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(54) Title: CURABLE COMPOSITIONS OF ACYL EPOXIDES, CYCLOALIPHATIC EPOXIDES, AND ARYL POLYOLS,
AND NETWORK POLYMERS THEREFROM

(57) Abstract: Curable compositions comprising polyepoxy acyl esters or amides, polyepoxy cycloaliphatic compounds, and aryl
polyols, and improved network polymers formed by curing them. The polyepoxy acyl esters can be provided by epoxidized biological
oils.



WO 2005/019297 A1

CURABLE COMPOSITIONS OF ACYL EPOXIDES, CYCLOALIPHATIC EPOXIDES, AND ARYL POLYOLS, AND NETWORK POLYMERS THEREFROM

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BACKGROUND

The present invention relates to the field of epoxy polymers and, in particular, to the field of epoxy polymers formed from epoxidized oils obtained from biological sources. For a number of decades, plant and animal oils containing unsaturated carboxylic acyl esters, as well as compositions containing unsaturated carboxylic acyl amides prepared therefrom, have been epoxidized for use as starting materials for making polymers. See, e.g., R Raghavachar et al., "Cationic Thermally Cured Coatings Using Epoxidized Soybean Oil," *J Coatings Technol.* 72(909):125-33 (Oct. 2000); HJ Falkena et al., "Environmental Life Cycle Assessment of Epoxidized Linseed Oil and TGIC (triglycidylisocyanurate), Applied as Crosslinkers in Powder Coatings," *Proceedings of the Sixth Symposium on Renewable Resources, in Series: Renewable Raw Materials*, Vol. 14, pp. 466-69 (1999) (Landwirtschaftsverlag GmbH, Muenster, Germany).

However, these epoxidized carboxylic acyl ester and amide compositions produce, upon curing, polymers with only moderate thermal stability and relatively low mechanical properties, e.g., relatively low modulus and strength. This is true, for example, even in the case of polymers formed by curing epoxidized linseed oil-based compositions; epoxidized linseed oil has the highest degree of epoxy functionality for typically used epoxidized biological oils, and, thus, produces the best-performing of the traditional epoxy oil polymers. However, these polymers have a glass transition temperature of about 45 to about 90°C, and they exhibit a strength of about 4,500 psi (about 31 MPa) to about 12,500 psi (about 86 MPa), and a modulus of about 100 ksi (about 690 MPa) to about 330 ksi (about 2,280 MPa).

As a result, these polymers are not useful for applications in which good thermal stability and relatively high mechanical properties are required. Therefore, a need exists in the field for improved curable compositions of epoxidized carboxylic acyl esters and/or amides that can be cured to provide polymers having substantially improved thermal stability and mechanical properties.

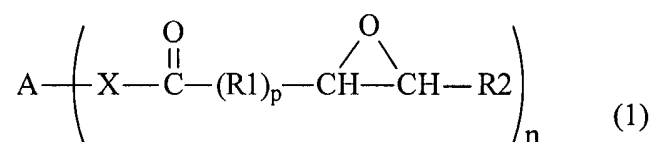
SUMMARY

The present invention provides improved curable compositions of epoxidized carboxylic acyl esters and/or amides that can be cured to provide polymers having substantially improved thermal stability and mechanical properties. This is accomplished by combining an epoxycycloaliphatic compound with the epoxidized carboxylic acyl compound, along with a polyol that is preferably an aryl or alkylaryl polyol; the resulting composition is then cured to obtain the improved polymer.

The present invention provides:

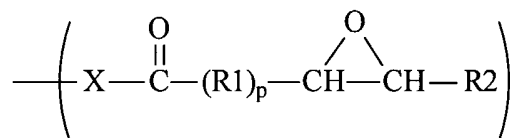
Curable compositions comprising

(I) at least one acyl epoxy compound represented by the following formula (1)



wherein,

(A) for each epoxy acyl unit



in each acyl epoxy compound of formula (1),

R1 independently represents a substituted or unsubstituted homo- or hetero-aliphatic divalent group,

R2 independently represents a substituted or unsubstituted homo- or hetero-aliphatic monovalent group,

p is independently an integer equal to 0 or 1,

X independently represents divalent oxygen



or a divalent amino group



with R3 independently representing H or a substituted or unsubstituted homo- or hetero-hydrocarbon monovalent group,

(B) each A independently represents a homo- or hetero-hydrocarbon polyvalent group, and

(C) each n is independently an integer equal to or greater than 2;

(II) at least one cycloaliphatic epoxy containing at least two epoxide groups;

(III) at least one homo- or hetero-hydrocarbon compound containing at least two hydroxyl

5 groups;

and

(IV) optionally, at least one curing catalyst selected from organic onium salts, imidazoles, and organic phosphines.

10 Curable compositions, wherein the acyl epoxy compound(s) are epoxy ester(s), epoxy amide(s), epoxy ester-amide(s), or a combination thereof.

Curable compositions, wherein each of R1 and R2 independently contains up to 40 main chain atoms and up to 5 epoxy groups; each R3, if present, is H or contains about 10 or fewer
15 skeleton atoms; each A contains from 1 to about 50 skeleton atoms; and each n is 2 to 10; each cycloaliphatic epoxy compound contains about 50 or fewer skeleton atoms; and each polyhydroxy hydrocarbon compound has a molecular weight of about 110 to about 3,000.

Curable compositions, wherein the acyl epoxy compound(s) are provided by epoxidated
20 biological oil(s), for example, epoxidated soybean oil and/or epoxidated linseed oil, or are provided by biological oil(s) obtained from biological organism(s) synthesizing epoxy acyl esters or amides.

Curable compositions, wherein the cycloaliphatic epoxy compound(s) contains at least two
25 epoxycycloaliphatic groups, such as a polykis(epoxy-cycloaliphatic) compound, or contains at least one aliphatic oxiranyl-substituted epoxycycloaliphatic compound, or both.

Curable compositions, wherein said homo- or hetero-hydrocarbon compound containing at least two hydroxyl groups is an aryl or alkylaryl polyol, such as a diphenol, a phenolic
30 novolac, or a phenolic resole.

Curable compositions, wherein the curing catalyst is an organic onium salt, imidazole, or organic phosphine.

Processes for forming such curable compositions. Processes for forming network polymers by curing such curable compositions. Network polymers formed thereby. Molded parts, coatings, adhesives and bonding agents, and composite materials containing the network polymers.

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DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

DEFINITIONS

10

Epoxy

As used herein, the terms "epoxy" and "epoxy group" refer to oxirane groups, and the term "epoxide" refers to compounds containing at least one oxirane group. As used herein, the term "aliphatic oxirane" refers to an aliphatic molecule or group that contains at least one oxirane group; among such groups are oxirane groups proper, i.e. epoxy ethyl groups.

15

Hydrocarbon & Aliphatic

As used herein, the term "hydrocarbon" means an aliphatic or aromatic compound, or a compound containing a combination of aliphatic and/or aromatic structures. The term "hydrocarbyl" means a mono-radical of an aliphatic or aromatic compound, or of a compound containing a combination of aliphatic and/or aromatic structures. Parallel definitions apply to hydrocarbon structural groups containing multiple radicals. As used herein, the term "aliphatic" means a cyclic, acyclic, and/or alicyclic hydrocarbon compound or group, excluding aromatic compounds. As used herein, the term "alicyclic" refers to aliphatic compounds and groups containing a carbocyclic ring structure which may be saturated or unsaturated, but may not be a benzenoid or other aromatic system.

20

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Poly- and Polykis-

As used herein, the prefixes "poly-" and "polykis-" indicate "at least two."

30

Ring Structures

Except where otherwise specified, the term "ring structure" means a monocyclic structure, a bridged ring, a fused polycyclic structure, a ring assembly, a mono- or poly-spiro ring structure, or a structure that is a combination thereof.

35

As used herein, the term "ring assembly" means a structural group in which a plurality of ring structures are covalently joined to one another by one or more single and/or double bond(s), and/or by one or more homo- or hetero-aliphatic structure(s), and/or by one or more non-carbon-based structure(s); examples of such non-carbon-based structures include, e.g., an oxa
5 (i.e. oxy) group, a thia group, a phospho group, a phosphine group, an aza group, an azo group, an azino group, an amino group, an aminooxy group, a phosphoxy group, a sulfoxy group, a nitroxy group, a silane group, a siloxy group, or a combination thereof.

Skeleton and Main Chain Atoms

10 The terms "skeleton" and "main chain," used in reference to atoms in a molecule or group, indicate the core or "backbone" atoms of the structure. Branched chains are assessed according to their longest chain structure; combination structures, such as alicyclic and alkylaryl structures, are assessed according to the sum of their ring skeleton atoms and the longest chain structure in each of their aliphatic ring substituents. For example, the acyl
15 group of decanoic acid contains ten main chain "skeleton" atoms, furan contains five ring "skeleton" atoms, a phenyl groups contains six ring "skeleton" atoms, styrene contains eight "skeleton" atoms, and so forth.

Substituents

20 Substituent groups may be present in any of the groups and molecules discussed herein. Where substituents are present, preferably these are one or more of oxo, hydroxy, sulfo, sulphydryl, and/or amino substituents, or homohydrocarbon substituent groups and/or heterohydrocarbon substituent groups, each of the groups independently having a molecular weight that is preferably about 250 or less, more preferably about 200 or less, even more
25 preferably about 150 or less, still more preferably about 100 or less, and yet more preferably about 80 or less, yet even more preferably 60 or less, and still even more preferably about 40 or less. Particular preferred substituent groups include, e.g., oxo, hydroxy, amino substituents and C1-C3 aliphatic substituent groups, preferably C1-C3 alkyl substituent groups.

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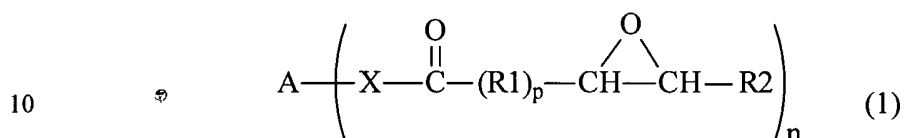
Valencies

As used herein, in the context of describing parts of molecules, terms such as "monovalent" and "polyvalent" (e.g., "divalent," "trivalent") refer to groups whose enumerated "valancies"

are actively participating in covalent bonds as bonding valencies within the molecule, and are not free valencies present in the molecule.

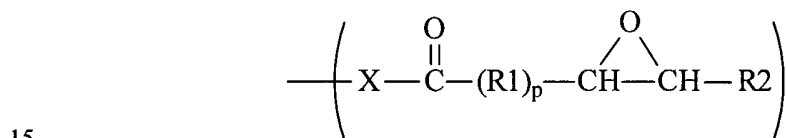
The present invention provides curable compositions and network polymers formed by curing
5 said compositions comprising

(I) at least one acyl epoxy compound represented by the following formula (1)



wherein,

(A) for each epoxy acyl unit



in each acyl epoxy compound of formula (1),

R1 independently represents a substituted or unsubstituted homo- or hetero-aliphatic divalent group,

R2 independently represents a substituted or unsubstituted homo- or hetero-aliphatic
20 monovalent group,

p is independently an integer equal to 0 or 1,

X independently represents divalent oxygen



or a divalent amino group



with R3 independently representing H or a substituted or unsubstituted homo- or hetero-hydrocarbon monovalent group,

(B) each A independently represents a homo- or hetero-hydrocarbon polyvalent group, and

30 (C) each n is independently an integer equal to or greater than 2;

(II) at least one cycloaliphatic epoxy compound containing at least two epoxide groups;

(III) at least one homo- or hetero-hydrocarbon compound containing at least two hydroxyl groups;

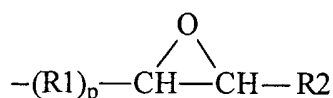
and

(IV) optionally, at least one curing catalyst selected from organic onium salts, imidazoles, and organic phosphines.

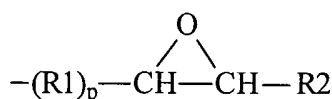
Preferably each of R1 and R2 will independently contain less than 40 main chain atoms, more preferably up to 30, even more preferably up to 20, still more preferably about 18 or fewer, yet more preferably about 15 or fewer, yet even more preferably about 12 or fewer, yet still more preferably 10 or fewer main chain atoms. In a preferred embodiment, each of R1 and R2 will independently contain 13 or fewer main chain atoms. In a particularly preferred embodiment for each acyl group, R1 will contribute 7 and R2 will contribute 8 main chain atoms, or R1 will contribute 10 and R2 will contribute 5 main chain atoms, or R1 will contribute 13 and R2 will contribute 2 main chain atoms.

Preferably, the total main chain atoms contributed to the acyl chain by the combination of R1 and R2 together will be less than 40. In a preferred embodiment, the main chain atoms provided by R1 and R2 will be about 37 or fewer, more preferably about 33 or fewer, even more preferably about 3 to about 27, still more preferably about 7 to about 23, yet more preferably about 9 to about 21, yet even more preferably about 13 to about 19, and yet still more preferably about 15 to about 17 main chain atoms. In a particularly preferred embodiment, the main chain atoms provided by R1 and R2 will be 15. Preferably R1 and R2 will each be unsubstituted aliphatic groups, preferably unsubstituted alkyne and alkyl groups, i.e. straight chain groups.

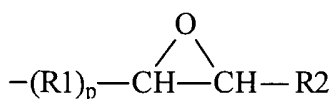
Thus, in a preferred embodiment, each



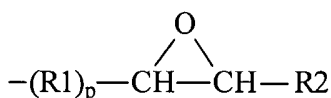
group will independently provide 41 or fewer main chain atoms to the acyl chain of an epoxy acyl unit of the acyl epoxy compound, preferably up to 39, more preferably up to 37, yet more preferably up to 35, even more preferably up to 33, still more preferably up to 31, and yet even more preferably up to 29 main chain atoms. In a preferred embodiment, each



group will independently provide 5 or more main chain atoms to the acyl chain of an epoxy acyl unit of the acyl epoxy compound, preferably at least 7, more preferably at least 9, yet more preferably at least 11, even more preferably at least 13, and still more preferably at least 15 main chain atoms. Preferably, each such group will independently provide 17 main chain atoms to the acyl chain of an epoxy acyl unit of the acyl epoxy compound. In a preferred embodiment, each



group of the acyl epoxy compounds will provide the same number of main chain atoms to the acyl chain of each epoxy acyl unit thereof. In a preferred embodiment, each such group will provide the same number of epoxy groups to each epoxy acyl unit of the acyl epoxy compound. In a preferred embodiment, each



group in the acyl epoxy compound will be identical.

In a preferred embodiment, each of R1 and R2 will independently contain up to 5 epoxy groups, preferably up to 4, even more preferably up to 3, and still more preferably up to 2 epoxy groups. In a preferred embodiment, the total epoxy groups contributed to the epoxy acyl group by the combination of R1 and R2 together will be 9 or fewer, more preferably 7 or fewer, even more preferably 5 or fewer, still more preferably 4 or fewer, yet more preferably 3 or fewer, yet even more preferably up to 2 epoxy groups.

In a preferred embodiment, each R3 will be hydrogen or will independently contain up to 10 main structure atoms (i.e. main chain, ring skeleton, or main chain-and-ring skeleton atoms), more preferably up to 8, even more preferably up to 6, and still more preferably up to 4 main structure atoms. In a particularly preferred embodiment, each R3 is independently hydrogen, n-propyl, isopropyl, ethyl, methyl, phenyl, cyclohexyl, cyclohexenyl, or cyclohexadienyl. In a preferred embodiment, all R3 in a given acyl epoxy molecule will be identical; more preferably all R3 in all acyl epoxy molecules will be identical.

In a preferred embodiment, A in each acyl epoxy compound will independently contain from 1 to about 50 main chain and cyclic skeletal structure atoms, more preferably 2 to about 30, and even more preferably 3 to about 21 such atoms.

In a preferred embodiment, n in each acyl epoxy compound will independently be an integer from 2 to 10, more preferably from 2 to 8, even more preferably from 2 to 6, still more preferably from 2 to 5, yet more preferably from 2 to 4. In a particularly preferred embodiment, n in each acyl epoxy compound will independently be an integer from 2 to 3.

In a particularly preferred embodiment, the average value of n among all acyl epoxy compounds utilized in a given curable composition will be between 2 and 4, inclusive, more preferably between 2 and 3, inclusive.

ACYL EPOXY COMPOUNDS

Acyl epoxy compounds useful herein include epoxy esters, epoxy amides, and epoxy ester-amides.

EPOXY ESTER COMPOUNDS

Epoxy esters useful herein may be provided in a number of different ways, either as homo-esters, hetero-esters, mixtures of esters, or mixtures of an ester(s) with another compound(s). In a preferred embodiment, the esters are obtained by epoxidation of unsaturated carboxylic acyl esters. In a preferred embodiment, these carboxylic acyl esters will be unsaturated fatty acyl esters that are part of a mixed oil composition expressed or extracted from a biological source, e.g., a plant, animal, or other organism, or an organ or organelle thereof.

Thus, in a preferred embodiment, the epoxy esters are obtained by epoxidation of unsaturated carboxylic acyl homo-di-esters, homo-tri-esters, hetero-di-esters, hetero-tri-esters, mixtures thereof, or mixtures thereof with another compound(s). In a preferred embodiment, the unsaturated carboxylic acyl esters are homo-esters. In a particularly preferred embodiment, the unsaturated carboxylic acyl esters are unsaturated fatty acyl esters that are: di- and/or tri-

olein, di- and/or tri-linolein, di- and/or tri-linolenin, mixtures thereof, or mixtures thereof with another compound(s).

5 In a particularly preferred embodiment, the epoxy esters are obtained as part of a mixed oil composition expressed or extracted from a plant that biosynthesizes epoxy fatty acyl esters.

Epoxidation of Unsaturated Carboxylic Acyl Esters

10 Epoxy esters may be provided in the form of epoxidated oils, which are obtained by performing an epoxidation reaction on oils containing at least di-esters of unsaturated carboxylic acids, preferably unsaturated fatty acyl di- and/or tri-glycerides. During epoxidation, at least one double bond in each of at least two unsaturated carboxylic acyl groups within an ester molecule are converted into oxirane groups. Epoxidation reactions may be carried out according to any of the many procedures known in the art as effective for
15 epoxidation of unsaturated carboxylic acyl esters, e.g., by treatment with an oxidant. Preferred examples of oxidants include, e.g., peracetic or performic acid.

Examples of oils useful for such epoxidation include, but are not limited to, "drying oils" and "semi-drying oils." In a preferred embodiment, the oils are obtained from at least one
20 biological source. Preferred examples of biological oils include, but are not limited to: seed oil "drying" and "semi-drying" oils, e.g., soybean oil, linseed oil, tung oil, oiticica nut oil, perilla oil, and hemp seed oil; and fish oil "drying" and "semi-drying" oils, e.g., oils obtained from fishes of the taxon *Clupeinae*, such as menhaden oil (*Brevoortia* spp.). These and other unsaturated oils may be used raw, or may be boiled, refined, and/or dehydrated before
25 epoxidation. For example, in a preferred embodiment, dehydrated castor bean oil and/or dehydrated *Lesquerella* spp. seed oil (e.g., from *L. fendleri*, *L. lindheimeri*, or *L. pallida*) is used.

30 As used herein, the term "oil" indicates an organic liquid not miscible with water. As used herein, the term "drying oil" indicates an oil containing unsaturated carboxylic acid esters and having an iodine value of about 140 cg iodine per gram of oil (cg/g) or more, when iodine is reacted with the oil. Iodine values are determined according to the ASTM D-1959 standard procedure (also called the "Wijs" method), or where conjugated fatty acyl esters are present, the ASTM D-1541 standard procedure may be substituted. The term "semi-drying oil"

indicates an oil containing unsaturated carboxylic acid esters and having an iodine value between about 100 cg/g and about 140 cg/g.

The term "non-drying oil" indicates an oil containing unsaturated carboxylic acid esters and typically having an iodine value less than 100 cg/g. Fats, which are organic compositions, containing carboxylic acid esters or ester mixtures, that are solid at room temperature, typically have an iodine value of less than 70 cg/g. Non-drying oils that have an iodine value between about 70 and 100 cg/g can also be used herein, though these are less preferred. An oil or fat composition's iodine value can be increased by dehydrogenation before the composition is epoxidized. Thus, non-drying oils having an iodine value significantly less than 70 cg/g (e.g., about 50 cg/g or less), and even fats having a non-zero iodine value, can be used, provided that they are first dehydrogenated to increase the iodine value to about 70 cg/g or more, more preferably to about 100 cg/g or more.

Thus, other examples of useful oils include, e.g., walnut oil, poppy seed oil, sunflower oil, safflower oil, cottonseed oil, canola oil, palm oil, peanut oil, tall oil, and neatsfoot oil. In addition, oils from plants discovered, selected, and/or engineered (e.g., hybridized, mutated, and/or transgenically manipulated) to produce, or to enhance production of, one or more unsaturated fatty acyl esters may also be used.

Synthetically prepared and/or synthetically modified unsaturated carboxylic acyl esters may also be used. Carboxylic acyl esters and mixtures thereof may also be formed and/or modified by interesterification, intraesterification, and/or transesterification of esters present in a starting material.

The unsaturations present in the unsaturated carboxylic acyl groups may be arranged as conjugated multiple bonds, non-conjugated multiple bonds, allenic double bonds, acetylenic bonds, or a combination thereof. In a preferred embodiment, all unsaturations are double bonds. In a preferred embodiment, some or all of the unsaturations are arranged as conjugated double bonds. In a preferred embodiment, all unsaturations are arranged as non-conjugated double bonds. In a particularly preferred embodiment, all unsaturations are arranged as alternating, non-conjugated double bonds according to the pattern of a 1,4-diene, i.e. as is found in the arrangement $-C=C-C-C=C-$. Particularly preferred are unsaturated carboxylic acyl groups in which all the unsaturation(s) occupy only one or more of the 3, 6, 9,

12, 15, 18, 21, 24, and 27 positions, or only one or more of the 4, 7, 10, 13, 16, 19, 22, 25, and 28 positions, or only one or more of the 2, 5, 8, 11, 14, 17, 20, 23, 26, and 29 positions in the acyl group. Preferably, each unsaturated carboxylic acyl group will contain less than 10 unsaturations. In a preferred embodiment, each unsaturated carboxylic acyl group will
5 contain up to 8 unsaturations, more preferably up to 6, even more preferably up to 5, still more preferably up to 4, and even more preferably up to 3 unsaturations.

In a preferred embodiment, an oil or fat composition selected for epoxidation will have an iodine value greater than 100 cg/g, more preferably about 120 cg/g or more, even more
10 preferably about 130 cg/g or more, still more preferably about 140 cg/g or more, yet more preferably about 150 cg/g or more, yet even more preferably about 160 cg/g or more. In a preferred embodiment, an oil or fat composition selected for epoxidation will have an iodine value less than 500 cg/g, more preferably about or less than 450 cg/g. Preferably the iodine value of the oil or fat will be up to about 420, more preferably up to about 390, even more
15 preferably up to about 360, still more preferably up to about 330, yet more preferably up to about 300, yet even more preferably up to about 270, and yet still more preferably up to about 240 cg/g. In a preferred embodiment the oil or fat will have an iodine value of about 100 to about 300, more preferably about 120 to about 270, even more preferably about 130 to about 240, still more preferably about 140 to about 230, yet more preferably about 150 to about
20 220, yet even more preferably about 160 to about 210, and yet still more preferably about 170 to about 200 cg/g.

The oils or fats may also or alternatively be at least partially fractionated to remove other components from the oil, e.g., free fatty acids, fatty acyl mono-esters, saturated fatty acyl
25 esters, terpenes, sterols, aldehydes, lignins, and/or peptides and proteins (e.g., ricin). If only a specific fraction of useful esters is desired, then before or after epoxidation these esters may be at least partially fractionated from one another in order to retain only the desired “enriched” portion thereof, e.g., only esters having a given size or size range and/or having a given number or range of unsaturations and/or having a given number or range of epoxy
30 groups and/or other functionalities. Any useful separation or fractionation technique(s) known in the art may be employed therefor. Where a pre-epoxidized oil or fat composition contains less than 50 mol% of useful unsaturated carboxylic acyl esters (i.e. those esters containing at least two unsaturated carboxylic acyl groups), the composition will preferably be fractionated, before epoxidation, in order to obtain at least one fraction in which these

esters make up about 50 mol% or more of the fraction(s). Then, these “enriched” fraction(s) are preferably selected for epoxidation.

Biosynthetic Epoxy Esters

Similarly, seed oils obtained from plants synthesizing esters of epoxy fatty acids may also be used, and no further epoxidation is required for these, treatment with an epoxidation reaction being optional (and being optionally used only where the oil also contains unsaturations).

For example, *Vernonia anthelmintica*, *V. galamensis*, *Crepis palaestina*, *Euphorbia lagascae*, and *Stokesia laevis* produce seeds whose oil already contains epoxy fatty acyl esters, e.g., di- and/or tri-glycerides of vernolic acid (12,13-epoxy-9-octadecenoic acid).

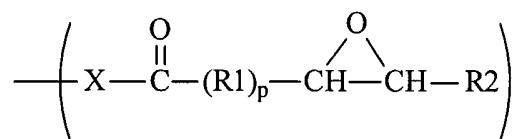
Other examples of seed oils that contain plant-synthesized esters of epoxy fatty acids are *Alchornea cordifolia* seed oil, which contains esters of alchornoic acid (14,15-epoxy-11-eicosenoic acid), and *Chrysanthemum coronarium* seed oil, which contains esters of coronaric acid (9,10-epoxy-12-octadecenoic acid). Other examples of plants reported to have seed oils in which epoxy fatty acyl esters are biosynthesized include *Cephalocroton pueschelii*, *Erlangea tomentosa*, *Faidherbia albida*, and *Schlechtendalia luzulaefolia*.

In addition, oils from plants discovered, selected, and/or engineered (e.g., hybridized, mutated, and/or transgenically manipulated) to produce, or to enhance production of, one or more epoxy fatty acyl esters may also be used.

Preferred Epoxy Ester Characteristics

In a preferred embodiment, the carboxylic acyl groups of the epoxy esters will each independently contain from 4 to about 40 main chain atoms. In a preferred embodiment, the carboxylic acyl groups of the epoxy esters will each independently contain from 4 to about 36 main chain atoms, more preferably about 6 to about 30, even more preferably about 10 to about 26, still more preferably about 12 to about 24, yet more preferably about 16 to about 22, and yet even more preferably about 18 to about 20 main chain atoms. In a particularly preferred embodiment, the carboxylic acyl groups of the epoxy esters will contain 18 main chain atoms.

Where at least one of the epoxy acyl units



in an epoxy ester of formula (1), contains more than one epoxy group, preferably all epoxy groups in the epoxy acyl unit(s) will be non-vicinal, i.e. no two epoxy groups occupying immediately neighboring positions, e.g., such as is found in 3,4:4,5-diepoxy compounds.

Preferably, all epoxy groups in each such epoxy acyl unit will be at least geminal, i.e. two proximate epoxy groups occupying adjacent pairs of carbon atoms, e.g., such as is found in 3,4:5,6-diepoxy compounds. More preferably, all epoxy groups in each such epoxy acyl unit will be separated by an aliphatic group, i.e. separated by at least a methylene group, connecting each epoxy group to its nearest neighboring epoxy group.

The epoxy esters may also retain one or more (non-epoxidated) unsaturations. For example, unsaturated carboxylic acyl esters, or mixtures containing them, may be either fully or partially epoxidated to obtain useful epoxy ester compositions. In a preferred embodiment, the epoxy esters will contain about or less than 25% by weight epoxy oxygen, more preferably about 20% by weight or less, even more preferably about 18% by weight or less, still more preferably about 15% by weight or less, and yet more preferably about 12% by weight or less epoxy oxygen. In a preferred embodiment, the epoxy esters will contain at least 2.5% by weight epoxy oxygen, more preferably about 3% by weight or more, even more preferably about 5% by weight or more, and still more preferably about 7% by weight or more epoxy oxygen. In a particularly preferred embodiment, the epoxy esters will contain about 8% to about 10% by weight epoxy oxygen.

Where a mixture of epoxy di-, and/or tri-, and/or larger poly-esters with other component(s) is utilized, preferably the epoxy esters will make up about 50 mole percent (mol%) or more of the composition, more preferably about 60 mol% or more, even more preferably about 70 mol% or more, still more preferably about 80 mol% or more, and yet more preferably about 90 mol% or more of the composition. Where the mixture contains less than 50 mol% of these epoxy esters, the mixture will preferably be fractionated to obtain at least one fraction in which the epoxy esters make up about 50 mol% or more of the fraction(s).

In a preferred embodiment, the epoxy esters are homo-di-esters, homo-tri-esters, hetero-di-esters, hetero-tri-esters, mixtures thereof, or mixtures thereof with another compound(s). In a preferred embodiment, the epoxy esters are homo-esters. In a particularly preferred embodiment, the epoxy esters are fully or partially epoxidized fatty acyl esters that are: di- and/or tri-olein, di- and/or tri-linolein, di- and/or tri-linolenin, mixtures thereof, or mixtures thereof with another compound(s). In a preferred embodiment, the epoxy esters will be provided by epoxidized soybean oil and/or epoxidized linseed oil. Useful epoxidized seed oils containing epoxidized fatty acyl di- and tri-glycerides are also available from the commercial market. For example, Charlotte Chemical Inc. (Mexico City, Mexico) sells epoxidized soybean oil, and Atofina Chemicals, Inc. (Philadelphia, PA, USA) sells epoxidized soybean oil (as VIKOFLEX 7170) and epoxidized linseed oil (as VIKOFLEX 7190).

EPOXY AMIDE COMPOUNDS

Epoxy amides are also useful herein and may be prepared by reacting a polyamino-hydrocarbon (i.e. an organic diamine or greater amine) with unsaturated free carboxylic acids, unsaturated acyl halides, and/or unsaturated carboxylic acid esters, preferably unsaturated free fatty acids, unsaturated fatty acyl halides, and/or unsaturated fatty acyl esters. In a preferred embodiment, all the amines of the polyamino-hydrocarbon will be primary and/or secondary amines. Preferably, the polyamino-hydrocarbon will be an aliphatic polyamine. In a particularly preferred embodiment using an aliphatic polyamine, the aliphatic polyamine will contain only primary amines. For example, a straight-chain aliphatic diamine may be used, e.g., 1,3-propyl diamine, or a branched-chain aliphatic diamine may be used, e.g., 2-aminomethyl-1,3-propyl diamine.

The preferred sizes and other features of the carboxylic acid(s) used and resulting acyl groups, the predominance of the resulting epoxy compounds in the organic reaction product mixture, and the amide compounds' epoxy content and arrangement, are respectively as described above for the epoxy ester compounds.

Mixtures of epoxy ester compounds and epoxy amide compounds, each as described above, may also be used herein.

EPOXY ESTER-AMIDE COMPOUNDS

Epoxy ester-amides are also useful herein. In these compounds, the epoxy acyl groups share a common heterohydrocarbon esterification-and-amidation partner, which is the amidation-
5 and-esterification reaction product of a "pre-partner," e.g., an aminoalcohol (e.g., an alkanolamine), a polyolamine, a polyamino-alcohol (e.g., a polyamino-alkanol), or a polyamino-polyol reactant. The epoxy acyl groups in these compounds include both N-acyl and O-acyl groups. In a preferred embodiment, the amino groups of the partnering reactant will be primary and/or secondary amino groups, more preferably primary amino groups.

10 Examples of preferred esterification-amidation partners include, but are not limited to, C2-C8 amino- and hydroxy-substituted aliphatic compounds, e.g.: ethanolamines, e.g. 2-amino-ethanol; amino-propane-diols; diamino-propanols; and amino- and hydroxy-substituted cyclohex-anes, -enes, and -dienes.

15 Epoxy ester-amides can be made, for example, by first forming an unsaturated acyl ester-amide(s) and then epoxidating it. Acyl ester amides can be formed by reacting a pre-partner, e.g., an alkanolamine, with an unsaturated fatty acid (e.g. oleic acid) or its methyl ester (e.g., methyl oleate) or its acid halide (e.g., oleoyl chloride), using any catalyst known effective therefor in the art. U.S. Patent No. 5,045,222 also describes a procedure for forming acyl
20 ester amides, though this procedure is less preferred. The unsaturated acyl ester-amide molecule(s) can then be epoxidized using an oxidant, such as peracetic acid.

The preferred sizes and other features of the carboxylic acid(s) used and resulting acyl groups, the predominance of the resulting epoxy compounds in the organic reaction product
25 mixture, and the ester-amide compounds' epoxy content and arrangement, are respectively as described above for the epoxy ester compounds.

CYCLOALIPHATIC EPOXY COMPOUNDS

30 A cycloaliphatic epoxy compound according to the present invention is a hydrocarbon compound containing at least one non-aryl ring structure and containing at least two epoxy groups, at least one of which epoxy groups is fused to a non-aryl hydrocarbon ring structure, but in which compound no glycidic group(s) is present. Glycidic groups include glycidol (2,3-epoxy-1-propanol)-based groups and glycidic acid (2,3-epoxy-propanoic acid)-based
35 groups, examples of which include: glycidyl ether groups, glycidoyl ester groups, glycidoyl

amide groups, and so forth. Thus, all the epoxy groups (i.e. all the oxirane groups) in the cycloaliphatic epoxy compound are: cycloaliphatic-ring-fused epoxy groups (such as is the fused epoxy group structure found in 1,2-epoxycyclohexane); or a combination of cycloaliphatic-ring-fused epoxy groups and aliphatic oxirane groups per se, representative
5 examples of the aliphatic oxirane groups being, e.g., epoxyethyl, epoxypropyl, epoxypropylamino, epoxybutyl, epoxypentylidene, diepoxyhexyl, epoxyhexenyl groups, and so forth. Preferably, the aliphatic oxirane groups are all epoxy-homoaliphatic groups, more preferably epoxy-homoaliphatic monovalent groups. Preferred aliphatic oxirane groups are C2-C6, more preferably C2-C4, and even more preferably C2-C3 aliphatic oxirane groups.

10 The cycloaliphatic epoxy compound may be: a polyepoxycycloaliphatic compound, i.e. one that contains more than one epoxycycloaliphatic group or more than one (fused) epoxy group per cycloaliphatic group, or both; a polykis-epoxycycloaliphatic compound, i.e. one that contains more than one identical epoxycycloaliphatic group; and/or an aliphatic oxiranyl-
15 epoxycycloaliphatic compound, i.e. one that contains at least one aliphatic oxiranyl-substituted epoxycycloaliphatic group.

In a preferred embodiment, the cycloaliphatic epoxy compound will contain two epoxy groups. In a preferred embodiment, the two epoxy groups will reside on a single
20 cycloaliphatic ring; preferred examples of this are the di-epoxy cyclohexanes and di-epoxy cyclohexene. In a preferred embodiment, one of the two epoxy groups will reside on a cycloaliphatic ring, and the other will reside on an aliphatic substituent of the ring; preferred examples of these are the aliphatic oxiranyl-epoxycyclohexanes and aliphatic oxiranyl-cyclohexene.

25 In a preferred embodiment, each of the two epoxy groups will reside on a different cycloaliphatic ring in the compound; preferred examples of this are: bis-epoxycyclohex-anes and -enes and bis-epoxycyclopent-anes and -ene, e.g., esters of epoxidized cyclic alcohols with a polycarboxylic acid or with an epoxidized cyclic acid, such as cyclohexanoic acid, as
30 well as other compounds containing two terminal cycloaliphatic epoxy groups (one at each terminus). In a preferred embodiment, the cycloaliphatic epoxy compound will contain more than two epoxy groups, and the types of linkages and arrangements illustrated with the above description of di-epoxy compounds demonstrate exemplary linkage and arrangements therefor, and can be combined therein.

Specific examples of preferred cycloaliphatic diepoxy compounds include, but are not limited to: vinyl cyclohexane diepoxides, e.g., 4-oxiranyl-cyclohexane (ERL-4206 from Union Carbide Corp.); (3,4-epoxycyclohexyl)methyl 3,4-epoxycyclohexanecarboxylate (ERL-4221 from Union Carbide Corp.); bis[(3,4-epoxycyclohexyl)methyl]dicarboxylates, e.g., the adipate (ERL-4229 from Union Carbide Corp.), the succinate, and so forth; bis[(3,4-epoxy-6-methylcyclohexyl)methyl]dicarboxylates, e.g., the adipate (ERL-4289 from Union Carbide Corp.), the pimelate, and so forth; bis(2,3-epoxycyclopentyl)ether (ERL-0400 from Union Carbide Corp.); 2-(3,4-epoxycyclohexyl)-5,5-spiro(2,3-epoxycyclohexane)-m-dioxane; 2-(3,4-epoxycyclohexyl)-5,5-spiro(3,4-epoxy cyclohexane)-m-dioxane (ERL-4234 from Union Carbide Corp.); (3,4-epoxy-6-methylcyclohexyl)methyl 3,4-epoxy-6-methylcyclohexane carboxylate (ERL-4201 from Union Carbide Corp.); limonene dioxide (ERL-4269 from Union Carbide Corp.); dicyclopentadiene dioxide; and 1,2-bis(2,3-epoxycyclopentyl)ethane. Methods for producing a variety of useful cycloaliphatic epoxy compounds is taught in various patents including U.S. Pat. Nos. 2,716,123, 2,750,395, 2,884,408, 2,890,194, 2,948,688, 2,985,667, 3,027,357 and 3,247,144.

In a preferred embodiment, the cycloaliphatic epoxy compound will have about or up to 50 main chain and ring skeleton atoms total, more preferably about 40 or fewer, even more preferably about 30 or fewer.

POLYHYDROXY HYDROCARBON COMPOUNDS

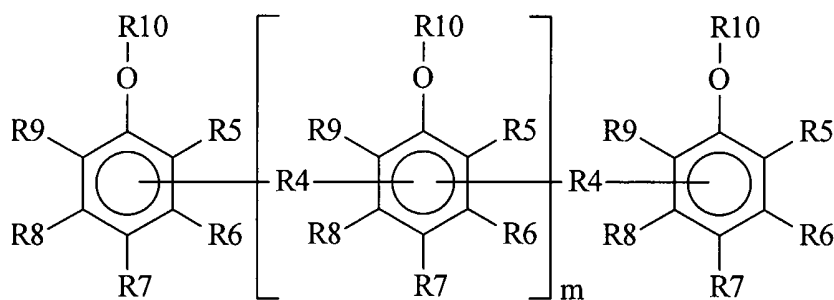
The polyhydroxy hydrocarbon compounds used herein are homo- or hetero-hydrocarbon compounds containing at least two hydroxyl groups, preferably up to or about 10 hydroxyl groups, more preferably up to or about 6 hydroxyl groups. Preferably, the polyhydroxy hydrocarbon compound will have a molecule weight from about 110 to about 3,000, more preferably about 200 to about 1,000.

In a preferred embodiment, the polyhydroxy hydrocarbon compound(s) will be aryl or alkylaryl polyhydroxy compound(s). In a particularly preferred embodiment, the polyhydroxy hydrocarbon compound(s) will be diphenol(s), phenolic novolac(s), and phenolic resole(s).

Particularly preferred phenolic novolac compounds include those having the following structure:

5

10



wherein,

m is an integer;

for each pair of proximal phenolic units in the compound,

15 each R4 independently represents a homo- or hetero-hydrocarbon divalent group;

and

for each phenolic unit in the compound,

each R5, R6, R7, R8, and R9 independently represents H or a homo- or hetero-hydrocarbon monovalent group, and

20 each R10 independently represents H or a homo- or hetero-hydrocarbon monovalent group; provided that at least two of R10 in the compound are H.

Preferably, each R4 represents a homo- or hetero-aliphatic divalent group, more preferably a homo-aliphatic divalent group, and even more preferably a homo-alkyl divalent group. In a preferred embodiment R4 contains a total number of core atoms (i.e. a total of main chain and, where branching is present, side chain atoms, including all carbon atoms and including all chain hetero-atoms, e.g., aza-atoms, oxa-atoms, thia-atoms, phospho-atoms, and sila-atoms; but excluding any non-core atoms that are present, i.e. hydrogen atoms and, e.g., halo-atoms, azo-atoms, oxo-atoms, thio-atoms, and phospho-atoms) that is from 1 to about 40.

30 In a preferred embodiment, R4 contains from 1 to about 30 core atoms, more preferably 1 to about 25, even more preferably 1 to about 20, still more preferably 1 to about 15, yet more preferably 1 to about 10, and yet even more preferably 1 to about 5 core atoms. In a particularly preferred embodiment, R4 contains 1 to 4 core atoms. In a particularly preferred embodiment, all R4 in the phenolic novolac compound are identical.

Preferably, each R5, R6, R7, R8, and R9 independently represents hydrogen or a homo- or hetero-aliphatic monovalent group, more preferably hydrogen or a homo-aliphatic monovalent group, and even more preferably hydrogen or a homo-alkyl monovalent group.

- 5 In a preferred embodiment, each R5, R6, R7, R8, and R9 independently represents hydrogen or a homo- or hetero-aliphatic monovalent group containing 1 to about 10 core atoms, even more preferably 1 to about 5 core atoms, and still more preferably 1 to 3 core atoms. In a particularly preferred embodiment, all R5 groups in the phenolic novolac compound are identical; also in a particularly preferred embodiment, all R6, R7, R8, and R9 groups,
10 respectively, are identical independently of one another (i.e. independently for all R5 groups from all R6 groups from all R7 groups from all R8 groups from all R9 groups). In a particularly preferred embodiment, all of one or two of the R5 groups, R6 groups, R7 groups, R8 groups, or R9 groups are methyl, and all of the remaining groups are hydrogen; i.e. the phenolic novolac is based on a cresol (a methyl phenolic unit) or on a dimethyl phenolic unit.
15 In a particularly preferred embodiment, all of the R5, R6, R7, R8, and R9 groups are hydrogen; i.e. the phenolic novolac is based on phenol (a phenolic unit).

- Preferably, each R10 independently represents hydrogen or a homo- or hetero-aliphatic monovalent group, more preferably hydrogen or a homo-aliphatic monovalent group, and
20 even more preferably hydrogen or a homo-alkyl monovalent group. In a preferred embodiment, each R10 independently represents hydrogen or a homo- or hetero-aliphatic monovalent group containing 1 to about 10 core atoms, even more preferably 1 to about 5 core atoms, and still more preferably 1 to 3 core atoms. In a preferred embodiment from 2 to about 10 of the R10 groups in a phenolic novolac compound will be hydrogen, more
25 preferably from 2 to about 6 of the R10 groups will be hydrogen. In a particularly preferred embodiment, all R10 will be hydrogen. Preferred examples of non-hydrogen R10 groups include, e.g., CH₃ and -CO-R-COOH half ester groups produced by reaction of the phenolic hydroxyl groups with aliphatic or aromatic anhydride compounds, wherein R preferably contains fewer than 20, more preferably about 15 or fewer, even more preferably about 12 or
30 fewer main chain and cyclic skeletal atoms.

A wide variety of useful aryl polyol, alkylaryl polyol, and polycyclic aromatic polyol compounds are available on the commercial market, including many phenolic novolacs. A

preferred example of a commercially available phenolic novolac is PERACIT 4439X1 (phenolic novolac resin, from Dynea USA Inc., Toledo, OH, USA).

5 CURING CATALYSTS

Curing catalysts useful in the present invention include organic onium salts, imidazoles, and organic phosphines. Preferred onium salts for use as catalysts include ammonium salts and phosphonium salts. Preferred examples of ammonium salts include, e.g.

10 tetrabutylammonium bromide. [Preferred examples of phosphonium salts include, e.g., tetraphenylphosphonium bromide, tetraphenyl phosphonium tetraphenyl borate, and butyl triphenyl phosphonium chloride.

Suitable imidazoles for use as catalysts include, for instance, aliphatic-group-substituted
15 imidazoles. In a preferred embodiment, the imidazole will be a 2,4-dialkyl-imidazole, for example, 2-ethyl-4-methylimidazole.

Suitable organic phosphine for use catalysts include, for example, hydrocarbon-group-substituted phosphines, preferably tertiary phosphines, e.g., triphenylphosphine and tris(4-
20 methoxyphenyl) phosphine.

PROCESS

Curable compositions according to the present invention can be cured thermally either with
25 or without a curing catalyst.

PROCESS WITHOUT CURING CATALYST

Where no curing catalyst is used, the components of the curable composition are preferably provided according to the following mass ratios, wherein Roman numerals indicate the
30 component listed in formula (1). Thus, (I) refers to the epoxy ester/amide, (II) refers to the cycloaliphatic epoxy compound, (III) refers to the polyol; also, (IV) refers to the curing catalyst. The mass ratio of (I):(II) can range from about 20:1 to about 1:20, preferably from about 10:1 to about 1:10. The mass ratio of [(I) + (II)]:(III) can range from about 1:0.3 to about 1:2, preferably about 1:0.4 to about 1:1.

35

The three components (I), (II), and (III) can be added in any order, although it is particularly preferred to add (I), then combine (II) therewith, then (III) therewith. Other preferred orders of addition include combining (III) with (I) before adding (II), combining (III) with (II) before adding (I), and combining (III) with each of (I) and (II) separately before mixing [(I) + (III)] and [(II) + (III)] together.

Preferably, all additions will be accompanied by stirring until the mixture is homogeneous. During preparation, the composition should be heated in order to dissolve (III) into (I) and/or into (II), or into [(I) + (II)]. Preferably, whichever of (I) and/or (II) or [(I) + (II)] is selected as the medium into which (III) will be dissolved is first preheated; then, heating is maintained until (III) is dissolved. Where (I) and (II) are first combined, preferably one or both of these will be preheated before they are brought into contact with one another. For all these steps, heating is applied to bring the composition to a temperature from 80 to 160°C, preferably a temperature from 100 to 140°C.

PROCESS WITH CURING CATALYST

Where a curing catalyst is used, the components of the curable composition are preferably provided according to the following mass ratios, wherein Roman numerals indicate the component listed in formula (1), as discussed above. The mass ratio of [(I) + (II) + (III)]:(IV) can range from about 500:1 to about 10:1, preferably from about 200:1 to about 100:1. Otherwise, the mass ratios of (I):(II):(III) are the same as described above for catalyst-free compositions.

In all cases, the curing catalyst should be added last. The orders of addition and heating for components (I), (II), and (III) will be the same as for the above-described case in which no curing catalyst is used. Preferably, all additions will be accompanied by stirring until the mixture is homogeneous.

The combination of (I) + (II) + (III) should be heated, before addition of the catalyst; then, after addition of the catalyst, the resulting mixture should be maintained at elevated temperature until the catalyst is dispersed throughout the mixture. In these last two heating steps, heating is applied to bring the composition to a temperature from 60 to 160°C, preferably a temperature from 80 to 130°C.

In order to cure the resulting curable composition or catalyst-curable composition, the composition is then heated at about 150 to about 180°C for a sufficient time to cure, thereby forming a network polymer.

5

USES

The curable compositions and network polymers formed therefrom may be used in a variety of formats and applications including, but not limited to: coatings, adhesives and other bonding agents, laminates, films, foams, molded parts, machined parts, and matrices for composite materials.

Coatings, composites, adhesives and other bonding agents containing the network polymers may be prepared by combining the curable composition(s) with one or more solvent, filler, flow modifier, pigment, and/or UV stabilizer. These may then be applied to substrates, for example, metal, plastic, wood, or glass substrates, followed by thermally curing the resulting combination. In addition, the curable compositions may also be directly used as liquid or powder coatings, composites, adhesives and other bonding materials, without requiring the preparation of such formulations.

20

Molded parts may be formed by placing the curable composition into a mold, followed by heating the composition to thermally cure it. Machined parts may be formed from such molded parts by removing material therefrom, e.g., by use of a shaving, carving, cutting, or abrading technique.

25

Composite materials may be prepared by combining the curable composition(s) with one or more reinforcing agent, followed by thermally curing the resulting combination. The composite materials may be unstructured materials, such as may result from curing of combination containing a randomly distributed, substantially homogeneous suspension of reinforcing material(s). The composite materials may be structured materials, such as may result from curing a combination of, e.g., a two- or three-dimensionally arranged distribution of reinforcing agent(s); preferred examples of such dimensionally arranged reinforcing agents include, e.g., fiber weaves, and fiber mats. The composite materials may also be mono-layer

30

materials or multi-layered materials and the layers may differ in composition from one another, for example, as by use of different matrix materials and/or by different types or distributions of reinforcing agents.

Preferred examples of reinforcing agents include fibrous materials and/or non-fibrous (e.g., particulate) materials. In a preferred embodiment, the reinforcing agent will comprise a fibrous material, which may be synthetic or naturally-occurring. Preferred examples of fibrous materials include, but are not limited to: glass fibers, carbon fibers, polyamide fibers, polyester fibers, and cellulosic fibers. Preferred naturally-occurring cellulosic fibers include, but are not limited to: wood fibers, jute fibers, ramie fibers, flax fibers, kenaf fibers, hemp fibers, and sisal fibers. Preferred examples of non-fibrous, e.g., filler, materials include, but are not limited to: carbon particles, glass particles, silica particles, sand, or particles of a naturally-occurring organic material.

EXAMPLES

EXAMPLE 1

Preparation of a Curable Composition of Epoxidized Linseed Oil, Bis-Cycloaliphatic Epoxy, and Phenolic Novolac, and Network Polymer Formed Therefrom.

13.83 g of epoxidized linseed oil (having an epoxide equivalent weight = 167.8) is combined with 13.83 g of 3,4-epoxycyclohexyl-methyl-3',4'-epoxycyclohexane carboxylate (ERL 4221 from Union Carbide Corp.; having an epoxide equivalent weight of 137.1) and the mixture is heated to 135°C in a glass bottle. 18.59 g of phenolic novolac (PERACIT 4439X1, from Dynea) is then added to the mixture and, with stirring, the mixture is reheated to 140°C, and stirring is maintained at that temperature until the phenolic novolac is dissolved. The resulting mixture is then placed in a bell jar and de-gassed under vacuum. The mixture is then cooled to 125°C. 0.97 mL of 2-ethyl-4-methylimidazole is then added to the mixture and, with stirring, the mixture is reheated to 120°C.

The resulting mixture is then poured into a rectangular, 5 in. × 3 in. × 0.125 in. (12.7 cm × 7.62 cm × 0.32 cm) glass mold that had been pre-heated to 150°C in a convection oven, and the filled mold is then placed back into the 150°C convection oven. After 1 hour at 150°C, the

oven temperature is increased to 180°C; after 2 hours at 180°C, the oven is cooled to room temperature and the resulting clear casting is removed from the mold.

A sample of the casting was analyzed by differential scanning calorimetry at a heating rate of 10C° per minute, from -50°C to 250°C. This analysis demonstrated that the cured network polymer has a glass transition temperature of 148°C. The casting was also tested for flexural properties using ASTM method D-790. This analysis demonstrated that the casting's flexural strength was 17,548 psi (about 121 MPa) and its modulus was 452 ksi (about 3,116 MPa).

EXAMPLE 2 - Comparative Example

Preparation of a Curable Composition of Epoxidized Linseed Oil and Phenolic Novolac, and Polymer Formed Therefrom.

26.12 g of epoxidized linseed oil (having an epoxide equivalent weight = 167.8) is placed into a glass bottle and heated to 135°C. 16.19 g of phenolic novolac (PERACIT 4439X1, from Dynea) is then added and, with stirring, the mixture is reheated to 140°C, and stirring is maintained at that temperature until the phenolic novolac is dissolved. The resulting mixture is then placed in a bell jar and de-gassed under vacuum. The mixture is then cooled to 125°C. 0.89 mL of 2-ethyl-4-methylimidazole is then added to the mixture and, with stirring, the mixture is reheated to 120°C.

The resulting mixture is then poured into a rectangular, 5 in. × 3 in. × 0.125 in. (12.7 cm × 7.62 cm × 0.32 cm) glass mold that had been pre-heated to 150°C in a convection oven, and the filled mold is then place back into the 150°C convection oven. After 1 hour at 150°C, the oven temperature is increased to 180°C; after 2 hours at 180°C, the oven is cooled to room temperature and the resulting clear casting is removed from the mold.

A sample of the casting was analyzed by differential scanning calorimetry at a heating rate of 10C° per minute, from -50°C to 250°C. This analysis demonstrated that the cured polymer has a glass transition temperature of 72°C. The casting was also tested for flexural properties using ASTM method D-790. This analysis demonstrated that the casting's flexural strength was 12,514 psi (about 86 MPa) and its modulus was 319.2 ksi (about 2,200 MPa).

A comparison of the results of Experiment 1 with those of Experiment 2 demonstrates that the addition of the cycloaliphatic epoxy component resulted in an unexpected 40% increase in flexural properties of the epoxidized vegetable oil polymer, as well as a doubling of the (Celsius) glass transition temperature. Thus, the addition of a cycloaliphatic epoxy component, surprisingly, makes it is now possible to produce epoxidized vegetable oil network polymers that are useful in applications where good thermal stability and high mechanical properties are required.

EXAMPLE 3 – Further Examples and Comparative Examples

The results of further examples and comparative examples are shown in Table 1. Table 1 reports properties for polymers prepared from epoxidized linseed oil (ELO), epoxidized soybean oil (ESO), and blends of ELO or ESO with a commercial epoxy component, i.e. with either vinylcyclohexene dioxide (available as ERL-4206 from Union Carbide Corp.) or 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexene carboxylate (available as ERL-4221 from Union Carbide Corp.). All compositions were cured using PERACIT 4439X1 phenolic novolac (available from Perstorp Chemitech S.A., France) and, as a catalyst, 2% w/v 2-ethyl-4-methylimidazole (EMI). Resin compositions contained the following components:

- Resin 1.ELO (as per comparative Example 2);
- Resin 2.ESO (as a comparative example);
- Resin 3.ELO:ERL-4221 in a 2:1 ratio;
- Resin 4.ELO:ERL-4206 in a 2:1 ratio;
- Resin 5.ELO:ERL-4221 in a 1:1 ratio (as per Example 1);
- Resin 6.ESO:ERL-4221 in a 1:1 ratio; and
- Resin 7.ERL-4221 (as a comparative example).

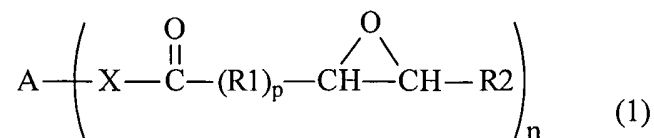
Glass transition temperatures of the resulting polymers were measured using differential scanning calorimetry (DSC). Table 1 reports flexural strength (measured in psi), percent of flexural strain at the break point, and flexural modulus (measured in ksi). "B-Time" is the time required for the liquid resin mixture to transition to the "B-state," i.e. the state in which the composition has achieved a cohesive semi-solid consistency throughout and the composition no longer behaves as a viscous liquid; at the time the composition first enters into the "B-state," it is typically rubbery and pieces of the mass can be torn off from the bulk of the mass.

Table 1. Properties for Resins 3, 4, 5, and 6 and for Comparative Resins 1, 2, and 7								
Resin		1	2	3	4	5	6	7
Wt. % ERL-4221 in Formulation		0	0	19.6	0	29.0	30.4	55.8
Tg by DSC, °C		72	48	107	125	148	137	178
Flex Strength	MPa	86	32	121	131	121	104	162
	psi	12514	4673	17610	18960	17548	15059	23500
Flex Strain at Break, %		8.1	>17.5	5.4	6.0	4.8	7.2	4.5
Flex Modulus	MPa	2198	758	2997	3197	3114	2384	4058
	ksi	319	110	435	464	452	346	589
Viscosity at 100°C, centipoises		700	275	950	>4000	1150	575	1900
B-Time of Formulation at 150°C, minutes		13.7	29.0	12.5	3.2	12.5	15.7	15.8
B-Time of Formulation at 180°C, minutes		4.2	7.5	4.1	1.0	3.9	4.0	4.3

CLAIMS

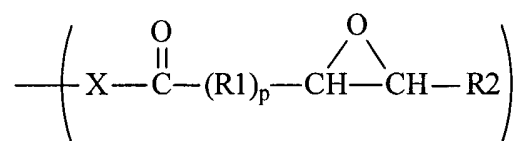
1. A curable composition comprising

(I) at least one acyl epoxy compound represented by the following formula (1)



wherein,

(A) for each epoxy acyl unit



in each acyl epoxy compound of formula (1),

R1 independently represents a substituted or unsubstituted homo- or hetero-aliphatic divalent group,

R2 independently represents a substituted or unsubstituted homo- or hetero-aliphatic monovalent group,

p is independently an integer equal to 0 or 1,

X independently represents divalent oxygen



or a divalent amino group



with R3 independently representing H or a substituted or unsubstituted homo- or hetero-hydrocarbon monovalent group,

(B) each A independently represents a homo- or hetero-hydrocarbon polyvalent group, and

(C) each n is independently an integer equal to or greater than 2;

(II) at least one cycloaliphatic epoxy containing at least two epoxide groups;

(III) at least one homo- or hetero-hydrocarbon compound containing at least two hydroxyl groups;

and

(IV) optionally, at least one curing catalyst selected from organic onium salts, imidazoles, and organic phosphines.

2. The curable composition according to Claim 1, wherein said acyl epoxy compound is at least one epoxy ester, at least one epoxy amide, or a combination thereof.

3. The composition according to Claim 1, wherein each of R1 and R2 independently contains up to 40 main chain atoms and up to 5 epoxy groups; if present, each R3 is H or contains about 10 or fewer skeleton atoms; each A contains from 1 to about 50 skeleton atoms; and each n is 2 to 10; each cycloaliphatic epoxy compound contains about 50 or fewer skeleton atoms; and each polyhydroxy hydrocarbon compound has a molecular weight of about 110 to about 3,000.

4. The composition according to Claim 3, wherein each of R1 and R2 independently contains about 15 or fewer main chain atoms and up to 2 epoxy groups; if present, each R3 is H or contains about 6 or fewer skeleton atoms; each A contains from 2 to about 30 skeleton atoms; and each n is 2 to 6; each cycloaliphatic epoxy compound contains about 30 or fewer skeleton atoms; and each polyhydroxy hydrocarbon compound has a molecular weight of about 200 to about 1,000.

5. The composition according to Claim 4, wherein, for each acyl group, R1 contains 7, 10, or 13 main chain atoms and R2 respectively contains 8, 5, or 2 main chain atoms.

6. The curable composition according to Claim 2, wherein said epoxy ester or esters are provided by at least one epoxidated biological oil or by an epoxidated combination of biological oils.

7. The curable composition according to Claim 6, wherein said epoxidated biological oil is epoxidated soybean oil, epoxidated linseed oil, a combination thereof, or an epoxidated combination of soybean and linseed oils.

8. The curable composition according to Claim 2, wherein said epoxy ester is obtained from an organism capable of synthesizing epoxy esters.

9. The curable composition according to Claim 1, wherein said cycloaliphatic epoxy compound is at least one bis(epoxy-cycloaliphatic) compound.

10. The curable composition according to Claim 9, wherein said bis(epoxy-cycloaliphatic) compound is a bis(epoxy-cyclohexane), a bis(epoxy-cyclohexene), a bis(epoxy-cyclopentane), a bis(epoxy-cyclopentene) compound, or a combination thereof.

11. The curable composition according to Claim 10, wherein said bis(epoxy-cyclohexane) compound is (3,4-epoxycyclohexyl)methyl 3,4-epoxycyclohexanecarboxylate, a bis[(3,4-epoxycyclohexyl)methyl]dicarboxylate, a bis[(3,4-epoxy-6-methylcyclohexyl)methyl]dicarboxylate, bis(2,3-epoxycyclopentyl)ether, 2-(3,4-epoxycyclohexyl)-5,5-spiro(2,3-epoxycyclohexane)-m-dioxane, 2-(3,4-epoxycyclohexyl)-5,5-spiro(3,4-epoxycyclohexane)-m-dioxane, (3,4-epoxy-6-methylcyclohexyl)methyl 3,4-epoxy-6-methylcyclohexane carboxylate, bis(2,3-epoxycyclopentyl)ether, 1,2-bis(2,3-epoxycyclopentyl)ethane, or a combination thereof.

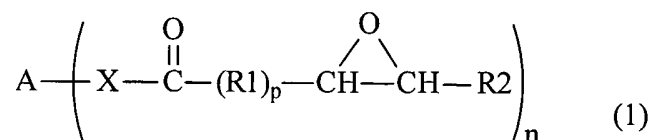
12. The curable composition according to Claim 1, wherein said cycloaliphatic epoxy compound is at least one aliphatic oxiranyl-substituted epoxycycloaliphatic compound.

13. The curable composition according to Claim 12, wherein said aliphatic oxiranyl-substituted epoxycycloaliphatic compound is an oxiranyl epoxy-cyclohexane, an oxiranyl epoxy-cyclohexene, an oxiranyl epoxy-cyclohexadiene, an oxiranyl epoxy-cyclopentane, an oxiranyl epoxy-cyclopentene, or an oxiranyl epoxy-cyclopentadiene.

14. The curable composition according to Claim 1, wherein said homo- or hetero-hydrocarbon compound containing at least two hydroxyl groups is an aryl or alkylaryl polyol.

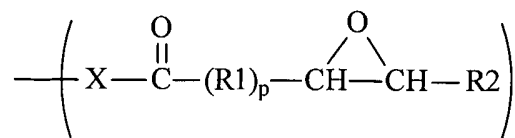
15. The curable composition according to Claim 14, wherein said aryl or alkylaryl polyol is a diphenol, a phenolic novolac, or a phenolic resole.

16. A process for forming a curable composition comprising
(Step 1) mixing, with stirring and with heating at about 80 to about 160°C,
(I) at least one acyl epoxy compound represented by the following formula (1)



wherein,

5 (A) for each epoxy acyl unit



in each acyl epoxy compound of formula (1),

10 R1 independently represents a substituted or unsubstituted homo- or hetero-aliphatic divalent group,

R2 independently represents a substituted or unsubstituted homo- or hetero-aliphatic monovalent group,

p is independently an integer equal to 0 or 1,

15 X independently represents divalent oxygen



or a divalent amino group



20 with R3 independently representing H or a substituted or unsubstituted homo- or hetero-hydrocarbon monovalent group,

(B) each A independently represents a homo- or hetero-hydrocarbon polyvalent group, and

(C) each n is independently an integer equal to or greater than 2,

with

25 (II) at least one cycloaliphatic epoxy containing at least two epoxide groups,

and with

(III) at least one homo- or hetero-hydrocarbon compound containing at least two hydroxyl groups,

to form a curable composition; and

30 (Step 2) optionally mixing with said curable composition, with stirring and with heating at about 60 to about 180°C, at least one curing catalyst selected from organic onium salts, imidazoles, and organic phosphines, to form a catalyst-curable composition.

17. A process for forming a network polymer comprising heating a curable composition or a catalyst-curable composition produced by the process according to Claim 16, at a temperature of about 150 to about 180°C until the composition hardens.

5 18. A network polymer formed according to the process of Claim 17.

19. A network polymer formed by curing a curable composition according to Claim 1.

20. A molded part comprising the network polymer of Claim 19.

10

21. A coating comprising the network polymer of Claim 19.

22. An adhesive or bonding agent comprising the network polymer of Claim 19.

15 23. A composite comprising the network polymer of Claim 19 and at least one reinforcing agent.

24. The composite of Claim 23, wherein the reinforcing agent comprises a fibrous material.

20 25. The composite of Claim 24, wherein the fibrous material comprises at least one of glass fibers, carbon fibers, polyamide fibers, or polyester fibers.

26. The composite of Claim 24, wherein the fibers are naturally-occurring organic fibers.

25 27. The composite of Claim 26, wherein the fibers are cellulosic fibers.

28. The composite of Claim 27 wherein the fibers are at least one of wood fibers, jute fibers, ramie fibers, flax fibers, kenaf fibers, hemp fibers, or sisal fibers.

30 29. The composite of Claim 23, wherein the reinforcing agent comprises a non-fibrous filler.

30. The composite of Claim 29, wherein the non-fibrous filler comprises at least one of carbon particles, glass particles, silica particles, sand, or particles of a naturally-occurring organic material.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/022943

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G59/00 C08L63/00 C08G59/40

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 7 C08G C08L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 057 402 A (GRIEVE ALAN ET AL) 2 May 2000 (2000-05-02) claims 4,10; example 2 -----	1-30
X	US 6 242 513 B1 (GRIEVE ALAN ET AL) 5 June 2001 (2001-06-05) column 5, lines 22-44; claims; examples -----	1-30
X	DATABASE WPI Section Ch, Week 199801 Derwent Publications Ltd., London, GB; Class A23, AN 1998-004261 XP002302588 & JP 09 272757 A (TEIJIN KASEI LTD) 21 October 1997 (1997-10-21) abstract ----- -/--	1-30

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/022943

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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