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(54) Title: SUBSTANTIALLY SOLVENT-FREE EPOXY FORMULATIONS

(57) Abstract: Embodiments include substantially solvent-free epoxy formulations having a resin component and a hardener component. The resin component can include an epoxy compound that is that is selected from the group consisting of aromatic epoxy compounds, alicyclic epoxy compounds, aliphatic epoxy compounds, and combinations thereof, and a diluent, where the diluent includes dicyclopentadiene diepoxide. The hardener component can be selected from the group consisting of an amine, an anhydride, a carboxylic acid, a phenol, a thiol, and combinations thereof.



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SUBSTANTIALLY SOLVENT-FREE EPOXY FORMULATIONS

Field of Disclosure

[001] This disclosure relates to epoxy formulations and in particular to substantially solvent-free epoxy formulations that include a resin component and a hardener component, where the resin component includes a diluent.

Background

[002] Epoxy systems consist of two components that can chemically react with each other to form a cured epoxy, which is a hard, inert material. The first component is an epoxy resin and the second component is a curing agent, sometimes called a hardener. Epoxy resins are substances or mixtures that contain epoxide groups. The hardener includes compounds which are reactive to the epoxide groups of the epoxy resins.

[003] The epoxy resins can be crosslinked, also referred to as curing, by the chemical reaction of the epoxide groups and the compounds of the hardener. This curing converts the epoxy resins, which have a relatively low molecular weight, into relatively high molecular weight materials by chemical reaction with the hardener.

[004] Epoxy systems can be used to make composite materials. Composite materials are materials that are made from two or more components that have distinct mechanical properties.

[005] For example, a composite material may be formed of multiple layers of a reinforcing fiber with an epoxy resin that is employed as a matrix material. Each layer that makes up the composite material is often separately impregnated with the resin prior to molding. These layers are referred to as prepregs. Prepregs can be formed, for example, by first diluting an epoxy resin in a solvent, such as N-methyl-2-pyrrolidinone (NMP), and then impregnating it into the reinforcing fiber. The prepregs can then be laid into a mold and then cured by application of heat and/or pressure to form the composite material. The heat and/or pressure causes the epoxy resin to penetrate and join all layers of the prepreg together as the epoxy resins cures.

[006] Composite materials can also be made by various processes employing a liquid epoxy resin. These processes can be characterized as either a wet lay-up process or an infusion process.

[007] Wet lay-up processes are carried out in an open mold. For the wet lay-up processes each layer of reinforcement material must be individually coated with resin and carefully positioned by hand on the open mold. This manual coating and positioning results in a highly labor intensive process. Additionally, composite materials formed by the wet lay-up process tend to have a lower average quality than infused composite materials. This lower average quality can be attributed to inconsistent thicknesses and fiber volumes resulting from the manual coating and positioning, as well as air bubble entrapment that can occur when resin is being applied.

[008] In recent years, however, there have been environmental concerns regarding the use of solvents. As such, there has been an increased effort to develop composite materials that use a minimum amount of solvent. One approach has been solvent free, closed system processes for forming composite materials. Infusion processes are solvent free and are carried out in closed systems where a mold is injected with liquid epoxy resin to infuse the reinforcing material. Infusion processes provide for better control over thicknesses and fiber volume fractions. Infusion processes can also infuse resin with a vacuum. The vacuum helps to prevent air bubble entrapment. Infusion processes employing a vacuum, also referred to as vacuum infusion, are described under different acronyms including VARTM—Vacuum Assisted Resin Transfer Molding, VARIM—Vacuum Assisted Resin Infused Molding, SCRIMP—Seemann Composites Resin Infusion Molding Process, VBRTM—Vacuum Bag Resin Transfer Molding, and VARI—Vacuum Assisted Resin Infusion process. While there can be differences amongst the vacuum infusion processes, each employs the process of impregnating a dry reinforcement material with liquid epoxy resin driven under vacuum.

[009] These solvent free, closed infusion processes help to address the environmental concerns regarding the use of solvents in the prepreg and wet lay-up processes, while providing composite materials that are superior to the prepreg and wet lay-up composite materials. There are many possible uses for infusion processes, and there are a great variety of characteristics that may be desirable for particular applications.

Summary

[010] The present disclosure provides one or more embodiments of substantially solvent-free epoxy formulations. For one or more of the embodiments,

the substantially solvent-free epoxy formulations include a resin component and a hardener component. The resin component includes an epoxy compound that is selected from the group consisting of aromatic epoxy compounds, alicyclic epoxy compounds, aliphatic epoxy compounds, and combinations thereof. The resin component also includes a diluent. The diluent can include dicyclopentadiene diepoxide. The hardener component is selected from the group consisting of an amine, an anhydride, a carboxylic acid, a phenol, a thiol, and combinations thereof.

[011] For one or more of the embodiments, the present disclosure provides methods of forming composites. The methods can include providing a mold, providing a reinforcement component to the mold, infusing the reinforcement component with a substantially solvent-free epoxy formulation, as disclosed herein, and curing the infused substantially solvent-free epoxy formulation to form the composite.

Brief Description of the Figures

[012] Figure 1 illustrates viscosity increase during cure for Comparative Example B and Example 4 through Example 7.

[013] Figure 2 illustrates peak cure temperatures for Comparative Example B and Example 7.

Detailed Description

[014] Embodiments of the present disclosure provide substantially solvent-free epoxy formulations having a resin component that includes a diluent. For one or more of the embodiments, the diluent includes dicyclopentadiene diepoxide. While some other diluents, such as some aliphatic epoxy compounds, can contribute to a lower relative viscosity of a formulation, those other diluents can also contribute to a greater peak temperature attained during curing, as compared to the substantially solvent-free epoxy formulations disclosed herein. Surprisingly it was found that the substantially solvent-free formulations having diluents that include dicyclopentadiene diepoxide have a viscosity that is comparable to some formulations with another diluent, such as some aliphatic epoxy compounds, while also providing a relatively lower peak cure temperature. The relatively lower peak temperature attained during curing can help to control exothermic reactions that occur during curing. Additionally, the relatively lower peak temperature can help prevent resin

decomposition, defect formation, and/or damage to manufacturing equipment that can occur at the relatively greater peak temperature attained during curing

[015] The substantially solvent-free epoxy formulations, disclosed herein, can include a solvent that is no more than 3 weight percent of a total weight of the formulation. For some preferred embodiments, the substantially solvent-free epoxy formulations do not include a solvent. Examples of solvents include, but are not limited to, ketones, amides, alcohols, and esters. Examples of ketones include, but are not limited to, acetone, methyl ethyl ketone, and cyclohexanone. Examples of amides include, but are not limited to, dimethylformamide, dimethylacetamide, and N-methylpyrrolidinone. Examples of alcohols include, but are not limited to, methanol, ethanol, isopropanol, and DowanolTM PM. Examples of esters include, but are not limited to, methyl acetate, ethyl acetate, and DowanolTM PMA.

[016] The substantially solvent-free epoxy formulations of the present disclosure include a resin component and a hardener component. For one or more of the embodiments, the resin component includes an epoxy compound. A compound is a substance composed of atoms or ions of two or more elements in chemical combination and an epoxy compound is a compound in which an oxygen atom is directly attached to two adjacent or non-adjacent carbon atoms of a carbon chain or ring system.

[017] The epoxy compound can be selected from the group consisting of aromatic epoxy compounds, alicyclic epoxy compounds, aliphatic epoxy compounds, and combinations thereof. Examples of aromatic epoxy compounds include, but are not limited to, glycidyl ether compounds of polyphenols, such as hydroquinone, resorcinol, bisphenol A, bisphenol F, 4,4'-dihydroxybiphenyl, phenol novolac, cresol novolac, trisphenol (tris-(4-hydroxyphenyl)methane), 1,1,2,2-tetra(4-hydroxyphenyl)ethane, tetrabromobisphenol A, 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane, and 1,6-dihydroxynaphthalene.

[018] Examples of alicyclic epoxy compounds include, but are not limited to, polyglycidyl ethers of polyols having at least one alicyclic ring, or compounds including cyclohexene oxide or cyclopentene oxide obtained by epoxidizing compounds including a cyclohexene ring or cyclopentene ring with an oxidizer. Some particular examples include, but are not limited to, hydrogenated bisphenol A diglycidyl ether; 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexyl carboxylate; 3,4-epoxy-1-methylcyclohexyl-3,4-epoxy-1-methylhexane carboxylate; 6-methyl-3,4-

epoxycyclohexylmethyl-6-methyl-3,4-epoxycyclohexane carboxylate; 3,4-epoxy-3-methylcyclohexylmethyl-3,4-epoxy-3-methylcyclohexane carboxylate; 3,4-epoxy-5-methylcyclohexylmethyl-3,4-epoxy-5-methylcyclohexane carboxylate; bis(3,4-epoxycyclohexylmethyl)adipate; methylene-bis(3,4-epoxycyclohexane); 2,2-bis(3,4-epoxycyclohexyl)propane; dicyclopentadiene diepoxide; ethylene-bis(3,4-epoxycyclohexane carboxylate); dioctyl epoxyhexahydrophthalate; and di-ethylhexyl epoxyhexahydrophthalate.

[019] Examples of aliphatic epoxy compounds include, but are not limited to, polyglycidyl ethers of aliphatic polyols or alkylene-oxide adducts thereof, polyglycidyl esters of aliphatic long-chain polybasic acids, homopolymers synthesized by vinyl-polymerizing glycidyl acrylate or glycidyl methacrylate, and copolymers synthesized by vinyl-polymerizing glycidyl acrylate or glycidyl methacrylate and other vinyl monomers. Some particular examples include, but are not limited to glycidyl ethers of polyols, such as 1,4-butanediol diglycidyl ether; 1,6-hexanediol diglycidyl ether; a triglycidyl ether of glycerin; a triglycidyl ether of trimethylol propane; a tetraglycidyl ether of sorbitol; a hexaglycidyl ether of dipentaerythritol; a diglycidyl ether of polyethylene glycol; and a diglycidyl ether of polypropylene glycol; polyglycidyl ethers of polyether polyols obtained by adding one type, or two or more types, of alkylene oxide to aliphatic polyols such as propylene glycol, trimethylol propane, and glycerin; and diglycidyl esters of aliphatic long-chain dibasic acids.

[020] The resin component further includes a diluent. The diluent can be a non-reactive diluent or a reactive diluent depending upon the particular substantially solvent-free formulation employed and/or application. A non-reactive diluent is a compound that does not participate in a chemical reaction with the epoxy compound during the curing process such that the non-reactive diluent substantially remains in the substantially solvent-free formulation after curing. A reactive diluent is a compound which participates in a chemical reaction with the epoxy compound during the curing process, and becomes incorporated into the cured composition.

[021] For one or more of the embodiments, the diluent includes dicyclopentadiene diepoxide. For some substantially solvent-free formulations dicyclopentadiene diepoxide is a substantially non-reactive diluent. For some other substantially solvent-free formulations dicyclopentadiene diepoxide is a reactive diluent.

[022] The diluent including dicyclopentadiene diepoxide can vary the viscosity and/or cure characteristics of the substantially solvent-free formulations for various applications. As discussed herein, while some other diluents, such as some aliphatic epoxy compounds, can contribute to a lower relative viscosity of a formulation, those other diluents also contribute to a greater peak temperature attained during curing, as compared to some formulations not including those diluents. The substantially solvent-free epoxy formulations where the diluent includes dicyclopentadiene diepoxide can provide a peak cure temperature relatively lower than the peak cure temperature of some formulations having a diluent that includes some aliphatic epoxy compounds. This relatively lower peak temperature can help to control exothermic reactions that occur during curing.

[023] The substantially solvent-free epoxy formulations include a hardener component. The hardener component is selected from the group consisting of an amine, an anhydride, a carboxylic acid, a phenol, a thiol, and combinations thereof. For one or more of the embodiments, the hardener component includes an amine. An amine is a compound that contains an N-H moiety. The amine is selected from the group consisting of aliphatic polyamines, arylaliphatic polyamines, cycloaliphatic polyamines, aromatic polyamines, heterocyclic polyamines, polyalkoxy polyamines, dicyandiamide and derivatives thereof, aminoamides, amidines, ketimines, and combinations thereof.

[024] Examples of aliphatic polyamines include, but are not limited to, ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), trimethyl hexane diamine (TMDA), hexamethylenediamine (HMDA), N-(2-aminoethyl)-1,3-propanediamine (N₃-Amine), N,N'-1,2-ethanediylbis-1,3-propanediamine (N₄-amine), dipropylenetriamine, and reaction products of an excess of these amines with an epoxy resin, such as bisphenol A diglycidyl ether. Examples of arylaliphatic polyamines include, but are not limited to, m-xylylenediamine (mXDA), and p-xylylenediamine. Examples of cycloaliphatic polyamines include, but are not limited to, 1,3-bisaminocyclohexylamine (1,3-BAC), isophorone diamine (IPDA), and 4,4'-methylenebiscyclohexaneamine. Examples of aromatic polyamines include, but are not limited to, m-phenylenediamine, diaminodiphenylmethane (DDM), and diaminodiphenylsulfone (DDS). Examples of heterocyclic polyamines include, but are not limited to, N-aminoethylpiperazine (NAEP), and 3,9-bis(3-aminopropyl) 2,4,8,10-tetraoxaspiro(5,5)undecane. Examples of polyalkoxy

polyamines include, but are not limited to, 4,7-dioxadecane-1,10-diamine; 1-propanamine; (2,1-ethanediyl-oxy)-bis-(diaminopropylated diethylene glycol) (ANCAMINE® 1922A); poly(oxy(methyl-1,2-ethanediyl)), alpha-(2-aminomethylethyl)omega-(2-aminomethylethoxy) (JEFFAMINE® D-230, D-400); triethyleneglycoldiamine ;and oligomers (JEFFAMINE® XTJ-504, JEFFAMINE® XTJ-512); poly(oxy(methyl-1,2-ethanediyl)), alpha, alpha'-(oxydi-2,1-ethanediyl)bis(omega-(aminomethylethoxy)) (JEFFAMINE® XTJ-511); bis(3-aminopropyl)polytetrahydrofuran 350; bis(3-aminopropyl)polytetrahydrofuran 750; poly(oxy(methyl-1,2-ethanediyl)); a-hydro-w-(2-aminomethylethoxy) ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (JEFFAMINE® T-403); and diaminopropyl dipropylene glycol. Examples of dicyandiamide derivatives include, but are not limited to, guanazole, phenyl guanazole, and cyanoureas. Examples of aminoamides include, but are not limited to, amides formed by reaction of the above aliphatic polyamines with a stoichiometric deficiency of anhydrides and carboxylic acids, as described in U.S. Patent 4,269,742. Examples of amidines include, but are not limited to, carboxamidines, sulfinamidines, and phosphinamidines. Examples of ketimines include compounds having the structure $R_2C = NR'$, where R is an alkyl group and R' is an alkyl group or hydrogen.

[025] For one or more of the embodiments, the hardener component includes an anhydride. An anhydride is a compound having two acyl groups bonded to the same oxygen atom. The anhydride can be symmetric or mixed. Symmetric anhydrides have identical acyl groups. Mixed anhydrides have different acyl groups. The anhydride is selected from the group consisting of aromatic anhydrides, alicyclic anhydrides, aliphatic anhydride and combinations thereof.

[026] Examples of aromatic anhydrides include, but are not limited to, 3,3',4,4'-benzophenonetetracarboxylic dianhydride and pyromellitic anhydride. Examples of alicyclic anhydrides include, but are not limited to methyltetrahydrophthalic anhydride, tetrahydrophthalic anhydride, methyl nadic anhydride, hexahydrophthalic anhydride, and methylhexahydrophthalic anhydride. Examples of aliphatic anhydrides include, but are not limited to propionic anhydride and acetic anhydride.

[027] For one or more of the embodiments, the hardener component includes a carboxylic acid. Examples of carboxylic acids include oxoacids having the structure $RC(=O)OH$, where R is an alkyl group or hydrogen.

[028] For one or more of the embodiments, the hardener component includes a phenol. Examples of phenols include, but are not limited to, bisphenols, novolacs, and resoles that can be derived from phenol and/or a phenol derivative.

[029] For one or more of the embodiments, the hardener component includes a thiol. Examples of thiols include compounds having the structure RSH, where R is an alkyl group.

[030] For some embodiments, the resin components of the substantially solvent-free formulations that include the diluent including dicyclopentadiene diepoxide have a viscosity from 500 centipoise (cP) to 10,000 cP at 25 °C. For some embodiments, the substantially solvent-free formulations that include the diluent dicyclopentadiene diepoxide have a peak cure temperature that is below 200 °C. For one or more of the embodiments, the substantially solvent-free formulations that include the diluent dicyclopentadiene diepoxide have a peak cure temperature that is below 60 °C. For one or more of the embodiments, the diluent is from 5 weight percent to 30 weight percent of a total weight of the substantially solvent-free formulation. For one or more of the embodiments, the substantially solvent-free formulations have a glass transition temperature of 70 °C to 135 °C.

[031] Composite materials, sometimes referred to more simply as composites, are materials that are formed from two or more components that have distinct mechanical properties. For one or more of the embodiments, the composites include a matrix component and a reinforcement component.

[032] The matrix component surrounds and/or supports the reinforcement component. The reinforcement component imparts mechanical and/or physical properties to the composite. The matrix component and the reinforcement component of the composite provide a synergism. This synergism provides that the composites have mechanical and/or physical properties that are unattainable with only the individual components. The substantially solvent-free epoxy formulations, as disclosed herein, are useful as matrix components of composites. The reinforcement component can be an organic material and/or an inorganic material. Examples of products formed from composites include, but are not limited to, boat hulls, bicycle frames, racing car bodies, wind turbine blades, fishing rods, storage tanks, and aerospace components including tails, wings, fuselages, propellers, among others.

[033] As discussed above, for one or more of the embodiments, the present disclosure provides methods of forming composites. The composites can be formed

by an infusion process. Examples of infusion processes include, but are not limited to, VARTM, VARIM, SCRIMP, VBRTM, and VARI.

[034] For one or more of the embodiments, the methods of forming composites include providing a mold. The mold can have different sizes, shapes, and/or compositions for different applications. The size, shape, and/or composition of the mold can depend upon the composite being formed and/or the infusion process being employed.

[035] The methods of forming composites include providing a reinforcement component to the mold. The reinforcement component can be a fiber, a fabric, and combinations thereof.

[036] Examples of fibers include, but are not limited to, glass, aramid, carbon, polyester, polyethylene, quartz, metal, ceramic, biomass, and combinations thereof. The fibers can be coated. An example of a fiber coating includes, but is not limited to, boron.

[037] Examples of glass fibers include, but are not limited to, A-glass fibers, E-glass fibers, C-glass fibers, R-glass fibers, S-glass fibers, and T-glass fibers. Aramids are organic polymers, examples of which include, but are not limited to, Kevlar® and Twaron®. Examples of carbon fibers include, but are not limited to, those fibers formed from polyacrylonitrile, pitch, rayon, and cellulose. Examples of metal fibers include, but are not limited to, stainless steel, chromium, nickel, platinum, titanium, copper, aluminum, beryllium, and tungsten. Examples of ceramic fibers include, but are not limited to, those fibers formed from aluminum oxide, silicon dioxide, zirconium dioxide, silicon nitride, silicon carbide, boron carbide, boron nitride, and silicon boride. Examples of biomass fibers include, but are not limited to, those fibers formed from wood and non-wood. The fibers can be provided to the mold by placing the fibers in the mold.

[038] The reinforcement component can be a fabric. The fabric can be formed from the fiber reinforcement component materials. The fabric can be formed into fabric layers. The fabric layers can be pressed into a shape of the mold and can be held together by a binder. These pressed fabric layers are sometimes referred to as preforms and can be provided to the mold by placing the preform in the mold. A single layer of the fabric can be provided to the mold. Examples of fabrics include, but are not limited to, stitched fabrics and woven fabrics. The fabric can be unidirectional or multiaxial.

[039] The methods of forming composites include infusing the reinforcement component with the substantially solvent-free epoxy formulation. Infusing the reinforcement component with the substantially solvent-free epoxy formulation can include injecting the substantially solvent-free formulation into a mold that contains the reinforcement component. The substantially solvent-free epoxy formulation can be injected until the mold is filled to a desired level and/or the reinforcement component has been desirably wetted, which may be referred to as impregnated.

[040] The methods of forming composite materials include curing the infused substantially solvent-free epoxy formulation to form the composite material. For one or more embodiments, the methods can include heating the infused substantially solvent-free epoxy formulation to a temperature from 70 °C to 140 °C. For one or more embodiments, the methods can include heating the infused substantially solvent-free epoxy formulation to a temperature from 50 °C to 300 °C. For some embodiments a heating can be subsequent to a prior heating and can help provide a more complete cure of the infused substantially solvent-free epoxy formulation.

[041] The methods of forming composite materials can include providing a mold core. The mold core can be formed from a material or combination of materials and is placed inside the mold prior to infusing the reinforcement component with the substantially solvent-free epoxy formulation. Examples of materials that the mold core can be formed from include, but are not limited to, end grain balsa wood, expanded polymeric foams, blown polymeric foams, syntactic foams, aramid paper, and/or aluminum honeycomb. The mold core can have different sizes and/or shapes for different applications. For some applications the mold core is less dense the combination of cured matrix component and reinforcement component.

EXAMPLES

[042] MATERIALS

[043] Aromatic epoxy compound: D.E.R.TM 383, Chemical Abstracts Service (CAS) registry number 25085-99-8, available from The Dow Chemical Company.

[044] Comparative diluent: Butanediol diglycidyl ether, (BDDGE), available from The Dow Chemical Company.

[045] Amine: JEFFAMINE® D-230 Polyoxypropylenediamine (D-230), available from Huntsman International LLC.

[046] Amine: Isophorone diamine (IPDA), available from Evonik Industries.

[047] Amine: Aminoethylpiperazine (AEP), available from The Dow Chemical Company.

[048] Diluent: Dicyclopentadiene diepoxide, (DCPD DE), (diluent), available from Sigma Aldrich.

[049] Amine: D.E.H.TM 52, Chemical Abstracts Service (CAS) registry number 111-40-0/31326-29-1, available from The Dow Chemical Company.

[050] Anhydride: Methylhexahydrophthalic anhydride (MHHPA), available from Dixie Chemical Company.

[051] Amine: Benzyl dimethylamine (BDMA), available from Sigma Aldrich.

[052] Resin component preparation

[053] Resin components 1 through 9 were prepared by adding D.E.R.TM 383 to a respective glass container for each of the resin components. Either BDDGE or DCPD DE was added to each of the respective glass containers. The container contents including BDDGE were stirred while the temperature was maintained at about 20 °C and the container contents including DCPD DE were stirred while the temperature was maintained at about 45 °C. Epoxide equivalent weight (EEW) was calculated as the mass of respective resin component constituent containing one mole of epoxide groups. The D.E.R.TM 383 had an EEW of 179.5 grams/equivalent (g/eq), the BDDGE had an EEW of 120 g/eq, and the DCPD DE had an EEW of 277 g/eq.

[054] Table 1 shows the weight percent (Wt %) of each constituent of resin components 1 through 9 based upon a total weight of the respective formulations Example 1 through Example 7 and Comparative Examples 1 and 2, as described below. The viscosity was determined for resin components 1 through 3 using the ASTM D-2393 test method. Table 1 shows the viscosity of resin components 1 through 3.

Table 1

	D.E.R. TM 383 (aromatic epoxy compound)	Butanediol diglycidyl ether	Dicyclopentadiene diepoxide	Viscosity (cP)
	Wt %	Wt %	Wt %	
Resin Component 1	65.6	10.7	-	1500

	(based on total weight of Comparative Example 1)	(based on total weight of Comparative Example 1)		
Resin Component 2	66.0 (based on total weight of Example 1)	-	11.6 (based on total weight of Example 1)	5300
Resin Component 3	58.7 (based on total weight of Example 2)	-	19.6 (based on total weight of Example 2)	3800
Resin Component 4	42.5 (based on total weight of Example 3)	-	7.5 (based on total weight of Example 3)	-
Resin Component 5	64.9 (based on total weight of Comparative Example 2)	11.45 (based on total weight of Comparative Example 2)	-	-
Resin Component 6	58.7 (based on total weight of Example 4)	-	19.6 (based on total weight of Example 4)	-
Resin Component 7	55.0 (based on total weight of Example 5)	-	23.6 (based on total weight of Example 5)	-
Resin Component 8	55.0 (based on total weight of Example 6)	-	23.6 (based on total weight of Example 6)	-
Resin Component 9	58.7 (based on total weight of Example 7)	-	19.6 (based on total weight of Example 7)	-

[055] Hardener component preparation

[056] Hardener components 1 through 9 were prepared by adding D-230, IPDA, AEP, D.E.H.TM 52, MHHPA and/or BDMA to a respective glass container for each of the hardener components. The each of the containers contents were stirred while the temperature was maintained at about 20 °C.

Hydrogen equivalent weight (HEW) was calculated as the molecular weight of the respective hardener component constituent divided by the number of sites on a molecule thereof that was capable of opening an epoxy ring. The D-230 had a HEW of 60 g/eq, the IPDA had a HEW of 43 g/eq, the AEP had a HEW of 43 g/eq, the D.E.H.TM 52 had a HEW of 44 g/eq, and the MHHPA had a HEW of 190 g/eq.

[057] Table 2 shows the weight percent (Wt %) of each constituent of the respective hardener components 1 through 9 based upon the total weight of respective

formulations Example 1 through Example 7 and Comparative Examples 1 and 2, as described below.

Table 2

	D-230 (Polyoxypropylenediamine)	Isophorone diamine	Aminoethylpiperazine	D.E.H. TM 52 (amine)	Methylhexahydrophthalic anhydride	Benzyl dimethylamine
	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %
Hardener component 1	17.3 (based on total weight of Comparative Example 1)	3.2 (based on total weight of Comparative Example 1)	3.2 (based on total weight of Comparative Example 1)	-	-	-
Hardener component 2	14.3 (based on total weight of Example 1)	7.4 (based on total weight of Example 1)	-	0.7 (based on total weight of Example 1)	-	-
Hardener component 3	13.9 (based on total weight of Example 2)	7.1 (based on total weight of Example 2)	-	0.7 (based on total weight of Example 2)	-	-
Hardener component 4	-	-	-	-	48.5 (based on total weight of Example 3)	1.5 (based on total weight of Example 3)
Hardener component 5	15.2 (based on total weight of Comparative Example 2)	7.8 (based on total weight of Comparative Example 2)	-	0.7 (based on total weight of Comparative Example 2)	-	-
Hardener component 6	13.9 (based on total weight of	7.2 (based on total weight of	-	0.7 (based on total weight of	-	-

	Example 4)	Example 4)		Example 4)		
Hardener component 7	13.7 (based on total weight of Example 5)	7.1 (based on total weight of Example 5)	-	0.6 (based on total weight of Example 5)	-	-
Hardener component 8	13.7 (based on total weight of Example 6)	6.2 (based on total weight of Example 6)	-	1.5 (based on total weight of Example 6)	-	-
Hardener component 9	13.9 (based on total weight of Example 7)	5.6 (based on total weight of Example 7)	-	2.2 (based on total weight of Example 7)	-	-

[058] Examples 1-7 preparation

[059] Substantially solvent-free formulations Example 1 through Example 7 were prepared by combining the resin components 1 through 9 with the hardener components 1 through 9 at a room temperature of approximately 23 °C. Example 1 was prepared by combining resin component 2 with hardener component 2; Example 2 was prepared by combining resin component 3 with hardener component 3; Example 3 was prepared by combining resin component 4 with hardener component 4; Example 4 was prepared by combining resin component 6 with hardener component 6; Example 5 was prepared by combining resin component 7 with hardener component 7; Example 6 was prepared by combining resin component 8 with hardener component 8; Example 7 was prepared by combining resin component 9 with hardener component 9.

[060] Comparative Examples A-B preparation

[061] Comparative Examples A and B were prepared as Examples 1-7, except that Comparative Examples A and B were prepared by combining resin component 1 with hardener component 1, and resin component 5 with hardener component 5, respectively.

[062] Examples 8-10 preparation

[063] The respectively combined resin components and hardener components were poured into a mold and cured. Example 1-3 were each cured at 70 °C for 7 hours and were post cured at 120 °C for 2 hours to provide Examples 8-10

respectively. Examples 8-10 were products obtained by curing the substantially solvent-free epoxy formulations.

[064] Comparative Example C preparation

[065] Comparative Example C was prepared as Examples 8-10, except that Comparative Examples A was employed.

[066] Properties of Examples 8-10 were determined. Glass transition temperature was determined by ASTM D7028; tensile strain was determined by ASTM D 3039; tensile modulus was determined by D638; determine tensile stress by D638; flexural modulus was determined by ASTM D790; flexural strength was determined by ASTM D790; Table 3A shows the results of the aforementioned tests.

Table 3A

	Tg (°C)	Tensile strain (%)	Tensile modulus (MPa)	Tensile stress (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)
Example 8	108	5.3	3676	75.6	3476	127
Example 9	94	3.9	3489	77.6	3800	137
Example 10	122	2.5	3763	73.9	-	-

[067] Properties of Comparative Example C were determined as described for Examples 8-10; Table 3B shows the results of the tests.

Table 3B

	Tg (°C)	Tensile strain (%)	Tensile modulus (MPa)	Tensile stress (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)
Comparative Example C	80	6.4	3377	72.1	3151	110

[068] Table 3A and Table 3B data shows that Examples 8, 9 and 10 each have a glass transition temperature that is greater than the Comparative Example C glass transition temperature. Table 3A data shows that Example 8 and Example 10 have a both a greater tensile modulus and tensile stress than those of Comparative

Example C. Table 3A data further shows that Example 8 has both a greater flexural modulus and flexural strength than Comparative Example C.

[069] Viscosity increase during curing of Comparative Example B and Example 4 through Example 7 was determined using a TA Instruments ARES Rheometer Model 4000-0047 with 40 millimeter diameter parallel plates. The viscosity increase was determined at a constant temperature of 40 °C over a time period of 60 minutes. After the 60 minute time period the viscosity increase was further determined while the temperature was increased 0.25 °C per minute from 40 °C to 70 °C. After the temperature had reached 70 °C the viscosity increase was further determined while the temperature was maintained at 70°C until Comparative Example B and/or Example 4 through Example 7 reached a gel point. The gel point is determined when the G' (the storage modulus) is equal to G'' (the loss modulus). Table 4A shows the determined viscosities of Example 4 through Example 7. Table 4B shows the determined viscosities of Comparative Example B. Table 4A and Table 4B data shows that Comparative Example B, which includes the diluent BDDGE, and Example 4 through Example 7, which include the diluent DCPD DE, each have a viscosity that is less than 0.16 Mpa·s at time 0.0. Table 4B data shows Comparative Example B has the lowest viscosity at time 0.0, which is 0.090 Mpa·s. Table 4A and Table 4B data shows that Comparative Example B reaches a viscosity of at least 0.53 Mpa·s, as seen at time 105.0, before any of Example 4 through Example 7.

Table 4A

		Example 4	Example 5	Example 6	Example 7
Time (min)	Temp (°C)	Viscosity (Mpa·s)	Viscosity (Mpa·s)	Viscosity (Mpa·s)	Viscosity (Mpa·s)
0.0	40.235	0.140	0.143	0.148	0.156
5.0	40.235	0.138	0.146	0.157	0.171
10.0	40.235	0.147	0.153	0.166	0.181
15.0	40.235	0.154	0.160	0.175	0.194
20.0	40.235	0.162	0.167	0.184	0.205
25.0	40.235	0.171	0.174	0.194	0.219
30.0	40.235	0.180	0.182	0.203	0.234
35.0	40.235	0.189	0.190	0.215	0.249
40.0	40.235	0.199	0.198	0.227	0.267
45.0	40.235	0.212	0.207	0.239	0.286
50.0	40.235	0.224	0.217	0.253	0.307
55.0	40.235	0.238	0.228	0.268	0.331
60.0	40.235	0.253	0.239	0.285	0.360
65.0	41.509	0.247	0.234	0.280	0.358
70.0	42.751	0.244	0.227	0.275	0.354
75.0	43.993	0.242	0.222	0.270	0.358

80.0	45.237	0.245	0.219	0.270	0.365
85.0	46.513	0.249	0.219	0.272	0.377
90.0	47.755	0.258	0.221	0.277	0.398
95.0	48.999	0.270	0.224	0.286	0.425
99.9	50.241	0.287	0.230	0.299	0.465
105.0	51.512	0.312	0.241	0.317	0.520
110.0	52.740	0.345	0.255	0.340	0.585
115.0	53.987	0.392	0.277	0.376	0.683
120.0	55.257	0.454	0.310	0.424	0.824
125.0	56.495	0.542	0.352	0.485	1.023
130.0	57.740	0.667	0.413	0.570	1.310
135.0	58.988	0.845	0.495	0.686	1.741
140.0	60.231	1.106	0.604	0.853	2.410
145.0	61.508	1.514	0.776	1.097	3.493
150.0	62.763	2.136	1.016	1.447	5.222
155.0	64.003	3.117	1.365	1.972	8.155
160.0	65.243	4.720	1.917	2.773	13.328
165.0	66.486	7.416	2.745	4.059	23.125
170.0	67.761	12.292	4.127	6.197	47.315
175.0	68.988	21.003	6.331	9.729	114.678
180.0	70.052	40.884	10.649	15.575	378.853
185.0	69.998	90.501	18.013	29.741	1320.304
190.0	69.997	229.425	32.151	60.558	-
195.0	70.004	685.961	58.401	143.381	-
200.0	70.009	1296.488	109.334	378.030	-

Table 4B

		Comparative Example B
Time (min)	Temp (°C)	Viscosity (Mpa·s)
0.0	40.235	0.090
5.0	40.235	0.088
10.0	40.235	0.093
15.0	40.235	0.100
20.0	40.235	0.108
25.0	40.235	0.116
30.0	40.235	0.127
35.0	40.235	0.138
40.0	40.235	0.152
45.0	40.235	0.167
50.0	40.235	0.184
55.0	40.235	0.203
60.0	40.235	0.224
65.0	41.509	0.230
70.0	42.751	0.238
75.0	43.993	0.250
80.0	45.237	0.268
85.0	46.513	0.293
90.0	47.755	0.326
95.0	48.999	0.376
99.9	50.241	0.439
105.0	51.512	0.535
110.0	52.740	0.659
115.0	53.987	0.855

120.0	55.257	1.156
125.0	56.495	1.625
130.0	57.740	2.373
135.0	58.988	3.625
140.0	60.231	5.790
145.0	61.508	9.809
150.0	62.763	17.271
155.0	64.003	34.462
160.0	65.243	74.764
165.0	66.486	195.240
170.0	67.761	670.320
175.0	68.988	2602.506
180.0	70.052	-
185.0	69.998	-
190.0	69.997	-
195.0	70.004	-
200.0	70.009	-

[070] The data of Table 4A and Table 4B indicates that Comparative Example B has a greater reactivity than any of Example 4 through Example 7. The greater reactivity is indicated by the greater viscosity increase rate of Comparative Example B, as compared to the viscosity increase rates of each of Example 4 through Example 7. Figure 1 is a graphical representation of Table 4A and Table 4B. Figure 1 illustrates that Comparative Example B has the lowest relative viscosity at 40 °C, corresponding to time 0, but has the fastest relative cure rate, as illustrated by portions of Figure 1 where lines tangent to Comparative Example B have a greater slope than lines respectively tangent to Example 4, Example 5, Example 6, or Example 7. The relatively linear and relatively horizontal portions of the curves for Comparative Example B and Examples 4-7 indicate that the formulations are relatively latent at the corresponding temperatures.

[071] Peak cure temperatures for Comparative Example B and Example 7 were determined by placing a 100 gram mass of each into a respective container and then inserting a temperature measuring probe in the geometric center of the respective mass. The temperature was recorded over time until the temperature reached a maximum and began to cool. Figure 2 shows the peak cure temperature for Comparative Example B is greater than 140 °C while the peak cure temperature for Example 7 is less than 60 °C. The lower exotherm of Example 7 indicates that Example 7 is less reactive than Comparative Example B.

Claims

What is claimed:

1. A substantially solvent-free epoxy formulation comprising:
a resin component that includes;
an epoxy compound that is selected from the group consisting of aromatic epoxy compounds, alicyclic epoxy compounds, aliphatic epoxy compounds, and combinations thereof; and
a diluent that includes dicyclopentadiene diepoxide; and
a hardener component that is selected from the group consisting of is selected from the group consisting of an amine, an anhydride, a carboxylic acid, a phenol, a thiol, and combinations thereof.
2. The formulation of claim 1, where the amine is selected from the group consisting of aliphatic polyamines, arylaliphatic polyamines, cycloaliphatic polyamines, aromatic polyamines, heterocyclic polyamines, polyalkoxy polyamines, dicyandiamide and derivatives thereof, aminoamides, amidines, ketimines, and combinations thereof.
3. The formulation of any one of the preceding claims, where the anhydride is selected from the group consisting of aromatic anhydrides, alicyclic anhydrides, aliphatic anhydride and combinations thereof.
4. The formulation of any one of the preceding claims, where the diluent is from 5 weight percent to 35 weight percent of a total weight of the formulation.
5. The formulation of any one of the preceding claims, where the epoxy compound includes an aromatic epoxy compound, the hardener component is from 15 weight percent to 25 weight percent of a total weight of the formulation and includes polyoxypropylenediamine and isophorone diamine, the diluent is from 10 weight percent to 25 weight percent of the total weight of the formulation, and the formulation has a glass transition temperature from 70 °C to 135 °C.

6. A product obtained by curing the substantially solvent-free epoxy formulation as in any one of claims 1-5.
7. A method of forming a composite comprising:
 - providing a mold
 - providing a reinforcement component to the mold;
 - infusing the reinforcement component with a substantially solvent-free epoxy formulation, where the substantially solvent-free epoxy formulation includes:
 - a resin component having:
 - an epoxy compound that is selected from the group consisting of aromatic epoxy compounds, alicyclic epoxy compounds, aliphatic epoxy compounds, and combinations thereof; and
 - a diluent that includes dicyclopentadiene diepoxide; and
 - a hardener component that is selected from the group consisting of an amine, an anhydride, a carboxylic acid, a phenol, a thiol, and combinations thereof; and
 - curing the infused substantially solvent-free epoxy formulation to form the composite.
8. The method of claim 7, where curing the substantially solvent-free epoxy formulation to form the composite includes heating the infused substantially solvent-free epoxy formulation to a temperature from 70 °C to 140 °C.
9. The method as in any one of claims 7-8, where the method includes providing a mold core to the mold.
10. The method as in any one of claims 7-9, where infusing the reinforcement component with a substantially solvent-free epoxy formulation includes providing a vacuum.

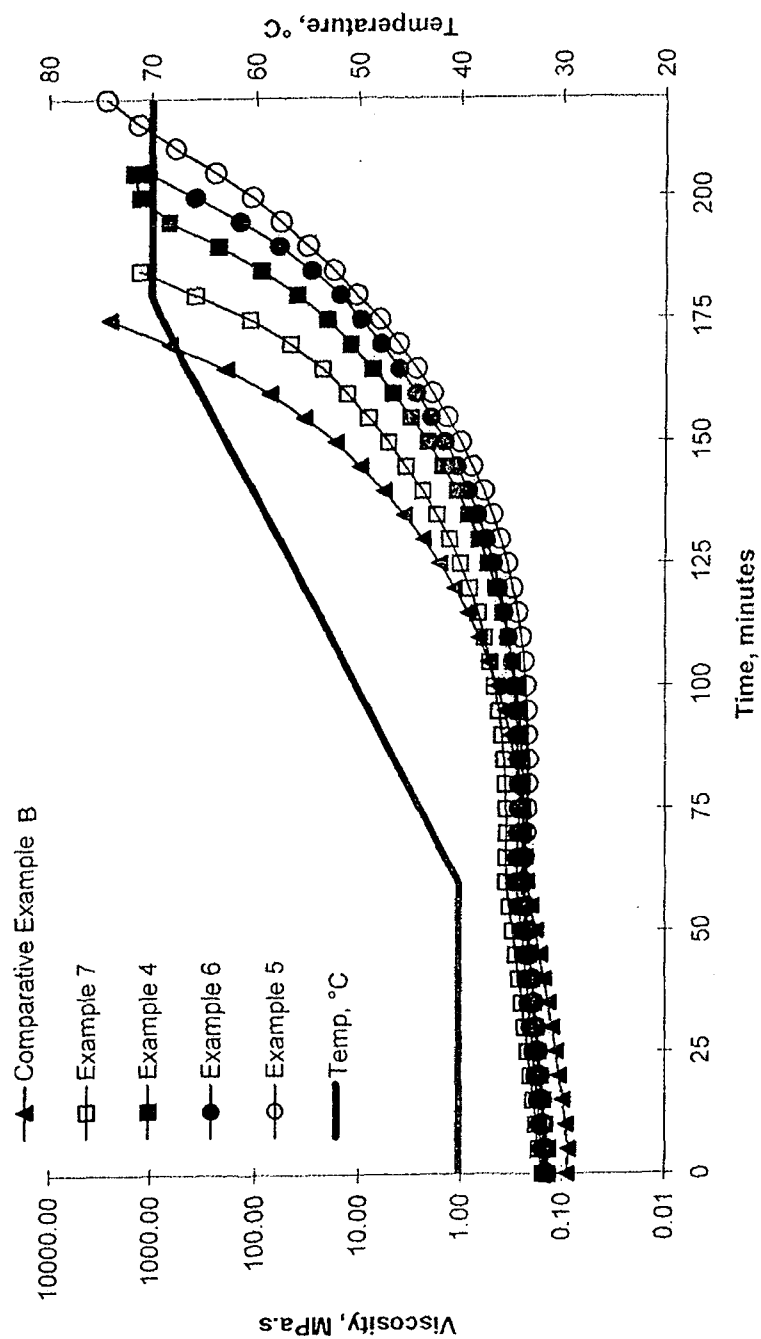


Figure 1

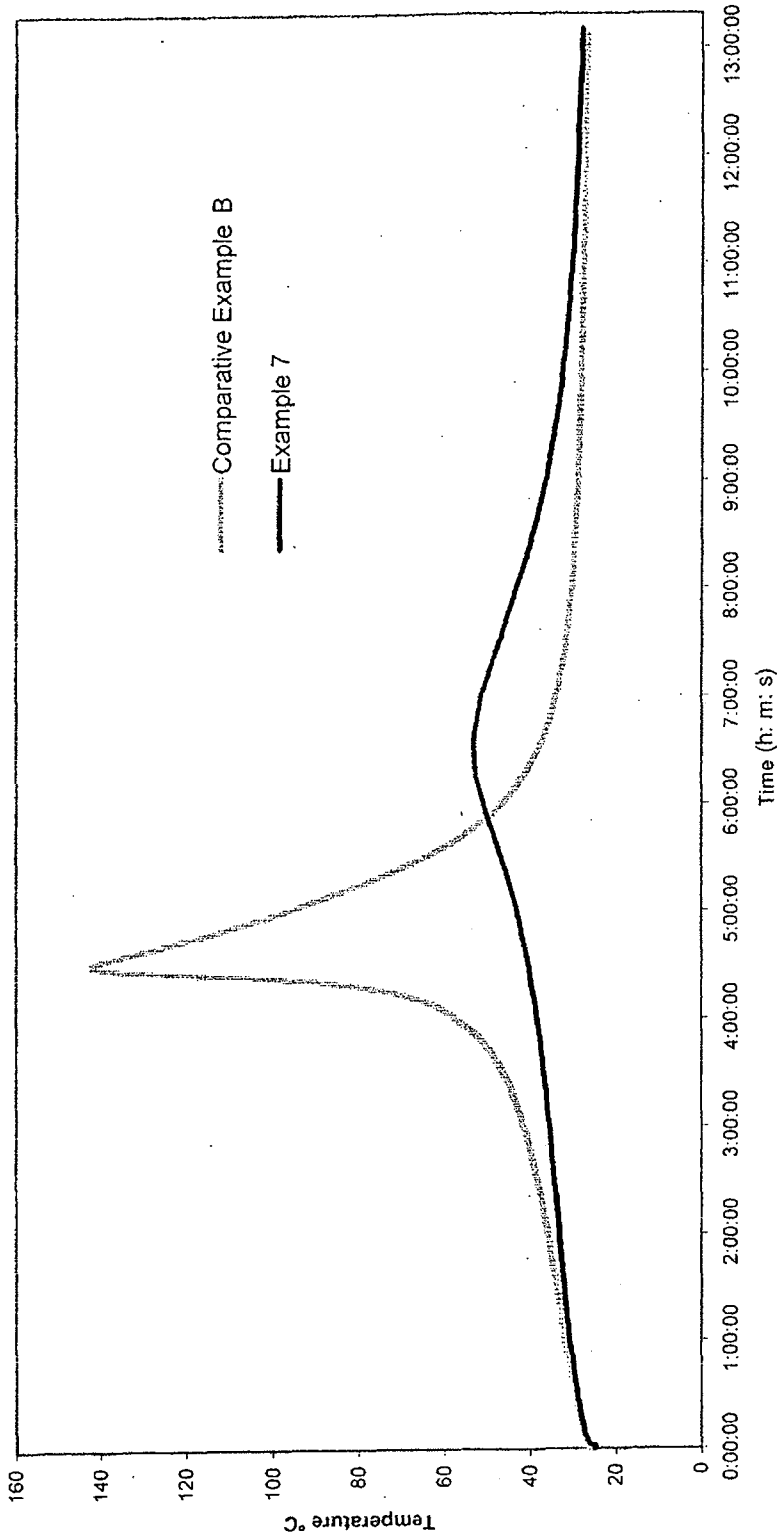


Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/003117

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G59/22 C08G59/24 C08L63/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C08L C09D C09J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.



See patent family annex.

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

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"&" document member of the same patent family

Date of the actual completion of the international search

23 June 2011

Date of mailing of the international search report

07/07/2011

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/003117

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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