



(51) International Patent Classification:

C08G 18/80 (2006.01) *C09J 163/00* (2006.01)
C08K 5/109 (2006.01) *C08G 63/00* (2006.01)
C08K 5/205 (2006.01)

(21) International Application Number:

PCT/US2014/019419

(22) International Filing Date:

28 February 2014 (28.02.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/778,651 13 March 2013 (13.03.2013) US

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(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, IR, IS, JP, KE, KG, 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, SA, 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, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

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

(54) Title: METHODS OF MAKING LOW SHRINKAGE AND EXPANDABLE COMPOSITIONS AND EXPANDABLE MONOMERS

(57) Abstract: The present invention pertain to a method of making a composition as well as low shrinkage and expandable compositions comprising an expandable monomer comprising at least two cyclic carbonate end groups; an epoxy resin; and a curing agent that concurrently reacts with the cyclic carbonate of the expandable monomer and epoxy groups of the epoxy resin. Also described are favored expandable monomers, comprising the reaction product of a cyclic carbonate compound having a hydroxyl group and a polyisocyanate comprising at least two hexamethylene groups and at least one uretdione, biuret, and/or isocyanurate group. The low shrinkage and expandable compositions and expandable monomers are suitable for various used such as (e.g. structural) adhesive wherein two substrates are bonded by the cured composition described herein.



METHODS OF MAKING LOW SHRINKAGE AND EXPANDABLE
COMPOSITIONS AND EXPANDABLE MONOMERS

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Background

According to paragraphs 0006 and 0007, US2002/1083474 describe “a method for preparing a carbonate urethane compound by reacting a carbonate containing compound that also contains a reactive hydroxyl group with a compound containing at least two isocyanate groups. The reaction is performed in a solvent and in the presence of a base.

Another form of the present invention is a composition for a curing agent that is a compound containing two or more first carbamate linkages, where each first carbamate linkage is connected to a second carbamate linkage. The ester side of the first carbamate linkages are connected to the ester side of corresponding second carbamate linkages. In addition, there is a terminal amine group connected to the amido side of the second carbamate linkages.

Yet another form of the present invention is a method for preparing a curing agent by reacting a compound containing at least two carbamate linkages, where each carbamate linkage is connected to at least one carbonate, with an excess of a diamine.”

20 **Summary**

Without intending to be bound by theory, it has been found that when a cyclic carbonate compound is ring opened concurrently with the ring opening of an epoxy resin, the expansion of the cyclic carbonate can offset or surpass the shrinkage caused by the ring opening of the epoxy compound.

25 In one embodiment, a method of making a composition is described comprising providing an expandable monomer derived from reacting a cyclic compound comprising a carbonate group and a hydroxyl group with a hydroxyl-reactive compound; and combining the expandable monomer with an epoxy resin and a curing agent, wherein the curing agent concurrently reacts with the carbonate of the expandable monomer and epoxy groups of the epoxy resin.

30 In another embodiment, a low shrinkage composition is described comprising an expandable monomer comprising at least two cyclic carbonate end groups; an epoxy resin; and a curing agent that concurrently reacts with the cyclic carbonate of the expandable monomer and epoxy groups of the epoxy resin.

35 In yet another embodiment, an expandable composition is described comprising an expandable monomer comprising at least two cyclic carbonate end groups; an epoxy resin; and a curing agent that reacts with the cyclic carbonate of the expandable monomer and epoxy groups of the epoxy resin; wherein the expandable composition exhibits an increase in volume after curing.

In yet other embodiments, favored expandable monomers are described comprising the reaction product of a cyclic compound having a hydroxyl group and a carbonate group and a polyisocyanate comprising at least two hexamethylene groups and at least one uretdione, biuret, and/or isocyanurate group.

The low shrinkage and expandable compositions and expandable monomers are suitable for various uses such as (e.g. structural) adhesive wherein two substrates are bonded by the cured composition described herein.

Detailed Description

The present invention pertains to expandable monomers. The expandable monomer is derived from a cyclic compound comprising a carbonate group and a hydroxyl group. The carbonate group forms a portion of the cyclic group. The cyclic group may be considered a cyclic aliphatic carbonate.

The hydroxyl group of a cyclic carbonate compound can be reacted with an isocyanate compound to form an expandable monomer having urethane linkages. Some representative reaction schemes are depicted in US2002/0183474. The reaction scheme of Desmodur 3300 with glycerine carbonate is depicted in the forthcoming examples.

The expandable monomer preferably comprises a residue of a polyisocyanate and urethane linkages terminating with a cyclic carbonate moiety. A representative structure of the expandable monomers is as follows:



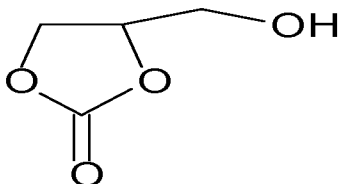
wherein R_i is a residue of a polyisocyanate;

R_c comprises a cyclic carbonate group; and

n averages greater than 1.

The total number of atoms that form the cyclic carbonate group (inclusive of the oxygen atoms of the carbonate group) is typically at least 4 or 5 and no greater than 8 or 6. An alkylene (C_2 - C_6) spacer group is typically present between the terminal cyclic carbonate group and the oxygen atom of the urethane linkage. In some embodiments, n averages 2 to 4 or 2 to 3.

One commercially available cyclic carbonate compound comprising a hydroxyl group is glycerine carbonate. Glycerine carbonate, depicted as follows, is commercially available from Hunstman under the trade designation "JEFFSOLTM GLYCERINE CARBONATE" and has been described as being readily biodegradable and having a renewable content of 76%.



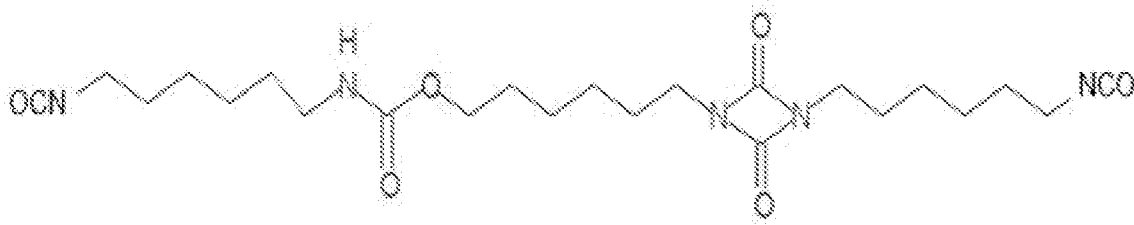
In typical embodiments, the hydroxyl group of the cyclic carbonate is reacted with a polyisocyanate compound to form an expandable monomer. "Polyisocyanate" refers to any organic compound that has two or more reactive isocyanate (-NCO) groups in a single molecule such as diisocyanates (n=2), triisocyanates (n=3), tetraisocyanates (n=4), etc., and mixtures thereof. Cyclic and/or linear polyisocyanate molecules may usefully be employed. For improved weathering and diminished yellowing the polyisocyanate(s) are typically aliphatic.

Useful aliphatic polyisocyanates include, for example, bis(4-isocyanatocyclohexyl) methane, such as available from Bayer Corp., Pittsburgh, Pa. under the trade designation "Desmodur W"; isophorone diisocyanate (IPDI) such as commercially available from Huels America, Piscataway, N.J.; hexamethylene diisocyanate (HDI) such as commercially available from Aldrich Chemical Co., Milwaukee, Wis.; trimethyl hexamethylene diisocyanate such as commercially available from Degussa, Corp., Dusseldorf, Germany under the trade designation "Vestanate TMDI"; and m-tetramethylxylene diisocyanate (TMXDI) such as commercially available from Aldrich Chemical Co., Milwaukee, Wis. Although typically less preferred, aromatic isocyanates such as diphenylmethane diisocyanate (MDI) such as commercially available from Bayer Corp., Pittsburgh, Pa. under the trade designation "Mondur M"; toluene 2,4-diisocyanate (TDI) such as commercially available from Aldrich Chemical Co., Milwaukee, Wis., and 1,4-phenylene diisocyanate.

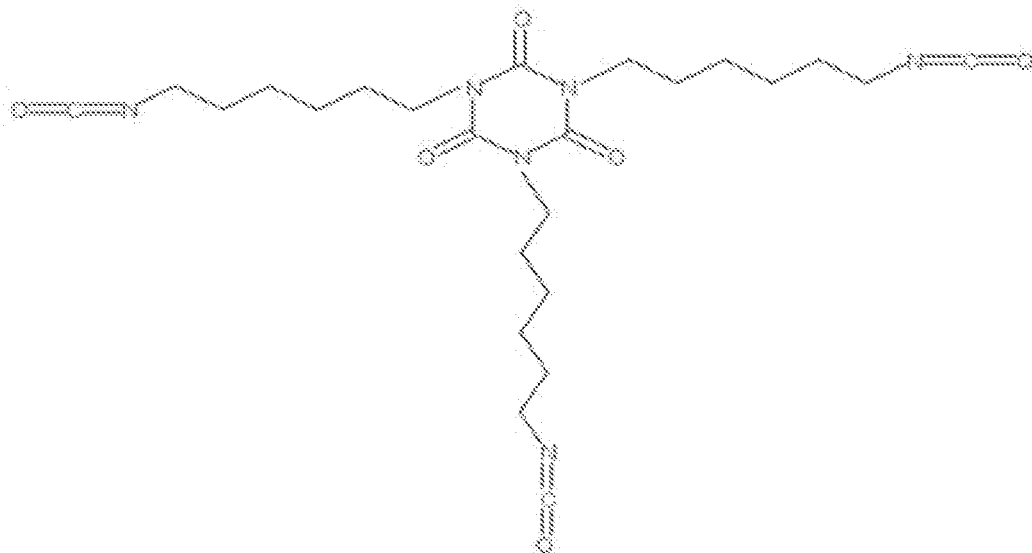
In favored embodiments, the polyisocyanates are derivatives of the above-listed monomeric polyisocyanates, such as derivatives of hexamethylene-1,6-diisocyanate that comprise an uretdione, biuret, and/or isocyanurate. In this embodiment, the residue of the polyisocyanate typically comprises at least two or three hexamethylene groups and at least one uretdione, biuret, and/or isocyanurate.

These derivatives include, but are not limited to, biuret adducts of HDI, such as available from Bayer Corp. under the trade designation "Desmodur N 3200"; HDI uretdione polyisocyanates, such as available from Bayer Corporation under the trade designation "Desmodur N 3400"; HDI polyisocyanurates, such as available from Bayer Corp under the trade designation "Desmodur N 3300"; and polyisocyanate prepolymer resins based on HDI, such as available from Bayer Corp. under the trade designation "Desmodur XP 2599".

The structures for a few representative derivatives of hexamethylene diisocyanate are depicted as follows:



Desmodur DESN 3200



Desmodur DESN 3300

The expandable monomer prepared from derivatives of hexamethylene diisocyanate can be represented by the following formula:



wherein R_i is a residue of a hexamethylene polyisocyanate comprising least one uretdione, biuret, or isocyanurate group ;

R_c comprises a cyclic carbonate group; and

n averages greater than 1, as previously described.

Preferred aliphatic polyisocyanate are solvent-free and are substantially free of isocyanate (e.g. HDI) monomer, i.e. less than 0.5 % and more preferably no greater than 0.3 % as measured according to DIN EN ISO 10 283.

The polyisocyanate is selected such that the expandable monomer synthesized therefrom is compatible with the epoxy resin. For example, when the epoxy resin is a diglycidyl ether of Bisphenol A such as "EPON 828" it has been found that expandable monomers derived from aliphatic isocyanates, such as HDI derivative, can exhibit better compatibility than those derived from toluene diisocyanate or isophorone diisocyanate, particularly when the expandable monomer is present at a weight ratio of about 1:3 or greater relative to the concentration of the epoxy resin. One indication of poor compatibility is phase separation. However, expandable monomers derived from aromatic polyisocyanates, such as toluene diisocyanate, or cyclic aliphatic polyisocyanates, such as isophorone diisocyanate may be sufficiently compatible with other types of epoxy resins.

Various commercially available epoxy resins can be utilized. In particular, epoxides that are readily available include resins of octadecylene oxide, epichlorohydrin, styrene oxide, vinyl cyclohexene oxide, glycidol, glycidyl methacrylate, diglycidyl ethers of Bisphenol A (for example, EPON 828, EPON 825, EPON 1004, and EPON 1001 from Momentive Specialty Chemicals) as well as DER 221, DER 332, and DER 334 from Dow Chemical Co., Midland, MI), vinylcyclohexene dioxide (for example, ERL 4206 from Union Carbide), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexene carboxylate (for example, ERL 4221, CYRACURE UVR 6110, and CYRACURE UVR 6105 from Union Carbide), 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexene carboxylate (for example, ERL 4201 from Union Carbide), bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate (for example, ERL 4289), bis(2,3-epoxycyclopentyl) ether (for example, ERL 0400), aliphatic epoxy modified from polypropylene glycol (for example, ERL 4050 and ERL 4052), dipentene dioxide (for example, ERL 4269), epoxidized polybutadiene (for example, OXIRON 2001 from FMC Corp.), silicone resin containing epoxy functionality, flame retardant epoxy resins such as brominated bisphenol-type epoxy resins (for example, DER 580), 1,4-butanediol diglycidyl ether of phenol formaldehyde novolak (for example, DEN 431 and DEN 438 from Dow Chemical), resorcinol diglycidyl ether (for example, KOPOXITE from Koppers Company, Inc.), bis(3,4-epoxycyclohexylmethyl)adipate (for example, ERL 4299 or CYRACURE UVR 6128), 2-(3,4-epoxycyclohexyl-5, 5-spiro-3,4-epoxy) cyclohexane-meta-dioxane (for example, ERL-4234), vinylcyclohexene monoxide, 1,2-epoxyhexadecane (for example, CYRACURE UVR- 6216), alkyl glycidyl ethers such as alkyl C₈-C₁₀ glycidyl ether (for example, HELOXY MODIFIER 7 from Resolution Performance Products), alkyl C₁₂-C₁₄ glycidyl ether (for example, HELOXY MODIFIER 8 from Momentive Specialty Chemicals), butyl glycidyl ether (for example, HELOXY MODIFIER 61 from), cresyl glycidyl ether (for example, HELOXY MODIFIER 62), p-tert-butylphenyl glycidyl ether (for example, HELOXY MODIFIER 65), polyfunctional glycidyl ethers such as diglycidyl ether of 1,4-butanediol (for example, HELOXY MODIFIER 67), diglycidyl ether of neopentyl glycol (for example, HELOXY MODIFIER 68), diglycidyl ether of cyclohexanedimethanol (for example, HELOXY MODIFIER 107), trimethylol ethane triglycidyl ether (for example, HELOXY MODIFIER 44), trimethylol propane triglycidyl ether (for example, HELOXY 48), polyglycidyl ether of an

aliphatic polyol (for example, HELOXY MODIFIER 84), polyglycol diepoxide (for example, HELOXY MODIFIER 32), bisphenol F epoxides (for example, EPON 862 and Araldite GY-281 from Huntsman Advanced Materials), and 9,9-bis[4-(2,3-epoxypropoxy)-phenyl]fluorenone (for example, EPON 1079 from Momentive Specialty Chemicals).

Other useful epoxy-containing materials include those that contain cyclohexene oxide groups such as epoxycyclohexanecarboxylates, typified by 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, and bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate. A more detailed list of useful epoxides of this nature is set forth in U.S. 3,117,099 (Proops et al).

Other useful epoxy resins are well known and contain such epoxides as epichlorohydrins, alkylene oxides (for example, propylene oxide), styrene oxide, alkenyl oxides (for example, butadiene oxide), and glycidyl esters (for example, ethyl glycidate). Still other useful epoxy resins include epoxy-functional silicones such as those described in U.S. 4,279,717 (Eckberg et al.), which are commercially available from the General Electric Company. These epoxy resins are polydimethylsiloxanes in which 1 to 20 mole percent of the silicon atoms have been substituted with epoxyalkyl groups (preferably, epoxy cyclohexylethyl, as described in U.S. 5,753,346 (Leir et al.)).

Blends of various epoxy-containing materials can also be utilized. Suitable blends can include two or more weight average molecular weight distributions of epoxy-containing compounds such as low molecular weight epoxides (e.g., having a weight average molecular weight below 200 g/mole), intermediate molecular weight epoxides (e.g., having a weight average molecular weight in the range of about 200 to 1000 g/mole), and higher molecular weight epoxides (e.g., having a weight average molecular weight above about 1000 g/mole). Alternatively or additionally, the epoxy resin can contain a blend of epoxy-containing materials having different chemical natures such as aliphatic and aromatic or different functionalities such as polar and non-polar.

The method of making the composition comprises providing an expandable monomer derived from reacting a cyclic compound comprising a carbonate group and a hydroxyl group (e.g. glycerine carbonate) with a hydroxyl-reactive compound (e.g. a polyisocyanate); and combining the expandable monomer with an epoxy resin and a curing agent. The curing agent reacts with the carbonate of the expandable monomer and epoxy groups of the epoxy resin. The reaction of the curing agent with the carbonate results in ring-opening and an expansion in volume, whereas the reaction of the curing agent with the epoxy results in a contraction in volume, commonly known as "shrinkage". The order of addition or synthesis is such that the curing agent concurrently reacts with the carbonate of the expandable monomer and epoxide groups of the epoxy resin. When concurrently reacted in this manner the expansion of the ring opened cyclic compound can offset or surpass the shrinkage.

When the concentration of expandable monomer is relatively low, for example the weight ratio of expandable monomer to epoxy resin is no greater than about 1:9, the mixture can be a low

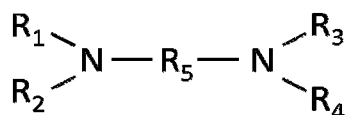
shrinkage composition typically having a shrinkage of no greater than 0.5%, or 0.4%, or 0.3%, or 0.2%, 0.1%, or even 0 as measured according to the Shrinkage Test Method described in the forthcoming examples. However, as the concentration of expandable monomer increases, the expansion caused by the ring opening of the cyclic carbonate group surpasses the shrinkage and the resulting composition can exhibit an increase in volume, or in other words a positive shrinkage. In some embodiments, the weight ratio of expandable monomer to epoxy resin is at least 1:8, or 1:7, or 1:6, or 1:5, or 1:4, or 1:3 or 1:2. The weight ratio of expandable monomer, to epoxy resin is typically no greater than 1:1. It is typically favored to utilize the minimum amount of expandable monomer that will provide the desired low shrinkage or expansion. In some embodiments, the amount of expandable monomer is least about 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 wt-% of the total polymerizable composition. The amount of expandable monomer may range up to 15, 20 or 25 wt-% of the total polymerizable composition. In some embodiments the thermal expansion of the epoxy resin does not significantly change by inclusion of up to 25 wt-% of expandable monomer. For example, the second heat may rise by about 10 – 15°C. In some embodiments the glass transition temperature (T_g) of the epoxy resin is reduced by inclusion of up to 25 wt-% of expandable monomer. For example, the T_g may decrease by 30-35°C.

The curing agent is reactive with the epoxy groups of the epoxy resin and the cyclic carbonate group of the expandable monomer. One class of curing agents having such reactivity are polyamines, such as diamines.

The polyamine crosslinker may be straight-chain, branched, and in some favored embodiments cyclic. In some embodiments, the polyamine crosslinker is aliphatic. In other embodiments, the polyamine crosslinker is aromatic.

Useful polyamine are of the general formula R₅-(NR₁R₂)_x wherein R₁ and R₂ are independently H or alkyl, R₅ is a polyvalent alkylene or arylene, and x is at least two. The alkyl groups of R₁ and R₂ are typically C₁ to C₁₈ alkyl and most typically methyl. R₁ and R₂ may be taken together to form a cyclic amine. In some embodiment x is two (i.e. diamine). In other embodiments, x is 3 (i.e. triamine). In yet other embodiments, x is 4.

Useful polyamines include diamines having at least two amino groups, wherein the two amino groups are primary, secondary, tertiary or a combination thereof. Diamines may be represented by the general formula:



wherein R₁, R₂, R₃ and R₄ are independently H or alkyl, and R₅ is a divalent alkylene or arylene. In some embodiments, R₁, R₂, R₃ and R₄ are each H and the diamine is a primary amine. In other

embodiments, R_1 and R_4 are each H and R_2 , and R_3 are each independently alkyl; and the diamine is a secondary amine. In yet other embodiments, R_1 , R_2 , R_3 and R_4 are independently alkyl and the diamine is a tertiary amine.

In some embodiments, primary and secondary amines are preferred.

5 Examples include hexamethylene diamine; 1,10-diaminodecane; 1,12-diaminododecane; 2-(4-aminophenyl)ethylamine; isophorone diamine; 4,4'-diaminodicyclohexylmethane; and 1,3-bis(aminomethyl)cyclohexane. Illustrative six member ring diamines include for example piperazine and 1,4-diazabicyclo[2.2.2]octane ("DABCO").

10 Other useful polyamines include polyamines having at least three amino groups, wherein the three amino groups are primary, secondary, or a combination thereof. Examples include 3,3'-diaminobenzidine and hexamethylene triamine.

Polymeric polyamines can also be utilized; including for example poly(4-vinylpyridine) and branched polyethylenimine.

15 Polyamines that are solids at room temperature have low odor due to having low vapor pressures. Polyamines having such property are straight-chain or branched polyamines having an alkylene group comprising at least 5 or 6 carbons. Cyclic polyamines are also favorably solids at room temperature. In some embodiments, the polyamine has a melting point of at least 100°C, 125°C, or 150°C. The melting point is typically no greater than 300°C, and in some embodiments no greater than 250°C, or 225°C, or 200°C, or 175°C.

20 The molecular weight of useful polyamines that are solids at room temperature (e.g. 25°C) is typically at least 100, 105, 110, or 115 g/mole. For embodiments wherein polymeric polyamines are employed, the (weight average) molecular weight of the polyamine can range up 100,000 g/mole; yet is typically less than the molecular weight of the isobutylene copolymer. In some embodiments, the (weight average) molecular weight of the polyamine is no greater than 75,000 g/mole, 50,000 g/mole
25 or 25,000 g/mole. When non-polymeric polyamines are employed the molecular weight of the polyamine is typically no greater than 1500 g/mole and in some embodiments no greater than 1000 or 500 g/mole.

30 The composition may further comprise optional additives such as antioxidants, inhibitors, (e.g. silane-treated) fillers, anti-sag additives, thixotropes, processing aids, waxes, and UV stabilizers. Examples of typical fillers include glass bubbles, fumed silica, alumina, mica, feldspar, and wollastonite.

The low shrinkage or expandable composition is suitable for various uses such as for use as a (e.g. structural) adhesive.

35 Although the (e.g. adhesive) composition may take many forms, the composition is typically provided as multipack or two-part adhesive systems where one package or part contains the epoxy resin and expandable monomer and a second package or part contains the (e.g. amine) curing agent. The two parts are mixed together at the time of use in order to initiate the concurrent reaction of the

epoxy and expandable monomer with the curing agent. The typical means for dispensing the (e.g. adhesive) composition are two-chambered cartridges equipped with static mixers in the nozzle, and for larger scale application, meter mix dispensing equipment. After mixing the individual packages, one or both surfaces to be joined are coated with the mixed adhesive system and the surfaces are placed in contact with each other.

The (e.g. structural) adhesive may be used to bond metal surfaces, such as steel, aluminum and copper, to a variety of substrates, including metal, plastics, and other polymers, reinforced plastics, fibers, glass, ceramics, wood and the like. The adhesive provides effective bond strength at room temperature, thus heat is not required either for applying the adhesive systems to the substrates or for developing handling strength and dimensional stability.

The (e.g. structural) adhesive may be brushed, rolled, sprayed, dotted, knifed, cartridge-applied, especially from a dual cartridge; or otherwise applied to one substrate or both substrates to desired thickness.

Although the present invention has been described with reference to particular embodiments, it should be recognized that these embodiments are merely illustrative of the principles of the present invention. Those of ordinary skill in the art will appreciate that the compositions, apparatus and methods of the present invention may be constructed and implemented in other ways and embodiments. The invention is further illustrated by the following examples.

Examples:

Shrinkage Test Method

Measurements were obtained by measuring the density of the systems before and after curing. The liquid density (before curing) was measured by weighing a precise amount of liquid formulation. The density of cured films (after curing) was measured by means of a Mettler Toledo Balance with density determination kit. The Archimedes principle is applied for determining the specific gravity of a solid with this measuring device:

A solid immersed in a liquid is exposed to the force of buoyancy. The value of this force is the same as that of the weight of the liquid displaced by the volume of the solid. The density measurements have been performed with the balance which enables to weigh the solid in air as well as in a liquid; the specific gravity of the solid is determined when the density of the liquid causing buoyancy is known, through the following formula:

$$\rho = W(a) \cdot \rho(1) / W(a) - W(1)$$

where ρ is the specific gravity of the solid; $\rho(l)$, the density of the liquid; $W(a)$, the weight of the solid in air; and $W(l)$ is the weight of the solid in liquid. The chosen liquid was D.I water with a density value at 25°C of $d_{25} = 0.9972$ g/mL.

5 The Shrinkage during polymerization was calculated with the following formula:

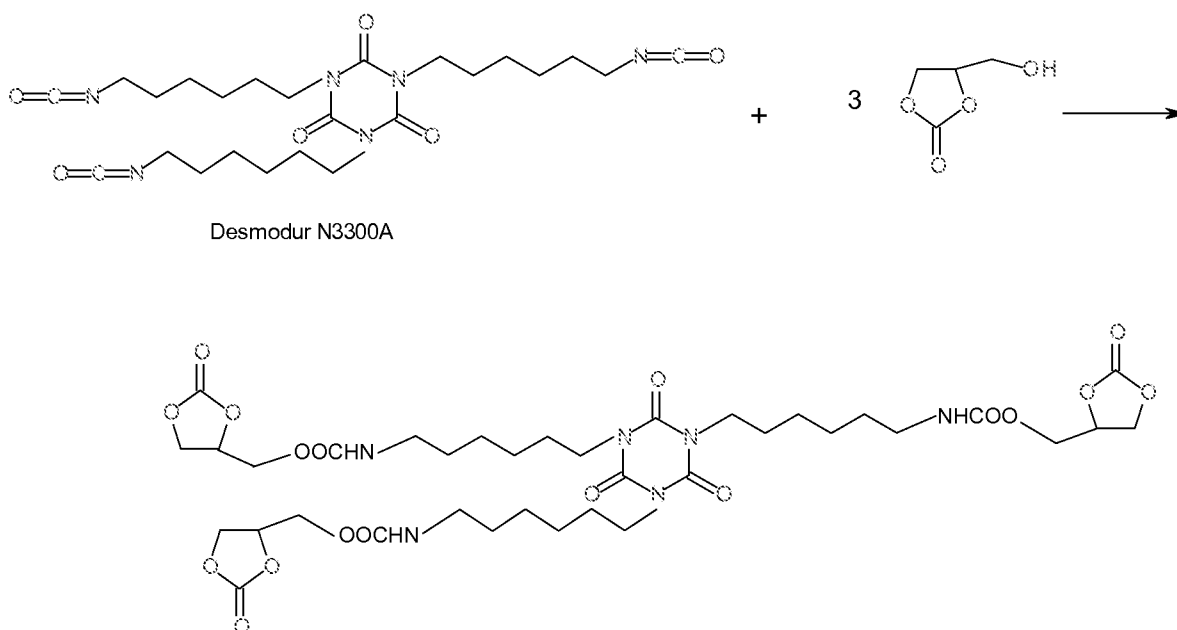
$$\% \text{ Shrinkage} = \rho(l) - \rho(a) / \rho(l) * 100$$

10 Synthesis of Expanding Monomers

Two different expanding monomer were prepared from two different polyisocyanates (Desmodur 3200 and Desmodur 3300). The expanding monomers will subsequently be referred to as EM-3200 (prepared from Desmodur 3200) and EM-3300 (prepared from Desmodur 3300).

15 For each synthesis, polyisocyanate (0.05 mols) was dissolved in dry MEK (50mL). To the stirred solution, glycerol carbonate (0.05 mols) was added and to the magnetically stirred solution, catalyst DBU (1 wt %) was added. An exothermic reaction followed and the reaction was monitored by FTIR (disappearance of 2270 cm⁻¹ isocyanate peak). After reaction was completed, the solvent was removed by rotavapor. The resulting viscous liquid was used directly for mixing with epoxy resin.

20 Following is a representative reaction scheme for Desmodur 3300 and glycerol carbonate.



Concurrent Polymerization of Expanding Monomer with Epoxy Resin and Amine Curing Agent

The expanding monomers synthesized above was mixed with Epon 828 and cured with isophorone diamine (30 phr). To get a bubble-free sample for density measurements, the polymerization was carried out in silicon oil. The intimate mixture of monomer and hardener was placed in silicon oil and heated to 70°C for complete polymerization. After keeping for 1h, the solidified sample was taken out and wiped thoroughly to remove the silicone oil.

The volume shrinkage of the cured composition was determined as previously described. The test results are as follows:

Volume Shrinkage of the Cured Composition

Example	Expanding Monomer	Weight Ratio of Epoxide to Expanding Monomer	Density of Monomer Mix	Density of polymer	% Volume Shrinkage
Comparative (no expanding monomer)		100:0	1.166	1.214	- 4.11
Example 1	EM-3300	50:50	1.210	1.189	+ 1.73
Example 2	EM-3300	75:25	1.201	1.191	+ 0.8
Example 3	EM-3300	90:10	1.192	1.194	- 0.2
Example 4	EM-3200	50:50	1.221	1.186	+ 2.9
Example 5	EM-3200	75:25	1.208	1.189	+ 1.6
Example 6	EM-3200	90:10	1.194	1.198	- 0.3

What is claimed is:

1. A method of making a composition comprising:

5 providing an expandable monomer derived from reacting a cyclic carbonate compound having a hydroxyl group with a hydroxyl-reactive compound; and combining the expandable monomer with an epoxy resin and a curing agent, wherein the curing agent concurrently reacts with the carbonate of the expandable monomer and epoxide groups of the epoxy resin.

10 2. The method of claim 1 wherein the expandable monomer is combined with the epoxy resin prior to combining with the curing agent.

15 3. The method of claim 1 wherein the expandable monomer is derived from reacting a glycerol carbonate compound with a polyisocyanate.

4. The method of claim 3 wherein the polyisocyanate averages at least two or three isocyanate groups.

20 5. The method of claims 3 or 4 wherein the polyisocyanate is an aliphatic isocyanate.

6. The method of claim 3 wherein the polyisocyanate comprises at least two hexamethylene groups and at least one uretdione, biuret, and/or isocyanurate group.

25 7. The method of claims 3-6 wherein the isocyanate is a viscous liquid at 25°C.

8. The method of claims 1-6 wherein the curing agent is a polyamine compound.

9. The method of claim 8 wherein the polyamine comprise a cyclic aliphatic group.

30 10. The method of claims 1-9 wherein the low shrinkage composition exhibits a reduction in shrinkage of at least 25%, 50%, or 75% relative to the combination of the epoxy and amine in the absence of the expandable monomer.

35 11. The method of claims 1-9 wherein the low shrinkage composition exhibits an increase in volume after curing.

12. A low shrinkage composition comprising:

an expandable monomer comprising at least two carbonate end groups;

an epoxy resin; and

a curing agent that concurrently reacts with the carbonate of the expandable monomer and epoxide groups of the epoxy resin.

13. An expandable composition comprising:

an expandable monomer comprising at least two carbonate end groups;

an epoxy resin; and

a curing agent that reacts with the carbonate of the expandable monomer and epoxide groups of the epoxy resin; wherein the expandable composition exhibits an increase in volume after curing.

14. The low shrinkage composition of claim 12 or expandable composition of claim 13 wherein the expandable monomer, epoxy resin, or curing agent are further described according to any one or combination of claims 1-10.

15. The low shrinkage composition of claim 12 or expandable composition of any one of claims 12-14 wherein the expandable composition is suitable for use as a structural adhesive.

16. An article comprising a first substrate bonded to a second substrate with a cured low shrinkage or expandable composition of any one of claims 12-15.

17. A method of making an expandable monomer comprising:

providing a cyclic compound having a hydroxyl group and a carbonate group; and

reacting the hydroxyl group of the cyclic compound with a polyisocyanate, the polyisocyanate comprising at least two hexamethylene groups and at least one uretdione, biuret, and/or isocyanurate group.

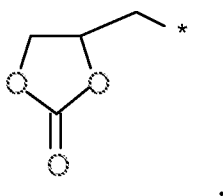
18. An expandable monomer comprising the reaction product of a cyclic compound having a hydroxyl group and a carbonate group and a polyisocyanate comprising at least two hexamethylene groups and at least one uretdione, biuret, and/or isocyanurate group.

19. The expandable monomer of claim 18 wherein the monomer has the formula:



- 5 wherein Ri is a residue of a hexamethylene polyisocyanate comprising least one uretdione, biuret, or isocyanurate group ;
 R_c comprises a cyclic carbonate group; and
 n averages greater than 1.

10 20. The expandable monomer of claim 1 wherein R_c is



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/019419

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/80 C08G63/00 C08K5/109 C08K5/205 C09J163/00
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 C08K 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 practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/064227 A1 (GAM ALLISA [US]) 3 April 2003 (2003-04-03) paragraphs [0024] - [0027] example 3 -----	1-20
X	US 2003/050424 A1 (BERNARD JEAN-MARIE [FR]) 13 March 2003 (2003-03-13) example 4 -----	17-20
X	US 2010/137507 A1 (BERNARD JEAN-MARIE [FR] ET AL) 3 June 2010 (2010-06-03) examples 1,3,4,7 table 6 -----	1-20

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Further documents are listed in the continuation of Box C.

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See patent family annex.

* Special categories of cited documents :

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

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

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"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 May 2014

Date of mailing of the international search report

27/05/2014

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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