight percent, preferably 3 to 40 percent 25 of the liquid coreactant or mixture of coreactants comprising molecules with one or more amino, epoxy, or cyanate groups and the like, as described above; 1 to about 40 percent, preferably 2 to 30 percent of other additives such as thermoplastic polymers.

The amount of carbon fiber in the composite is between about 10 and about 90 percent by weight, preferably between about 20 and about 85 percent by weight.

30 Additional components in the composition can include initiators for vinyl polymerization such as di-*t*-butyl peroxide, dicumyl peroxide, 1,1-bis *t*-butyl peroxy cyclohexane, azo bis isobutyronitrile and the like. The initiator comprises from 0 to 3 percent by weight of the total composition.

Inhibitors for vinyl polymerizations can also be used. They include, hydroquinone, *t*-butyl hydroquinone, benzoquinone, *p*-methoxyphenol, and 4-nitro-*m*-cresol. Inhibitors are present in amounts of from 0 to 2 35 percent by weight of the total composition.

By reacting a suitable reactive comonomer with any one or a mixture of the above-described bismaleimides a matrix resin having the physical characteristics necessary for use in a conventional process for producing prepreg can be obtained and combined with carbon fibers surface-treated according to the invention to make a preimpregnated reinforcement.

40 Preimpregnated reinforcement can be prepared by several techniques known in the art, such as wet winding or hot melt. In one method of making impregnated tow or unidirectional tape, the fiber is passed into a bath of the resin mixture. A non-reactive, volatile solvent such as methyl ethyl ketone may be optionally included in the resin bath to reduce viscosity. After impregnation, the reinforcement is passed through a die to remove excess resin, sandwiched between plies of release paper, passed through a set of heated rollers, 45 cooled, and taken up on a spool. It can be used within a few days or may be stored for months at 0° F. (-17.78° C)

Composites may be prepared by curing preimpregnated reinforcement using heat and, optionally, pressure. Vacuum bag/autoclave cures work well with these compositions. Laminates may also be prepared via wet layup followed by compression molding, resin transfer molding, or by resin injection, as described in 50 European Patent Application 0019149 published November 26, 1980. Typical cure temperatures are 100° F (37.78° C) to 500° F (260° C) preferably 180° F (82.22° C) to 450° F (232.22° C).

The composites of this invention may be used as aircraft parts such as wing skins, wing-to-body fairings, floor panels, flaps, radomes; as automotive parts such as driveshafts, bumpers, and springs; and as pressure vessels, tanks and pipes. They are also suitable for protective armor on military vehicles and 55 sporting goods applications such as golf shafts, tennis rackets, and fishing rods.

In addition to structural fibers, the composition may also contain particulate fillers such as talc, mica, calcium carbonate, aluminum trihydrate, glass microballoons, phenolic thermospheres, and carbon black. Up to half of the weight structural fiber in the composition may be replaced by filler. Thixotropic agents such as

fumed silica may also be used.

Example 1

Unsize and unshear treated carbon fiber samples commercially available in tows having about 12000 fibers/tow from Union Carbide Corporation under the trade designation T-300 were electrolytically treated in a nitric acid bath (conc. 0.5M) and/or an ammonium hydroxide bath (conc. 2.65M) except for control fiber which was not treated in a bath. The degree of shear treatment was evaluated by ESCA of the unsize fiber and by composite EDS testing using a bis-maleimide matrix resin consisting of a mixture of 54 parts by weight of methylene dianiline bismaleimide and 46 Parts by weight of 0,0-diallylbisphenol A. The polarity in each bath was the same. The composites were made by laying up ten plies of prepreg made by a hot melt process. The four centermost plies contained T-300 carbon fiber having a fiber area weight of about 145 gm/m². The other six outer plies (three on each side of the four center plies) were made with T-40 carbon fiber (available from Union Carbide Corporation) having a fiber area weight of about 136 gm/m². All composites were autoclave cured and the resin was bled to give a nominal cured composite fiber volume loading of 60%.

The ESCA and EDS results are given in Table I, along with the line speeds and bath current values. In the column designated "Electrolyte", a "+" indicates two separate baths.

Table I

T-300 12k Shear Treatment								
Electrolyte	Treatment Level (coul./g)	Line Speed		Current (amps)	ESCA*		EDS (ksi)	
		(ft/min)	(m/min)		O	N	As Made	Dry**
None	--	--	(--)	--	4.2	2.3	21.5	18.7
HNO ₃	9.8	5	(1.52)	0.2	10.9	1.9	40.1	33.3
NH ₄ OH	16.4	2	(0.61)	0.3	6.8	3.8	40.1	38.6
HNO ₃	4.9	10	(3.05)	0.2	8.2	1.8		
+ NH ₄ OH	8.2	4	(1.22)	0.3	7.2	4.6	44.4	42.1
HNO ₃	9.8	5	(1.52)	0.2	12.0	1.0		
+ NH ₄ OH	16.4	2	(0.61)	0.3	7.8	7.6	47.7	40.0

* Indicated the polarity of the electrodes in the bath.

** Dried overnight at 180 ° F. (82.22 ° C)

Those skilled in the art will readily appreciate that many modifications are possible in the above exemplary embodiments without materially departing from the novel teachings and advantages of this invention.

Claims

1. A method of surface-treating carbon fibers comprising the steps of:

(a) moving the carbon fiber, as anode, through a first electrolytic bath comprising an aqueous solution of an oxygen acid; then

(b) moving said carbon fiber, as anode, through a second electrolytic bath comprising an aqueous solution of an ammonium compound, said bath having a pH of at least about 8, wherein step b) is conducted at 0.5 to 5 mA/cm².

2. The method of claim 1 wherein said oxidizer is an oxygen acid selected from the group consisting of nitric acid, sulfuric acid and phosphoric acid.

3. The method of claim 1 wherein said oxidizer is present in from about 0.5 to about 20 wt%.

4. The method of claim 1 wherein said oxidizer is present from about 1 to about 10 wt%.

5. The method of claim 1 wherein said ammonium compound is ammonium hydroxide.

6. The method of claim 1 wherein the concentration of said ammonium compound is from about 0.02 M to about 5 M.
7. A method of surface-treating carbon fibers according to Cl. 1, comprising the steps of:
 - (a) moving said fiber, as anode, through a first electrolytic bath comprising an aqueous solution of from about 0.5 to about 20 wt% nitric acid, followed by
 - (b) moving said fiber, as anode, through a second electrolytic bath comprising from about 0.2 to about 5 M aqueous ammonium hydroxide wherein step b) is conducted at 0.5 to 5 mA/cm².
8. A carbon fiber which is surface-treated by the process of Claim 7 and having a surface elemental content of at least 7% oxygen and at least 4% nitrogen.

Revendications

1. Procédé de traitement de surface de fibres de carbone comprenant les étapes consistant à :
 - (a) déplacer la fibre de carbone, en tant qu'anode, à travers un premier bain électrolytique comprenant une solution aqueuse d'un acide d'oxygène ; puis
 - (b) déplacer la fibre de carbone, en tant qu'anode, à travers un second bain électrolytique comprenant une solution aqueuse d'un composé d'ammonium, le bain ayant un pH d'au moins environ 8, et dans lequel l'étape (b) est conduite à 0,5 jusqu'à 5 mA/cm².
2. Procédé selon la revendication 1, dans lequel l'agent oxydant est un acide d'oxygène choisi dans le groupe consistant en l'acide nitrique, l'acide sulfurique et l'acide phosphorique.
3. Procédé selon la revendication 1, dans lequel l'agent oxydant est présent en une quantité allant d'environ 0,5 jusqu'à environ 20 % en poids.
4. Procédé selon la revendication 1, dans lequel l'agent oxydant est présent en une quantité d'environ 1 jusqu'à environ 10 % en poids.
5. Procédé selon la revendication 1, dans lequel le composé d'ammonium est de l'hydroxyde d'ammonium.
6. Procédé selon la revendication 1, dans lequel la concentration du composé d'ammonium est d'environ 0,02 M jusqu'à environ 5 M.
7. Procédé de traitement de surface de fibres de carbone selon la revendication 1, comprenant les étapes consistant à :
 - (a) déplacer la fibre en tant qu'anode, à travers un premier bain électrolytique comprenant une solution aqueuse en une quantité d'environ 0,5 jusqu'à environ 20 % en poids d'acide nitrique, puis
 - (b) déplacer la fibre en tant qu'anode à travers un second bain électrolytique comprenant environ 0,2 jusqu'à environ 5 M d'hydroxyde d'ammonium aqueux, dans lequel l'étape (b) est conduite à 0,5 jusqu'à 5 mA/cm².
8. Fibre de carbone qui est traitée en surface par le procédé selon la revendication 7 et ayant une teneur élémentaire en surface d'au moins 7 % d'oxygène et au moins 4 % d'azote.

Patentansprüche

1. Verfahren zur Oberflächenbehandlung von Kohlenstoff-Fasern, umfassend die folgenden Stufen:
 - (a) das Bewegen der Kohlenstoff-Faser als Anode durch ein erstes Elektrolysebad, welches eine wäßrige Lösung einer Sauerstoffsäure umfaßt, und hiernach
 - (b) das Bewegen der Kohlenstoff-Faser als Anode durch ein zweites Elektrolysebad, welches eine wäßrige Lösung einer Ammoniumverbindung umfaßt, wobei das Bad einen pH von zumindest etwa 8 aufweist und wobei Stufe (b) bei 0,5 bis 5 mA/cm² durchgeführt wird.
2. Verfahren gemäß Anspruch 1, worin das Oxidationsmittel eine Sauerstoffsäure, ausgewählt unter Salpetersäure, Schwefelsäure und Phosphorsäure, ist.

3. Verfahren gemäß Anspruch 1, worin das Oxidationsmittel in etwa 0,5 bis etwa 20 Gew.-% vorliegt.
4. Verfahren gemäß Anspruch 1, worin das Oxidationsmittel in etwa 1 bis etwa 10 Gew.-% vorliegt.
- 5 5. Verfahren gemäß Anspruch 1, worin die Ammoniumverbindung Ammoniumhydroxid ist.
6. Verfahren gemäß Anspruch 1, worin die Konzentration der Ammoniumbindung etwa 0,02 M bis etwa 5 M beträgt.
- 10 7. Verfahren zur Oberflächenbehandlung von Kohlenstoff-Fasern gemäß Anspruch 1, umfassend die folgenden Stufen
- (a) das Bewegen der Faser als Anode durch ein erstes Elektrolysebad, welches eine wäßrige Lösung von etwa 0,5 bis etwa 20 Gew.-% Salpetersäure umfaßt, und hieran anschließend
- 15 (b) das Bewegen der Faser als Anode durch ein zweites Elektrolysebad, umfassend etwa 0,2 bis etwa 5 M wäßriges Ammoniumhydroxid, wobei Stufe (b) bei 0,5 bis 5 mA/cm² durchgeführt wird.
8. Nach dem Verfahren von Anspruch 7 oberflächenbehandelte Kohlenstoff-Faser mit einem Oberflächen-elementgehalt von zumindest 7% Sauerstoff und zumindest 4% Stickstoff.

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