

Description

FIELD OF THE INVENTION

This invention relates to improved epoxy resin compositions. In addition, it relates to curable epoxy resin compositions comprising reinforcing filaments and epoxy prepolymers, cured with a series of substituted bisurea catalysts derived from aryl monoisocyanates and diamines, alone, or combined with aromatic polyamines.

BACKGROUND OF THE INVENTION

Epoxy resin compositions are useful to encapsulate electronic components, and as structural adhesives. Reinforced epoxy resin composites having high strength to weight ratios have been found extensive use in the aircraft and aerospace industries, and in other applications where strength, corrosion resistance and light weight are desirable. For instance, fiber resin matrix materials have replaced aluminum and other metals in primary and secondary structures of modern military and commercial aircraft. Sporting equipment such as tennis rackets and golf clubs have also adopted fiber resin materials successfully.

Epoxy resin compositions and fiber modifications are abundant. Since the advent of fiber resin matrix materials, much effort has been expended in improving their properties and characteristics, including the development of many curing systems.

It is known to add curing agents functioning as accelerators or catalysts such as substituted ureas and boron trifluoride-amine complexes to such epoxy compositions to cure them, and also to significantly decrease the hardening temperature of such resin systems. Substituted ureas made from monoamines and polyisocyanates and used for this purpose are described, for example, in U.S. 3,386,955 and EP-A-0133281 and the use of boron trifluoride-amine complexes is also described and claimed in the latter. While such curing agents do lower gel times, they tend to lower the mechanical properties of high performance epoxy resins, especially those containing tetraglycidyl-diaminodiphenylmethane. Although they increase resin toughness, they lower hot/wet properties and glass transition temperatures.

Amine and polyamine curing agents have received wide acceptance for use alone with epoxys, or in combination with the substituted urea curing agents or the boron trifluoride-amine complexes. Among these can be mentioned, for example, polyamino aromatic compounds, such as m-phenylenediamine, 4,4'-diaminodiphenyl methane and 3,3'-diaminodiphenyl sulfone, as well as the aminobenzoates disclosed in U.K. Patent 1,182,377, U.S. 3,932,360, and in Gillham, Organic, Coatings and Applied Polymer Science Proceedings, Vol. 46, p 592-598, March-April, 1982. Such aromatic polyamines are effective as curing agents for a variety of polyepoxides, and the resulting cured compositions are useful as films, moldings, coatings and glass-reinforced laminates.

Further, GB-A-1 194 465 discloses the use of adducts of an organic monoisocyanate with a polyamine as a curing agent for epoxy resins.

Non-published EP-A-113 233 describes curable compositions comprising a polyepoxide, an aromatic urea curing agent and a condensation catalyst to promote the reaction between the polyepoxide and the curing agent.

While there is generally no indication in the properties presented in the prior art that the curing agents exemplified therein will produce the combination of toughness and strength under hot/wet conditions essential for use in the above-mentioned structural applications, the said copending application EP-A-0 133 281 describes fiber resin matrices comprising reinforcing filaments in a heat-curable epoxy resin composition comprising an epoxy prepolymer and a novel family of aromatic polyamine curing agents. The application describes neat resin formulations having, after cure, improved physical properties, e.g., higher elongation and satisfactory hot/wet modulus. Moreover, the epoxy compositions, cured with filaments, and catalyzed, exhibit improved inter-laminar toughness and residual compression strength after impact, while maintaining compression strength under hot/wet conditions.

It has now been discovered that a particular family of bisurea catalysts can be obtained by reacting an aryl monoisocyanate with an organic diamine, and that their use with epoxys alone or in further combination with polyamines provides desirable temperature-viscosity profiles during cure and unexpected resistance to degradation in hot/wet properties, as well as retention of thermal properties.

SUMMARY OF THE INVENTION

According to the present invention, there are provided heat curable compositions comprising:
(a) an epoxy prepolymer or combination of prepolymers having more than one epoxide group per molecule, and

(b)(i) an amount effective to cure said epoxy (a) of a bisurea compound comprising the reaction product of an organic diamine with at least two moles, per mole of diamine of an aryl monoisocyanate alone, or in an amount of 0.1 to 20 parts by weight per 100 parts of epoxy resin in further combination with
(b)(ii) an amount effective to cure of an amine functional aromatic curing agent.

Such compositions are useful in adhesives, potting compounds, encapsulating resins, molding resins, coatings and the like.

Also provided are such compositions combined with fibrous reinforcements and a modifying resin. According to this aspect there are provided fiber resin matrix compositions comprising

A. reinforcing filaments, and

B. a heat-curable epoxy resin composition comprising:

(a) an epoxy prepolymer or combination of prepolymers having more than one epoxide group per molecule, and

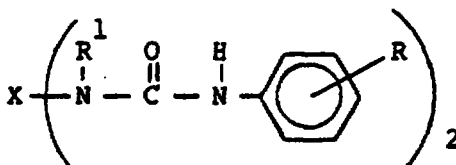
(b)(i) an amount effective to cure said epoxy of a bisurea compound comprising the reaction product of an aryl monoisocyanate and an organic diamine as defined above alone or in further combination with

(b)(ii) an amount effective to cure said epoxy (a) of an amine functional aromatic amine curing agent, alone, or in further combination with

(c) a second homogeneous or heterogeneous resin component blended and alloyed with components (a), (b)(i) and (b)(ii) in an amount sufficient to enhance toughness and resistance to failure under hot/wet stress conditions in composites produced from said composition. Resins of type (c) can be present homogeneously and also in the form known as interpenetrating polymer networks.

Preferably, in such compositions, in component B, (a) comprises 100 parts by weight, component (b)(i) comprises 0.25 to 20 parts by weight, (b)(ii) comprises 10 to 55 parts by weight, and component (c) comprises 5 to 50 parts by weight per 100 parts by weight total of B.

A preferred series of accelerators (b)(i) according to this invention is of the formula



wherein X is a divalent organic hydrocarbon radical, a divalent or trivalent hetero-interrupted hydrocarbon radical, or a divalent inertly-substituted hydrocarbon radical, R is hydrogen, a monovalent hydrocarbon radical, an amino or hydrocarbon substituted amino radical, a cyano radical, a hydrocarbonoxy radical or an inertly-substituted such radical, and R¹ is, independently hydrogen, a monovalent hydrocarbon radical, an inertly-substituted hydrocarbon radical, a single bond, or a divalent alkylene radical or inertly-substituted such radical.

Especially preferred are bisureas of the above formula wherein X is a divalent alkylene radical of from 2 to 12 carbon atoms, a trivalent nitrogen-interrupted alkylene radical of 4 to 12 carbon atoms, a divalent arylene or polyarylene radical of 6 to 30 carbon atoms interrupted with —CR²—, —O—, —S— or —SO₂— groups, wherein R² is hydrogen, a monovalent hydrocarbon radical or an inertly-substituted hydrocarbon radical, R is hydrogen, cyano, amino, methoxy, vinyl or ethinyl, and R¹ is hydrogen, alkyl of 1 to 6 carbon atoms, aryl of 6 to 12 carbon atoms, or divalent alkylene of from 2 to 3 carbon atoms.

Special mention is made of the most preferred bisureas. These are of the above formula wherein X is divalent alkylene of from 2 to 12 carbon atoms, trivalent nitrogen-interrupted alkylene of from 4 to 12 carbon atoms, divalent diaryl sulfone of from 12 to 20 carbon atoms, R is hydrogen, amino, vinyl, methoxy or ethinyl, and R¹ is hydrogen, or alkyl of 1 to 6 carbon atoms, or divalent alkylene of from 2 to 3 carbon atoms.

The term "inertly-substituted" as used herein means bearing substituents which will not react with epoxide groups, i.e., generally free of active hydrogen.

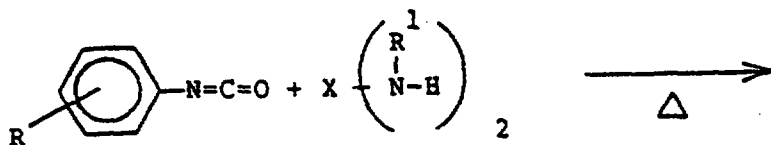
DESCRIPTION OF THE DRAWINGS

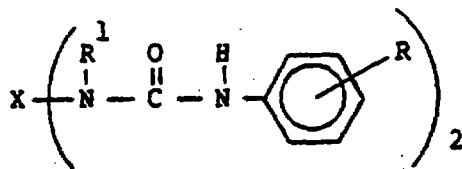
Figure 1 is a schematic of one method for preparing a fiber resin matrix prepreg tape of the present invention.

Figure 2 is an enlarged cross-sectional view of a strip of the fiber resin matrix prepreg tape of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The curing catalysts of this invention are prepared by reacting an aryl isocyanate with a diamine in a solvent, such as toluene, acetonitrile, or tetrahydrofuran, in accordance with the following:





The reaction conditions are not particularly critical. At least two moles of isocyanate are used per mole of diamine. Temperatures can be ambient, e.g., 20–25°C, or mild heating up to 100°C can be used. The reaction is over in a relatively short period of time, one hour usually being adequate. The products are recovered in conventional fashion, usually by precipitation, filtration and drying. They are usually obtained as white, crystalline solids, and can be further purified, if desired, by conventional means, such as by recrystallization.

The starting materials are either commercially available, or they can easily be made. Among the arylmonoisocyanates which can be employed are: phenyl isocyanate, 4-methylphenyl isocyanate, 4-methoxyphenyl isocyanate, 4-acetaminophenyl isocyanate, 4-cyanophenyl isocyanate, 4-vinylphenyl isocyanate, 4-ethinylphenyl isocyanate, 4-isopropenylphenyl isocyanate, 1-naphthyl isocyanate, 4-phenyl isocyanate, the 2- and 3-substituted isomers thereof, and the like. Preferably, phenyl isocyanate will be used.

The diamines likewise are available from a number of commercial sources and can be readily prepared by those skilled in this art. They will comprise diprimary, dissecondary and mixed diprimary and dissecondary amines. Illustrative are ethylenediamine, 1,3-propylenediamine, 1,2-propylenediamine, 1,4-tetramethylenediamine, 1,6-hexamethylenediamine, 1,12-dodecamethylenediamine, N,N'-dimethylethylenediamine, N,N'-diethyl-1,3-propanediamine, diethanolamine, N,N'-dimethylethanolamine, piperazine and N-(2-aminoethyl)piperazine. The preferred diamines comprise N,N'-dimethyl-1,6-hexamethylenediamine, N,N'-diethyl-1,3-propane-diamine, piperazine, N-(2-aminoethyl)piperazine and 1,3-propanediamine.

In general, the resin compositions of this invention are prepared by mixing the polyepoxide compounds with the bisurea catalyst in quantities, e.g., of 0.1 to 5 parts by weight per 100 parts by weight based on the epoxide. If polyamines are to be included, they will be added in conventional quantitative ratios, e.g., 1 epoxide equivalent to 0.3 to 3.0 NH- equivalents, preferably 1.0 to 3.0 NH- equivalents, and especially preferably 1.5 to 2.5 NH- equivalents. Mixing is accomplished optionally with heating, e.g., at a temperature in the range of 30 to 160°C, preferably at a temperature in the range of 80 to 140°C, until a melt is obtained and stirring is continued for a few additional minutes. The melt can then be poured into a mold and reacted, for example, for 2 hours at 135°C and then for 3 hours at 180°C, to form castings. The castings can then be cut into coupons and tested. They show outstanding flexural and thermal properties. The NH-equivalents is the quantity of aromatic polyamine in grams in which 1 gram-atom of hydrogen combined with amine nitrogen is present.

Fillers, pigments, dyes, reinforcements, such as glass fibers or woven cloths, plasticizers and mixtures thereof, may be added to the epoxy resin-bisurea catalyst composition before the reaction in order to modify ultimate properties, in known ways. Applications can also be made by trowelling, brush coating, immersion or dip-coating, spraying or any other convenient method.

The fiber resin matrix compositions according to the present invention can be prepared by embedding filaments, e.g., glass fibers and/or non-siliceous filaments in a curable resin composition to form a fiber resin matrix which can be manipulated and cured to a solid composite. Particular selection of the filament material, epoxy prepolymer, curing agent(s), and thermoplastic resin as well as including optional ingredients such as fillers, dyes, processing aids, etc., can give a range of curable compositions heretofore unknown in the art and exhibiting improved physical properties over known materials.

Glass filaments useful herein are well known. Non-siliceous filament components may be of any non-glass, non-silicon dioxide-containing material which improves the strength or other physical properties of the curable epoxy resin component (described *infra*). Such filaments include, but are not limited to, filaments comprised of carbon, graphite, silicon carbide, boron, aramid, polyester, polyamide, rayon, polybenzimidazole, polybenzothiazole, metal-coated such filaments, for example nickel-coated and/or silver-coated graphite fibers and filaments, or combinations of such filaments. Fibers (woven or non-woven), tows or mats of such filaments, or tapes (unwoven, flat bundles of the unidirectional filaments) may be employed as desired. In applications demanding high stiffness to weight ratio or shear strength, carbon fibers, graphite filaments, polyaramid filaments or nickel-plated graphite filaments, as disclosed in assignee's EP-A-88884 are most preferred.

The epoxy resins suitable for the present invention are compounds having more than one epoxide group per molecule available for reaction with the primary and secondary polyamines of the present invention (described *infra*). Such epoxy prepolymers include but are not limited to, polyglycidyl ethers of polyhydric phenols, for example pyrocatechol; resorcinol; hydroquinone; 4,4'-dihydroxydiphenyl methane; 4,4'-dihydroxy-3,3'-dimethyldiphenyl methane; 4,4'-dihydroxydiphenyl dimethyl methane; 4,4'-dihydroxydiphenyl methyl methane; 4,4'-dihydroxydiphenyl cyclohexane; 4,4'-dihydroxy-3,3'-dimethyl-

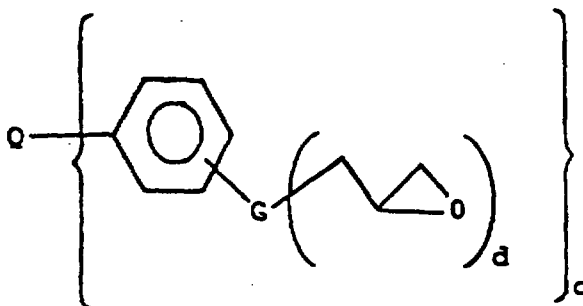
diphenyl propane; 4,4'-dihydroxydiphenyl sulphone; or tris-(4-hydroxyphenyl) methane; polyglycidyl ethers of the chlorination and bromination products of the above-mentioned diphenols; polyglycidyl ethers of novolacs (i.e., reaction products of monohydric or polyhydric phenols with aldehydes, formaldehyde in particular, in the presence of acid catalysts); polyglycidyl ethers of diphenols obtained by esterifying 2 mols of the sodium salt of an aromatic hydroxycarboxylic acid with 1 mol. of a dihalogenalkane or dihalogen dialkyl ether (U.K. 1,017,612); and polyglycidyl ethers of polyphenols obtained by condensing phenols and long-chain halogen paraffins containing at least 2 halogen atoms (U.K. 1,024,288).

Other suitable compounds include polyepoxy compounds based on aromatic amines and epichlorohydrin, for example N,N'-diglycidyl-aniline; N,N'-dimethyl-N,N'-diglycidyl-4,4'-diaminodiphenyl methane; N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane; and N-diglycidyl-4-aminophenyl glycidyl ether. Special mention is made of N,N,N',N'-tetraglycidyl-1,3-propylene bis(4-aminobenzoate).

Glycidyl esters and/or epoxycyclohexyl esters of aromatic, aliphatic and cycloaliphatic polycarboxylic acids, for example phthalic acid diglycidyl ether and adipic ester diglycidyl and glycidyl esters of reaction products of 1 mol of an aromatic or cycloaliphatic dicarboxylic acid anhydride and 1/2 mole of a diol or 1/n mol of a polyol with n hydroxyl groups, or hexahydrophthalic acid diglycidyl esters, optionally substituted by methyl groups, are also suitable.

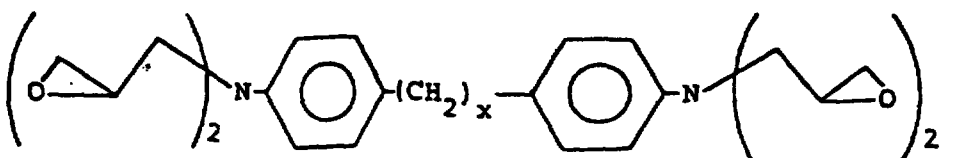
Glycidyl ethers of polyhydric alcohols, for example of 1,4-butanediol; 1,4-butenediol; glycerol; 1,1,1-trimethylol propane; pentaerythritol and polyethylene glycols may also be used. Triglycidyl isocyanurate; and polyglycidyl thioethers of polyvalent thiols, for example of bis mercaptomethylbenzene; and diglycidyltrimethylene sulphone, are also suitable.

Preferably the epoxy prepolymer component will be selected from compounds having the idealized formula:

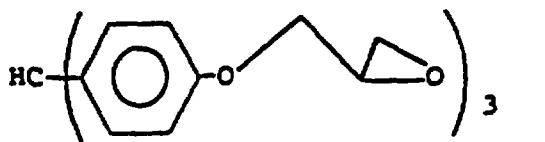


and halogen and alkyl substituted derivatives of such compounds, wherein c is 2, 3 or 4 and equal to the valence of Q; Q is a divalent, trivalent or tetravalent radical; G is —O—, NR'— or —N—; R is hydrogen or alkyl; and d is 1 or 2 depending on the valence of G.

The most preferred epoxy compounds will include the following:

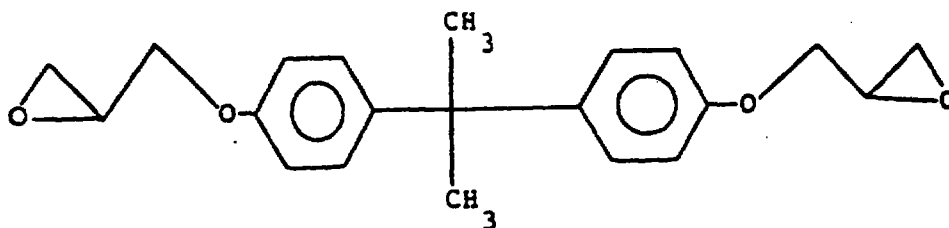


wherein x is an integer from 1 to 4, available commercially (where x = 1) as Araldite® MY-720 (Ciba-Geigy);

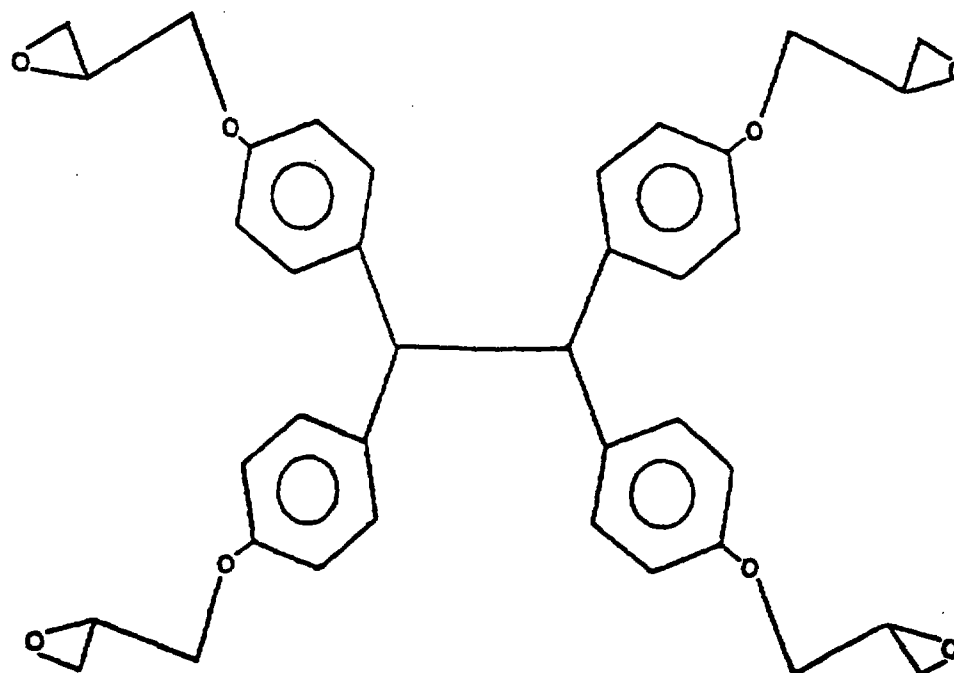


available commercially as XD7342 (Dow Chemical);

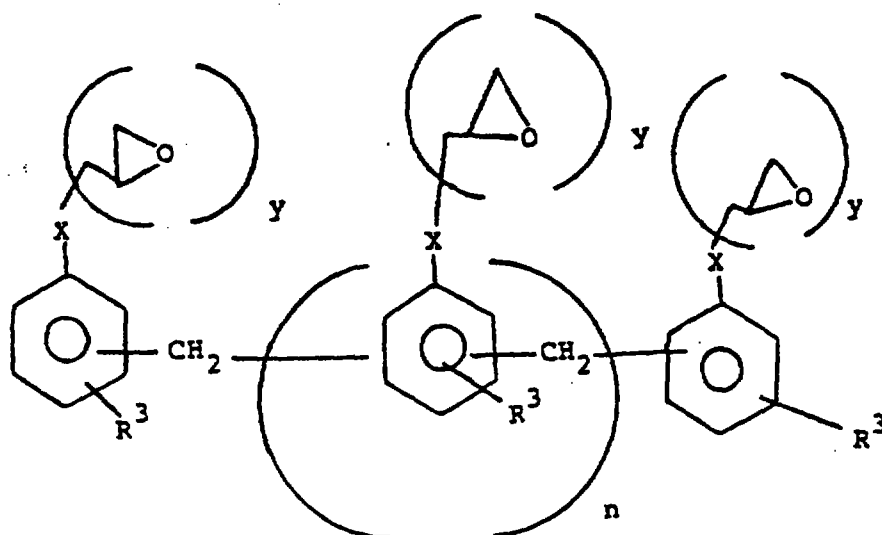
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available commercially as DER331 (Dow Chemical) or EPON® 828 (Shell);



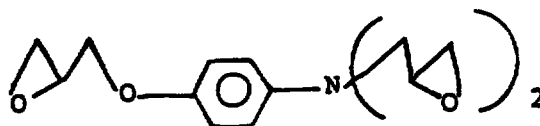
available commercially as EPON® 1031 (Shell);



wherein Y is 1 or 2, X is —O— or —N—, R³ is H or CH₃ and n is 2 to 8.

Compounds in which X is —O— are available as a mixture under the tradename DEN—438 from Dow Chemical Company.

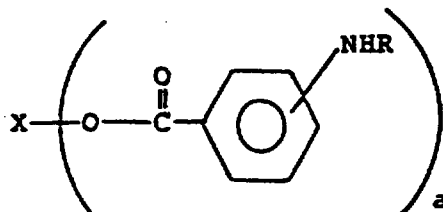
Also preferred are N,N,O-triglycidyl compounds of meta- and para-hydroxyaniline, e.g., represented by the formula:



These are available under the tradename ARALDITE® 0500, 0510 from Ciba-Geigy.

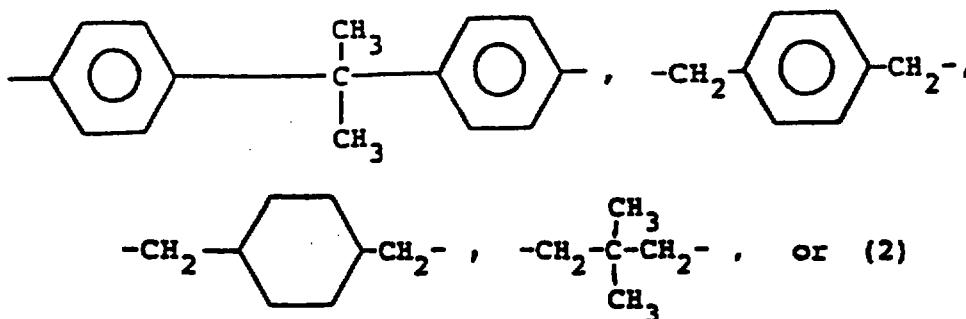
In general any polyaminoaromatic compound conventionally used for curing such epoxide prepolymers can be used in this invention. For example, m- and p-phenylenediamine, diamino-naphthalene, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfone and 4,4'-diaminodiphenylether, can be used. Among these, 3,3'-diaminodiphenylsulfone is preferred.

For those compositions which contain component (b)(ii), an especially preferred series of polyamine curing agents are of the formula:



wherein a is 2 or 3, R is hydrogen alkyl or aryl, and X is a divalent or trivalent organic hydrocarbon, hetero-interrupted hydrocarbon, or substituted hydrocarbon radical or —N—. They may be prepared for corresponding starting materials, e.g., nitro compounds, by reduction, for example, according to methods described in U.K. Patent 1,182,377. In addition, EP—A—0 133 281 shows an elegant method for N-methylation, using succinimide and formaldehyde with the primary amine, followed by reductive cleavage.

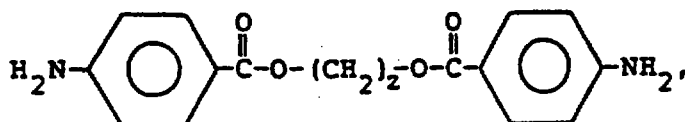
Preferred aromatic polyamine curing agents (b)(ii) are compounds according to the above formula in which R is hydrogen, C₁—C₃ alkyl, or phenyl and X is a divalent or trivalent radical of valence a, selected either from (1) a divalent group consisting of —(CH₂)_y—, wherein y is an integer of from 2 to 12, —(CH₂CH₂OCH₂CH₂OCH₂CH₂)—,



a trivalent group consisting of

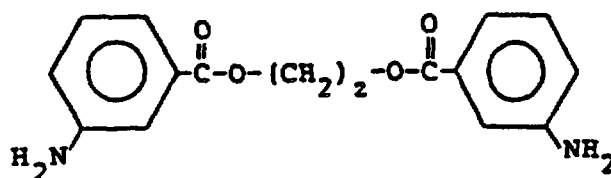


and —(CH₂)_n—CH—(CH₂)_m—, wherein n and m are the same or different integers from 1 to 4. More preferred curing agents are the following:

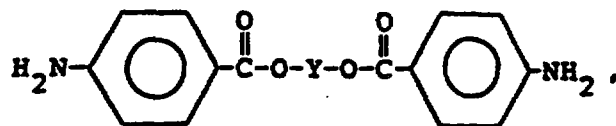


wherein z is an integer of from 2 to 12, preferably 2 to 6,

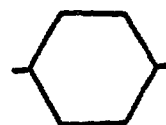
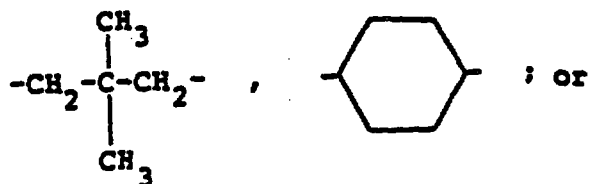
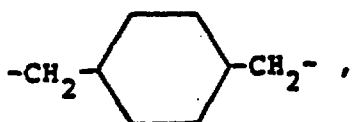
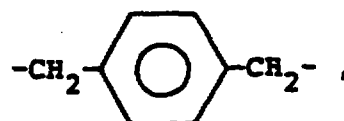
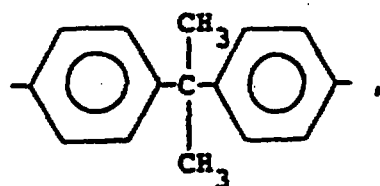
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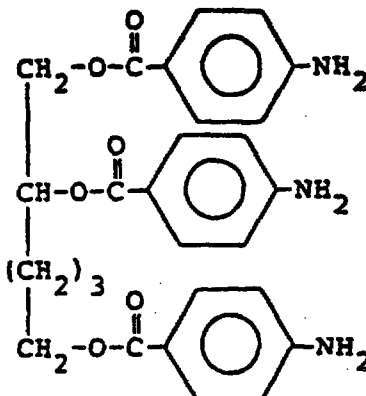
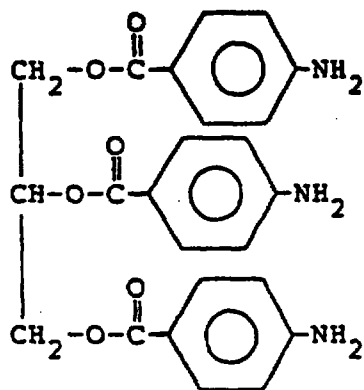
wherein z is an integer from 2 to 12, preferably 2 to 6,



wherein Y is $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$,

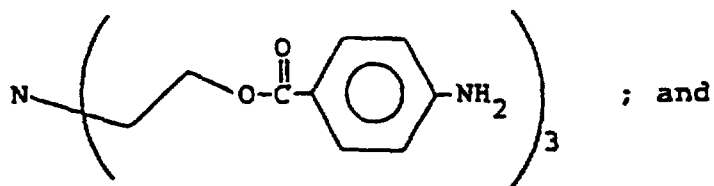


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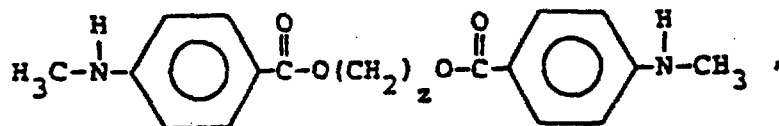


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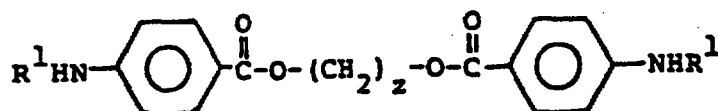


; and



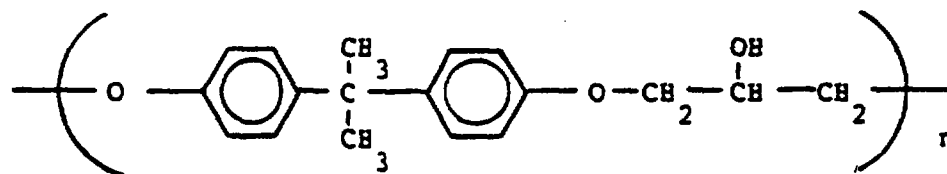
wherein z is an integer of from 2 to 12, preferably 2 to 6.

In the most preferred compounds, the primary diamine will include one or more of a compound of the formula:

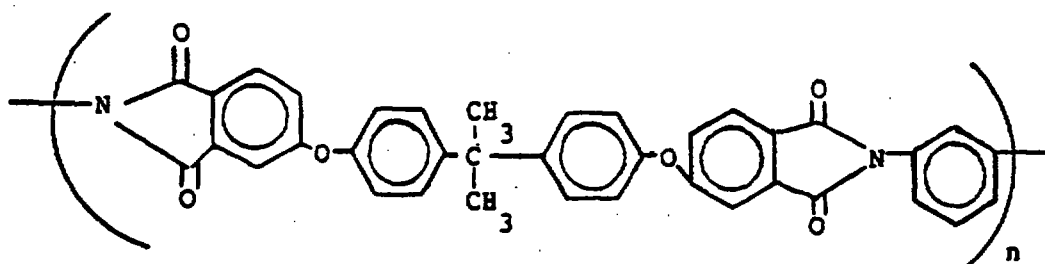


wherein R¹ is hydrogen or C₁—C₆ alkyl, e.g., methyl, and z is an integer of from 2 to 12, preferably 2 to 6, and most preferably 3. Also contemplated are the use of such compounds in combination with other conventional polyamines such as methylene dianiline or phenylene diamine.

The matrix resin compositions benefit from the inclusion of a resin modifier in an amount sufficient to impart improvements in mechanical properties, especially toughness, while preserving substantial resistance to failure under hot/wet conditions. Such resins can be present homogeneously and also in the form known as interpenetrating polymer networks. Particularly useful in this aspect are polyether resins derived from bisphenol A and epichlorohydrin, and which include repeating units of the formula:



and polyetherimide resins derived from the reaction product of bisphenol-A and a substituted phthalic anhydride, subsequently reacted with m-phenylenediamine and containing units of the formula:



wherein n in each is a number sufficient to provide a molecular weight in the range of 20,000 to 60,000. Amounts of 5 to 30, preferably 10 to 20 parts by weight per 100 parts by weight of epoxy prepolymer can be used. Such polymers are available commercially, respectively, from Union Carbide Co., Danbury, CT, U.S.A., under the tradename PKHH resin and from General Electric Company, Fairfield, CT, U.S.A., under the tradename, ULTEM resin. Their use in epoxy systems is described in the above-mentioned EP-A-0133281.

Other resins which can be used as thermoplastic modifiers include reactive and non-reactive butadiene-styrene-acrylonitrile core-shell modifiers, polyurethanes, nylons, carboxylated acrylonitrile-butadiene elastomers, e.g., those described in the above-mentioned U.S. 3,894,113, and many others. They will, in general, have molecular weights in the range of 5,000 to 60,000, and will be used in amounts set forth above.

One method of forming the fiber matrix composition of the invention is illustrated in the drawings. As seen in Figure 1, the basic fiber matrix material is produced by delivering fiber 2 through conventional eyeboards 4 and 6 to a pressure roller assembly 8. The resin composition is coated in a layer 10 from a conventional film coating applicator 12 onto a substrate such as release paper 14 and passed through the pressure roller assembly 8. Release paper 16 is also delivered to the pressure roller assembly 8.

The pressure rollers 8 are set at a temperature and pressure for imbedding the fibers 2 in the resin layer 10 to form a fiber matrix composition 18. Practice has taught that a temperature in the range of 88°C (190°F) and pressures of 454 kg (one thousand pounds) over 38.1 cm (fifteen inch) centers are suitable for producing fiber resin prepreg tape 18.

The fibers 2, the substrate 14 with resin layer 10 and the release paper 16 are delivered to the pressure rollers 8 and passed therethrough at the rate of 1.5—6.1 meters/min (5—20 feet/minute).

The feed of fiber 2 and resin layer 10 to the pressure rollers 8 is selected to produce a fiber matrix of about twenty to sixty weight percent resin and about eighty to forty weight percent fiber. For example, one hundred twenty spools of 6K carbon fibers are delivered within a twelve inch width to the pressure rollers 8 with a layer of resin 0.044 to 0.00635 kg/m² (0.009 to 0.0013 pounds per square foot). The resulting fiber resin matrix 18 results in a generally parallel array of fibers, shown by Figure 2.

Fillers, pigments, dyes, and other such conventional additives and processing aids may be added to

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the fiber matrix compositions of the invention before curing to influence the properties of the final resin composite.

The following examples will illustrate the practice of the present invention and are provided by way of demonstration and not by way of limitation.

5 The following procedure is used to prepare and cure neat resin compositions: the epoxide prepolymer is melted, and mixed with the bisurea at 100°C for 10 minutes. If a polyamine is used, the epoxide prepolymer and the polyamide component are mixed at 135°C for 10 minutes, and cooled to 100°C, the bisurea catalyst is mixed in, and the mixture is degassed for 10 minutes. The liquid resin is then poured into a mold and cured for 2 hours at 135°C and for 3 hours at 180°C. Properties are determined on coupons cut from the castings by the following procedures: The flexural test is described in ASTM D—790, Method I. Dynamic mechanical analysis was performed on a Dupont 981 Dynamic Mechanical Analyzer, and T_g was defined as the temperature at which the loss tangent, $\tan \delta$, is a maximum. ASTM D4065 test method covers this type of T_g measurement. Conditioning before testing is described by the phrases "wet" and "dry". "Wet" refers to conditioning for two weeks at 71°C, immersing in distilled water, prior to testing at 15 93°C. "Dry" means testing a sample, as prepared, at 23°C.

Examples 1—6

20 The series of substituted bisureas were prepared by stirring solutions of acetonitrile of phenyl isocyanate and the corresponding diamines for 0.5 to 2.0 hours, and isolating by filtration. The reactants used and the products obtained are outlined in Table 1:

TABLE 1. PREPARATION OF SUBSTITUTED BISUREAS

EXAMPLE	ISOCYANATE	DIAMINE	BISUREA	MELTING POINT, °C.
1		$\text{CH}_3\text{NH}-(\text{CH}_2)_6-\text{NHCH}_3$		138-140
2		$\text{CH}_3\text{CH}_2\text{NH}-(\text{CH}_2)_3\text{NHCH}_2\text{CH}_3$		125-126
3		$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$		--
4		$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{NH}_2$		223-224
5				250
6		$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}$		169-171

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Examples 7 and 8

Compositions comprising an epoxy prepolymer, the catalyst of Example 2, alone, and with two different diamines were prepared and gel time measurements were made isothermally at 180°C. For comparison purposes, a bisurea catalyst of the prior art, U.S. 3,386,955, Example 1, was also included. The formulations used and the results obtained are set forth in Table 2.

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TABLE 2. HEAT CURABLE COMPOSITIONS

EXAMPLE COMPOSITION (parts by weight)	7A*	7B*	7	7C*	8
N,N,N',N'-tetra-glycidyl 4,4'- diamino diphenyl methane	100	100	100	100	100
Diaminodiphenylsulfone	--	47	--	--	--
Trimethylene bis(p-amino benzoate)	47	--	47	47	--
Reaction product of phenyl isocyanate and N,N-diethyl- 1,3-propane diamine (Ex. 2)	--	--	1.4	--	1.4
Reaction product of toluene 2,4-diisocyanate and dimethylamine (U.S. 3,386,955, Ex. 1)	--	--	--	1	--
PROPERTIES					
Gel time at 180°C. in minutes	45	45	30	30	>30

* Control.

The practical effect of reducing gel times is demonstrated both by the catalyst of this invention (Example 7) and that of the prior art (Example 7C*).

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Examples 9—13

The general procedure for forming neat resin compositions was used with two catalysts according to this invention. For comparison purposes, an uncatalyzed, cured composition was prepared, as well as one catalyzed with the bisurea of the prior art. The formulations used and the properties obtained are set forth in Table 3.

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TABLE 3. BISUREA-CATALYZED EPOXY-POLAMINE CURED COMPOSITIONS AND PROPERTIES

EXAMPLE COMPOSITION (parts by weight)	9	10	11	12	13	11A*	11B*	11C*
N,N,N',N'-tetra-glycidyl 4,4'- diamino diphenyl methane	100	100	100	100	100	100	100	100
Trimethylene bis(p-amino benzoate)	47	47	47	47	47	47	47	47
Reaction product of phenyl isocyanate and N,N-dimethyl 1,6-hexamethylene diamine (Ex. 1)	1	2	--	--	--	--	--	--
Reaction product of phenyl isocyanate and N,N'-diethyl- 1,3-propanediamine (Ex. 2)	--	--	1	2	4	--	--	--
Reaction product of toluene 2,4-diisocyanate and dimethylamine	--	--	--	--	--	1	2	4
PROPERTIES								
Modulus, MSI								
dry	0.52	0.57	0.48	0.48	0.48	0.49	0.66	0.72
wet	0.31	0.29	0.30	0.28	0.27	0.29	0.11	0.03
Strength, KSI	23.8	25.5	22.9	24.5	23.2	21.7	27.9	28.1
Work-to-break, in-lbs./in.	1000	970	825	1220	1200	1125	915	630
T _g , °C.	203	171	207	201	187	197	146	130
* Control.	--	132	160	150	148	139	124	104

TABLE 3. BISUREA-CATALYZED EPOXY-POLYAMINE CURED COMPOSITIONS AND PROPERTIES

EXAMPLE COMPOSITION (parts by weight)	2	10	11	12	13	11A*	11B*	11C*
N,N,N',N'-tetra-glycidyl 4,4'- diamino diphenyl methane	100	100	100	100	100	100	100	100
Trimethylene bis(p-amino benzoate)	47	47	47	47	47	47	47	47
Reaction product of phenyl isocyanate and N,N-dimethyl 1,6-hexamethylene diamine (Ex. 1)	1	2	—	—	—	—	—	—
Reaction product of phenyl isocyanate and N,N'-diethyl- 1,3-propanediamine (Ex. 2)	—	—	1	2	4	—	—	—
Reaction product of toluene 2,4-diisocyanate and dimethylamine	—	—	—	—	—	1	2	4
PROPERTIES								
Modulus, Gigapascals dry	3.58	3.93	3.31	3.31	3.31	3.38	4.55	4.96
wet	2.14	2.00	2.07	1.93	1.86	2.00	0.76	0.21
Strength, Megapascals dry	164.1	175.8	157.9	168.9	159.9	149.9	192.3	193.7
Work-to-break, ³ kilojoules/m	6894	6687	5688	8411	8273	7756	6308	4343
T _g °C.	203	171	207	201	187	197	146	130
wet	—	132	160	150	148	139	124	104
* Control.								

The degradation in strength and thermal properties caused by the prior art catalyst is ameliorated by using the catalysts of this invention.

Example 14

The neat resin procedure was modified by curing at 121.1°C (250°F) for 1.5 hours and the degree of cure was determined by differential scanning calorimetry (DSC). The formulation employed, in parts by weight, was N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane, 61; bisphenol-A diglycidyl ether 39; m-diaminodiphenyl sulfone, 40; and the reaction product of phenyl isocyanate and N,N'-diethyl-1,3-propanediamine (Ex. 2), 7. The degree of cure by DSC was 80%, showing excellent latent catalytic activity.

Example 15

Two fiber resin matrix formulations were prepared from the following materials:

component A	CELION® 6K high strain graphite fiber
component (a)	ARALDITE® MY720 EPON® 1031 (see formulae, <i>supra</i> .)
catalysts (b)(i)	toluene-2,4-diisocyanate reaction product with dimethylamine (control); phenyl isocyanate reaction product with N,N'-diethyl-1,3-propanediamine (Ex. 2)
(curing agent) (b)(ii)	trimethylene bis-(p-aminobenzoate)
polymer modifier (c)	polyether alcohol (PKHH)

Using an apparatus shown generally in Figure 1, prepreg tapes of the structure shown generally in Figure 2, were prepared:

Example	15A*	15
<i>(28%) Resin Mixture (parts by weight)</i>		
N,N,N',N'-tetra(glycidyl-4,4'-diaminodiphenyl)methane	100	100
Trimethylene bis-(para-aminobenzoate)	48.4	48.4
Polymer modifier**	10	10
Catalyst (TDI/DMA)	1	—
(Ex. 2 herein)	—	1.4
<i>(72%) Filament (parts by weight)</i>		
(6K graphite fibers having a strain to failure of about 1.5%)		

* Control

** Reaction product of bisphenol A and epichlorohydrin (Union Carbide, PKHH).

These samples were cured and compared against commercial epoxy resin matrixes. The sheets of resin involved were as follows:

Quasi-Isotropic: 16 sheets [(+45/0/90)₂]_s.

The compressive strength was measured on a modified ASTM D695 specimen described in D. H. Woilsencraft et al., Composites, Oct., 1981, pages 275—280. Compressive strength after impact was measured as described in B.A. Byers, NASA Report No. CR 159293, August, 1980. This property is tested by subjecting a cured laminate specimen to 6672 joules/meter (1500 in.lb, per inch) of nominal thickness impact with a 0.62 diameter spherical tip impactor while supported by a rigid base (e.g., 8.89 cm (3.5 in) steel cutout). The panel is then tested in compression. The results are set forth in Table 4, as follows:

TABLE 4

EXAMPLE	CONDITION	16-PLY QUASIISSOTROPIC 23°C.	16-PLY QUASIISSOTROPIC 93°C.	COMPRESSIVE STRENGTH, KSI 132°C.	177°C.	FRACTURE TOUGHNESS GIC IN-LBS./IN ^{3/2}	COMPRESSIVE STRENGTH AFTER IMPACT PLY (KSI) 1500 in.-lb./in.
15A*	dry	90	73	59	16		
	wet	--	65	43	--	2.7	38.7
15	dry	97	91	87	56		
	wet	--	86	55	--	2.12	33.4

* See above.

TABLE 4

EXAMPLE	CONDITION	16-PLY QUASIISSOTROPIC 23°C.	16-PLY QUASIISSOTROPIC 93°C.	COMPRESSIVE STRENGTH, MEGAPASCALS 132°C.	177°C.	FRACTURE TOUGHNESS GIC joules/m ^{3/2}	COMPRESSIVE STRENGTH AFTER IMPACT PLY (MEGAPASCALS) 6672 joules/meter
15A*	dry	620.5	503.3	406.7	110.3		
	wet	--	448.1	296.4	--	472.5	266.8
15	dry	668.7	627.4	599.8	386.1		
	wet	--	592.9	379.17	--	371	230.3

*See above.

The data demonstrate that the reinforced, cured composition according to this invention (Example 15) does not lose its hot/wet compression strength to the same extent as the other two catalyzed matrix compositions (15A*).

Example 16

A resin composition is prepared by mixing the following (by weight)

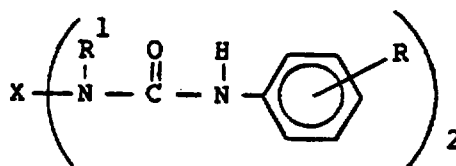
5	(a)	N,N,N',N'-tetraglycidyl-4,4'-diamino diphenyl methane	100 parts
10	(b)	Polyether polyimide resin (General Electric Ultem, formula above)	15 parts
15	(c)	trimethylene bis(p-amino-benzoate)	48 parts
20	(d)	reaction product of phenyl isocyanate and N,N'-diethyl-1,3-propanediamine (catalyst)	1.4 parts

A prepreg tape is prepared following the general procedure of Example 15, with a 35 to 45 preferably 40% resin/55 to 65, preferably, 60% graphite loading. When this is formed into laminates by the procedure of Example 14, excellent quality composites are produced. Preferred ranges of compositions are (a), 94—126 parts; (b), 14.25—15.75 parts; (c) 45.6—50.4 parts; and (d), 0.5—2.5 parts.

It is seen that the present invention produces articles of manufacture with beneficial properties, making them useful in a variety of applications. Many variations will suggest themselves to those skilled in this art in light of the foregoing detailed description.

Claims

1. A heat curable composition comprising
 - (a) an epoxy prepolymer or combination prepolymers having more than one epoxy group per molecule, and
 - (b) a curing catalyst for said epoxy comprising
 - (i) an amount effective to cure said epoxy of a bisurea compound comprising the reaction product of an organic diamine with a least two moles, per mole of diamine, of an aryl monoisocyanate, which is either used alone, or
 - (ii) in an amount of 0.1 to 20 parts by weight per 100 parts by weight of epoxy resin in further combination with an amine functional aromatic curing agent.
2. A composition as defined in Claim 1 wherein said bisurea compound (b)(i) is of the formula



wherein X is a divalent organic hydrocarbon radical, a divalent or trivalent hetero-interrupted hydrocarbon radical, or a divalent inertly-substituted hydrocarbon radical, R is hydrogen, a monovalent hydrocarbon radical, an amino or hydrocarbon substituted amino radical, a cyano radical, a hydrocarbonoxy radical or an inertly-substituted such radical, and R¹ is, independently, hydrogen, a monovalent hydrocarbon radical, an inertly-substituted hydrocarbon radical, a single bond, or a divalent alkylene radical or inertly-substituted such radical.

3. A composition as defined in Claim 2 wherein in said bisurea compound (b)(i) X is a divalent alkylene radical of from 2 to 12 carbon atoms, a trivalent nitrogen-interrupted alkylene radical of 4 to 12 carbon atoms, a divalent arylene or polyarylene radical of 6 to 12 carbon atoms or a divalent polyarylene radical of 6 to 30 carbon atoms interrupted with —CR²—, —O—, —S— or —SO₂— groups, wherein R² is hydrogen, a monovalent hydrocarbon radical or an inertly-substituted hydrocarbon radical, R is hydrogen, cyano, amino, methoxy, vinyl or ethinyl, and R¹ is hydrogen, alkyl of 1 to 6 carbon atoms, aryl of 6 to 12 carbon atoms, or a divalent alkylene of from 2 to 3 carbon atoms.

4. A composition as defined in Claim 3 wherein in said bisurea compound (b)(i), X is divalent alkylene of from 2 to 12 carbon atoms, trivalent nitrogen-interrupted alkylene of from 4 to 12 carbon atoms, divalent diaryl sulfone of from 12 to 20 carbon atoms, R is hydrogen, amino, vinyl, methoxy or ethinyl, and R¹ is

The data demonstrate that the reinforced, cured composition according to this invention (Example 15) does not lose its hot/wet compression strength to the same extent as the other two catalyzed matrix compositions (15A*).

Example 16

A resin composition is prepared by mixing the following (by weight)

(a)	N,N,N',N'-tetraglycidyl-4,4'-diamino diphenyl methane	100 parts
(b)	Polyether polyimide resin (General Electric Ultem, formula above)	15 parts
(c)	trimethylene bis(p-amino- benzoate)	48 parts
(d)	reaction product of phenyl isocyanate and N,N'-diethyl- 1,3-propanediamine (catalyst)	1.4 parts

A prepreg tape is prepared following the general procedure of Example 15, with a 35 to 45 preferably 40% resin/55 to 65, preferably, 60% graphite loading. When this is formed into laminates by the procedure of Example 14, excellent quality composites are produced. Preferred ranges of compositions are (a), 94—126 parts; (b), 14.25—15.75 parts; (c) 45.6—50.4 parts; and (d), 0.5—2.5 parts.

It is seen that the present invention produces articles of manufacture with beneficial properties, making them useful in a variety of applications. Many variations will suggest themselves to those skilled in this art in light of the foregoing detailed description.

Claims

1. A heat curable composition comprising

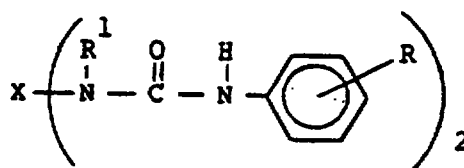
(a) an epoxy prepolymer or combination prepolymers having more than one epoxy group per molecule, and

(b) a curing catalyst for said epoxy comprising

(i) an amount effective to cure said epoxy of a bisurea compound comprising the reaction product of an organic diamine with a least two moles, per mole of diamine, of an aryl monoisocyanate, which is either used alone, or

(ii) in an amount of 0.1 to 20 parts by weight per 100 parts by weight of epoxy resin in further combination with an amine functional aromatic curing agent.

2. A composition as defined in Claim 1 wherein said bisurea compound (b)(i) is of the formula



wherein X is a divalent organic hydrocarbon radical, a divalent or trivalent hetero-interrupted hydrocarbon radical, or a divalent inertly-substituted hydrocarbon radical, R is hydrogen, a monovalent hydrocarbon radical, an amino or hydrocarbon substituted amino radical, a cyano radical, a hydrocarbonoxy radical or an inertly-substituted such radical, and R¹ is, independently, hydrogen, a monovalent hydrocarbon radical, an inertly-substituted hydrocarbon radical, a single bond, or a divalent alkylene radical or inertly-substituted such radical.

3. A composition as defined in Claim 2 wherein in said bisurea compound (b)(i) X is a divalent alkylene radical of from 2 to 12 carbon atoms, a trivalent nitrogen-interrupted alkylene radical of 4 to 12 carbon atoms, a divalent arylene or polyarylene radical of 6 to 12 carbon atoms or a divalent polyarylene radical of 6 to 30 carbon atoms interrupted with —CR²—, —O—, —S— or —SO₂— groups, wherein R² is hydrogen, a monovalent hydrocarbon radical or an inertly-substituted hydrocarbon radical, R is hydrogen, cyano, amino, methoxy, vinyl or ethynyl, and R¹ is hydrogen, alkyl of 1 to 6 carbon atoms, aryl of 6 to 12 carbon atoms, or a divalent alkylene of from 2 to 3 carbon atoms.

4. A composition as defined in Claim 3 wherein in said bisurea compound (b)(i), X is divalent alkylene of from 2 to 12 carbon atoms, trivalent nitrogen-interrupted alkylene of from 4 to 12 carbon atoms, divalent diaryl sulfone of from 12 to 20 carbon atoms, R is hydrogen, amino, vinyl, methoxy or ethynyl, and R¹ is



hydrogen, or alkyl of 1 to 6 carbon atoms, or divalent alkylene of from 2 to 3 carbon atoms.

5. A composition as defined in Claim 2 wherein in compound (b)(i) X is



R¹ is —CH₃, and R is —H.

6. A composition as defined in Claim 2 wherein in compound (b)(i) X is



R₁ is —CH₂CH₃, and R is —H.

7. A composition as defined in Claim 2 wherein in compound (b)(i) X is



and R and R¹ are —H.

8. A composition as defined in Claim 2 wherein in compound (b)(i), X is



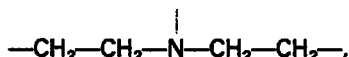
and R and R¹ are —H.

9. A composition as defined in Claim 2 wherein in compound (b)(i) X is



R is —H, one R¹ is a single bond and the other R¹ is $-(CH_2)_2-$, one end of which is linked to the single bond

10. A composition as defined in Claim 2 wherein in compound (b)(i) X is the trivalent radical



R is —H, one R¹ is —H and the other R¹ is $-(CH_2)_2-$, one end of which is linked to the single-bonded N in X.

Patentansprüche

1. Hitzehärtbare Masse, umfassend

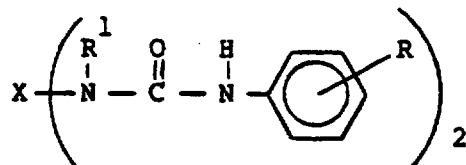
(a) ein Epoxy-Präpolymere oder eine Kombination von Präpolymeren mit mehr als einer Epoxygruppe pro Molekül und

(b) einen Härtungskatalysator für das erwähnte Epoxy, umfassend

(i) eine zur Härtung des Epoxy wirksame Menge einer bis-Harnstoffverbindung, umfassend das Reaktionsprodukt eines organischen Diamins mit mindestens 2 Mol, pro Mol des Diamins, eines Arylmono-isocyanats, die entweder allein verwendet wird oder

(ii) in einer Menge von 0,1 bis 20 Gewichtsteile pro 100 Gewichtsteile des Epoxyharzes in weiterer Kombination mit einem aromatischen Härtungsmittel mit Aminfunktionalität.

2. Masse gemäß Anspruch 1, wobei die bis-Harnstoffverbindung (b)(i) die folgende Formel hat



wobei X für einen divalenten organischen Kohlenwasserstoffrest, einen divalenten oder trivalenten Hetero-unterbrochenen Kohlenwasserstoffrest oder einen divalenten, inert-substituierten Kohlenwasserstoffrest steht, R für Wasserstoff, einen monovalenten Kohlenwasserstoffrest, einen Amino- oder Kohlenwasserstoff-substituierten Aminorest, einen Cyanorest, einen Kohlenwasserstoffoxyrest oder für einen inert-substituierten derartigen Rest steht und R¹ unabhängig für Wasserstoff, einen monovalenten Kohlenwasserstoffrest, einen inert-substituierten Kohlenwasserstoffrest, eine Einfachbindung oder einen divalenten Alkylenrest oder einen inert-substituierten derartigen Rest steht.

3. Masse gemäß Anspruch 2, wobei in der bis-Harnstoffverbindung (b)(i) X für einen divalenten Alkylenrest mit 2 bis 12 Kohlenstoffatomen, einen trivalenten Stickstoff-unterbrochenen Alkylenrest mit 4 bis 12 Kohlenstoffatomen, einen divalenten Arylen- oder Polyarylenrest mit 6 bis 12 Kohlenstoffatomen oder einen divalenten Polyarylenrest mit 6 bis 30 Kohlenstoffatomen, unterbrochen durch —CR²—, —O—,



—S— oder —SO₂— Gruppen steht, wobei R² für Wasserstoff, einen monovalenten Kohlenwasserstoffrest oder einen inert-substituierten Kohlenwasserstoffrest steht, R für Wasserstoff, Cyano, Methoxy, Vinyl oder Ethinyl steht und R¹ für Wasserstoff, Alkyl mit 1 bis 6 Kohlenstoffatomen, Aryl mit 6 bis 12 Kohlenstoffatomen oder ein divalent Alkyl mit 2 bis 3 Kohlenstoffatomen steht.

5 4. Masse gemäß Anspruch 3, wobei in der bis-Harnstoffverbindung (b)(i) X für divalent Alkyl mit 2 bis 12 Kohlenstoffatomen, trivalent Stickstoff-unterbrochenes Alkyl mit 4 bis 12 Kohlenstoffatomen, divalent Diarylsulfon mit 12 bis 20 Kohlenstoffatomen steht, R für Wasserstoff, Amino, Vinyl, Methoxy oder Ethinyl steht und R¹ für Wasserstoff oder Alkyl mit 1 bis 6 Kohlenstoffatomen oder divalent Alkyl mit 2 bis 3 Kohlenstoffatomen steht.

10 5. Masse gemäß Anspruch 2, wobei in Verbindung (b)(i) X für



steht, R¹ für —CH₃ steht und R für —H steht.

15 6. Masse gemäß Anspruch 2, wobei in Verbindung (b)(i) X für



steht, R¹ für —CH₂CH₃ steht und R für —H steht.

20 7. Masse gemäß Anspruch 2, wobei in Verbindung (b)(i) X für



steht, R und R¹ für —H steht.

25 8. Masse gemäß Anspruch 2, wobei in Verbindung (b)(i) X für



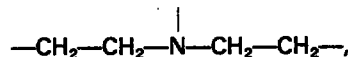
steht, R und R¹ für —H steht.

30 9. Masse gemäß Anspruch 2, wobei in Verbindung (b)(i) X für



35 steht, R für —H steht, ein R¹ für eine Einfachbindung steht und das andere R¹ für $-(CH_2)_2-$ steht, dessen eines Ende an die Einfachbindung geknüpft ist.

10. Masse gemäß Anspruch 2, wobei in Verbindung (b)(i) X für den trivalent Rest



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steht, R für —H steht, ein R¹ für —H steht und das andere R¹ für $-(CH_2)_2-$ steht, dessen eines Ende mit dem einfach gebundenen N in X verknüpft ist.

Revendications

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1. Composition thermodurcissable comprenant

(a) un prépolymère époxy ou une combinaison de prépolymères comportant plus d'un groupe époxy par molécule, et

(b) un catalyseur de durcissement pour ledit époxyde, comprenant

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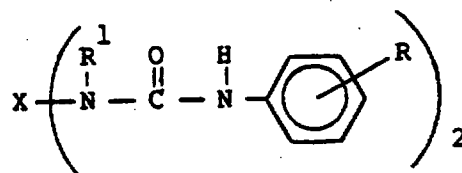
(i) une quantité, efficace pour le durcissement dudit époxyde, d'un composé de type bis-urée comprenant le produit de réaction d'une diamine organique avec au moins 2 moles, par mole de diamine, d'un monoisocyanate d'aryle qui est présent, soit seul, soit

(ii) en une quantité de 0,1 à 20 parties en poids, pour 100 parties de résine époxy, à nouveau en combinaison avec un agent durcisseur aromatique à fonction amine.

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2. Composition selon la revendication 1, dans laquelle ledit composé bis-urée (b)(i) est de formule

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65 dans laquelle X est un radical organique hydrocarboné bivalent, un radical hydrocarboné bivalent ou trivalent interrompu par des hétéroatomes, ou un radical hydrocarboné bivalent substitué par des



substituants inertes; R est un atome d'hydrogène ou un radical hydrocarboné monovalent, un radical amino ou amino substitué par des groupes hydrocarbonés, un radical cyano, un radical hydrocarboné-oxy ou un tel radical substitué par des substituants inertes; et R¹ est, indépendamment, un atome d'hydrogène ou un radical hydrocarboné monovalent, un radical hydrocarboné substitué par des substituants inertes,

3. Composition selon la revendication 2, caractérisée en ce que, dans ledit composé bis-urée (b)(I), X est un radical alkylène bivalent ayant de 2 à 12 atomes de carbone, un radical alkylène trivalent ayant de 4 à 12 atomes de carbone, interrompu par de l'azote, un radical arylène bivalent ou un radical polyarylène ayant de 6 à 12 atomes de carbone ou un radical polyarylène ayant 6 à 30 atomes de carbone, interrompu par —O—, —S— ou par des groupes —CR₂ ou —SO₂, R² étant un atome d'hydrogène ou un groupe hydrocarboné monovalent ou un groupe hydrocarboné substitué par des substituants inertes; R est un atome d'hydrogène ou un groupe cyano, amino, méthoxy, vinyle ou éthinyle; et R¹ est un atome d'hydrogène ou un groupe alkyle ayant de 1 à 6 atomes de carbone, aryle ayant de 6 à 12 atomes de carbone, ou un radical alkylène bivalent ayant 2 ou 3 atomes de carbone.

4. Composition selon la revendication 3, caractérisée en ce que, dans ledit composé bis-urée (b)(I), X est un radical alkylène bivalent ayant de 2 à 12 atomes de carbone, un radical alkylène trivalent ayant de 4 à 12 atomes de carbone, interrompu par de l'azote, un radical diarylsulfone bivalent ayant de 12 à 20 atomes de carbone; R est un atome d'hydrogène ou un groupe amino, vinyle, méthoxy ou éthinyle; et R¹ est un atome d'hydrogène ou un radical alkyle ayant de 1 à 6 atomes de carbone, ou un radical alkylène bivalent ayant 2 ou 3 atomes de carbone.

5. Composition selon la revendication 2, caractérisée en ce que, dans le composé (b)(I), X est



R¹ est —CH₃, et R est —H.

6. Composition selon la revendication 2, caractérisée en ce que, dans le composé (b)(I), X est



R¹ est —CH₂CH₃, et R est —H.

7. Composition selon la revendication 2, caractérisée en ce que, dans le composé (b)(I), X est



et R et R¹ sont —H.

8. Composition selon la revendication 2, caractérisée en ce que, dans le composé (b)(I), X est



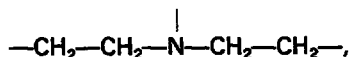
et R et R¹ sont —H.

9. Composition selon la revendication 2, caractérisée en ce que, dans le composé (b)(I), X est



R est —H, un R¹ est une simple liaison et l'autre R¹ est —(CH₂)₂—, dont une extrémité est liée à la simple liaison.

10. Composition selon la revendication 2, caractérisée en ce que, dans le composé (b)(I), X est le radical trivalent



R est —H, un R¹ est —H et l'autre R¹ est —(CH₂)₂—, dont une extrémité est liée à l'azote à simple liaison dans X.

