



(51) International Patent Classification:
C08G 65/00 (2006.01)

(21) International Application Number:
PCT/US2012/062708

(22) International Filing Date:
31 October 2012 (31.10.2012)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: EMPIRE TECHNOLOGY DEVELOPMENT LLC [US/US]; 2711 Centerville Road, Suite 400, Wilmington, DE 19808 (US).

(72) Inventor: ADAM, Georgius, Abidal; 46A Gwandalan Road, Edensor Park, new South Wales, 2176 (AU).

(74) Agents: SCOLNICK, Daniel, M. et al.; Pepper Hamilton LLP, Suite 5000, 500 Grant Street, Pittsburgh, PA 15219 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: MULTIFUNCTIONAL MELAMINE EPOXY RESINS, METHYLOLS AND AMINES

(57) Abstract: Multifunctional melamine epoxy resins, methylols and amines are provided. Methods of making multifunctional melamine epoxy resins, methylols and amines are also provided. An advantage of the methods and compounds described herein is that natural sources of melamine exist, which reduces the reliance on petrochemical resources. Therefore, the embodiments provided herein provide an opportunity to utilize melamine obtained from highly industrialized non-petrochemical processes and increase the functionality of the base molecule(s), allowing a range of new possible applications of melamine-based materials.



WO 2014/070155 A1

MULTIFUNCTIONAL MELAMINE EPOXY RESINS, METHYLOLS AND AMINES**FIELD**

[0001] Multi-functional epoxy resins for composite materials, methods of making, and uses thereof are provided.

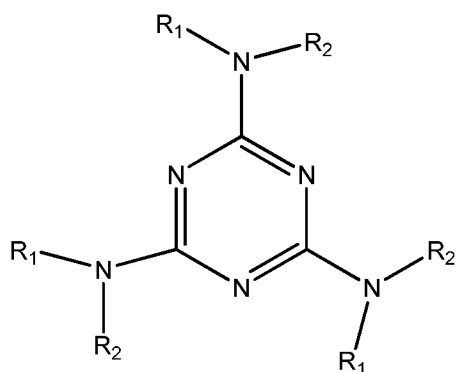
BACKGROUND

[0002] Epoxy resins are used as the predominant ingredient in the fabrication of composite parts and can be utilized both as matrix resin and as crosslinking agents. The degree of functionality of the resin is critical in determining the final properties and the range of end-use applications. Accordingly, production of new resins with enhanced functionality and improved toughness will have a wide range of applications in various fields of composites, coatings, paints, and Interpenetrating Polymer Networks (IPNs). New resins must not only have the requisite properties, but also can be obtained from non-petrochemical sources and have a demonstrably lower materials life cycle cost. The majority of polyfunctional epoxies are sourced from petrochemicals such as, for example, those based on Novolac epoxy. There are others based on polyhydroxy compounds such as glycerol, and epoxy esters derived from polycarboxylic acids as alternative multi-functional epoxy resins. Several melamine formaldehyde resins are known compounds and produced industrially such as :melamine oil, melamine hexamethylol esters .

[0003] There is still a need for improved melamine resins and for new uses and applications of the same with increased functionality. The present application fulfills these needs as well as others.

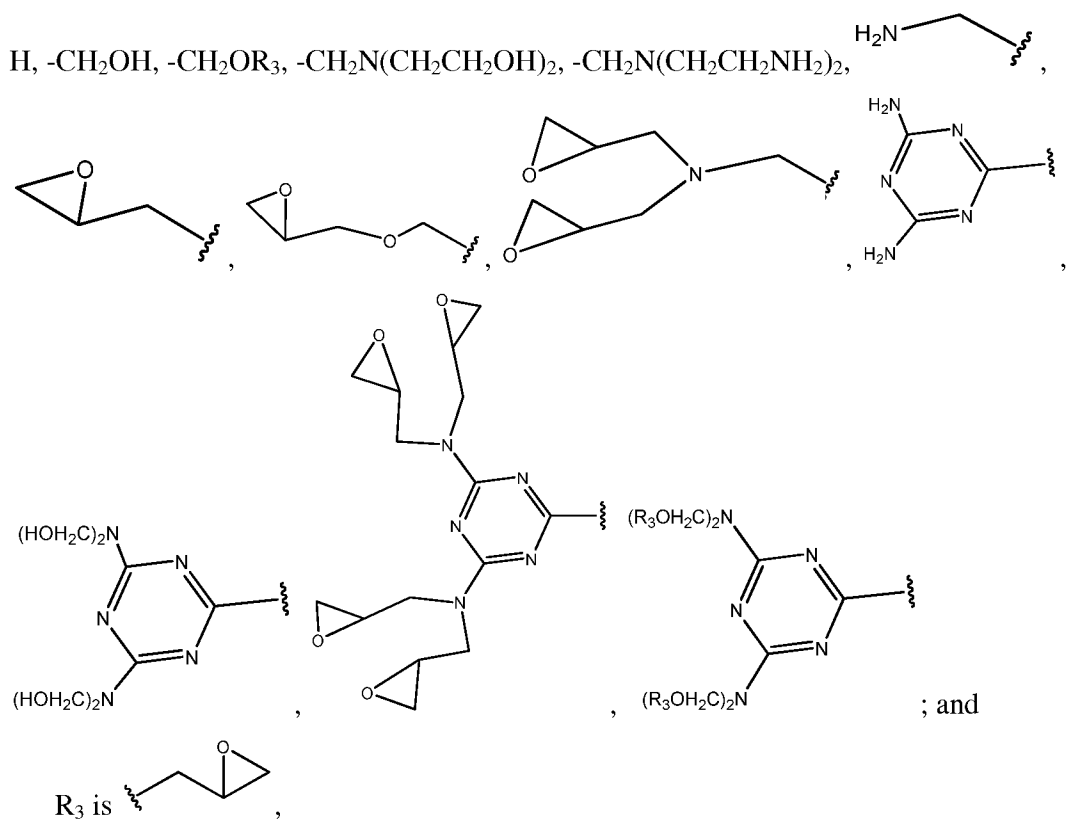
SUMMARY OF THE INVENTION

[0004] In some embodiments, compounds having the structure of Formula III:



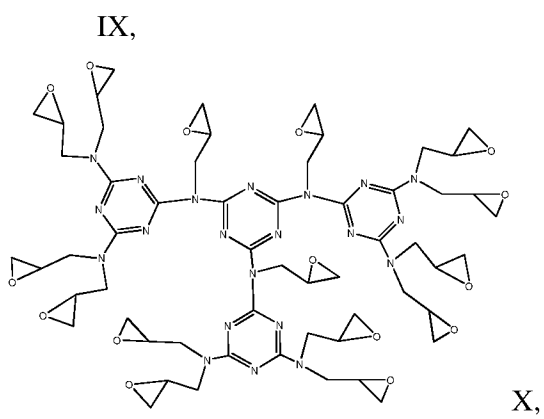
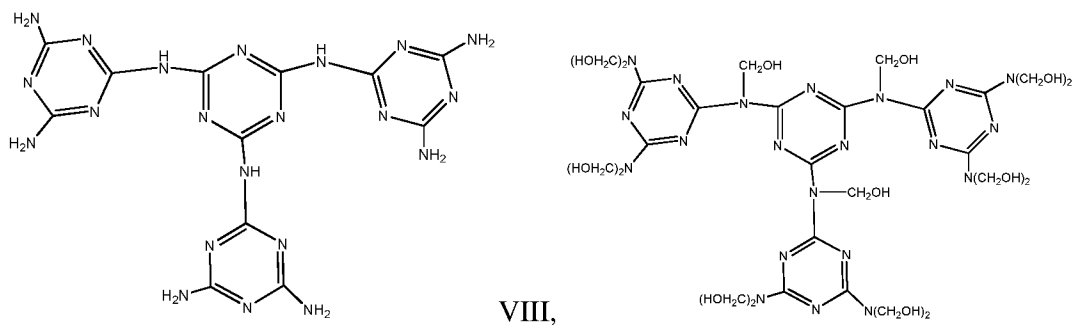
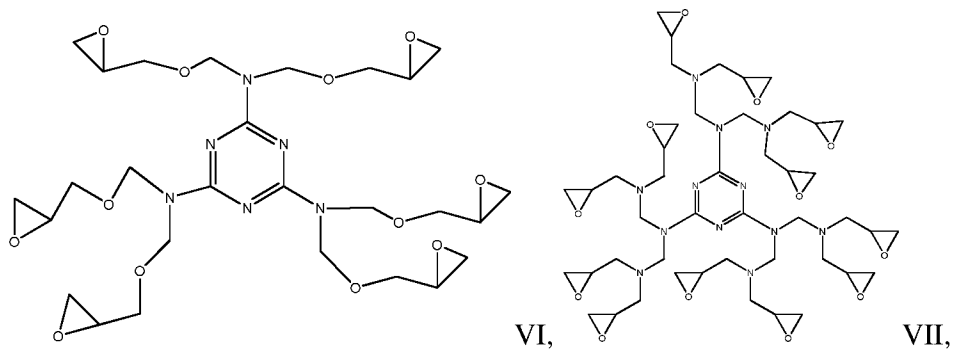
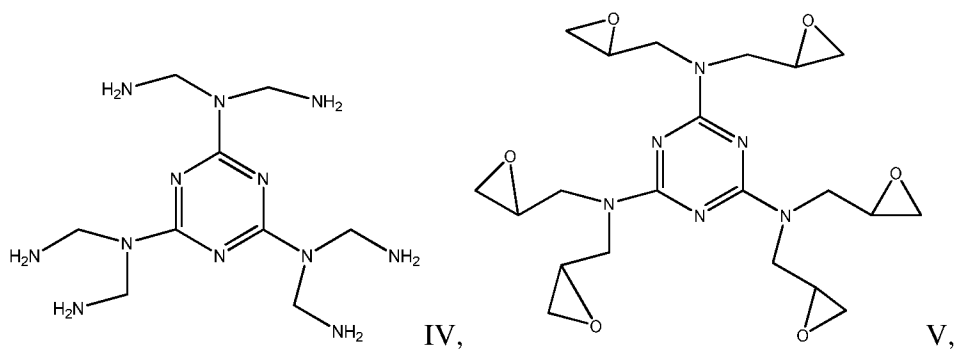
III,

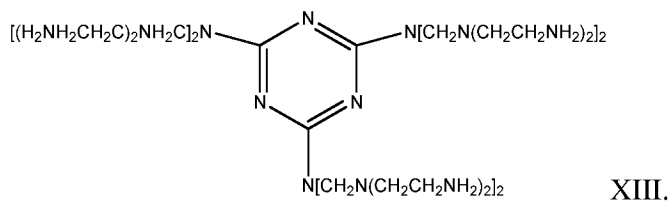
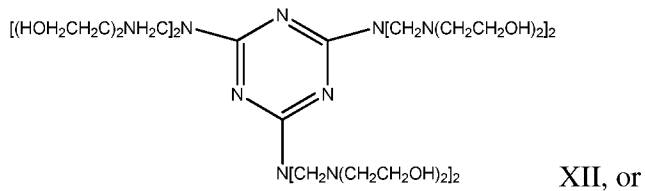
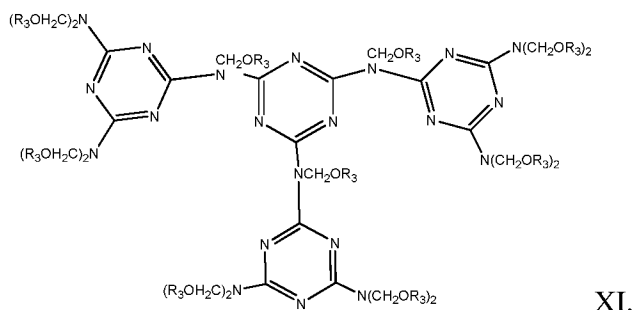
In some embodiments, R_1 and R_2 are each independently selected from the group consisting of:



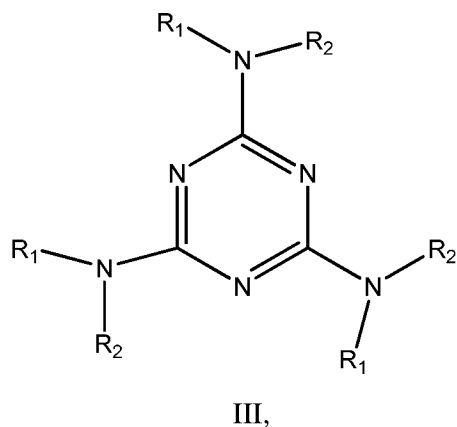
provided that when R_1 is H, R_2 is not H or $-\text{CH}_2\text{OH}$ are provided.

[0005] In some embodiments, the compound has the formula of:

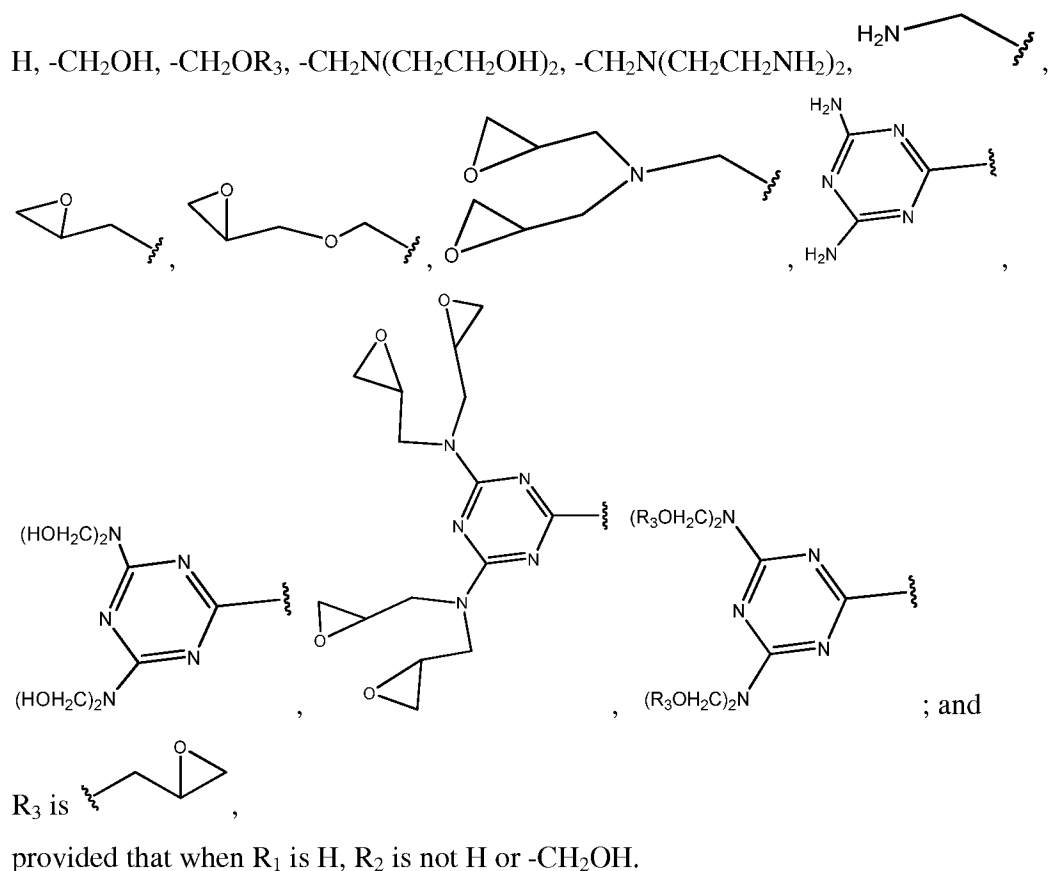




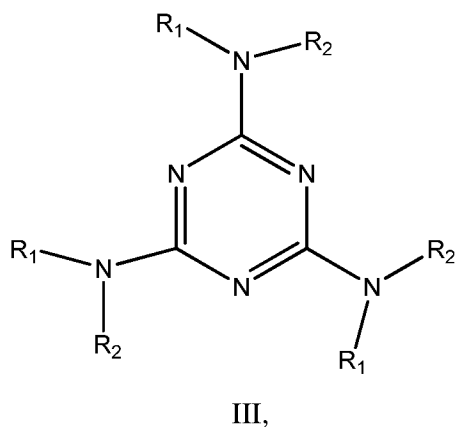
[0006] In some embodiments, compositions are provided, the compositions comprising one or more of the compounds having the formula of Formula III:



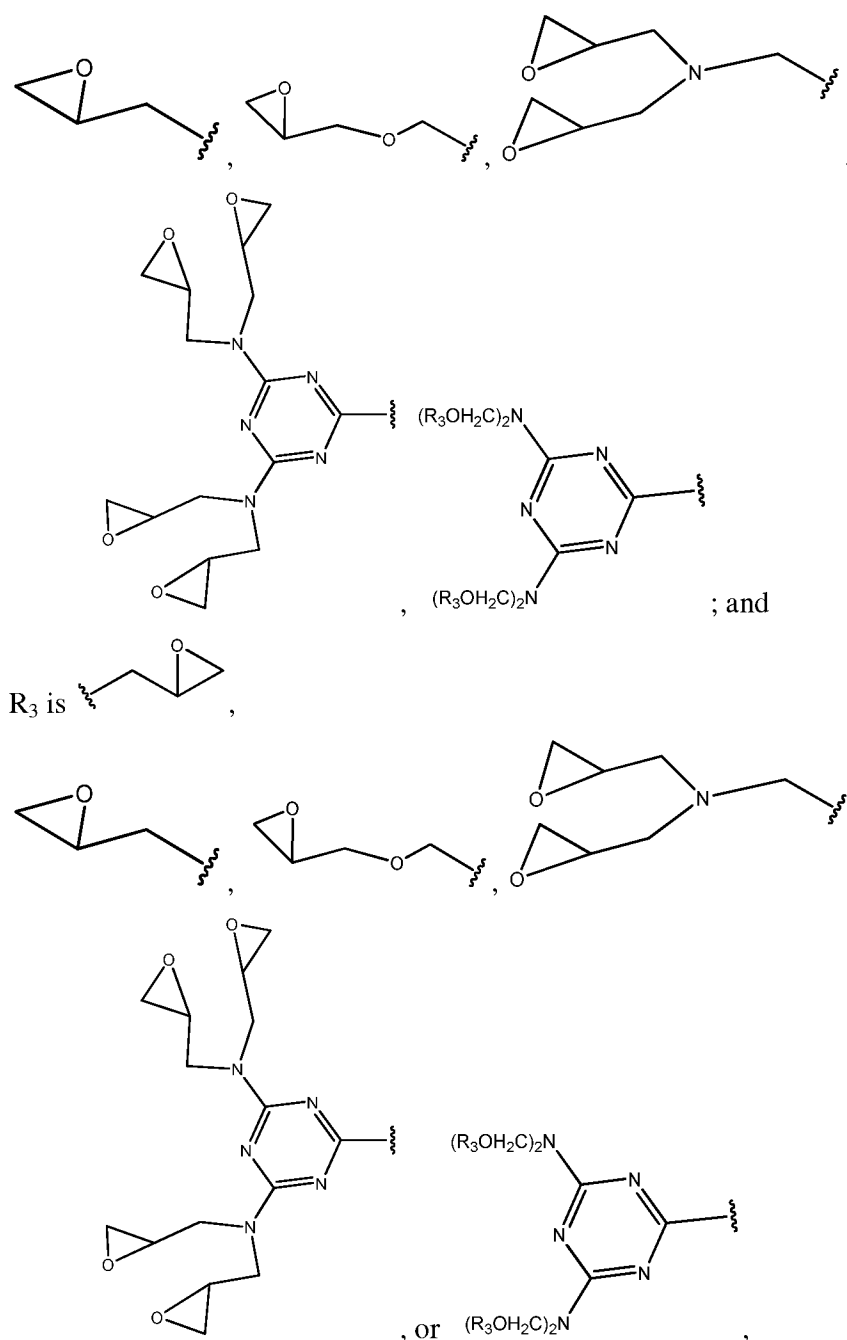
wherein R_1 and R_2 are each independently selected from the group consisting of:



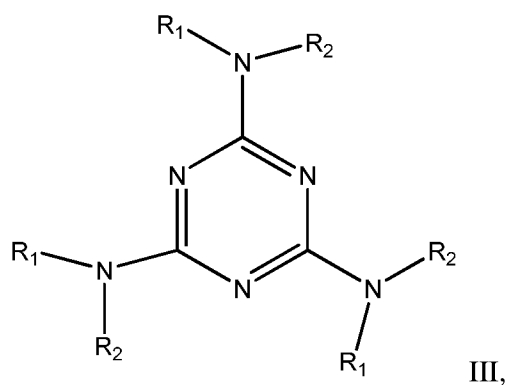
[0007] In some embodiments, epoxy resins are provided, the epoxy resins comprising a compound having the structure of Formula III:



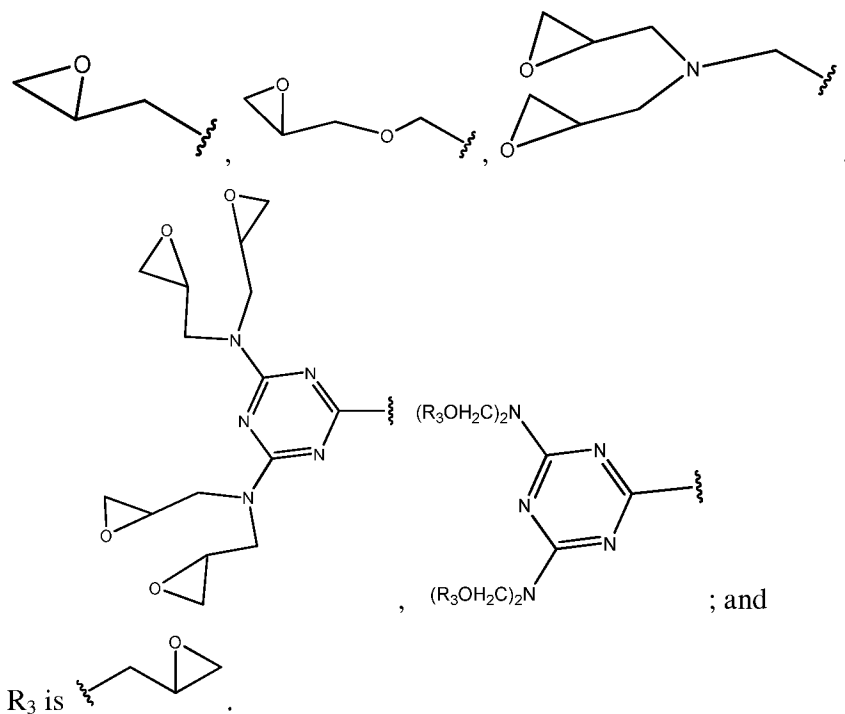
wherein R₁ and R₂ are each independently selected from the group consisting epoxy groups of:



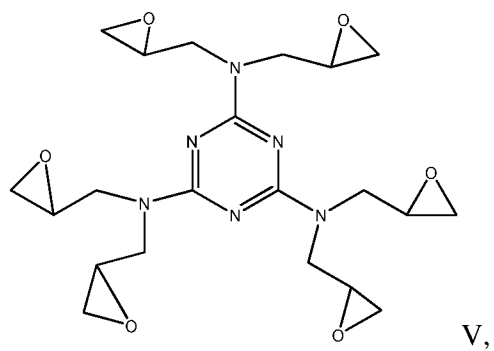
[0008] In some embodiments, carbon fiber composites are provided, the composites comprising a cured epoxy resin of an epoxy resin and amino hardeners, wherein the epoxy resin is a compound of Formula III

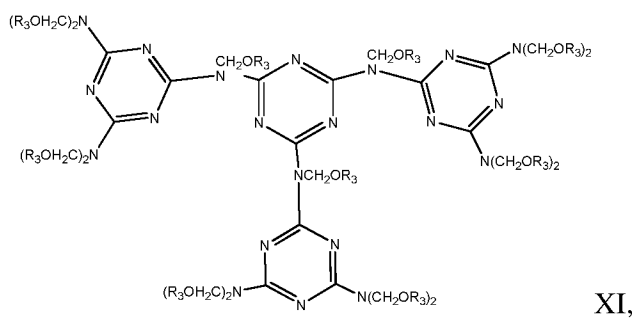
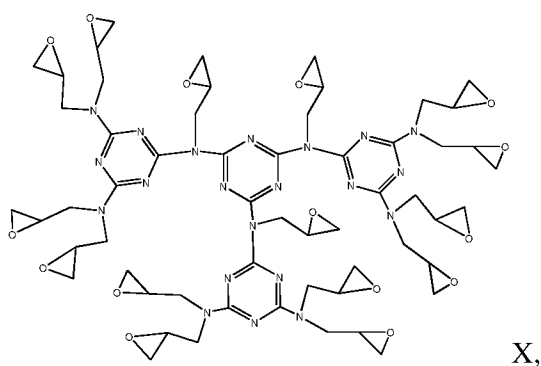
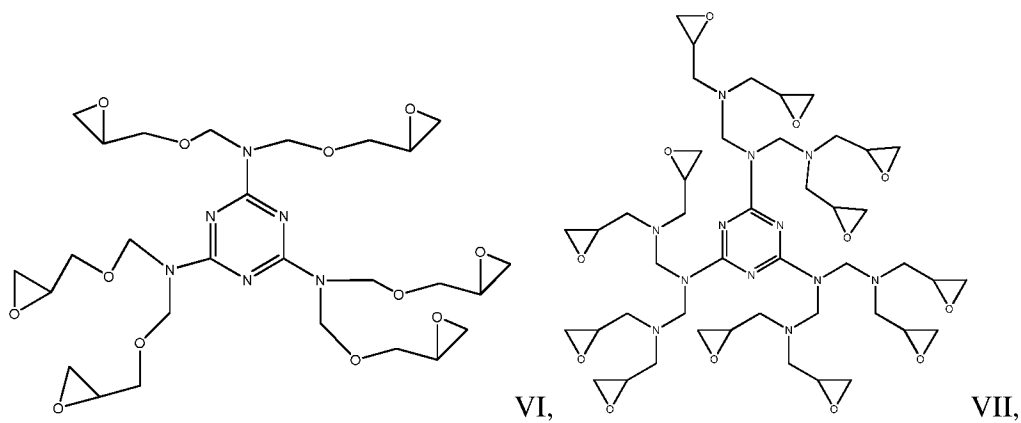


wherein R_1 and R_2 are independently selected from the group consisting of:



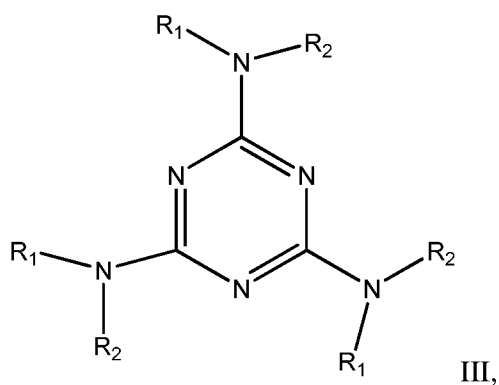
[0009] In some embodiments, the composite comprises an epoxy resin having a Formula of



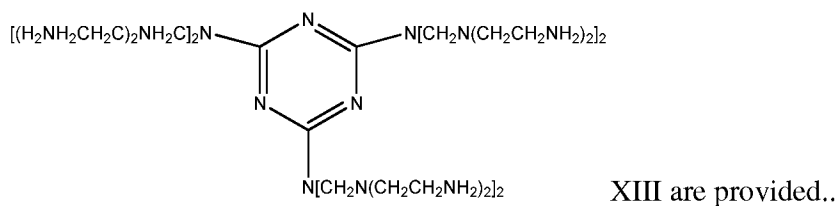
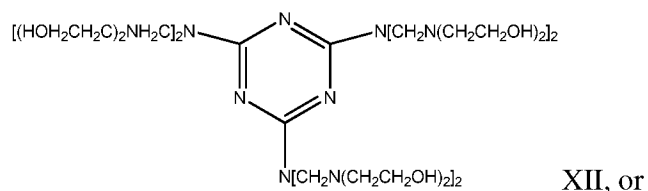
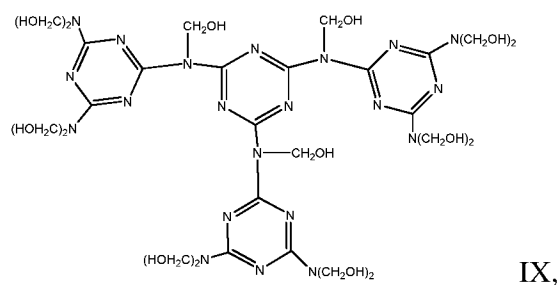
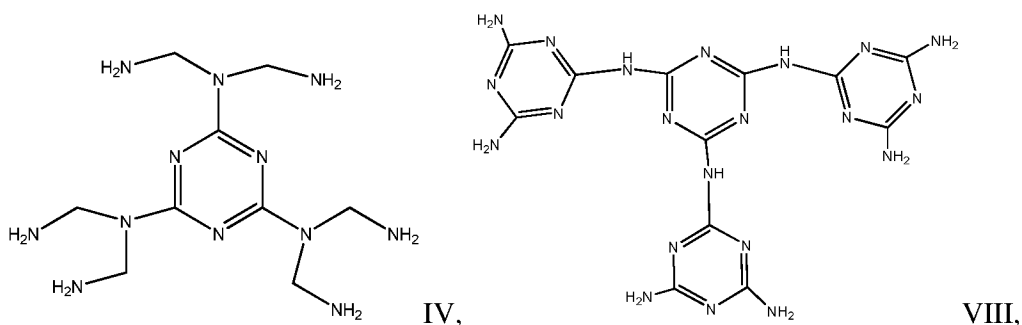


wherein R_3 is .

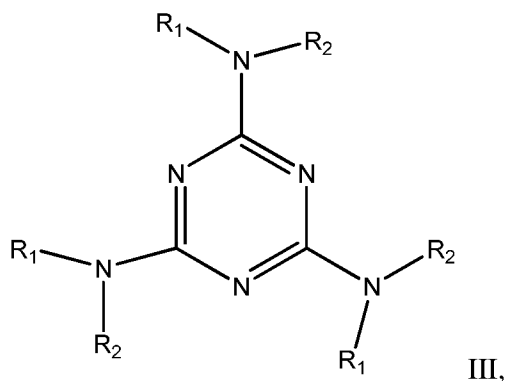
[0010] In some embodiments cross-linked isocyanate terminated polyurethanes, polyesters, or silicones, wherein the isocyanate terminated polyurethanes, polyester, or silicone are cross-linked with a compound of Formula III



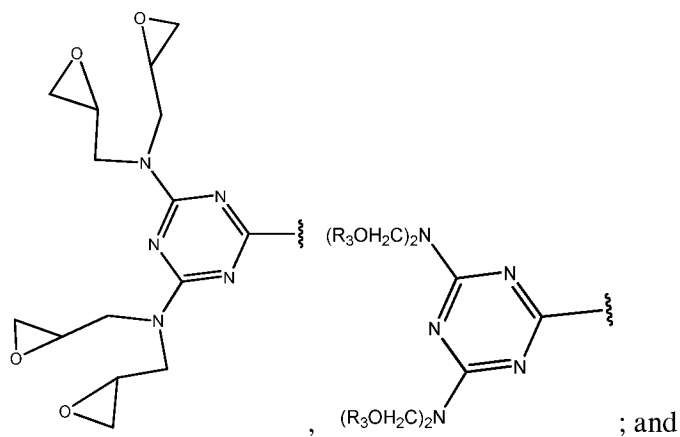
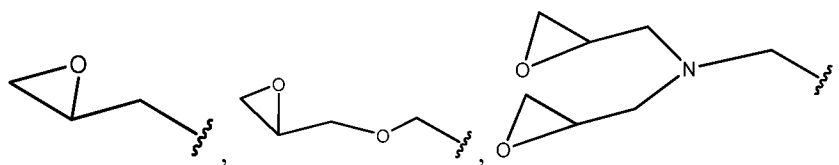
wherein R_1 and R_2 are independently selected from the group consisting of H, CH_2OH , CH_2NH_2 , and melaminy1, or are cross-linked with a compound having a formula of



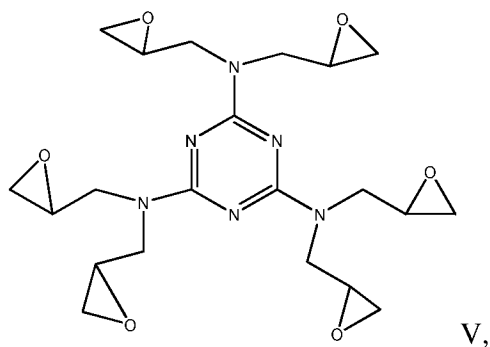
[0011] In some embodiments, composites are provided, the composites comprising one or more a cured epoxy resins of an epoxy resin of Formula III, wherein the epoxy resin is a compound of Formula III

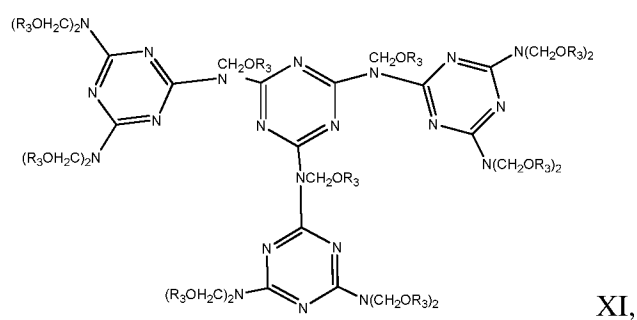
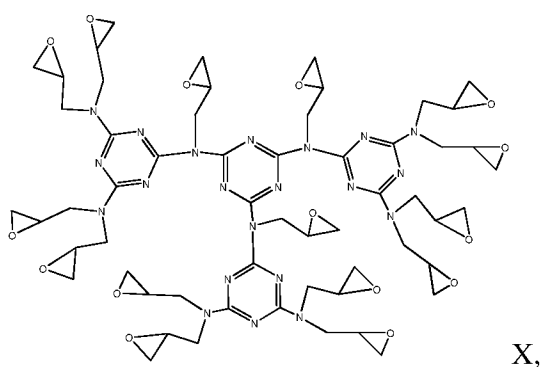
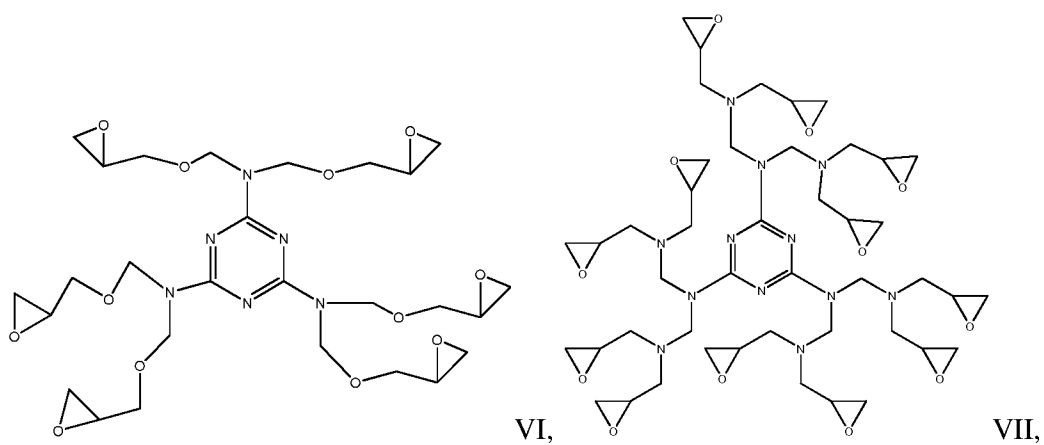


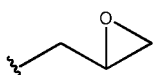
wherein R_1 and R_2 are independently selected from the group consisting of:



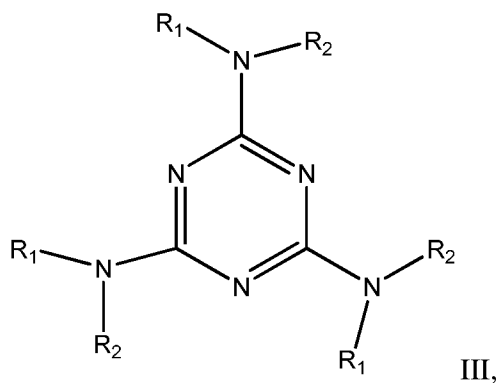
R_3 is . In some embodiments, the epoxy resin has a Formula of



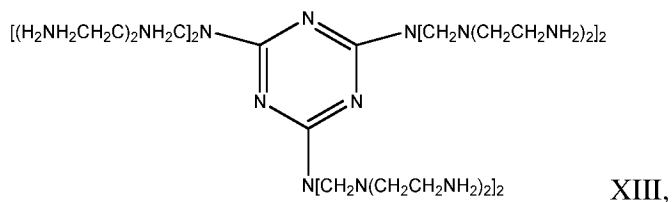
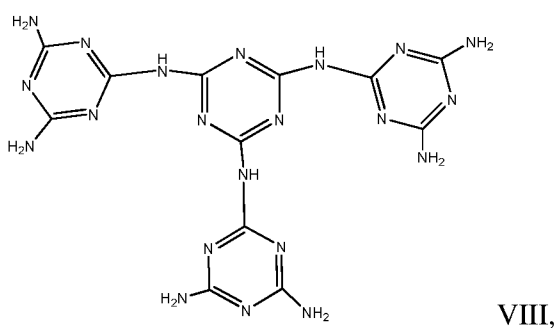
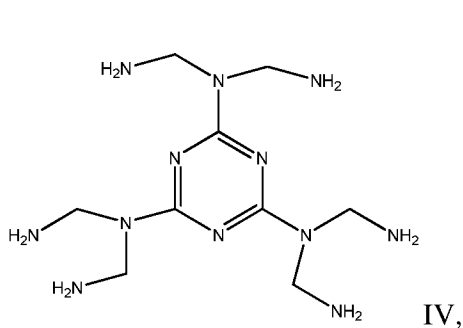


wherein R_3 is .

[0012] In some embodiments, methods of curing epoxy resins are provided, the methods comprising contacting an epoxy resin disclosed herein with amine compounds, a compound of Formula III

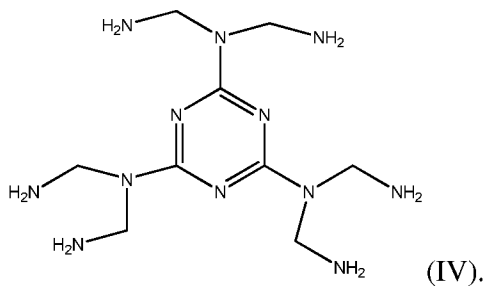


wherein R₁ and R₂ are independently selected from the group consisting of CH₂NH₂, and melaminyll, a compound having a formula of

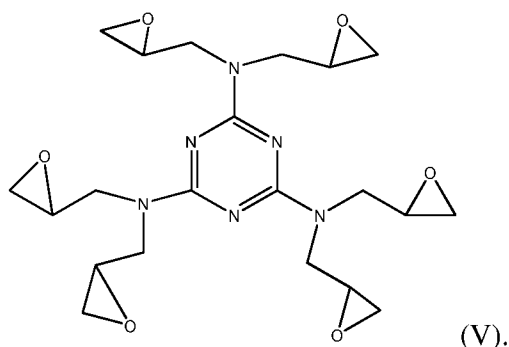


or with one or more hardeners under conditions sufficient to cure the epoxy resins.

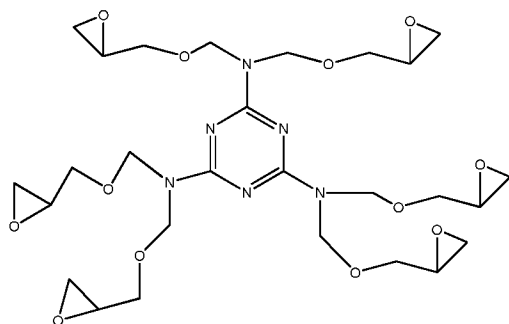
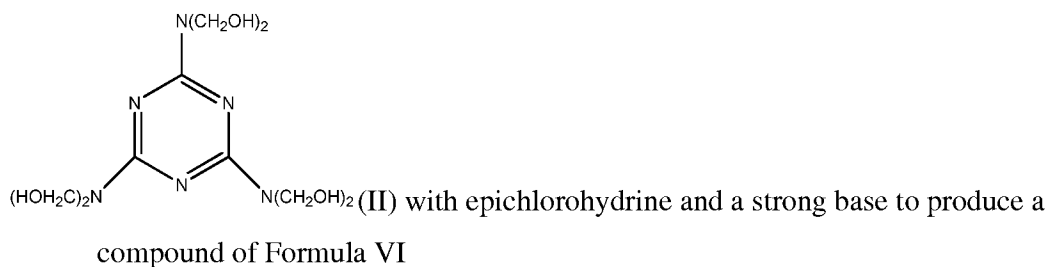
[0013] In some embodiments, methods of making a compound of Formula III are provided, the methods comprising contacting hexamethylol melamine with ammonia to produce a compound of Formula IV



[0014] In some embodiments, methods of making a compound of Formula V are provided, the methods comprising contacting melamine with epichlorohydrine and a strong base to produce a compound of Formula V

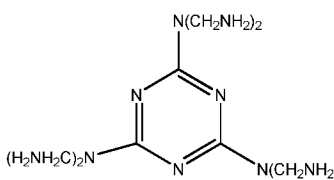


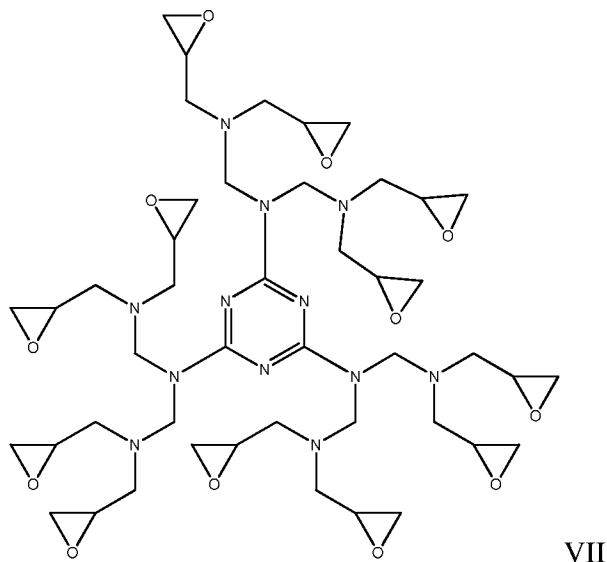
[0015] In some embodiments, methods of making a compound of Formula VI are provided, the methods comprising contacting a compound of Formula II



VI. In some embodiments, the method is performed in the presence of a catalyst and co-catalyst. Examples of a catalyst includes, a lewis acid catalyst. The lewis acid catalyst can be, for example, Lanthanium trifluoromethanesulphonate. Other examples of lewis acid catalysts are known to one of skill in the art. The co-catalyst can be, for example, tetramethylammonium chloride. The co-catalyst can be provided in an aqueous solution, such as a 50 % solution in water. Other suitable co-catalysts can also be used.

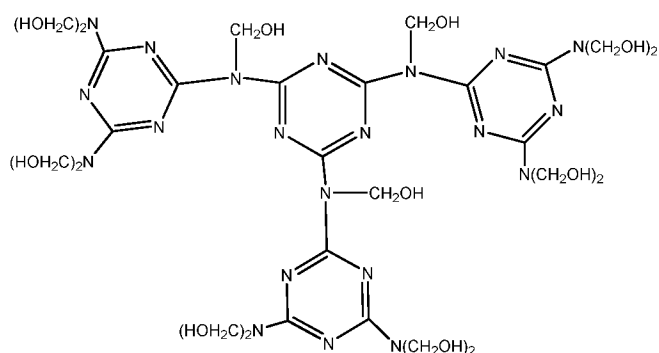
[0016] In some embodiments, methods of making a compound of Formula VII are provided, the methods comprising contacting a compound of Formula IV


CCNCC1=NC=NC(=N1)NCC (IV) with epichlorohydrine and a strong base at a temperature of about 0-80 °C to produce a compound of Formula VII



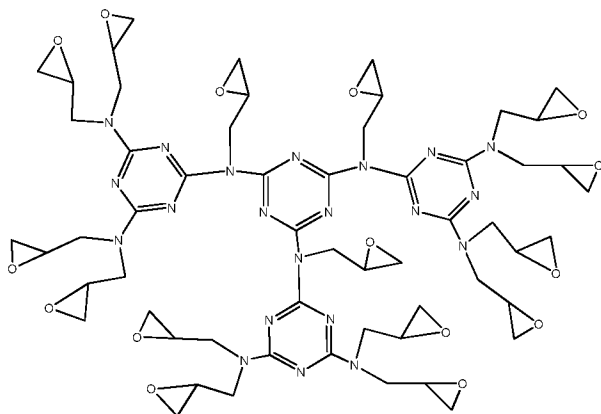
VII

[0017] In some embodiments, methods of making a compound of Formula IX are provided, the methods comprising contacting a compound of Formula VIII with excess formaldehyde and a strong base to produce a compound of Formula IX



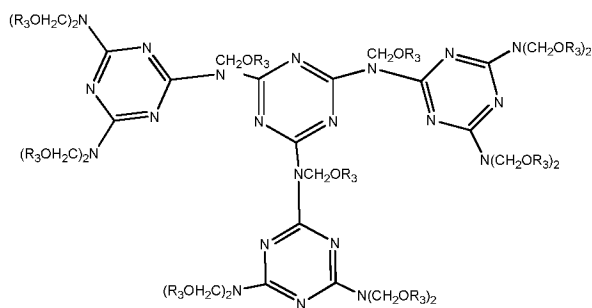
IX.

[0018] In some embodiments, methods of making a compound of Formula X are provided, the methods comprising contacting a compound of Formula VIII with epichlorohydrine and a strong base at a temperature of about 0-80 °C to produce a compound of Formula X



X.

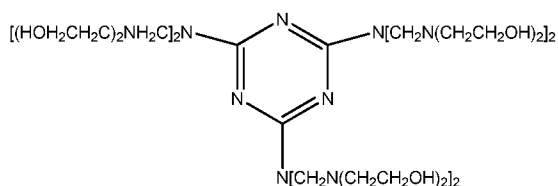
[0019] In some embodiments, methods of making a compound of Formula XI are provided, the methods comprising contacting a compound of Formula IX with an excess of epichlorohydrine and a strong base at a temperature of about 50-60 °C to produce a compound of Formula XI



XI,

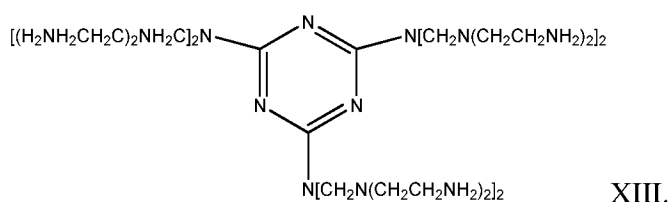
wherein R_3 is .

[0020] In some embodiments, methods of making a compound of Formula XII are provided, the methods comprising contacting a compound of Formula II with diethanol amine to produce a compound of Formula XII



XII.

[0021] In some embodiments, methods of making a compound of Formula XIII are provided, the methods comprising contacting a compound of Formula XII with ammonia or an aliphatic amine under a pressure of about 1-2 atm to produce a compound of Formula XIII



[0022] In some embodiments, methods of producing glycidyl ether derivatives of a compound of Formula XII or glycidylamines from any melamine amino derivatives, a compound of formula XIII are provided, the methods comprising contacting a compound of Formula XII or XIII with respectively with epichlorohydrine and a strong base at a temperature sufficient to produce a glycidyl ether derivative from compound of Formula XII or glycidylamines from compound of formula XIII.

[0023] In some embodiments, compositions comprising further generations of melamine derived epoxy resins are provided, the resins prepared by method described herein. In some embodiments, the methods comprise contacting a melamine methylol of Formula II, IX or Formula XII with an amine to produce a melamine amino derivatives; and optionally contacting the melamine amino derivative with an epichlorohydrine to yield glycidylamine derivative; or contacting the melamine amino derivative with formaldehyde and a strong base to yield a methylol derivatives.

DETAILED DESCRIPTION

[0024] This description is not limited to the particular processes, compositions, or methodologies described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and it is not intended to limit the scope of the embodiments described herein. Unless defined otherwise, all

technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. In some cases, terms with commonly understood meanings are defined herein for clarity and/or for ready reference, and the inclusion of such definitions herein should not necessarily be construed to represent a substantial difference over what is generally understood in the art. However, in case of conflict, the patent specification, including definitions, will prevail.

[0025] It must also be noted that as used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural reference unless the context clearly dictates otherwise.

[0026] As used in this document, terms “comprise,” “have,” and “include” and their conjugates, as used herein, mean “including but not limited to.” While various compositions, methods, and devices are described in terms of “comprising” various components or steps (interpreted as meaning “including, but not limited to”), the compositions, methods, and devices can also “consist essentially of” or “consist of” the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0027] Melamine represents a starting material from which, various resins can be custom designed for many applications including, but not limited to, in various fields of composites, coatings, paints, and Interpenetrating Polymer Networks (IPNs). Melamine has several distinct advantages over existing starting materials. Melamine is a heterocyclic aromatic amine structure, which has been classified as Generally Accepted As Safe (GAAS) (for human uses in industrial applications). All other aromatic amines have been confirmed as carcinogenic to humans and are gradually being phased out of use in Europe and the USA. Additional functionality of the molecule may be achieved with the methods described herein,

which will provide the opportunity to use the compounds in many applications and in future uses of resins.

[0028] Another advantage of the methods and compounds described herein is that natural sources of melamine exist, which reduces the reliance on petrochemical resources. Therefore, the embodiments provided herein provide an opportunity to utilize melamine obtained from highly industrialized non-petrochemical processes and increase the functionality of the base molecule(s), allowing a range of new possible applications of melamine-based materials.

[0029] The compounds and methods described herein are related to the preparation, characterization and evaluation of a series of multifunctional epoxies derived from melamine (Formula I, described herein), methylol melamines (Formula II & XII, described herein), melamine cyanurate (Formula VIII, described herein), methyloic derivatives of melamine cyanurate (Formula IX, described herein) and melamine amine derivatives (Formula IV & XIII, described herein). Some of these have the advantage of being water soluble, which allows them to be used in important applications, such as but not limited to, concrete and water based paint industries.

[0030] The multi-functional epoxies also show very high reactivity, which make them highly suitable, such as but not limited to, for photo curing, increasing the degree of crosslinking of commercial epoxy resins, powder coating, and to enhance the epoxy equivalent of ligno epoxy resins. Furthermore, the multi-functional amine derivatives of these raw materials have several outstanding applications, including but not limited to: hardeners, activators, crosslinking agents for polyurethane, silicones, and amino resins. Other advantages, for example, are related to their fire retardant characteristics, high thermal stability, and high glass transition temperatures. Thus, the natural and cost efficient sources of

melamine that exist can be exploited that will reduce reliance on petrochemicals and avoid their harmful derivatives.

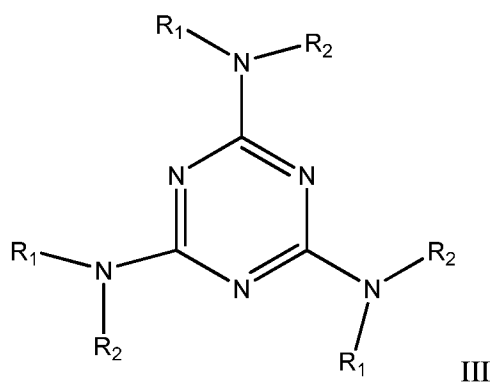
[0031] Melamine can be obtained from any source. It can also be obtained at a relatively reduced cost from urea. Urea, for example, can be industrially produced from synthetic ammonia and CO₂. The ammonia by-products of producing melamine from urea can be recycled for production of urea again if desired.

[0032] Melamine can also, for example, be sourced from, calcium cyanamide. The hydrolysis of calcium cyanamide in the presence of equal moles of CO₂ forms cyanamide, which polymerizes on heating to produce melamine. This process also has an advantage of consuming CO₂.

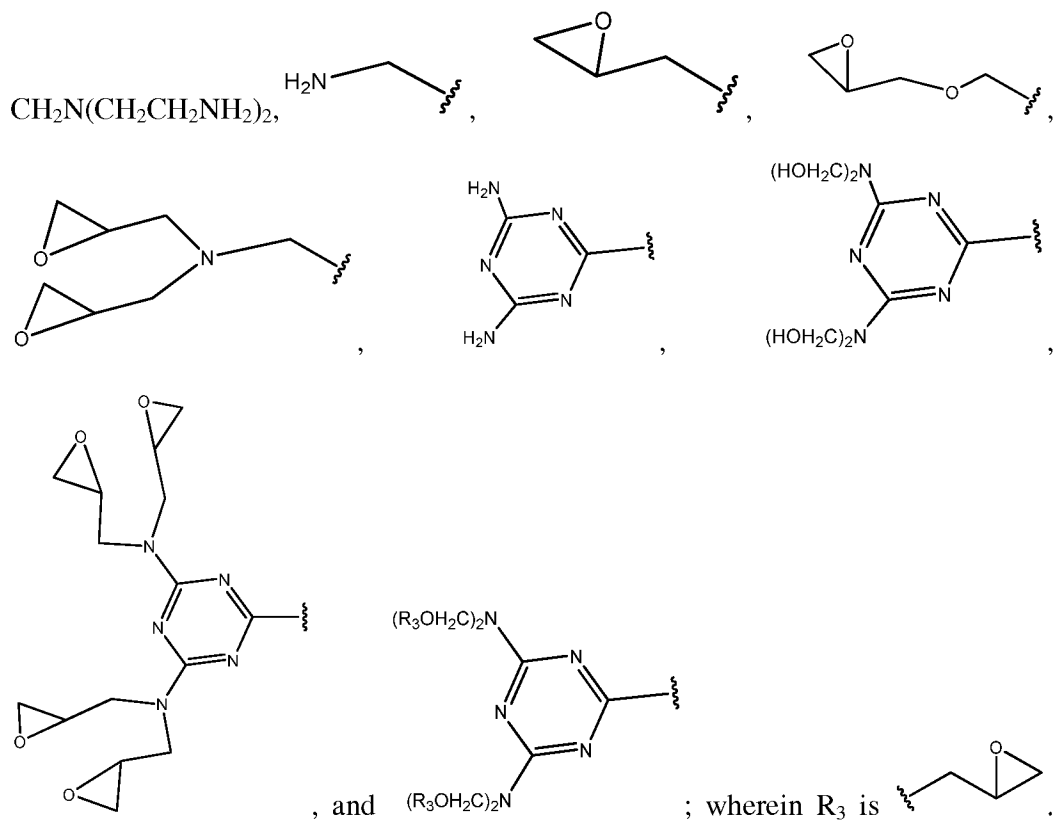
[0033] Melamine combined with formaldehyde has been demonstrated industrially to produce melamine formaldehyde resins, which is a durable thermoset used in various applications. Melamine and melamine polyphosphate are also known and used as excellent fire retardant and smoke suppressant additives in paints, plastics and paper. Melamine formaldehyde sulphonate resin (SMF) resins are known to be efficient concrete super-plasticizers. Hexamethylol melamine and its esters and ethers are also known as “melamine oils” are used also as effective crosslinking agents. The following reactions and schema represent novel and non-obvious opportunities for enhancing the properties of melamine based resins and additives and therefore extending its range of use. The compounds and methods described herein can be converted through uncomplicated and cost effective syntheses into a multifunctional epoxies, amines , glycidyl amines and glycidyl amine ethers. The products are valuable multi-functional epoxy resins and hardeners for, but not limited to, composite materials with carbon fibres and /or as cross linking agents for commercial epoxy ,polyurethanes ,polyesters, and silicones.

[0034] The methods, compounds, and compositions provide the following unexpected and surprising advantages over previous compounds used for similar purposes. For example, the compounds and compositions provides herein include, but are not limited to, epoxy resins with multi-functionality that have more than three epoxy groups per molecules and have improved physical, mechanical, and application properties. Additionally, some of the compounds and compositions can be made without the use of petrochemicals. The multi-functional epoxy resins have a higher degree of crosslinking that can lead to higher glass transition and improved resistant to solvents and corrosive chemicals. The Multi-functional epoxy (MFE) based on melamine are self-extinguishing products with outstanding fire retardant properties due to presence of melamine structures. These products are different from melamine formaldehyde resins. Some of the MFE epoxy amino derivatives or amino hardeners also have improved water miscibility than common aromatic epoxy. Therefore, these resins are suitable for applications in humid environments, wet surfaces, and water based epoxy for construction and water based paints. However, when they are cured with suitable hardeners they are completely water and solvent resistant . Thus, the compounds and compositions described herein have expanded uses as compared to the prior art. The compounds and compositions described herein can also be used as improved cross linking agents and/or fire retardants.

[0035] Accordingly, in some embodiments, compounds having the structure of Formula III

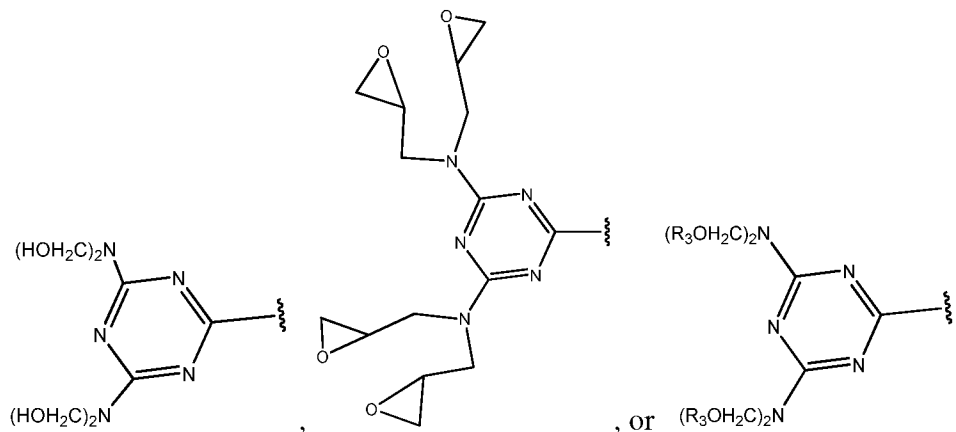
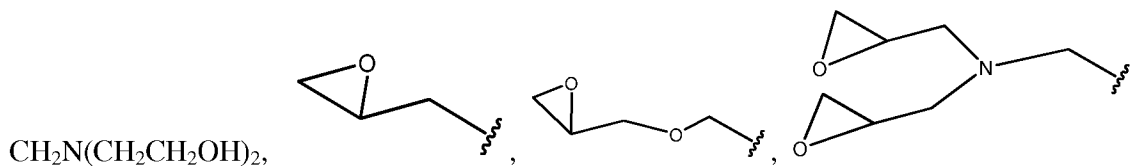


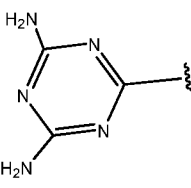
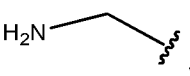
are provided. In some embodiments, R_1 and R_2 are each independently selected from the group consisting of: H, $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OR}_3$, $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$, $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$,



In some embodiments, when R_1 is H, R_2 is not H or $-\text{CH}_2\text{OH}$.

[0036] In some embodiments, when R_1 is $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OR}_3$, -

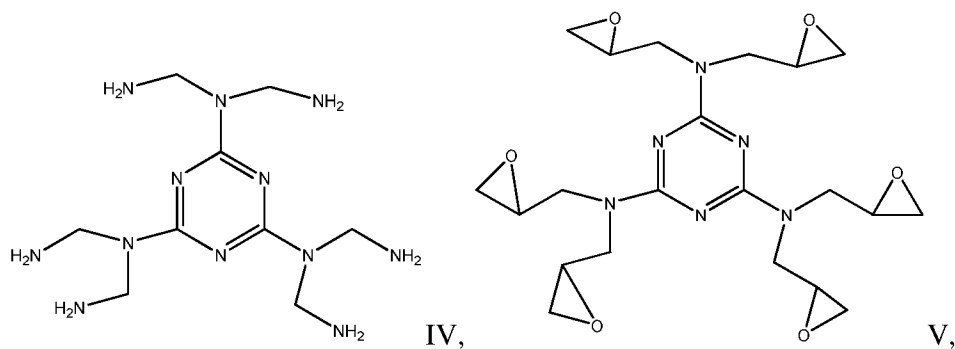


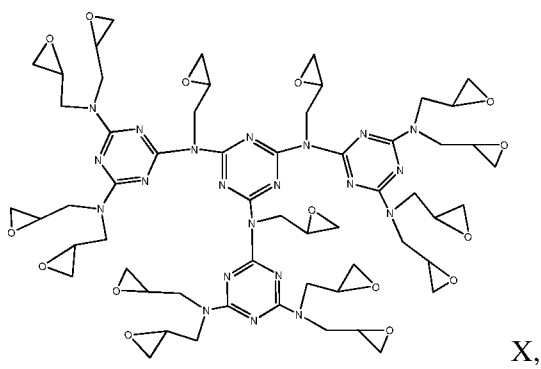
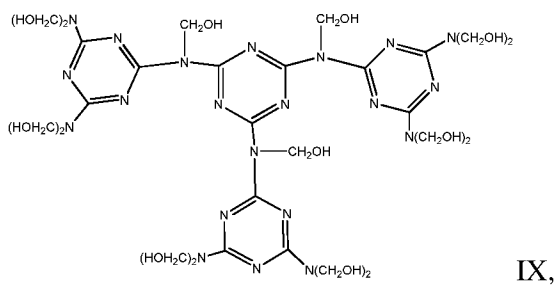
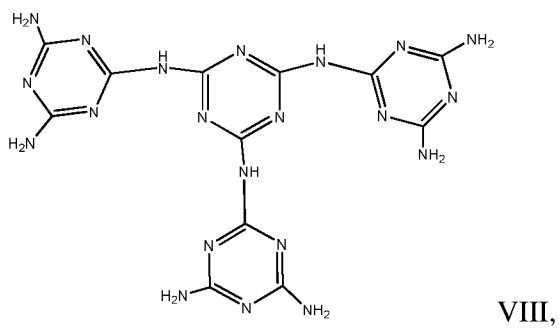
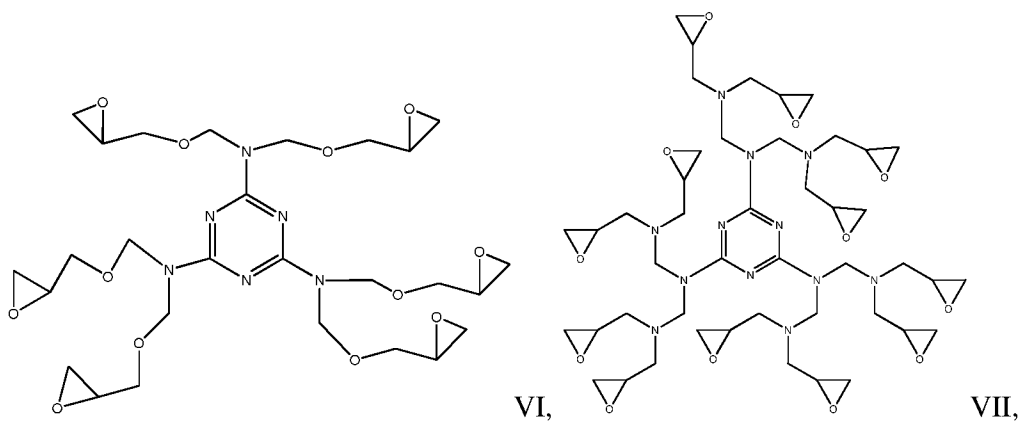
[0037] R_2 is not , $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$, or .

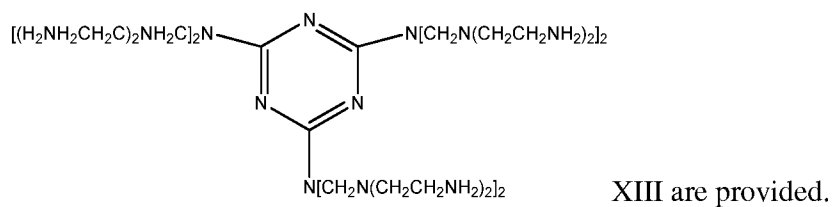
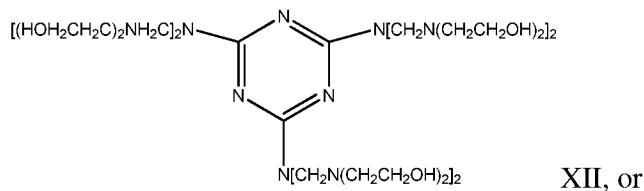
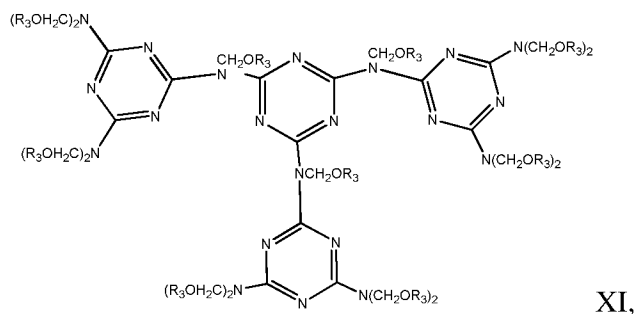
[0038] In some embodiments, when R_1 is H, R_2 is not $-\text{CH}_2\text{OR}_3$.

[0039] In some embodiments, R_1 and R_2 are the same.

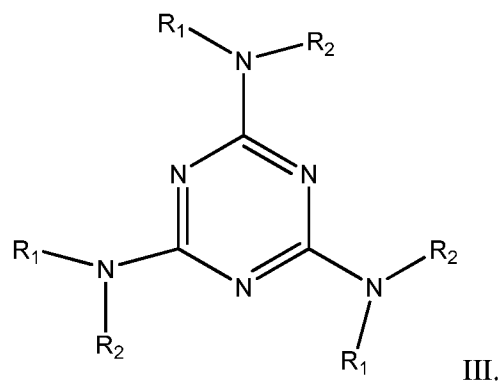
[0040] In some embodiments, compounds having the formula of:



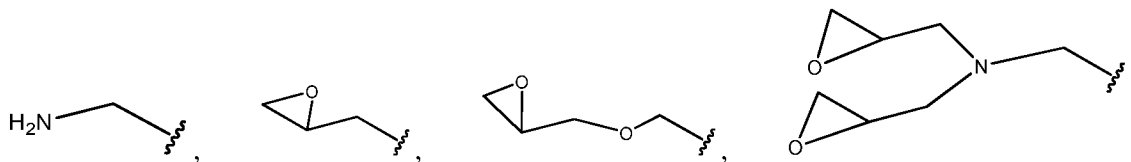


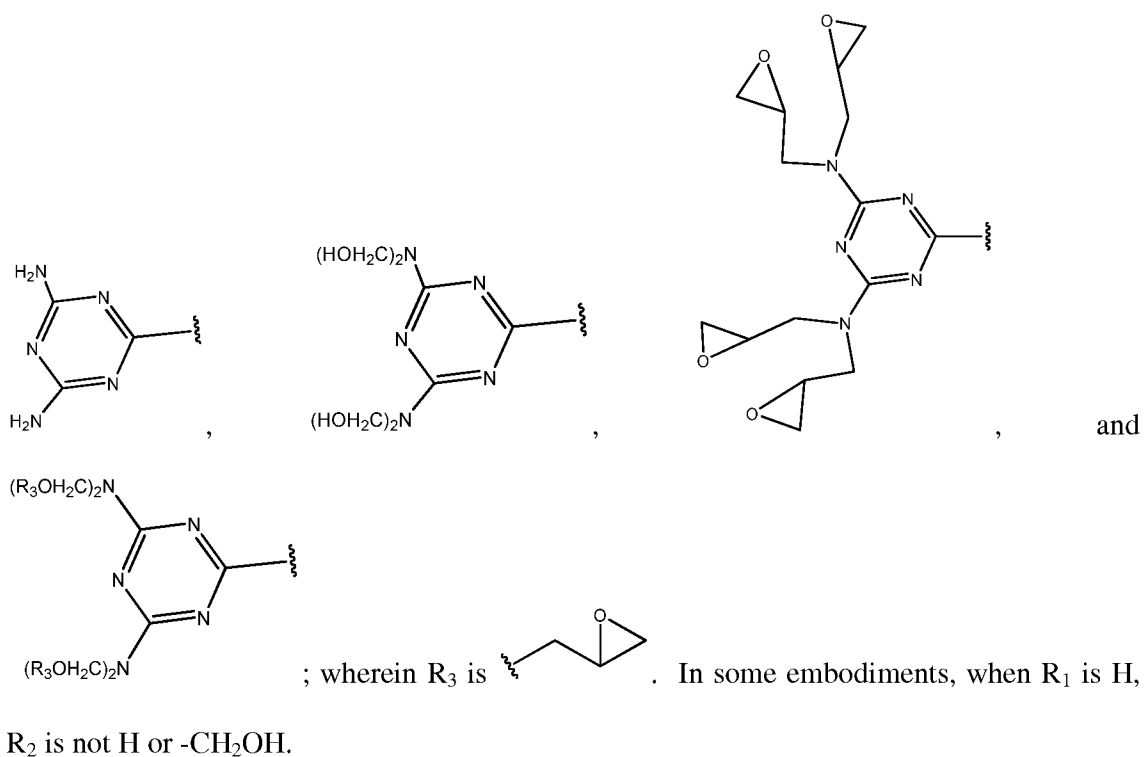


[0041] In some embodiments, a composition comprising one or more of the compounds having the formula of Formula III are provided:

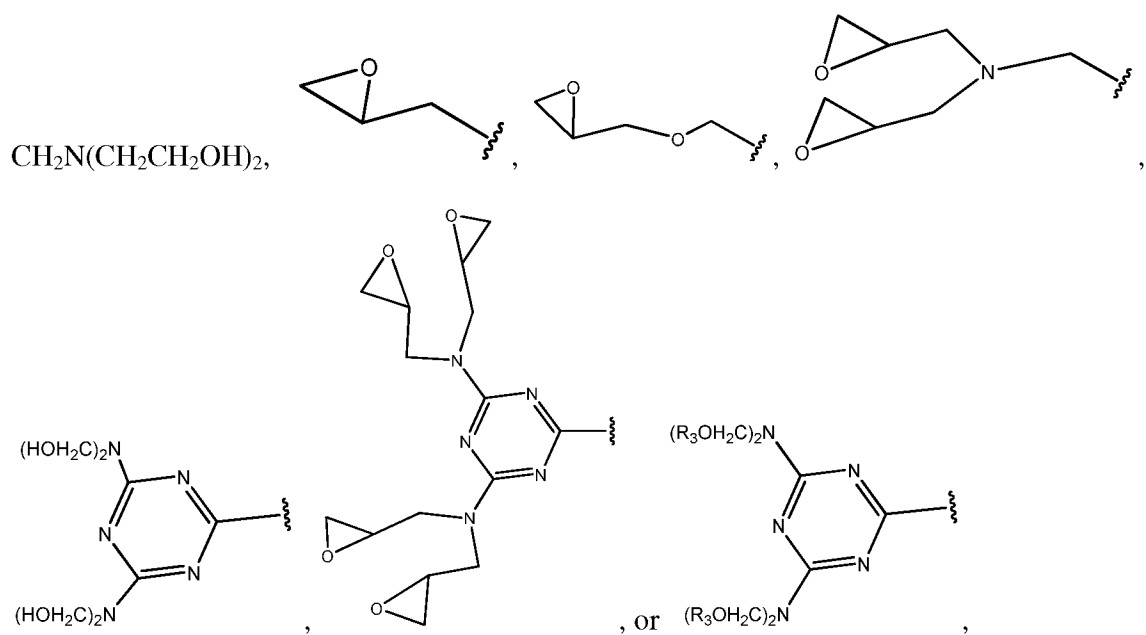


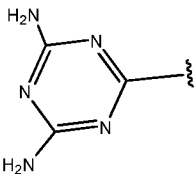
[0042] In some embodiments, R₁ and R₂ are each independently selected from the group consisting of: H, -CH₂OH, -CH₂OR₃, -CH₂N(CH₂CH₂OH)₂, -CH₂N(CH₂CH₂NH₂)₂,

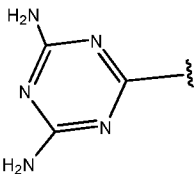
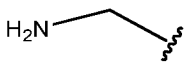




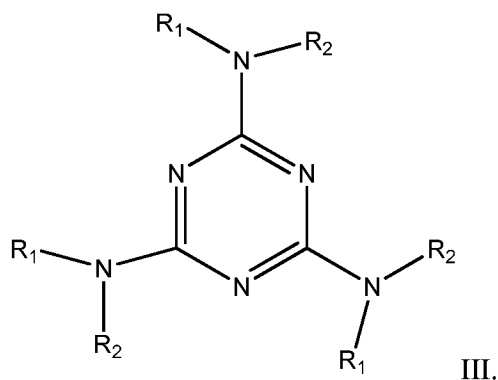
[0043] In some embodiments, when R1 is -CH₂OH, -CH₂OR₃, -



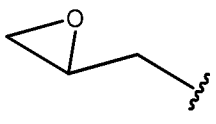
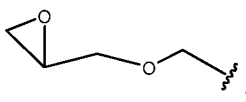


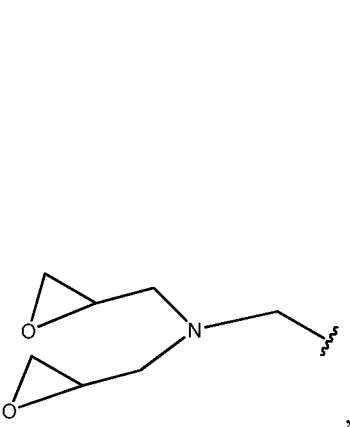
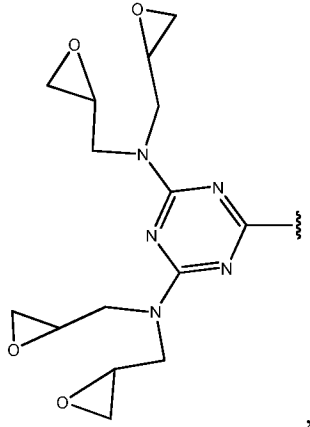
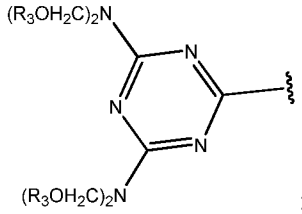
 R_2 is not , $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$, or . In some embodiments, R_2 does not comprise a terminal amino group.

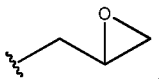
[0044] In some embodiments, an epoxy resin is provided. In some embodiments, the epoxy resin comprises a compound having the structure of Formula III:



[0045] In some embodiments, R_1 and R_2 are each independently selected from the

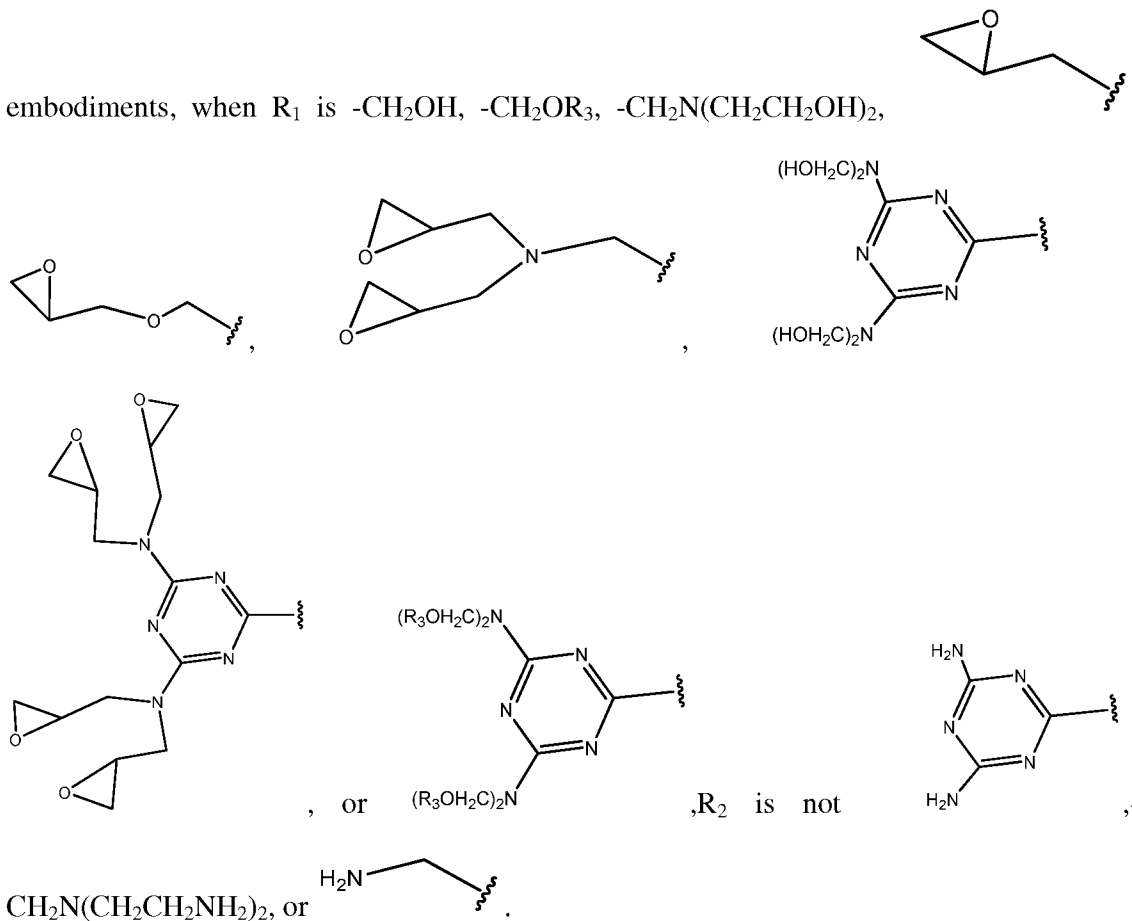
group consisting of epoxy groups , ,

, , and ;

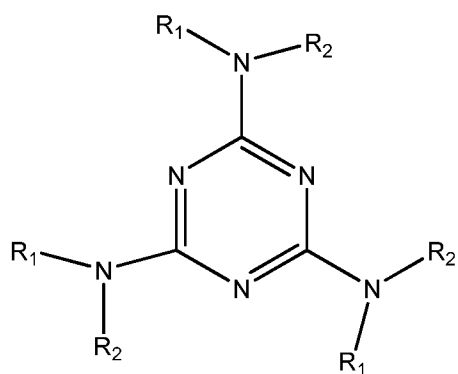
wherein R_3 is .

[0046] In some embodiments, when R₁ is H, R₂ is not H or -CH₂OH. In some

embodiments, when R_1 is $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OR}_3$, $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$,

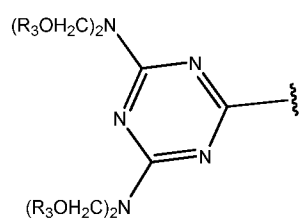
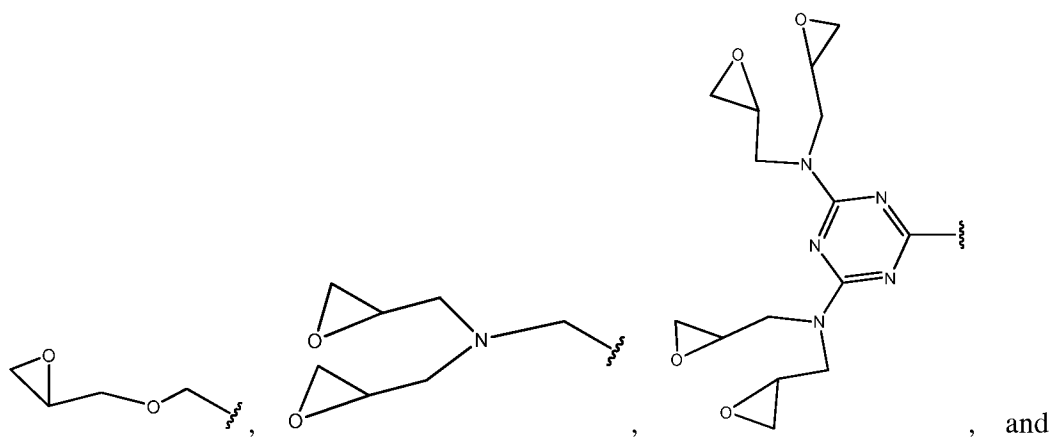
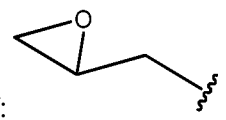


[0047] In some embodiments, carbon fibers or carbon fiber composites are provided. In some embodiments, the fiber or composite comprises a cured epoxy resin, which comprises an epoxy resin and amino hardeners. In some embodiments, the carbon fiber comprises a cured epoxy resin with suitable hardeners. In some embodiments, the epoxy resin is a compound of Formula III



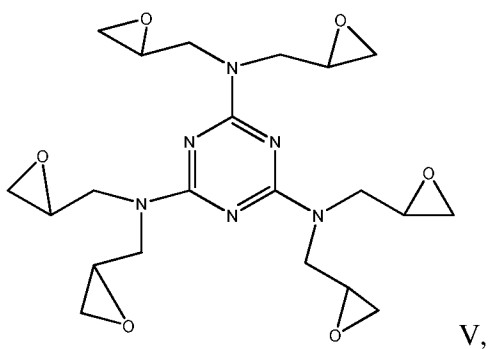
III. In some embodiments, R_1 and R_2 are

independently selected from the group consisting of:

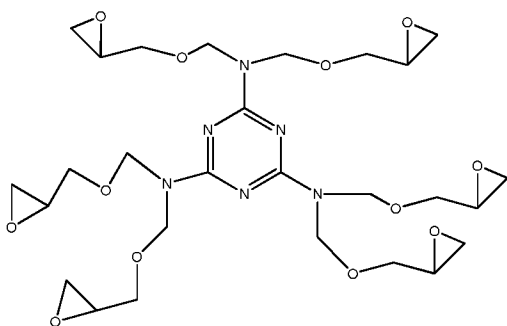


; wherein R_3 is .

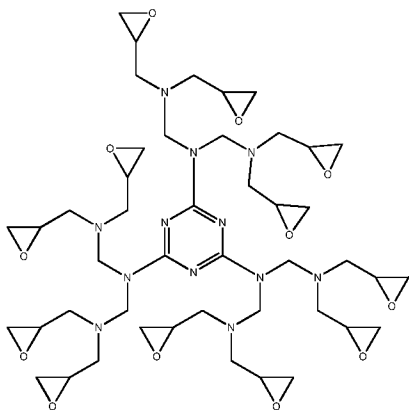
[0048] In some embodiments, the carbon fiber composite has an epoxy resin that has a Formula of



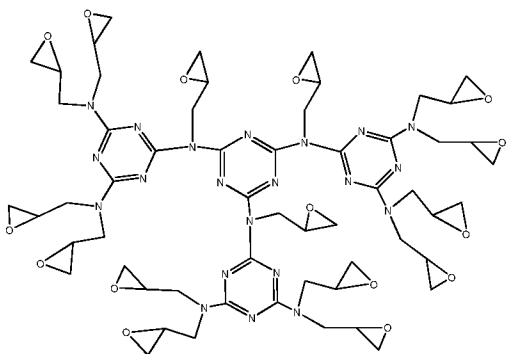
V,



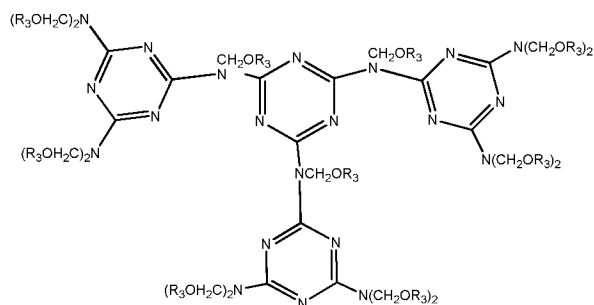
VI,

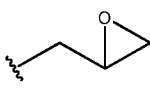


VII,



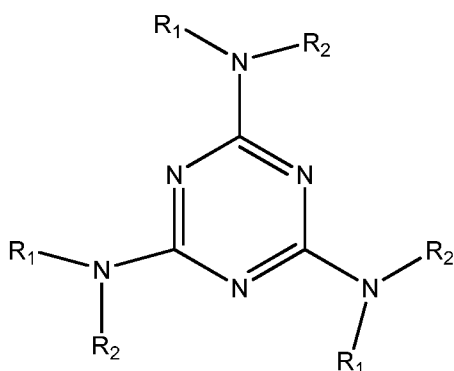
X,



XI, wherein R_3 is .

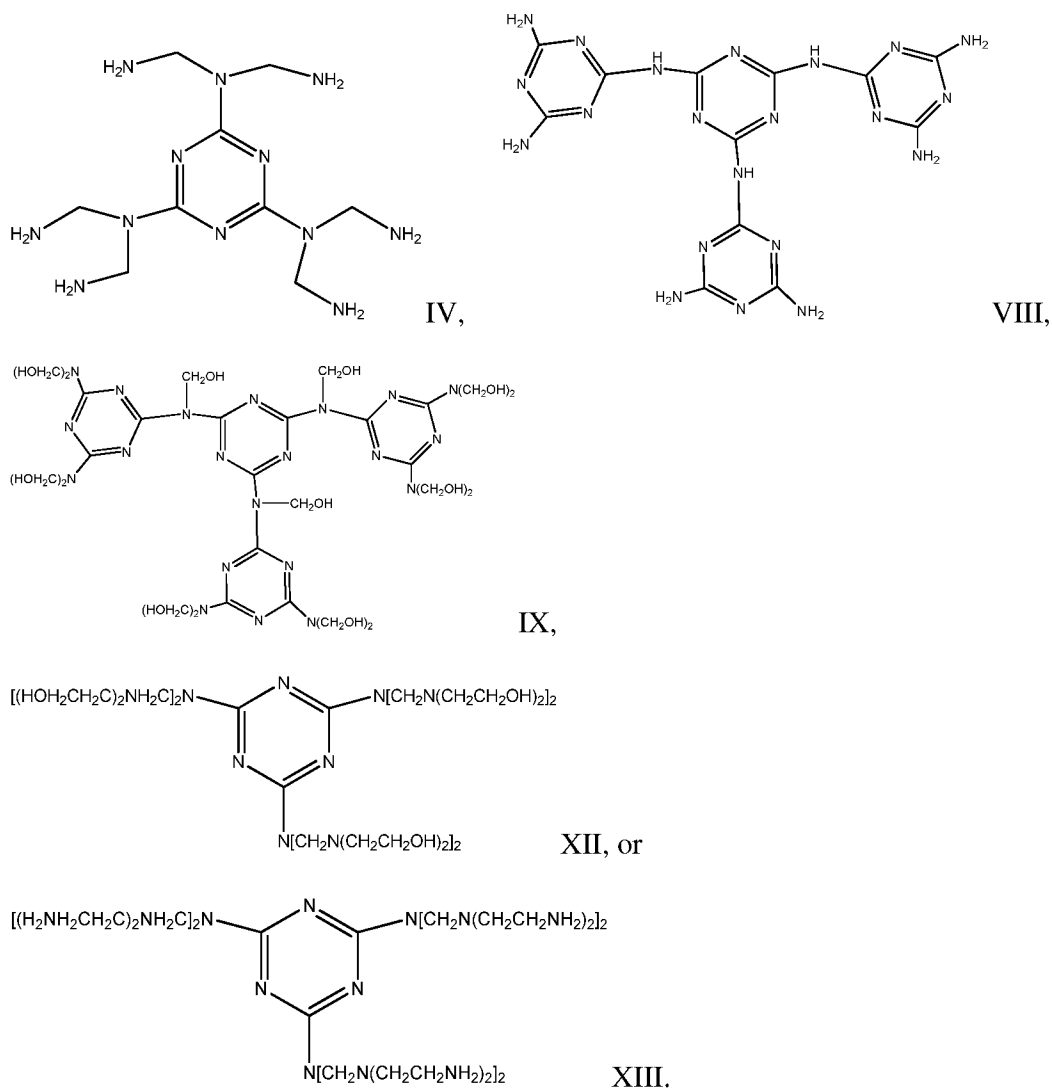
[0049] In some embodiments, the hardener has a compound of Formula III. In some embodiments, the resin comprises any melamine amino derivatives such as, but not limited to, a compound of Formula IV, VIII, or XIII.

[0050] In some embodiments, cross-linked polyurethanes, polyester, or silicone are provided, wherein the polyurethane, polyester, or silicone are cross-linked with a compound of Formula III

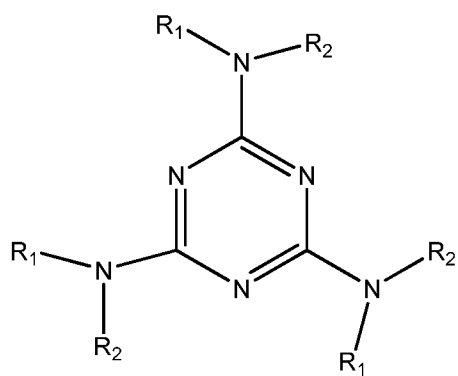


III, wherein R_1 and R_2 are independently

selected from the group consisting of H, CH_2OH , CH_2NH_2 , and melaminy, or are cross-linked with a compound having a formula of

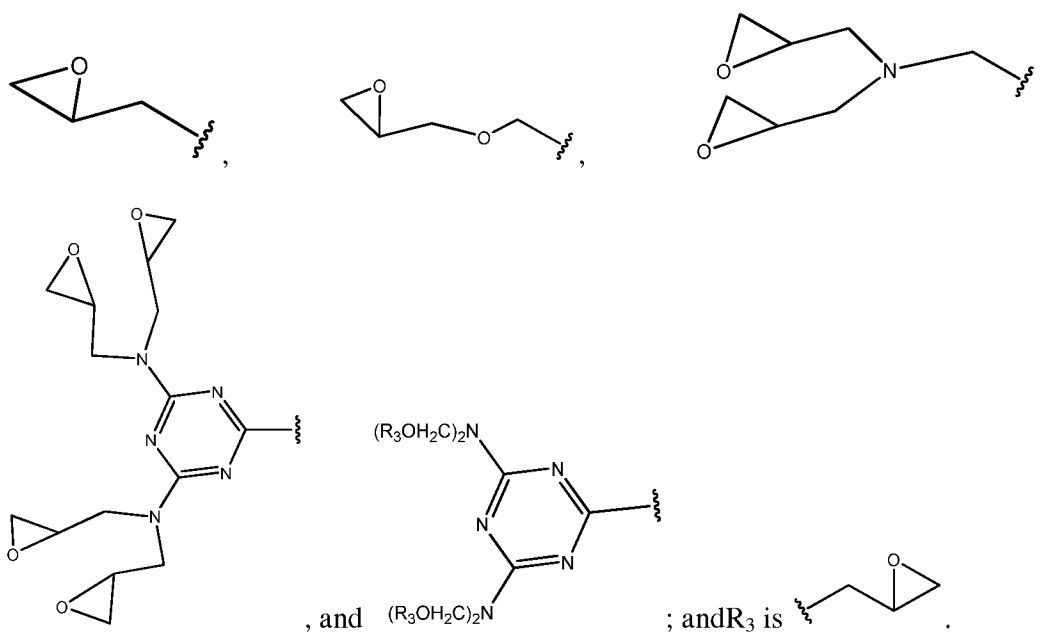


[0051] In some embodiments, a composite comprising one or more of a cured epoxy resins with suitable hardeners, wherein the epoxy resin is a compound of Formula III

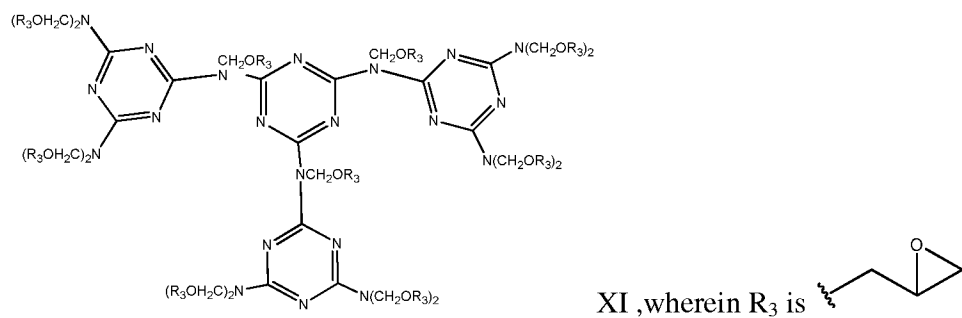
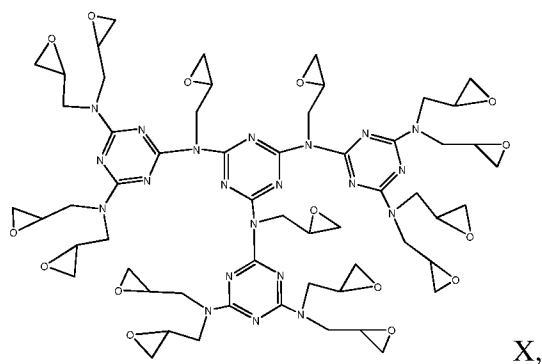
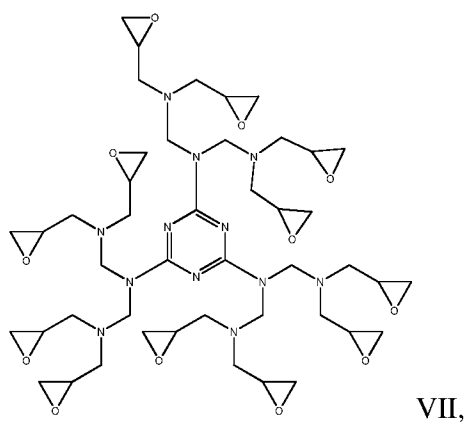
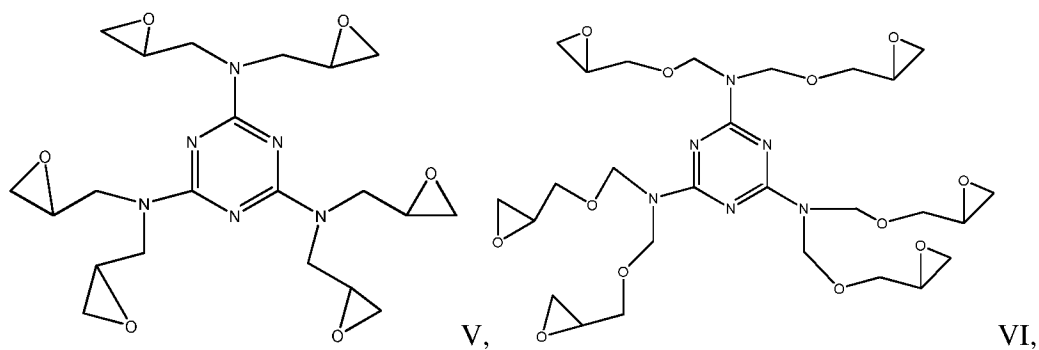


III are provided. In some embodiments, R₁ and

R_2 are independently selected from the group consisting of:

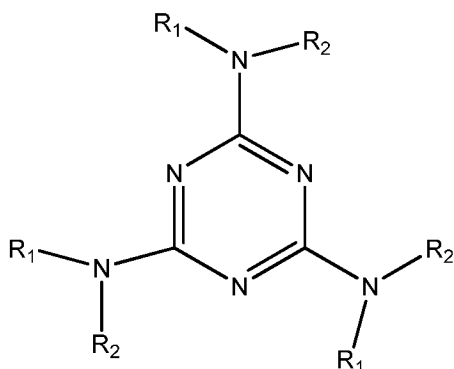


[0052] In some embodiments, the epoxy resin has a Formula of

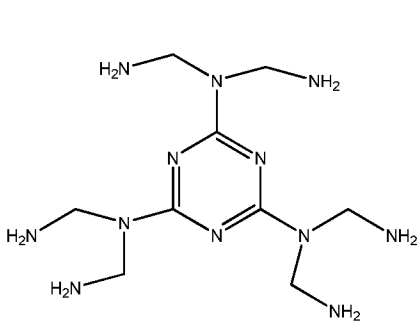


[0053] In some embodiments methods of curing an epoxy resin are provided. In some embodiments, the method comprises contacting the epoxy resin or the polyurethane

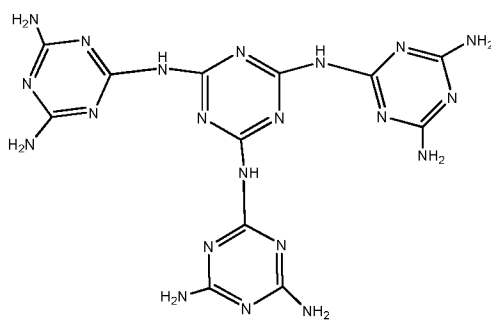
resins terminated with isocyanate groups such as polyester polyol terminated with isocyanate active groups with an amine compound, a compound of Formula III



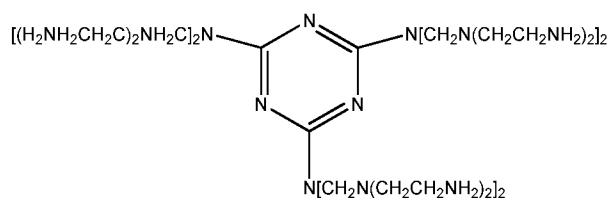
III, wherein R_1 and R_2 are independently selected from the group consisting of H, CH_2OH , CH_2NH_2 , and melaminyl, a compound having a formula of



IV,



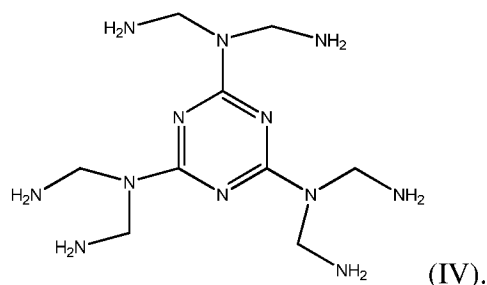
VIII,



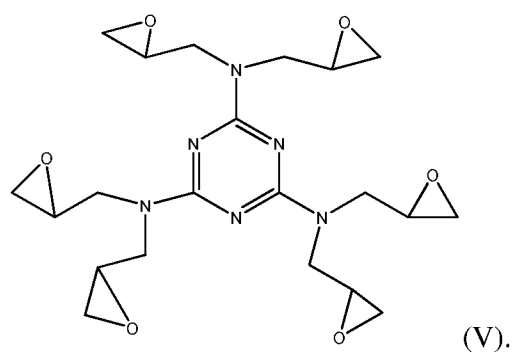
XIII, or with one or more

commercial hardeners under conditions sufficient to cure the epoxy resin.

[0054] In some embodiments, methods of making a compound of Formula III are provided. In some embodiments, the method comprises contacting hexamethylol melamine II with ammonia to produce a compound of Formula IV



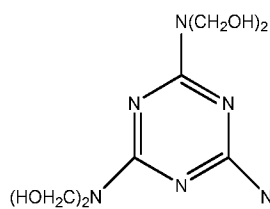
[0055] In some embodiments, methods of making a compound of Formula V are provided. In some embodiments, the methods comprises contacting melamine with epichlorohydrine and a strong base (*e.g.* sodium hydroxide or potassium hydroxide) to produce a compound of Formula V



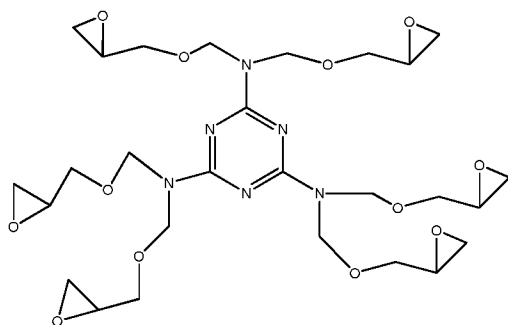
[0056] In some embodiments, the method is performed at a temperature of about 0-80 °C. In some embodiments, the method of making a compound of Formula V is performed at three temperature stages: a temperature of about 0-10 °C for the initial reaction of epichlorohydrine with melamine and its derivatives for the first stage, about 40- 80 °C for the second stage and about 50-65°C for final dehydrochlorination stage. In some embodiments, the method of making a compound of Formula V is performed at a temperature from about 0-80 °C.

[0057] In some embodiments, methods of making a compound of Formula VI are provided. In some embodiments, the methods comprise contacting a compound of Formula

II

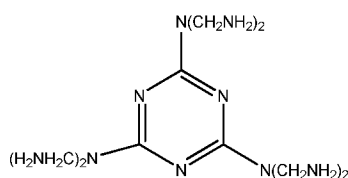


(II) with epichlorohydrine and a strong base (*e.g.* sodium hydroxide potassium hydroxide, and the like) to produce a compound of Formula VI

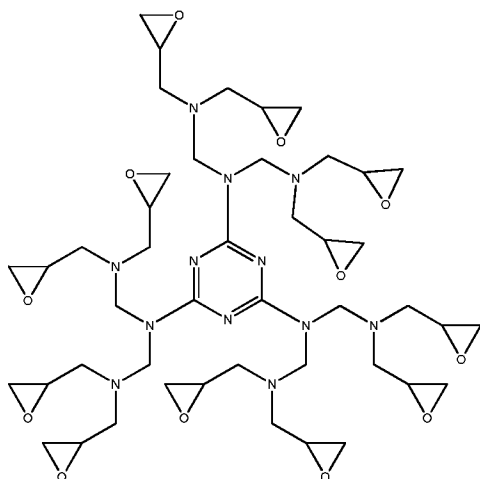


VI. In some embodiments, the method is performed at temperature of about 50-60 °C.

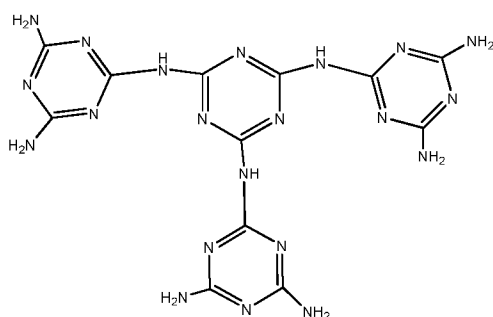
[0058] In some embodiments, methods of making a compound of Formula VII are provided. In some embodiments, the methods comprise contacting a compound of Formula IV



(IV) with epichlorohydrine a strong base (*e.g.* sodium hydroxide potassium hydroxide, and the like) at a temperature of about 0-80 °C, including, for example, at three different temperature stages as described herein, to produce a compound of Formula VII

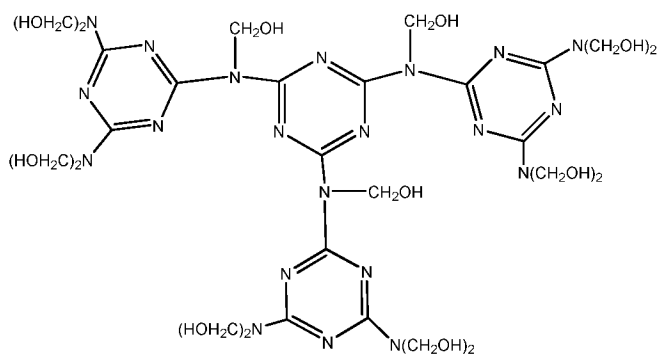


VII. In some embodiments, the method comprises contacting melamine with cyanuryl chloride to produce a compound of Formula VIII.



VIII.

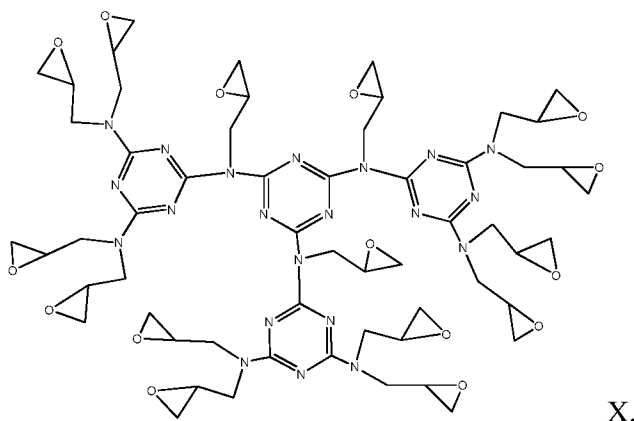
[0059] In some embodiments, methods of making a compound of Formula IX are provided. In some embodiments, the methods comprise contacting a compound of Formula VIII with excess formaldehyde with a strong base (*e.g.* sodium hydroxide potassium hydroxide, and the like) to produce a compound of Formula IX



IX.

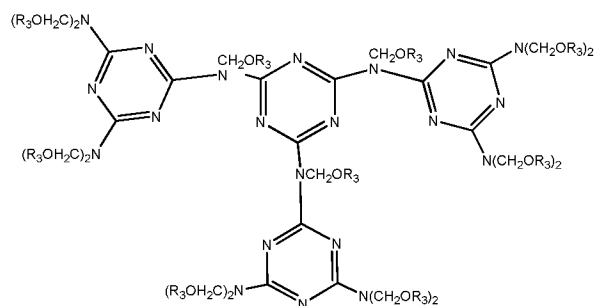
[0060] In some embodiments, methods of making a compound of Formula X are provided. In some embodiments, the methods comprise contacting a compound of Formula

VIII with epichlorohydrine and a strong base, such as, but not limited to, sodium hydroxide or potassium hydroxide at a temperature of about 0-80°C, including, for example, at three different temperature stages as described herein to produce a compound of Formula X



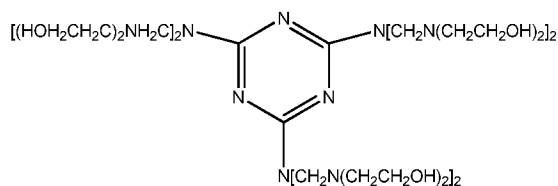
X.

[0061] In some embodiments, methods of making a compound of Formula XI are provided. In some embodiments, the methods comprise contacting a compound of Formula IX with an excess of epichlorohydrine and a strong base (*e.g.* sodium hydroxide potassium hydroxide, and the like) at a temperature of about 50-60 °C to produce a compound of Formula XI



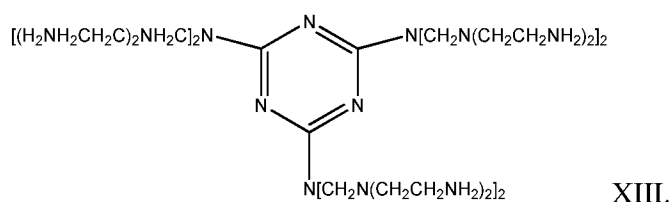
XI, wherein R₃ is 

[0062] In some embodiments, methods of making a compound of Formula XII are provided. In some embodiments, the methods comprise contacting a compound of Formula II with diethanol amine to produce a compound of Formula XII



XII.

[0063] In some embodiments, methods of making a compound of Formula XIII are provided. In some embodiments, the method comprises contacting a compound of Formula XII with ammonia or an aliphatic amine under a pressure of about 1-2 atm to produce a compound of Formula XIII



[0064] In some embodiments, methods of producing glycidyl ether derivatives from a melamine methylol derivative, such as but not limited to Formula XII or glycidylamines from a melamine amino derivatives, such as a compound of formula XIII (as an example of any melamine amino derivatives) are provided. In some embodiments, the methods comprise contacting a compound of, for example, Formula XII or XIII, respectively, with epichlorohydrine and a strong base (*e.g.* sodium hydroxide potassium hydroxide, and the like) at a temperature sufficient to produce a glycidyl ether derivative from compound of Formula XII or glycidylamines from compound of formula XIII.

[0065] A composition comprising further generations of melamine derived epoxy resin, the resin prepared by a method, the method comprising contacting a compound melamine methylols of formula II, IX or Formula XII or other melamine methylols with an ammonia or an amine to produce new melamine amino derivatives which could be either transferred to glycidylamine derivatives similar to V, VII, or X, as an example, by their direct reactions with an epichlorohydrine or to be transferred to new generation of methylol derivatives by their reaction with formaldehyde and a strong base similar to II, IX and XII, as an example. The new generation of methylols could be either transferred to their glycidylether derivatives or transferred to amino groups again to form the next generation of melamine amino derivatives. This can be continued for several sequences mainly for

producing powder solid epoxy for spray powder technology coating with epoxy resins. The limit of the sequence of generations is when the product is insoluble and/or infusible.

EXAMPLES

Example 1: Preparation of Resin II: Hexa methylol melamine.

[0066] Hexamethylolmelamine was prepared and characterized according to (Manley,T.R, Thermalstability of hexamethylolmelamine, Polymer,J.4,(1)111-113,1972) Three necked reaction vessel fitted with reflux, thermometer condenser and mechanical stirrer.The reaction vessel was charged with 126 g melamine (1 mole), and 650 g (8 moles) forlmaline solutionm 37%. 10% sodium carbonate solution was added (pH 8.5-9). The solution was heated to 65-70 °C for 3 hours with continuous efficient mixing after 3 hours the reaction mixture became transparent indicating that all melamine was transfered to its methylolic resins. The product was cooled to room temperature and excess of non reacted formaldehyde was removed. The solid product was used in the preparation of the new melamine derivatives of this invention. A modified procedure was also used by using sodium hydroxide as basic medium for the reaction.

Example 2: preparation of hexa aminomelamine: Resin III where R1,R2 are NH₂ (Compound IV).

[0067] A two liter auto clave system from Analis –Belgium fitted with mechanical stirrer, and controlled temperature and pressure was charged with 306 g hexamethylol melamine prepared in Example 1 and 500ml of methyl alcohol. The system was secured and connected to ammonia gas cylinder. The system was flashed with N₂,mixed for 10 minutes to dissolve the methylol resin. Ammonia gas was fed to the autoclave until the pressure reached 2 atm. The reaction temperature was controlled at 50-60 °C via the cooling jacket of the autoclave. The reaction was continued until no further increase in temperature was observed. The system was cooled to room temperature. The system was

flushed with N₂ gas to remove the unreacted ammonia gas. The white milky syrup product was evaporated and dried under vacuum. The solid product with a decomposition temperature of 387 °C was obtained. The product characterized by CHN analysis and molecular weight determination.

[0068] The obtained degree of amination as found from CHN analysis was 87%. The obtained resin was used in the preparation of glycidyl melamine resins as an epoxy hardener, as a crosslinking agent for polyurethane, as curing agent for: methylol melamine, resol, ,resolack, and as starting material for the second generation of melamine methylol derivatives compounds XII and XIII (Example 10).

Example 3 : Preparation of N-glycidyl melamine resins: Resin III where R₁,R₂ are glycidyl groups Compound (V).

[0069] A reactor consisting flanged top five necked reaction vessel fitted with: a mechanical stirrer, condenser, thermometer, dropping funnel, gas inlet tube, immersed in thermo stated oil bath. The reaction vessel was charged with 63 g melamine (0.5 mole) dissolved in 100 DMF one gram of Mg (ClO₄) dissolved in 5 ml 2-methoxy ethanol was added as catalyst. The system was flashed with nitrogen for 10 minutes and the reaction mixture was cooled to 10 °C. 350 ml of epichlorohydrine was added to the reaction mixture portion wise over one hour with continuous mixing for another 60 min then the temperature was increased gradually up to 60°C and the reaction was continued for an additional three hours with the temperature controlled between 60-80 °C. The reaction mixture was cooled to 65 °C. 12 g of tetra butyl ammonium chloride dissolved in 25 ml water was added with mixing followed by the addition of 250 ml of 50% sodium hydroxide solution, which was added portion wise with continuous efficient mixing over two hours. The mixture was heated to 70 °C for two hours. The reaction mixture was cooled to room temperature then the formed resin was separated by addition of 100-200 ml of water with mixing to ensure that all the

epoxy product is separated from DMF. The epoxy layer was separated, dissolved in toluene, filtered from any salt residue and washed with 40% solution of sodium chloride in water containing 1% acetic acid, dried with molecular sieves, evaporated under vacuum and dried under vacuum at 0.1mm Hg at 40 °C for 6 hours. A dark colored viscous resin was obtained. The epoxy equivalent of the resin was determined and found to be 5.34 equivalent/kg, viscosity at 40 °C was 91.4 Pa s, and active chlorine content (0.3%).

Example 4 : Effect of metal salt catalysts.

[0070] The procedure of Example 1 was repeated in the absence of catalyst and in the presence of LiCl, LiOH, and LiClO₄ catalysts. No appreciable changes were found in the yield of epoxy equivalent and viscosity by changing the catalyst. The absence of catalysts reduces the epoxy equivalent to 4.5 equivalent /kg and increases the viscosity of 110 Pa s.

Example :5 : Effect of phase transfer co catalyst.

[0071] Example 1 was repeated in the presence of several phase transfer catalysts, e.g. benzyltrimethylammonium bromide, cetyltrimethylammonium bromide, tetrabutylammonium hydroxide. No appreciable changes were found in the yield, epoxy equivalent and viscosity. The absence of phase transfer catalyst reduces the epoxy equivalent of the resin to 4.1 equivalent/kg and increases the viscosity to 95 Pa s.

Example-6: Effect of temperature.

[0072] Several reaction schemes were implemented at various temperatures from zero to 100 °C. It was found that the initial stage of addition of epichlorohydrine to melamine solutions in the presence of catalysts was highly exothermic when the reaction was fulfilled at temperatures above 50 °C which lead to formation of water soluble polymelamine epichlorohydrine polycondensate. The three stage temperature control presented in Example 1

was found to give the highest epoxy equivalent, lowest viscosity and lowest active chlorine content (0.3%).

Example 7: Preparation of hexamethylolmelamineglycidyl ether (compound VI).

[0073] The reaction set up used in Example 3 was used. The reaction vessel was charged with 153 g (0.5 mole) hexamethylol melamine prepared in Example 1 and 250ml of n-butanol. The mixture was neutralized with benzene sulphonic acid to pH-7-7.5. The system was flashed with N₂ for 10 minutes. 0.75 g Lanthanumtrifluoro- methanesulphonate was added as lewis acid catalyst and 5 g of tetra methylammonium chloride as a 50 % solution in water. The system was heated to 50 °C. 323.8 g (3.5 mole) of epichlorohydrine was added within 2 hours and then the mixture was heated to 75 °C for one hour. The mixture was cooled to 60 °C and then 280 g (3.5 mole) of 50% sodium hydroxide solution was added portionwise within one hour with continuous azeotropic removal of water from the system and with continuous mixing for further one hour at 60 C. The reaction mixture was cooled to room temperature. The solid residue was found to be crosslinked melamine resin and salt. Butanol was evaporated under vacuum. Highly viscous resin was obtained (epoxy equivalent 5.56 mol/kg, chlorine content was 1.9%, yield based on melaminehexamethylol resin was 72%).

Example 8: Preparation of the second generation of glycidyl melamine amino resins (Compound VII).

[0074] The same procedure used in example 3 is implemented but replacing melamine by hexaaminomelamine (resin IV) doubling the molar ratio of epichlorohydrine, catalyst, co-catalyst, and sodium hydroxide. The catalyst and co-catalyst are the same as were used in Example 7. The expected reaction product is solid epoxy resin with much higher epoxy equivalent than resin (V).

Example -9:Preparation of the N- glycidyl melamine cyanurate(Compound X).

[0075] The same procedure used in example 3 is implemented but replacing melamine by melamine cyanurate(resin VIII) using the molar ratio of epichlorohydrine, catalyst , co catalyst, and sodium hydroxide equivalent to the number of the amino groups present in resin VIII. The catalyst and co-catalyst are the same as were used in Example 7. The expected reaction product is solid epoxy resin with much higher epoxy equivalent than resin (V).

Example 10. Preparation of melamine cyanuratemethylol resin : (Compound IX).

[0076] The set up and procedure of Example 1 is used in the preparation of resin IX by using molar ratio of formaldehyde/amino as 2.2:1 using the same catalysts and reaction conditions.The expected melamine cyanurate methylol resin is waxy solid product.

Example 11 :Preparation of melamine cyanurateglycidyl ether : (Compound XI)

[0077] (Proffitic)The set up and chemicals used in Example 7 for preparation of melamine derivative glycidylether (compound VI) are used in the preparation of the melamine cyanurate glycidylether (compound XI) by replacing resin II by resin IX implementing the same procedure at the same reaction conditions and using the same molar ratio of epichlorohydrin:methylol:NaOH taking into consideration the number of methylol groups in compound IX.The product epoxy resin is solid with higher epoxy equivalent.

Example 12: Curing of glycidyl melamine resin.

[0078] A) 10 g of glycidylmelamine (IV) was cured with 3.5 grams of melamine mixed and cured at 80 °C for 16 hours. The resin was found cure to solid tough product with a glass transition temperature of 172 °C as measured by DSC. The sample at room temperature did not cure completely but the viscosity increased remarkably, which is an indication for partial curing at ambient temperature. B)10 g of glycidylmelamine (IV) was

cured with 2.5g of hexa amino melamine (III).The sample underwent curing at room temperature and at 60 °C. The post cured sample had a glass transition temperature of 187°C.C)10 g of glycidylmelamine(IV) was cured with 2.5g of amino melamine (VII).The sample underwent curing at room temperature and at 60 °C. The post cured sample had a glass transition temperature of 174°C.D)10 g of glycidyl melamine (IV) was cured with 3.5g of Huntsman commercial curing agent 1203, the resin cured to solid product at room temperature. The post cured sample had a glass transition temperature of 175 °C.

Example 13: Curing of melamine glycidylether (VI).

[0079] 10 g of melaminehexamethylolglycidyl ether (VI) was cured with equivalent ratios of the amino resins tested in Example 12. Compounds I, III, VII and Huntsman 1203 is a standard commercial hardener, which have hardener equivalent weights of 114 g/equivalent. The sample underwent curing at room temperature and at 60 °C with all curing agents except with compound I. The glass transition for the post cured sample Compound VI in the presence of compounds I, III, VII or Huntsman 1203 of was 168, 175, 177 and 168°C, respectively as measured by DSC at 10 degrees/minute.

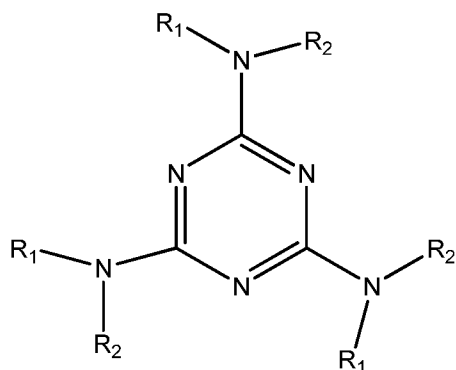
Example 14: Crosslinking and catalytic efficiency of melamine amino derivatives and melamine methylol resins.

[0080] **A)** Commercial polyether polyol terminated with isocyanate (10 g) liquid component was mixed with one gram of melamine amino resins IV. A solid polyurethane foam was formed instantly. The density of the foamed product, which is very important in polyurethane technology, can be controlled by the ratio of the aminocrosslinking agent added. **B)** Commercial polyether polyol terminated with isocyanate (10 g) liquid component was mixed with one gram of melamine methylol resins II. A flexible polyurethane foam was formed instantly.

CLAIMS

What is claimed is:

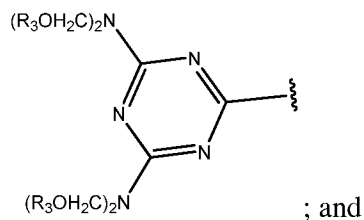
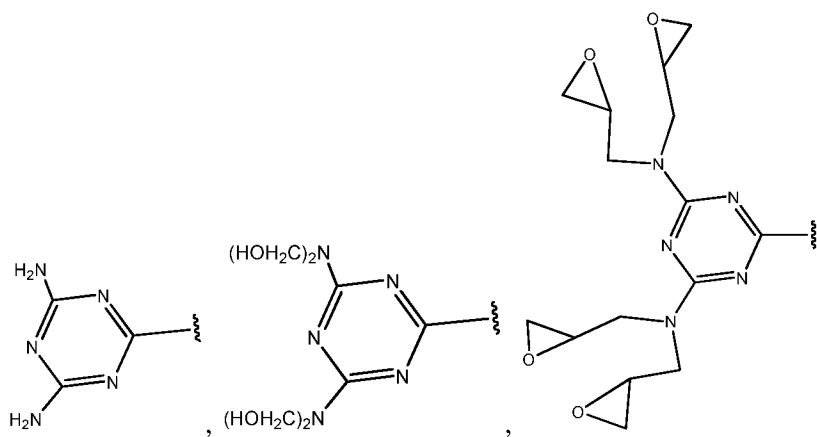
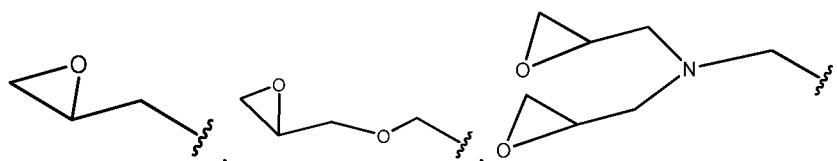
1. A compound having the structure of Formula III:



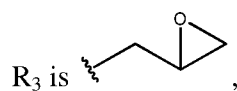
III,

wherein R₁ and R₂ are each independently selected from the group consisting of:

H, -CH₂OH, -CH₂OR₃, -CH₂N(CH₂CH₂OH)₂, -CH₂N(CH₂CH₂NH₂)₂, ,

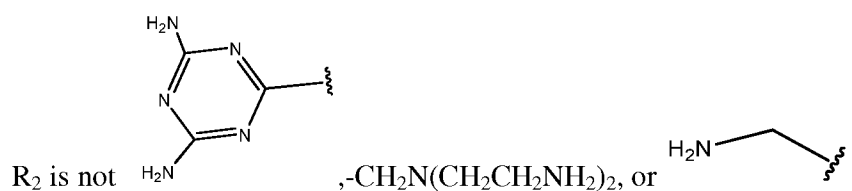
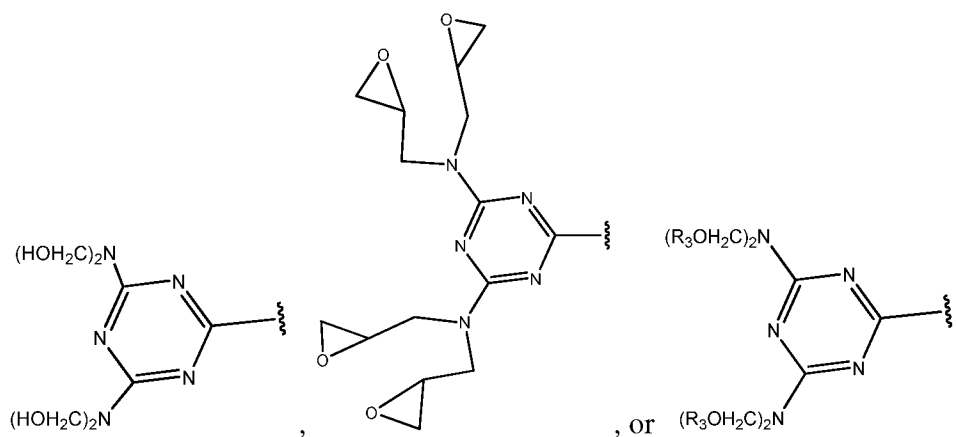
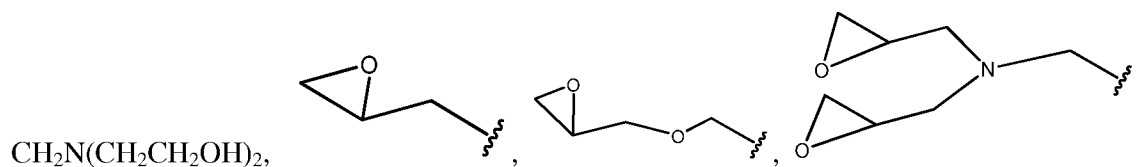


; and

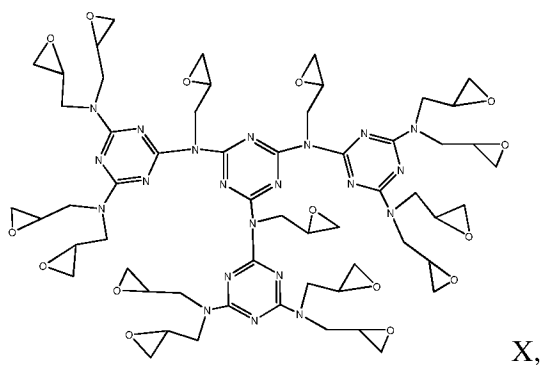
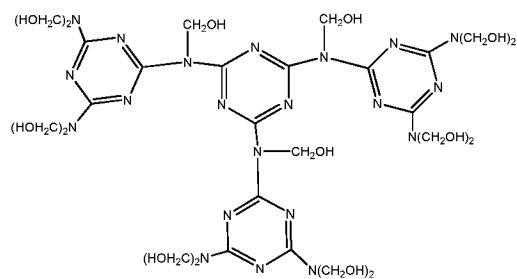
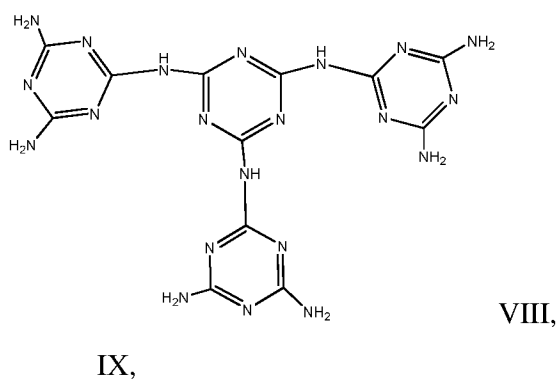
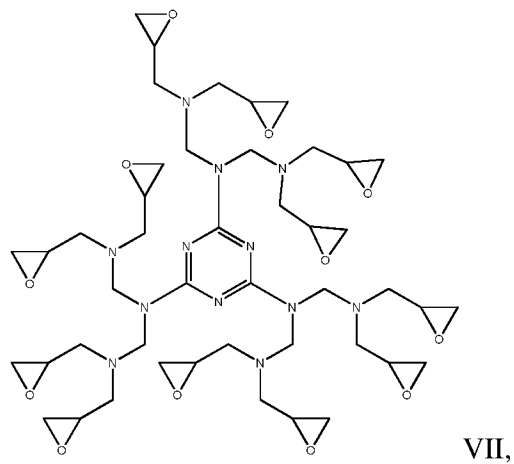
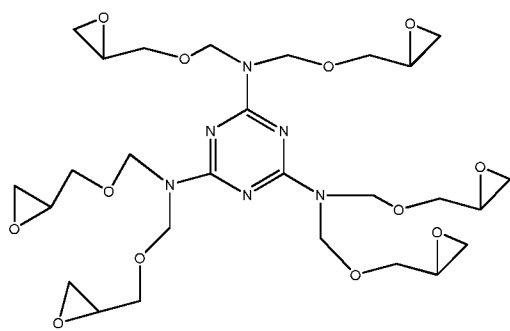
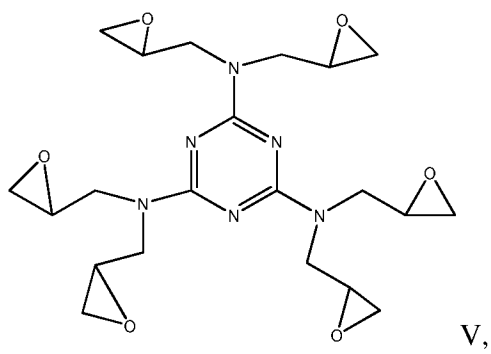
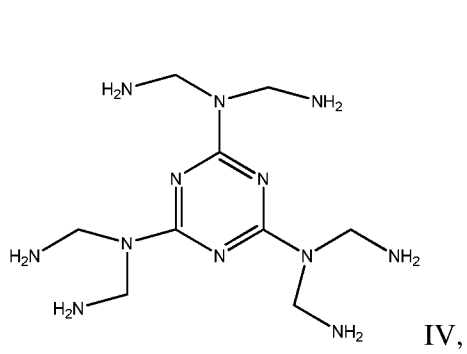


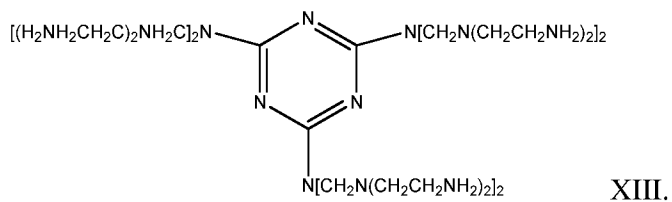
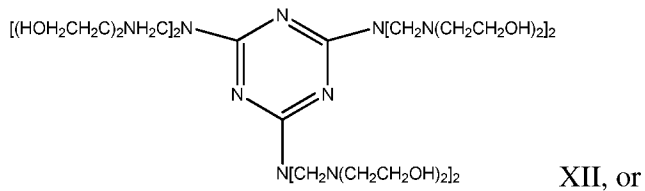
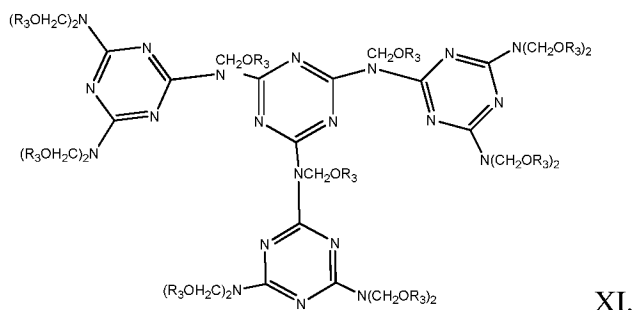
provided that when R_1 is H, R_2 is not H or $-\text{CH}_2\text{OH}$.

2. The compound of claim 1, provided that when R_1 is $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OR}_3$, -

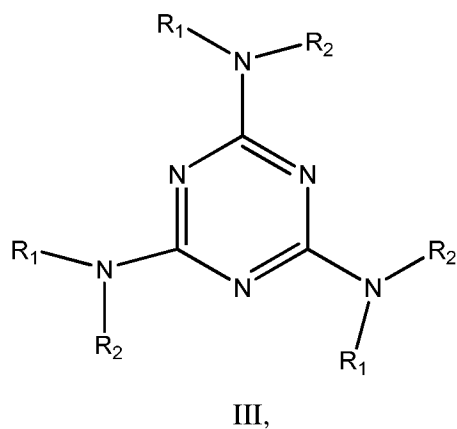


3. The compound of claim 1, provided that when R_1 is H, R_2 is not $-\text{CH}_2\text{OR}_3$.
4. The compound of claim 1, wherein R_1 and R_2 are the same.
5. The compound of claim 1, wherein the compound has the formula of:

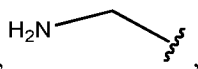


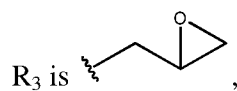
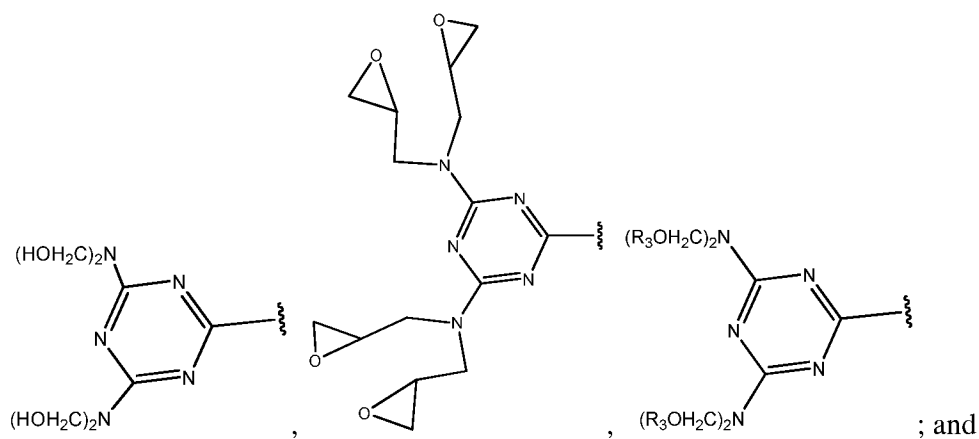
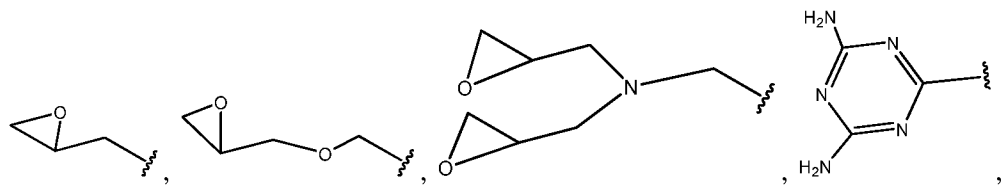


6. A composition comprising one or more of the compounds having the formula of Formula III:



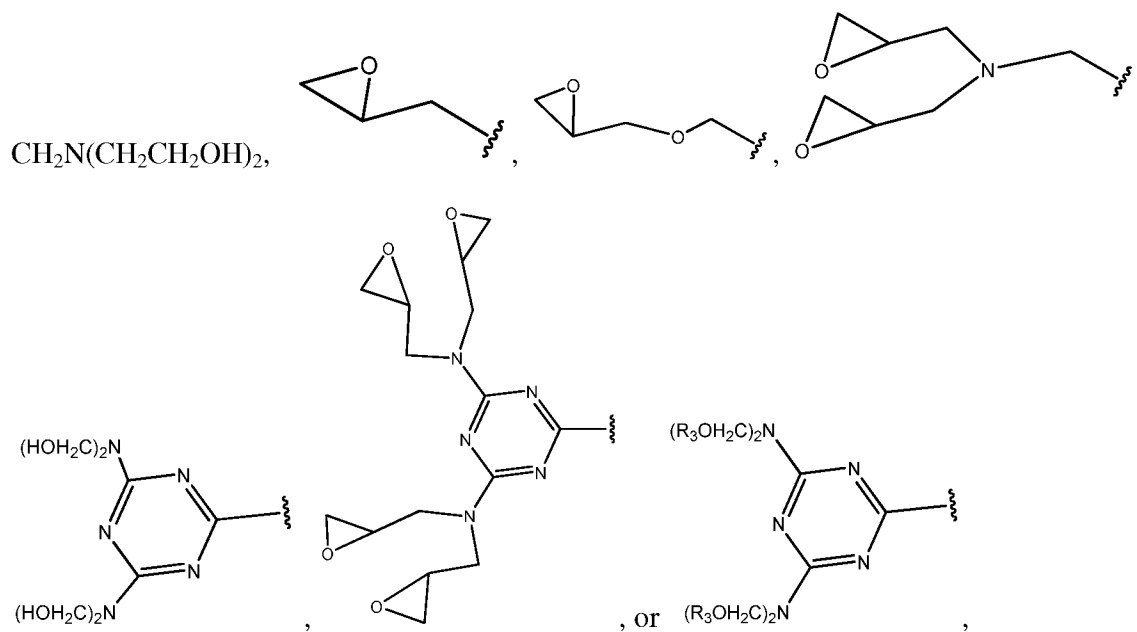
wherein R_1 and R_2 are each independently selected from the group consisting of:

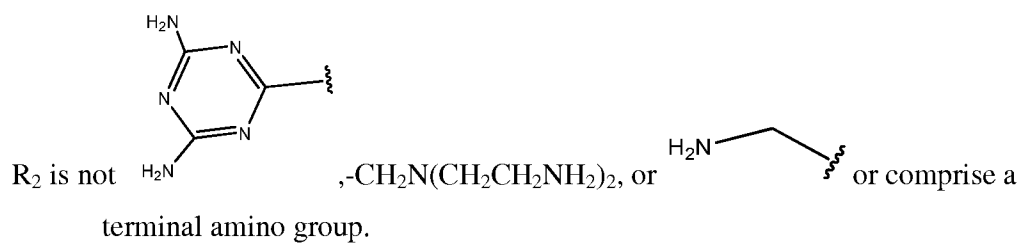
H, $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OR}_3$, $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$, $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$, ,



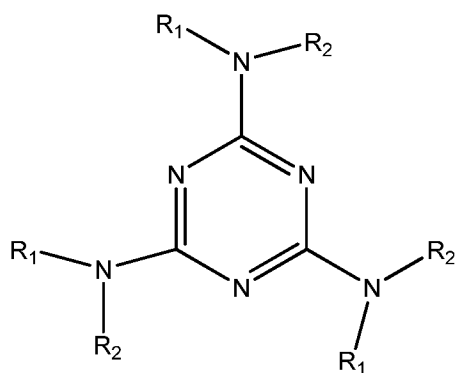
provided that when R_1 is H, R_2 is not H or $-\text{CH}_2\text{OH}$.

7. The composition of claim 6, provided that when R_1 is $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OR}_3$, $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$,



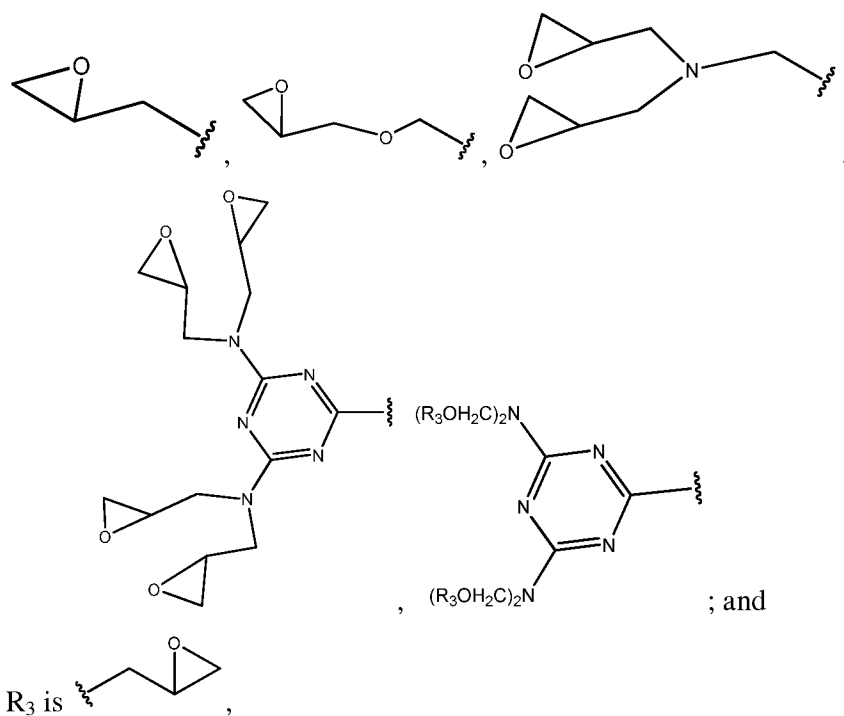


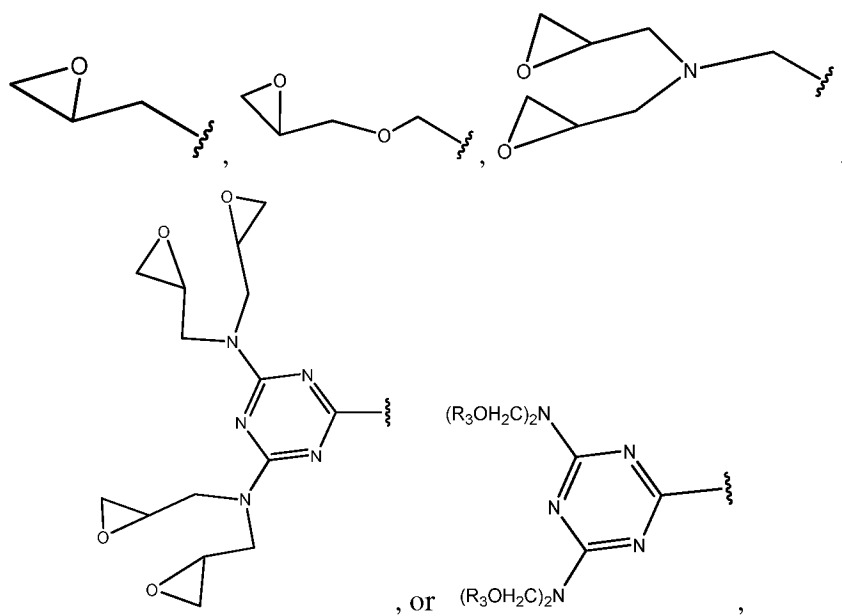
8. An epoxy resin comprising a compound having the structure of Formula III:



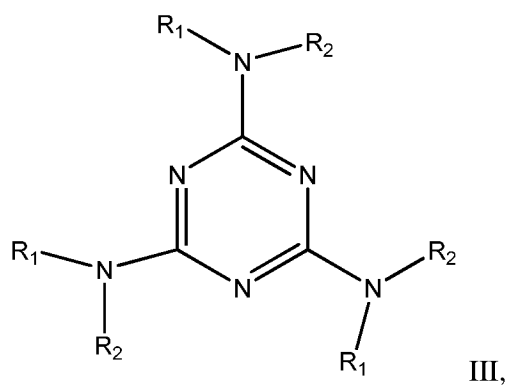
III,

wherein R_1 and R_2 are each independently selected from the group consisting epoxy groups of:

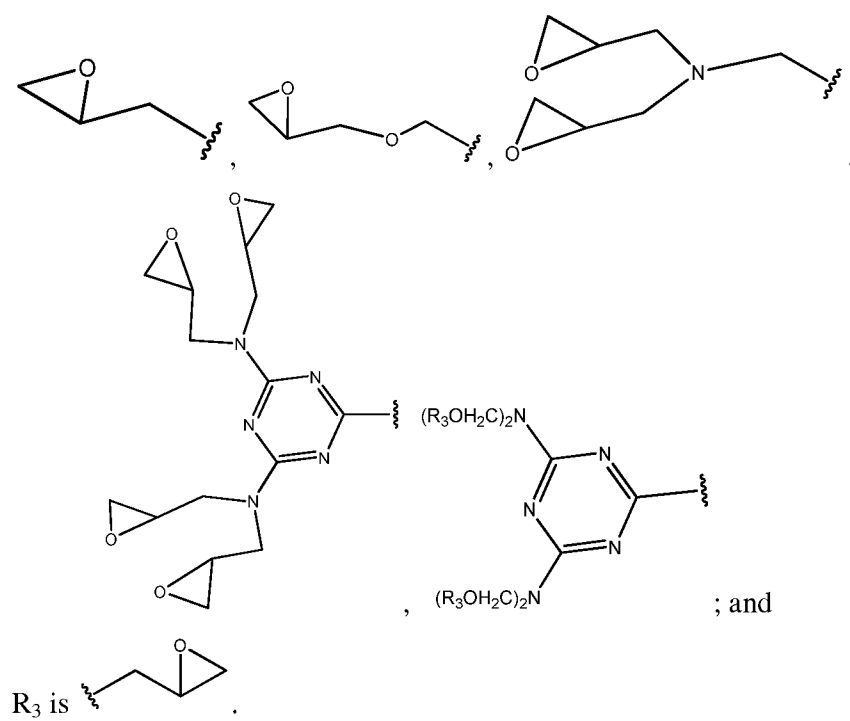




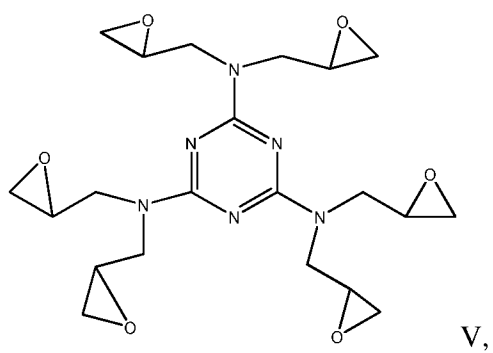
9. A carbon fiber composite comprising a cured epoxy resin of an epoxy resin and amino hardeners, wherein the epoxy resin is a compound of Formula III

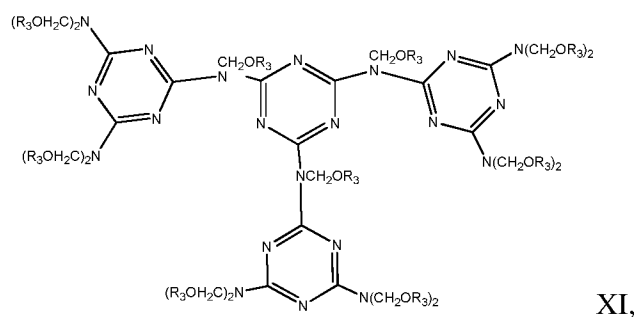
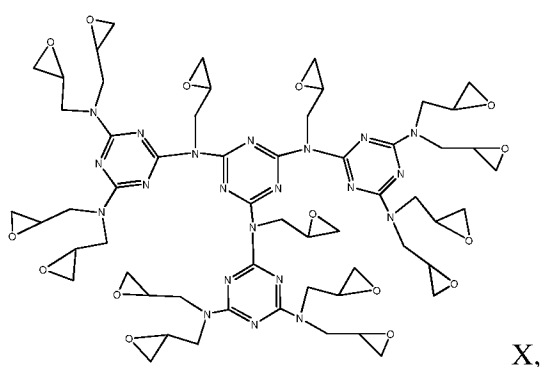
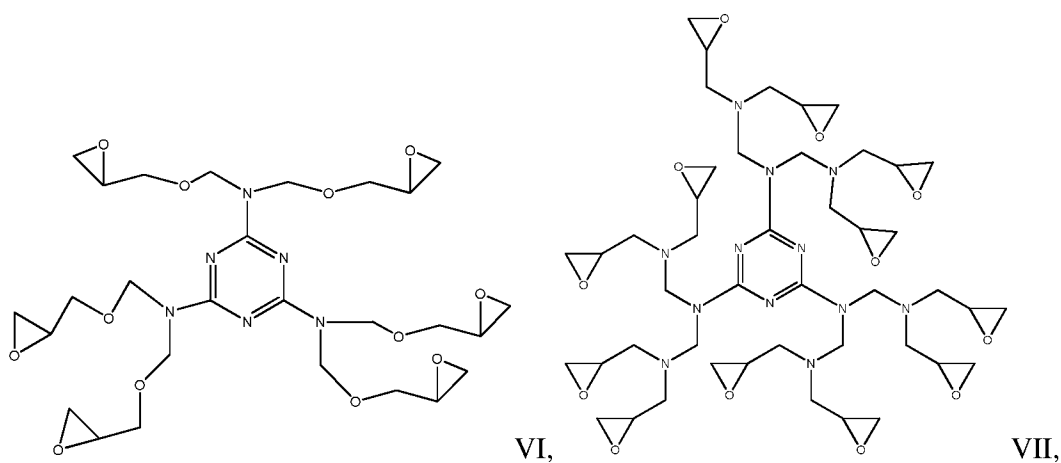


wherein R_1 and R_2 are independently selected from the group consisting of:



10. The carbon fiber composite of claim 9, wherein the epoxy resin has a Formula of

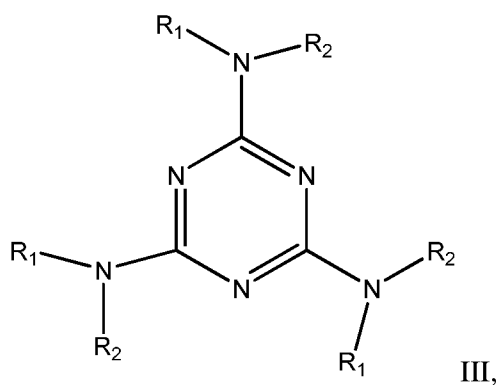




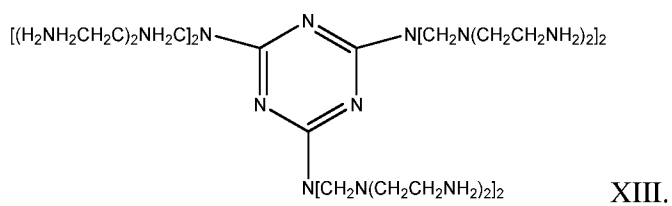
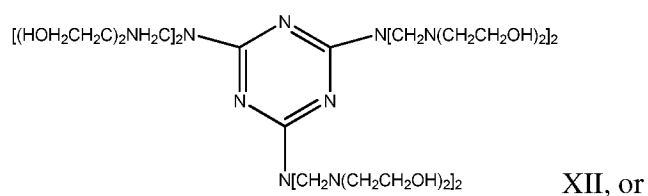
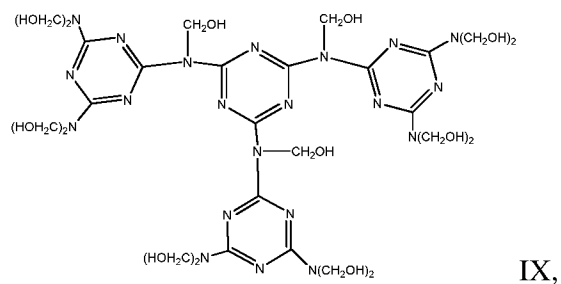
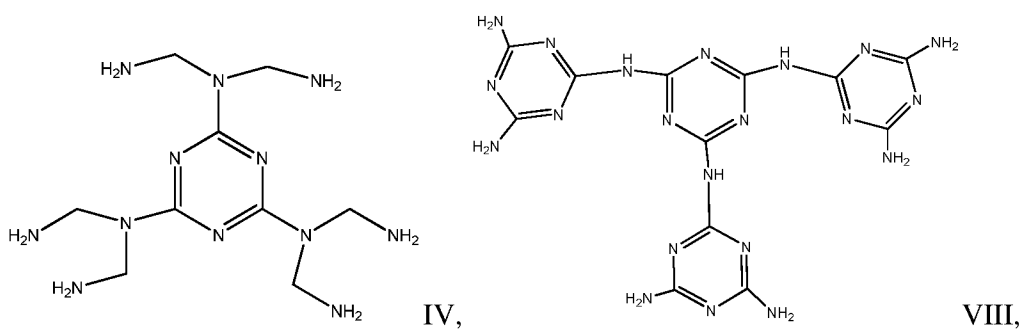
wherein R_3 is .

11. The carbon fiber composite of claim 9, wherein the amine hardener has a Formula of III, wherein R_1 and R_2 are any melamine amino derivatives.

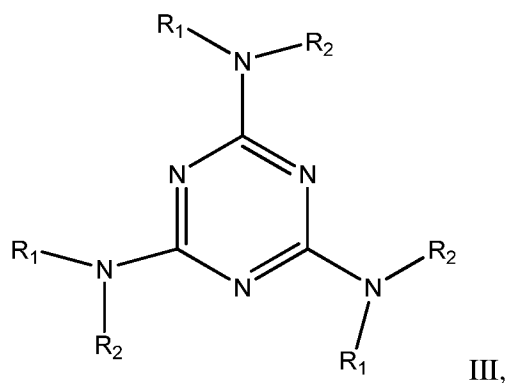
12. cross-linked polyurethane, polyester, or silicone, wherein the isocyanate terminated polyurethane, polyester, or silicone are cross-linked with a compound of Formula III



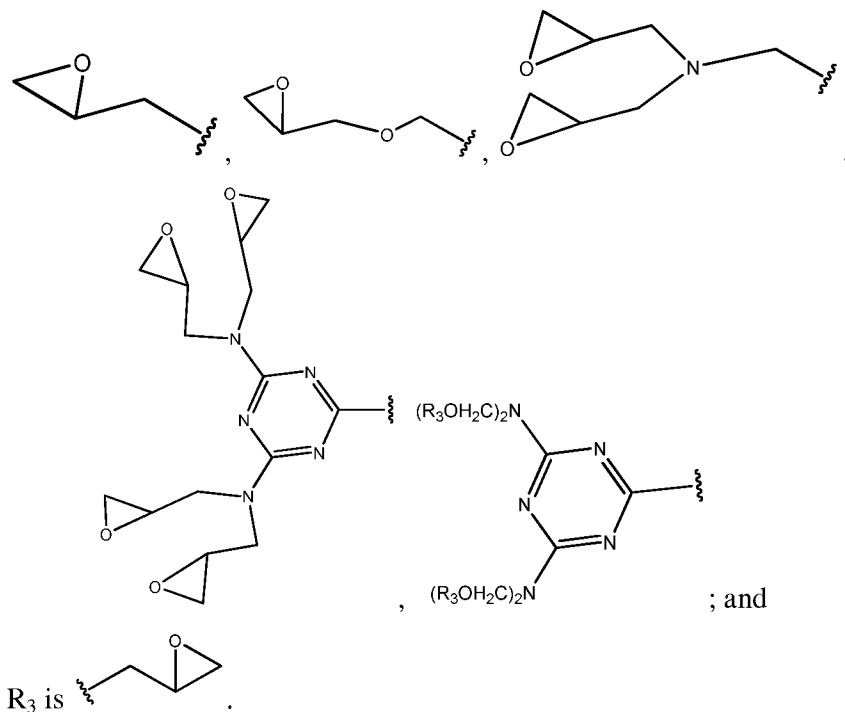
wherein R_1 and R_2 are independently selected from the group consisting of H, CH_2OH , CH_2NH_2 , and melaminy1, or are cross-linked with a compound having a formula of



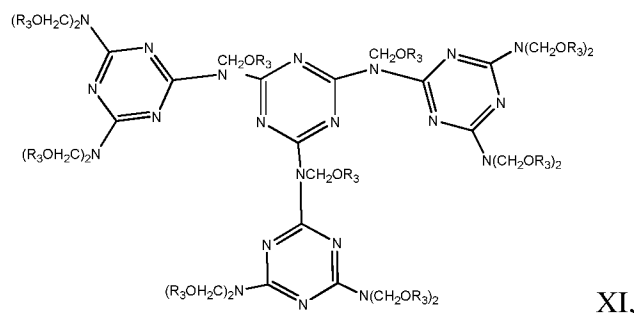
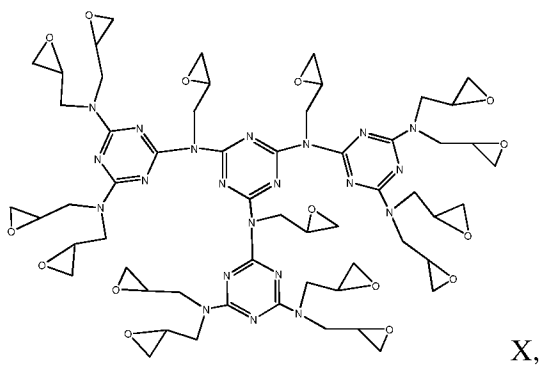
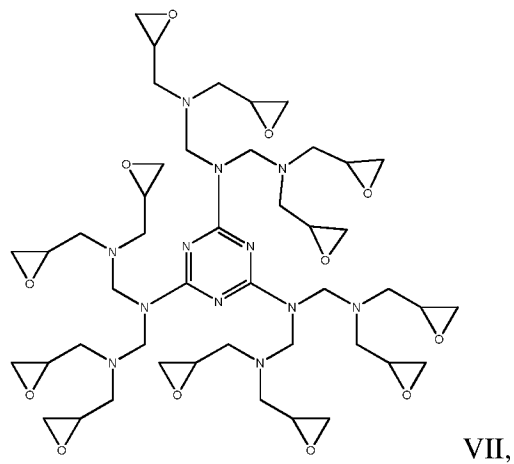
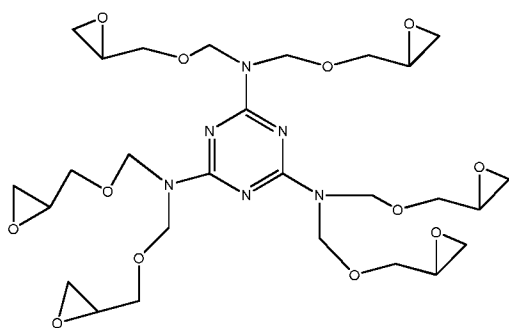
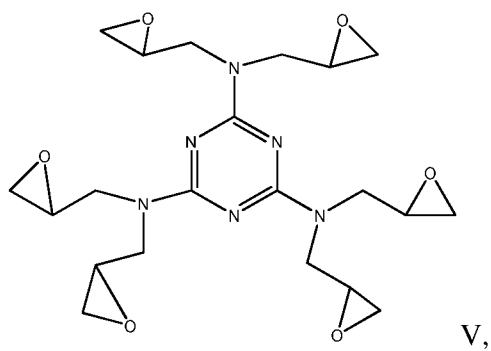
13. A composite comprising one or more a cured epoxy resins of an epoxy resin of Formula III, wherein the epoxy resin is a compound of Formula III



wherein R_1 and R_2 are independently selected from the group consisting of:

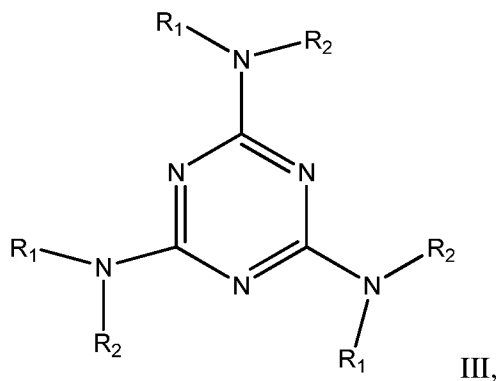


14. The composition of claim 13, wherein the epoxy resin has a Formula of

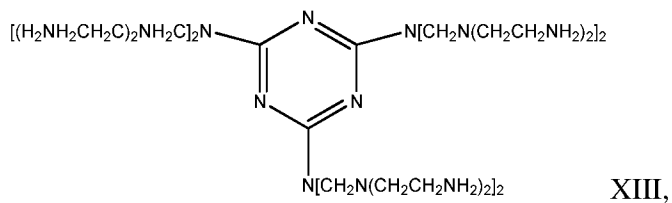
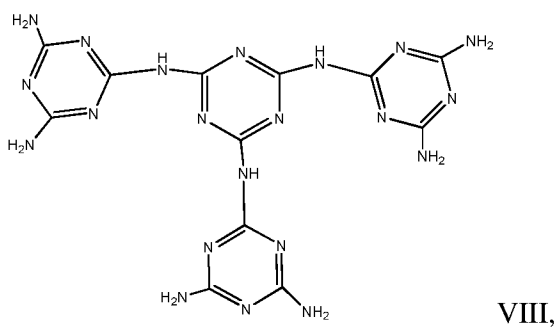
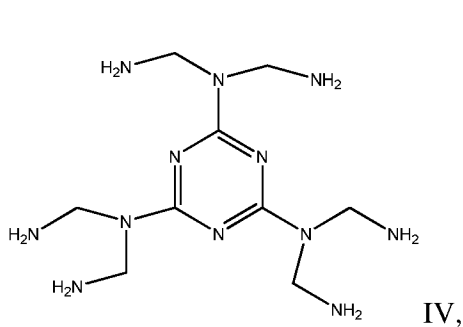


wherein R_3 is .

15. A method of curing an epoxy resin the method comprising contacting an epoxy resin of claim 13 and 14 with amine compounds, a compound of Formula III

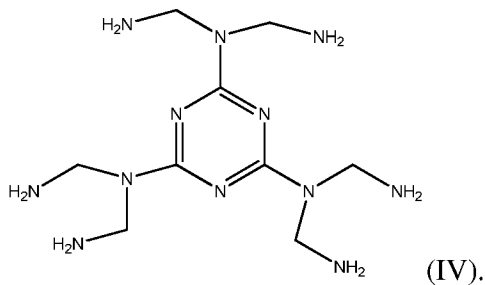


wherein R₁ and R₂ are independently selected from the group consisting of CH₂NH₂, and melaminy1, a compound having a formula of

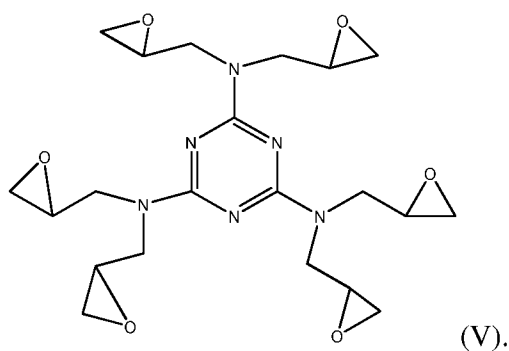


or with one or more hardeners under conditions sufficient to cure the epoxy resins.

16. A method of making a compound of Formula III, the method comprising contacting hexamethylol melamine with ammonia to produce a compound of Formula IV



17. A method of making a compound of Formula V, the method comprising contacting melamine with epichlorohydrine and a strong base to produce a compound of Formula V

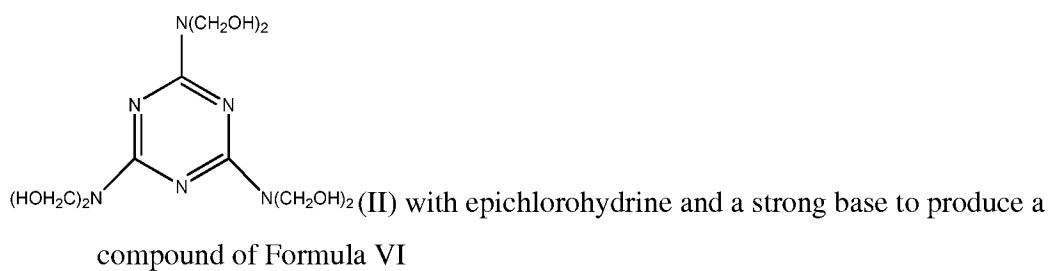


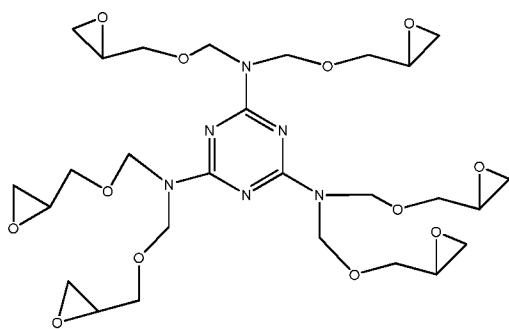
18. The method of claim 17, wherein the method is performed at a temperature of about

0-80 °C.

19. The method of claim 18, wherein the method is performed at three different temperature of about 0-10°C, about 40-80°C, and about 50-60 °C.

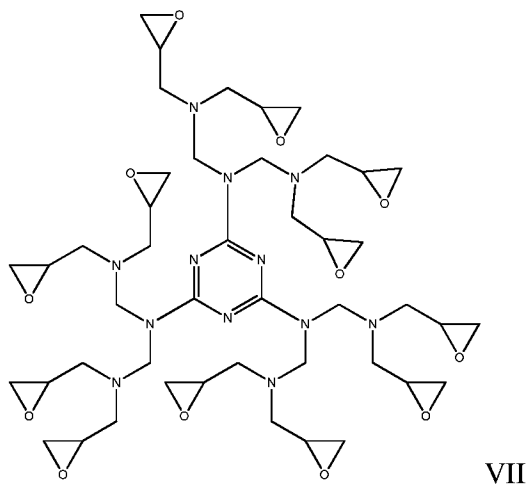
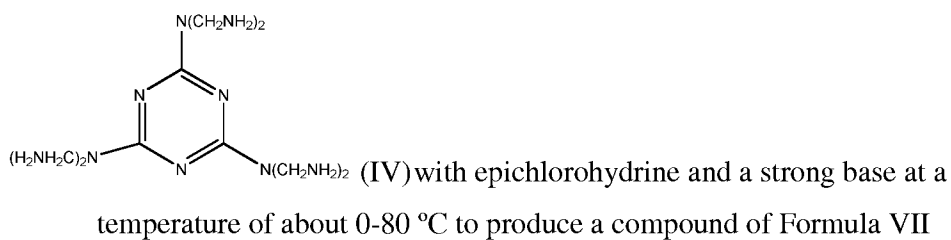
20. A method of making a compound of Formula VI, the method comprising contacting a compound of Formula II



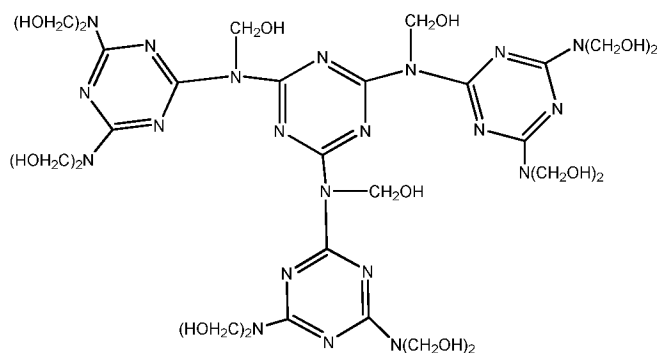


21. The method of claim 19, wherein the method is performed at temperature of about 50-60 °C.

22. A method of making a compound of Formula VII, the method comprising contacting a compound of Formula IV

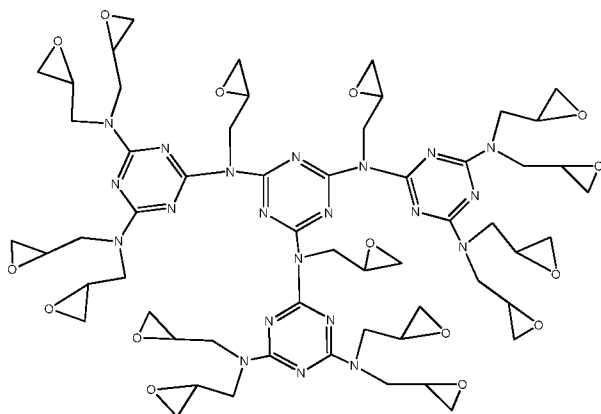


23. A method of making a compound of Formula IX, the method comprising contacting a compound of Formula VIII with excess formaldehyde and a strong base to produce a compound of Formula IX



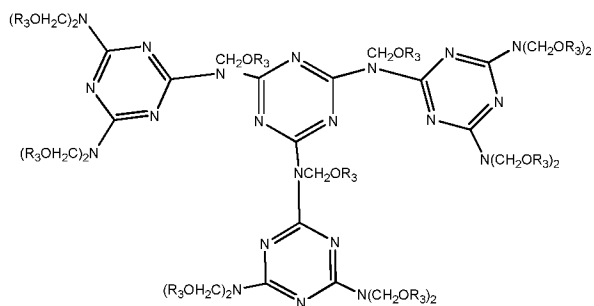
IX.

24. A method of making a compound of Formula X, the method comprising contacting a compound of Formula VIII with epichlorohydrine and a strong base at a temperature of about 0-80 °C to produce a compound of Formula X

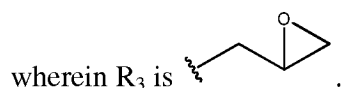


X.

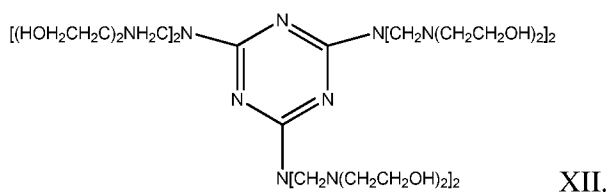
25. A method of making a compound of Formula XI, the method comprising contacting a compound of Formula IX with an excess of epichlorohydrine and a strong base at a temperature of about 50-60 °C to produce a compound of Formula XI



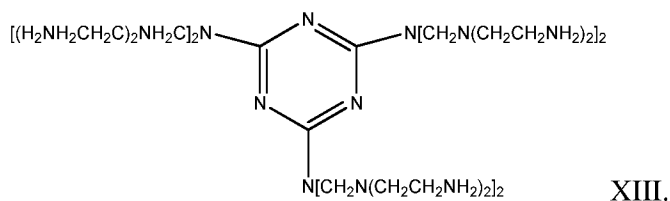
XI,



26. A method of making a compound of Formula XII, the method comprising contacting a compound of Formula II with diethanol amine to produce a compound of Formula XII



27. A method of making a compound of Formula XIII, the method comprising contacting a compound of Formula XII with ammonia or an aliphatic amine under a pressure of about 1-2 atm to produce a compound of Formula XIII



28. A method of producing glycidyl ether derivatives of a compound of Formula XII or glycidylamines from any melamine amino derivatives, a compound of formula XIII the method comprising contacting a compound of Formula XII or XIII with respectively with epichlorohydrine and a strong base at a temperature sufficient to produce a glycidyl ether derivative from compound of Formula XII or glycidylamines from compound of formula XIII.

29. A composition comprising further generations of melamine derived epoxy resin, the resin prepared by a method, the method comprising contacting a melamine methylol of Formula II, IX or Formula XII with an amine to produce a melamine amino derivatives; and optionally contacting the melamine amino derivative with an epichlorohydrine to yield glycidylamine derivative; or contacting the melamine amino derivative with formaldehyde and a strong base to yield a methylol derivatives.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2012/062708

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08G 65/00(2012.01)

USPC - 525/510

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)

IPC(8) - C07D 253/02; C08G 8/28, 59/40, 65/00 (2012.01)

USPC - 156/233, 282; 427/58; 525/510, 511; 528/118

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

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

Orbit.com, Google Patents, Google Scholar, ProQuest, STN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2,980,676 A (ZUPPINGER et al) 18 April 1961 (18.04.1961) entire document	1-8, 13, 14
A	LUBCZAK. Polyhydroxyalkyl derivatives and polyetherols obtained from azacyclic compounds, 2011, Vol.56(6), Polimery, Pages 452-459, entire document	1-14, 16-29
A	CASTRO et al. Melamine/epichlorohydrin prepolymers: syntheses and characterization, 2005, Vol. 46, Polymer, Pages 1766-1774, entire document	1-14, 16-29
A	US 4,661,568 A (KOENIG et al) 28 April 1987 (28.04.1987) entire document	1-14, 16-29

☐ Further documents are listed in the continuation of Box C.


* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

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

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

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

"T"

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

"X"

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

"Y"

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

"&"

document member of the same patent family

Date of the actual completion of the international search

19 December 2012

Date of mailing of the international search report

09 JAN 2013

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/062708

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

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

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

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

3. ☒ Claims Nos.: 15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

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

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.