

A RESIN-COMPOSITION AND METHOD FOR CURING A LINER

The present invention relates to a curable resin-composition and a method for curing a liner.

5 The resin-composition may be used for rehabilitation of line and tank systems used for liquids and gases, protecting tubes from corrosion or to reinforce pressurized pipes. Moreover, the resin-composition may be used in a composite for e.g. boat building and wind turbine blades. The resin-composition comprises one or more polymerizable and/or crosslinkable organic compounds, one or more photoinitiators, one or more copper complex, one or more photo

10 sensitizers and one or more redox or photochemical rearrangement organic compounds.

BACKGROUND ART

15 Resin-compositions, which are polymerizable and/or crosslinkable by electromagnetic radiation, such as electromagnetic radiation comprising UV, Visible and IR light, are suitable for use in many applications. One application is for curing a liner, e.g. in a pipeline in a relining process.

Pipelines and tanks are typically made of robust and heavy materials, such as steel, cast iron,

20 concrete, clay or very rigid plastic. Exchanging existing pipelines and tanks is usually a costly process, especially when the pipeline or tank is located underground or in difficult accessible places such as sewage pipelines. It is therefore preferable to renovate the defective pipeline or tank instead of replacing it. For example, a process called relining is used to renovate a defective pipeline, such as a leaking sewage pipeline, in which process a fiber liner is inserted

25 into the existing pipeline. The liner generally made of woven or non-woven fibers is resin-impregnated and after mounting and cure has a shape like a tube having approximately the same diameter as the pipeline or tank.

The resin-composition in the liner is allowed to cure after being inserted into the pipeline. When

30 cured, the liner will be robust, solid and fluid-tight. The inner surface of the liner will be very smooth, i.e. have a low surface roughness. Due to the decreased roughness, the flow rate with the liner installed will typically be improved compared to the flow rate without liner, even if the liner reduces the effective flow area of the pipeline.

Pull-in or Eversion are common technologies used for lining and relining existing pipelines. Eversion is made by fastening one end of the liner onto a turning head and subsequently inverting the liner into the pipeline by the use of pressurized fluid, e.g. water or steam. Electromagnetic radiation like UV light, visible light or hot fluid like water or steam is typically used to perform the subsequent curing of the liner in order to form a rigid and fluid-tight composite wall structure on the inner surface of the pipelines, tanks or other geometry structures.

An advantageous technology for curing a liner has been described in the international patent application PCT/DK2008/000073, published as WO 2008/101499. The above-mentioned patent application relates to an apparatus for curing a liner. The apparatus includes a light curing device comprising a mobile and flexible "light train" having a set of LEDs (light emitting diodes), which are used to cure the liner.

The light curing device is typically cooled by the use of compressed air, as it is readily available since it is used for the other above-mentioned purposes. In the prior art devices, the compressed air is led through heat sinks running straight through the light curing device. Other cooling media than air can be used as well.

However, there has been a long-felt need in the field of (photo)curing of curable resin-compositions to find improved and reliable resins and methods for providing cured structural parts, i.e. parts and resin objects having a thickness of at least 0.5 mm, and having appropriate mechanical properties such as tensile strength and modulus, hardness, adhesion and chemical resistance. Safety considerations also play a major role when curing a polymerizable or cross-linkable resin mixed with (co)polymerizable free monomer, i.e. in a reactive or non-reactive diluent. Reactive or non-reactive diluents are generally relatively volatile compounds that may be dangerous because of explosion risks at incidentally occurring high temperatures, and because of toxicity aspects during preparation of the cured materials.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a curable resin-composition suitable for curing an item, e.g. a resin impregnated liner, where the resin composition can be cured by using electromagnetic radiation, such as an LED-UV light emitter, in a reliable and controlled manner and provide a cured item with a sufficient degree of cure through the entire depth of the item.

A further object is to provide a curable resin-composition which can be cured in an efficient and cost-effective manner.

- 5 The principle of curing a resin-composition in a photo-induced polymerization or photo polymerization reaction consists in exposing the composition comprising monomers, oligomers and/or polymers bearing reactive functionalities (such as acrylic, vinyl, epoxy, etc.) to light radiation so as to produce active species (free radicals or cations) in order to initiate a polymerization. The generation of these species takes place by excitation of photosensitive components in the resin-composition, commonly via an additive denoted "photoinitiator".

- 15 A photoinitiator has a defined electromagnetic radiation wavelength interval in which it generates active species for polymerization initiation. It is possible to extend this interval by photosensitization using a photosensitizer in combination with the photoinitiator. A photosensitizer is a molecule which absorbs electromagnetic radiation wavelengths different than those absorbed by the photoinitiator and transfers this energy to the photoinitiator, thus extending its spectral sensitivity.

- Thus, in a first aspect, the present invention relates to a resin-composition which is curable and polymerizable by an electromagnetic radiation, said composition comprising:
- one or more polymerizable and/or crosslinkable organic compounds;
 - a photoinitiator comprising an iodonium salt;
 - one or more photosensitizers;
 - a copper-complex;
 - 25 a butanediol and its derivatives;
 - a pinacol and its derivatives;
 - one or more redox or photochemical rearrangement organic compounds; and
 - one or more diluents.

- 30 Although the resin-composition functions very well using one sensitizer, it has been found that it is possible to combine the photoinitiator with at least two photosensitizers. The photosensitizer's high triplet energy is used to sensitize the initiator and therefore the photolysis yield. Thus, a greater amount of reactive species are generated and, consequently, the polymerization is more rapid. As examples of photosensitizers may be mentioned: camphorquinone, an-

thraquinone, anthracene, pyrene, phenothiazine, pinacol (also denoted as tetramethyl-ethylene glycol), acetophenone, xanthenes, carbazole derivatives, ethoxynaphthalene derivatives, fluorenone and acylphosphine oxides.

- 5 The further combination with a copper-complex and at least one redox or photochemical rearrangement organic compound serves to improve the reactions in the resin-composition during curing (i.e. increase reaction), thereby enhancing the properties of the cured composition.

The diluents serve to adjust the resin-composition viscosity as well as to adjust the final properties after it is cured.

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Generally, the resin-composition comprises:

- 50 – 90% of one or more polymerizable and/or crosslinkable organic compounds;
0.1 – 5.0% of the photoinitiator;
15 0.1 – 6.5% of the one or more photosensitizers;
0.1 – 5.0% of a second photosensitizer;
0.01 – 5.0% of the copper-complex;
0.01 – 5.0% butanediol and its derivatives;
0.01 – 5.0% pinacol and its derivatives;
20 0.1 – 5.0% of one or more redox or photochemical rearrangement organic compound; and
5.0 – 45.0% of one or more diluents.

All percentages are weight percentages.

- 25 The resin-composition should always comprise one photosensitizer. However, the composition may also comprise a second or more photosensitizers, such as a third, fourth, fifth and sixth photosensitizer. Preferably, the photosensitizers are each present in an amount of 0.1 – 5.0% of the composition.
- 30 The combination of one or more photosensitizers, butanediol and its derivatives, pinacol and its derivatives, organic acid and copper-complex in the resin-composition gives a controlled cure rate and cure exotherm of the resin upon suited electromagnetic radiation. It is possible to formulate the composition so that the peak exotherm temperature will be between 100 to

230 °C, such as between 100 to 160 °C. The reaction is fully cured within stipulated time periods from 5 to 250 sec, more preferably from 5 to 100 sec. The system gives good adhesion on cast iron as well as aluminium surface with high mechanical strength.

- 5 The resin-composition is preferably based on epoxy compounds which, when included in a curable composition, can provide cured items with excellent sought-after properties, such as low shrinkage. Thus, preferably at least one polymerizable and/or crosslinkable organic compound is selected from compounds of propoxylated glyceryl triacrylate (GPTA), trimethylolpropane triacrylate and oxybis(methyl-2,1-ethandiyl)diacrylate, BPA epoxy resins such as liquid, semisolid and solid bisphenol A epoxy resin, novalac epoxy resin, halogenated and non-halogenated epoxy resins, cardanol based epoxy resin, cycloaliphatic epoxy resin, sorbitol based epoxy resin, bio epoxy resins, bisphenol F epoxy resins, and any combination thereof.

- 15 Iodonium salts have proven to function excellent as photoinitiators. Thus the photoinitiator in the resin-composition is based on an iodonium salt. Preferably, the iodonium salt is selected from Iodonium diphenyl- 4,4'-di-C10-13-alkyl derivatives, tetrakis (2,3,4,5,6-pentafluorophenyl) borates and (4-(1-methylethyl)phenyl)-(4-methylphenyl)Iodonium tetrakis(pentafluorophenyl)-borate(1-).

- 20 The photosensitizers in the resin-composition may be selected from e.g. camphorquinone and its derivatives, anthraquinone, anthracene, pyrene, phenothiazine, pinacol, acetophenone, xanthenes, carbazole derivatives, ethoxynaphtalene, fluorenone and acylphosphine oxides, which all function well as photosensitizers. Preferably, the photosensitizers are selected from camphorquinone, anthracene, such as 9,10-dibutoxyanthracene, ethoxynaphtalene, such as 1,4-diethoxynaphthalene.

- Inclusion of a copper-complex in the resin-composition improves the curing and hardening of the resin. Preferably, the copper-complex is selected from copper naphthanate, copper benzoate, copper sulfate, copper tetra fluoro borate, and copper carbonate.

- 30 The resin-composition also comprises a redox or photo chemical rearrangement organic compound which improves the curing by influencing the formation of Brøndsted acids. Preferably, the redox or photo chemical rearrangement organic compound is based on an organic acid selected from butanediol and its derivatives, ascorbic acid, 2,3-dimethyl 2,3-butanediol, and 4,4-diphenylcyclohexadienone.

The butanediol and its derivatives also influence the rate of reaction as well as help to improve the reactivity. The pinacol and its derivatives also help to improve the reactivity and through cure of the resin-filled fiber. Preferably the thickness of the filled resin is achieved till 4 to 10 mm.

The diluents serve to lower the viscosity of the resin-composition, and preferably the one or more diluents are selected from propoxylated glyceryl triacrylate, 1, 4-butanediol diglycidyl ether, C12-C14 alkyl glycidyl ether, o-cresyl glycidyl ether, phenol glycidyl ether, propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 1,6- hexanediol diglycidyl ether, trimethylol propane triglycidyl ether, cardanol based mono, di- and tri- functional epoxy reactive and non-reactive diluents, triethylene glycol divinyl ether, diethyleneglycol divinyl ether, cyclohexanedimethanol divinyl ether, hydroxybutyl vinyl ether, cyclohexyl vinyl ether, isobornyl acrylate, 3,3,5-trimethyl cyclohexyl acrylate, 4-tert-butyl cyclohexyl acrylate, cyclic trimethylol propane formal acrylate, tetrahydrofurfuryl acrylate, tripropylene glycol diacrylate, tri and tetra ethylene glycol diacrylate, tricyclodecane dimethanol diacrylate, propylene glycol 200 – 600 diacrylate, trimethylol propane triacrylate, glycerin (PO)₃ triacrylate, pentaerythritol tetraacrylate, isodecyl methacrylate, benzyl methacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, polyester acrylates such as mono, di, tri, tetra, hexa functional polyester acrylates, phosphate methacrylate, carboxyethyl acrylate, alkali strippable polyester acrylate.

Inclusion of the solid epoxy resin increases the adhesion properties on various substrate, such as cast iron, aluminium as well as PVC. The solid epoxy resin also helps to improve the reactivity as well as taking part to control the exothermic temperature. In combination, solid epoxy resin and propoxylated glyceryl triacrylate (GPTA) reduce the exothermic temperature up to 30 to 50%, such as reduced up to 100 C from 220 °C.

In an embodiment, the resin-composition after cure has a volume shrinkage of less than 5%, such as less than 3%, such as less than 2%. A low volume shrinkage is desirable, e.g. if the resin-composition is intended for repairing a pipe or tank by the relining method described, where the liner or structure comprising the resin should have a close fit after cure.

It is possible to cure the resin-composition using a wide range of electromagnetic radiation wavelengths comprising ultraviolet- (UV) and visible- (VIS), Infrared- (IR) light, and in an embodiment the resin-composition is polymerizable by an electromagnetic radiation of UV, IR and

VIS light, hereafter denominated light, in the wavelength from the light emitting source, emitting light in the range from 360 to 700 nm, preferably emitting light in the range from 380 to 480 nm.

- 5 Using a light in the wavelength range 380 to 480 nm provides a good curing of the resin-composition, even if the items to be cured have a thickness above 3 mm, such as between 3 and 6 mm, or a thickness up to 10 mm. The resin may be cured using light of one or a combination of two or more suitable wavelengths. Thus, the resin may be cured using light of two different wavelengths, such as e.g. 365 nm and 415 nm, or 415 nm and 472 nm. The suitable
- 10 light wavelengths can easily be selected by the skilled person and adapted in accordance with the sensitizers used, e.g. in such a way that a first wavelength is chosen as the wavelength where e.g. the first sensitizer absorbs most energy, and a second or third wavelength is chosen as the wavelength where a second sensitizer absorbs most energy.
- 15 The invention also relates to a resin-composition which is curable and polymerizable by electromagnetic radiation, said composition comprising:
one or more polymerizable and/or crosslinkable organic compounds;
a photoinitiator comprising an iodonium salt;
one or more photosensitizer;
20 one or more butanediol derivatives;
one or more pinacol derivatives;
one or more copper-complex; and
one or more redox or photo chemical rearrangement organic compounds;
wherein the resin-composition after cure has a volume shrinkage of less the 5%, such as less
25 than 3%, such as less than 2%.

A low volume shrinkage is desirable along with adhesion to various substrates, e.g. if the resin is intended for repairing a pipe or tank by the relining method described, where the liner comprising the resin should have a close fit after cure.

- 30 The one or more polymerizable and/or crosslinkable organic compounds are preferably based on epoxy compounds which, when included in a curable composition, can provide controlled exothermic reaction and cured items with excellent sought-after properties, such as good adhesion, low shrinkage, and high strength. Thus, the at least one polymerizable and/or cross-
- 35 linkable organic compound is preferably selected from compounds of propoxylated glyceryl

triacrylate, trimethylolpropane triacrylate and oxybis(methyl-2,1-ethandiyl) diacrylate, BPA epoxy resins such as liquid, semisolid and solid bisphenol A epoxy resin, novalac epoxy resin, halogenated and non-halogenated epoxy resins, cardanol based epoxy resin, cycloaliphatic epoxy resin, sorbitol based epoxy resin, bio epoxy resins, bisphenol F epoxy resins, and any
5 combination thereof.

The photoinitiator comprises an iodonium salt having good properties as photoinitiators. Preferably, the iodonium salt is selected from Iodonium diphenyl- 4,4'-di-C10-13-alkyl derivatives, tetrakis (2,3,4,5,6-pentafluorophenyl) borates and (4-(1-methylethyl)phenyl)-(4-methylphe-
10 nyl)Iodonium tetrakis(pentafluorophenyl)borate(1-).

The one or more photosensitizers in the resin-composition may be selected from e.g. camphorquinone and its derivatives, anthraquinone, anthracene, pyrene, phenothiazine, pinacol, acetophenone, xanthenes, carbazole derivatives, ethoxynaphthalene, fluorenone and acyl-
15 phosphine oxides, which all function well as photosensitizers. Preferably, the photosensitizers are selected from camphorquinone, anthracene, such as 9,10-dibutoxyanthracene, ethoxynaphthalene, such as 1,4-diethoxynaphthalene.

The resin-composition also comprises a redox or photo chemical rearrangement organic compound which improves the curing by influencing the formation of Brønsted acids. Preferably, the redox or photo chemical rearrangement organic compound is based on an organic acid selected from butanediol, pinacol, ascorbic acid, 2,3-dimethyl 2,3-butanediol, and 4,4- di-
20 phenylcyclohexadienone.

25 The resin-composition including a photoinitiator comprising an iodonium salt, one or more photosensitizer; one or more butanediol and its derivatives; one and more pinacol derivatives and one or more redox or photo chemical rearrangement organic compounds has proven to have excellent properties in respect of shrinkage. The resin also has good mechanical properties such as tensile strength and modulus, hardness, and chemical resistance. The resin composition has good adhesion on different substrates such as cast iron, aluminium and PVC.
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In an embodiment, the resin-composition also includes a copper-complex. Inclusion of a copper-complex in the resin-composition improves the curing and hardening of the resin. Preferably, the copper-complex is selected from copper naphthanate, copper benzoate, copper sulfate, copper tetra fluoro borate, and copper carbonate.
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The resin-composition may also comprise one or more diluents. The diluents serve to lower the viscosity as well as to control the exothermic reaction of the resin-composition and preferably, the one or more diluents are selected from propoxylated glyceryl triacrylate, 1, 4-butanediol diglycidyl ether, C12-C14 alkyl glycidyl ether, o-cresyl glycidyl ether, phenol
5 glycidyl ether, propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, trimethylol propane triglycidyl ether, cardanol based mono, di and tri functional epoxy reactive and non-reactive diluents, triethylene glycol divinyl ether, diethyleneglycol divinyl ether, cyclohexanedimethanol divinyl ether, hydroxybutyl vinyl ether, cyclohexyl vinyl ether, isobornyl acrylate, 3,3,5-trimethyl cyclohexyl acrylate, 4-tert-butyl cyclo-
10 hexyl acrylate, cyclic trimethylol propane formal acrylate, tetrahydrofurfuryl acrylate, tripropylene glycol diacrylate, tri and tetra ethylene glycol diacrylate, tricyclodecane dimethanol diacrylate, propylene glycol 200 – 600 diacrylate, trimethylol propane triacrylate, glycerin (PO)₃ triacrylate, pentaerythritol tetraacrylate, isodecyl methacrylate, benzyl methacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate,
15 polyester acrylates such as mono, di, tri, tetra, hexa functional polyester acrylates, phosphate methacrylate, carboxyethyl acrylate, alkali strippable polyester acrylate.

The invention also relates to a method for curing a composite material containing the resin-composition, e.g. a liner. The method comprises the steps of providing a resin-composition as
20 described above and impregnating the liner with the resin-composition and curing the resin-composition using ultraviolet- (UV) and visible- (VIS), Infrared- (IR) light in the range 360 to 700 nm to obtain a cured liner, or the resin-composition may be used in a composite for e.g. boat building and wind turbine blades.

25 Although it is possible to use any suitable light source as the cure light, the cure light is preferably provided by LEDs (light emitting diodes), which may generate light in a cost-effective manner. LEDs also have the benefit that they are wavelength specific, with narrow wavelength distributions. Thus the LED light source can be designed to emit light in narrow bands around chosen suited wavelengths, such as 380 nm, 390 nm, 415 nm, 450 nm, and 472 nm. The
30 emitted light may have an intensity between 0.001 W/cm² - 15 W/cm², such as an intensity between 0.005 W/cm² and 12 W/cm², such as an intensity between 0.01 W/cm² and 10 W/cm². The emitted light may pass along the surface of the liner with a speed of 3 to 200 m/h, such as a speed of 5 to 100 m/h, such as a speed of 10 to 90 m/h.

The resin may be contained in a carrier such as a fiber liner. Preferably the fibers are polymer fibers, carbon fibers, basalt fibers, natural fibers, or glass fibers. In an embodiment, the liner is intended for lining a pressurized or non-pressurized pipe, side connections, hat profiles (top-hat) and tee-hat.

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The method also comprises the steps:

- a: providing a resin-composition comprising a photo initiator selected from Iodonium diphenyl-4,4'-di-C10-13-alkyl derivatives, tetrakis (2,3,4,5,6-pentafluorophenyl) borates and (4-(1-methylethyl)phenyl)-(4-methylphenyl)Iodonium tetrakis(pentafluorophenyl)borate(1-) and
- 10 camphorquinone, pinacol and anthracene as sensitizers;
- b: adding solvent selected from ether or alcohol to the mixture;
- c: stirring till the mixture is dissolved in the solvent;
- d: adding solid epoxy resin, cycloaliphatic epoxy resin, bisphenol A glycidyl ether resin, bisphenol F glycidyl ether resin and epoxy diluents to obtain the curable composition along with
- 15 propoxylated glyceryl triacrylate.

In an embodiment, the method comprises the further step of adding ascorbic acid to the mixture before step b.

- 20 The method may also include adding at least one further component in step d, selected from polyester acrylates, epoxy acrylate, polyurethane acrylate, and/or polyether acrylate.

Moreover, the method may also comprise the further step of adding tetramethylethylene glycol, dibutanediol and copper salt or copper complex in step d.

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The method may include adding at least one further component in step d, selected from mono-, di- and/or tri- functional acrylate including Acyl, aromatic, ether, dioxolane, carboxylic acid amide with acryloyl group and oxetane acrylate.

- 30 In an embodiment, the method comprises the steps:

- e: applying the obtained curable resin-composition on a fiber liner;
- f: applying LED light of a wavelength 380 to 480 nm with an intensity between 0.01 W/cm² and 10 W/cm² to the surface of fiber liner with a speed of 5 to 90 m/hr;
- g: allowing the fiber reinforced liner to cool down to room temperature.

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The invention also relates to use of the resin-composition for repairing and/or curing a liner. The liner is impregnated with the resin-composition in a known manner, and the liner is mounted in the location where it should be cured, these processes are also well-known and well-established.

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The invention also relates to the use of the resin-composition for pipe rehabilitation with the use of liner systems, felt liner, glass liner and other carrier materials, vertically and horizontally, side connections, hat-profiles (top-hat) and tee-hat.

10 The invention also relates to use of the resin-composition for outside pipe-wrapping with a material like fiberglass, carbon fiber, basalt, polyester, where the material is wetted out with the resin-composition and cured. This may serve to protect pipes from corrosion or to reinforce pressurized pipes.

15 The invention also relates to the use of the resin-composition in a composite suitable for use in boatbuilding, wind turbine blades, spray coat, etc. The structural fibers like fiberglass, carbonfiber, basalt or polyester are wetted out with the resin-composition and cured.

Moreover, the invention also relates to the use of the resin-composition with added fillers of
20 reinforcement in the form of glass fibers, carbon fibers, carbon nanotubes, inorganic fillers and other materials, for repair and/or protection of surfaces of materials such as steel, concrete, clay, stone, rigid composites, rigid plastics and other rigid materials by the method of spray, roller, brush, dip and other application methods.

25 The invention also relates to the use of the resin-composition for coating and/or protection of surfaces of materials such as steel, concrete, clay, stone, plastics, rigid composites, rigid plastics and other rigid materials.

Moreover, the invention relates to the use of the resin-composition in 3D printing technology.

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The invention provides a resin-composition with sufficient degree of cure through the entire depth of the item to be cured, a resin-composition which can be cured using a broader UV range, and better heat control is obtained during curing.

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DETAILED DESCRIPTION OF THE INVENTION

The principles of the invention are explained below by means of examples.

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Example 1

Formulation of light curable thermochemical Bisphenol A glycidyl ether (BPA) resin.

10 A photoinitiator UV cata 243 (Iodonium diphenyl- 4,4'-di-C10-13-alkyl derivatives, tetrakis (2,3,4,5,6-pentafluorophenyl) borates photoinitiator delivered by BLUESTAR Silicones) was photosensitized by long-wave UV absorber camphorquinone along with Anthracene (Anthracure UVS 2171 delivered by Kawasaki Kasei Chemicals Ltd.) at a wavelength about 380 nm to 480 nm, which led to a very good degree of cure through the entire depth of the
15 resin impregnated item.

The reactions are as follows. The photoinitiator absorbs the light and by heterolytic or by homolytic cleavage of diphenyliodonium salt it produces an aryl cation which in presence of a hydrogen donor produces a proton, which coupled with an anion, provides Brønsted acid.

20

The Brønsted acid reacts with an epoxy group (in the BPA) to form a carbonium cation, which attacks another epoxy group to form polyether by ring opening cationic polymerisation. Heat is generated during the reaction between the epoxy group and the Brønsted acid, which is produced by the photochemical reaction.

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In the presence of ascorbic acid and heat, the Brønsted acid is produced again, and may again react with the epoxy groups and continue the reaction to form polyether.

An epoxy resin according to the invention was prepared. The resin had the following composition by weight:

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72%. BPA – BPF resin.

1% Iodonium diphenyl- 4,4'-di-C10-13-alkyl derivatives, tetrakis (2,3,4,5,6-pentafluorophenyl) borates

35

1% Camphorquinone

1% 9,10-dibutoxyanthracene

5 1% 1,4-diethoxynaphthalene

1% copper naphthalate

1% ascorbic acid

10

22% butandiol diglycidylether.

The resin-composition was prepared as follows. The UV cata 243 was weighed along with camphorquinone, Anthracure UVS 2171 and ascorbic acid. Ether or alcohol solvent was added in proportion and heated up to 40 to 50 °C. Stirring was continued till the mixture was completely soluble in the solvent. Then Bisphenol A glycidyl ether resin was added with epoxy diluents.

The above mix of BPA resin was applied on a 3 to 6 mm thick fiber liner in absence of light, i.e. under dark condition. Then the LED light source, emitting light in the wavelength range from 380 to 480 nm, was switched on. The light was emitted onto the surface of the resin filled fiber liner at the speed of 40 to 80 m/hr. The peak exotherm of the reaction was measured between 110 and 180 °C. The liner was left to cool down to room temperature and the mechanical properties were measured.

25

The resin was cured by light in the wavelength range 380 to 480 nm, and the mechanical properties were tested on pure resin seven days after cure. Eight samples were tested according to the procedures outlined in the standards ASTM D 638 – 2a, ASTM D 790 and ASTM D 2240.

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Tensile strength	55 - 75 MPa	(ASTM D 638 – 2a)
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Tensile modulus	30-3600 MPa	(ASTM D 638 – 2a)
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35 Flexural strength	125-150 MPa	(ASTM D 790)
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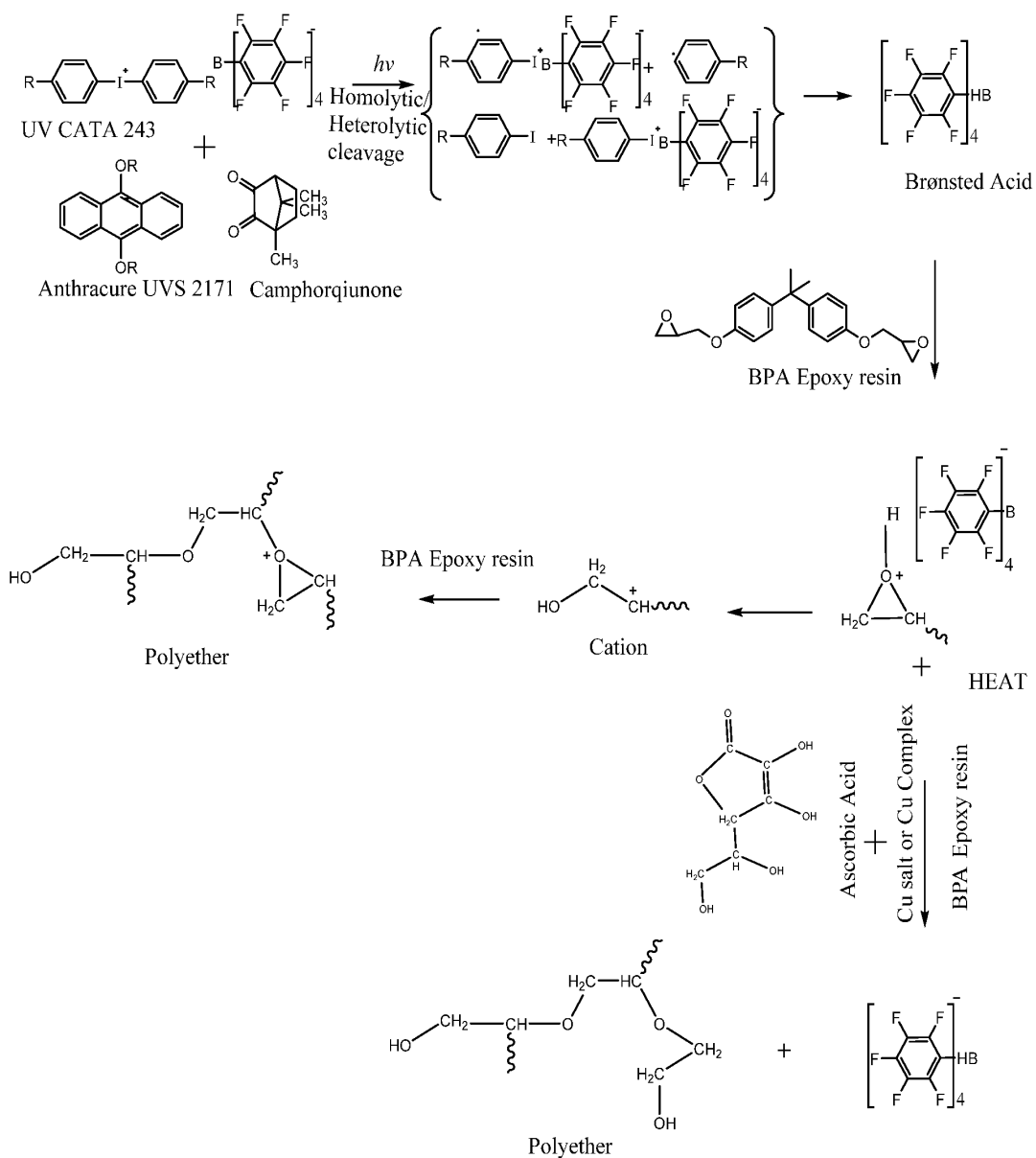
Flexural modulus	45-5400 MPa	(ASTM D 790)
Shore D hardness	87-90	(ASTM D 2240)

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The results showed that the resin-composition has mechanical properties fully satisfactory as resin in a liner for e.g. relining a sewer pipe.

- 10 The mechanical properties fulfilled the requirements, and it could be concluded that the resin composition is suitable for use in a liner.

The reaction scheme is shown below.



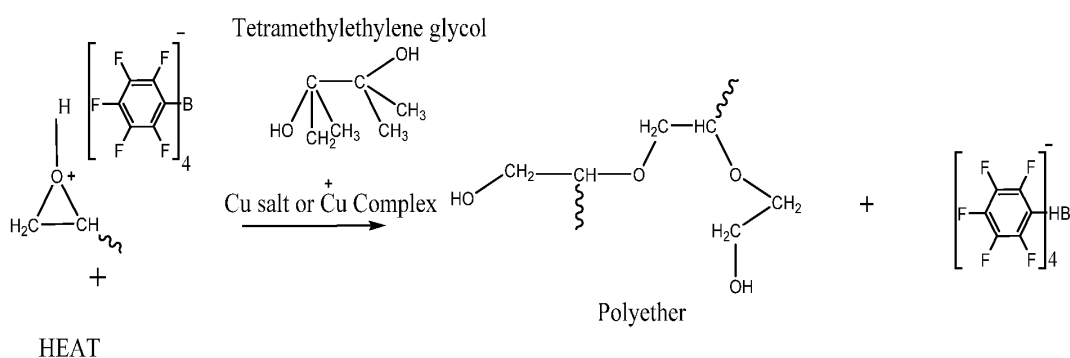
- 5 As an alternative to the described light-induced ring-opening or free radical photo curing, it is also possible to obtain a thermoredox light curing of Bisphenol A glycidyl ether resin (BPA resin) and its hybridization with light curable acrylates.

The thermoredox light cure of bisphenol A glycidyl ether was carried out in the presence of tetramethylethylene glycol (pinacol) and copper salt or copper complex.

The UV cata 243 was weighed up along with camphorquinone, Anthracure UVS 2171 and
 5 tetramethylethylene glycol. Ether or alcohol solvent was added in proportion and the mixture was heated up to 40 to 50 °C. Stirring was continued till the mixture was completely soluble in the solvent. Bisphenol A glycidyl ether was added along with epoxy diluents. Cu- salt or Cu-complex was added. The mixture was applied on a fiber liner and exposed to light in the wave-length range from 380 to 480 nm, until the cure was completed.

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The reaction scheme is shown below.



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Example 2

It is also possible to achieve a hybrid reaction by adding light curable acrylates to the above-mentioned mixture and carry out the curing process in presence of a light source with 380 to
 20 480 nm wavelength.

The invention also includes a hybrid reaction as follows. The addition of LED curable polyester acrylates or epoxy acrylate or polyurethane acrylate or polyether acrylate into the described LED curable mix Bisphenol A glycidyl ether resin with photo initiator and photosensitizers also
 25 modifies the reactivity as well as the mechanical and adequate thermal properties, e.g. tensile strength, elastic modulus and glass transition temperature.

Polyester acrylates/epoxy Acrylate/polyurethane acrylate/polyether acrylate was mixed with up to 20% Bisphenol A glycidyl ether, UV cata 243, UVS 2171, Camphorquinone, ascorbic acid and applied on a fiber liner and exposed to light in the wavelength range from 380 to 480 nm until the cure was completed.

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An epoxy acrylate resin according to the invention was prepared. The resin had the following composition by weight:

56 % Epoxidised compound of trimethylolpropantriacylat and oxybis(methyl-2,1-ethandiyl)di-
10 acrylat

20% BPA – BPF resin.

1% Iodonium diphenyl- 4,4'-di-C10-13-alkyl derivatives, tetrakis (2,3,4,5,6-pentafluorophenyl)
15 borates

1% Camphorquinone

1% 9,10-dibutoxyanthracene
20

1% 1,4-diethoxynaphthalene

1% copper naphthanate,

25 1% ascorbic acid

9% isobornyl acrylate

9% 1,4-Butanediol dimethacrylate.
30

The resin was cured by light in the range 380 to 480 nm, and the mechanical properties were tested on pure resin samples seven days after curing. The samples were tested according to the procedures outlined in the standards ASTM D 638 – 2a, ASTM D 790 and ASTM D 2240.

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	Tensile strength	35-50 MPa	(ASTM D 638 – 2a)
	Tensile modulus	21-2800 MPa	(ASTM D 638 – 2a)
5	Flexural strength	95-110 MPa	(ASTM D 790)
	Flexural modulus	27-4500 MPA	(ASTM D 790)
10	Shore D hardness	85-90	(ASTM D 2240)

Although a certain variety was found in respect of tensile modulus and flexural modulus, the results were fully acceptable.

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The resin-composition was also tested in non-woven polyester. This test is intended to simulate the resin-composition properties in a liner.

A 3 mm thick polyester liner was impregnated with the resin and positioned in a test setup comprising polyvinylchloride (PVC) and steel pipes. The resin impregnated liner within the pipe test setup was cured by light having wavelengths in the range 380 to 480 nm.

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The mechanical properties of in-line installed liner samples from both the PVC and steel pipes were measured after 3 weeks. The measurements were performed according to the standard ISO 7685.

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	Youngs-modulus:	1500-2500 MPa	(ISO 7685)
	Ring stiffness:	2,5 – 4 KN/m ²	(ISO 7685)
30	3% deflection by strain:	42 – 56 N	(ISO 7685)

The obtained result showed that the resin-composition provided excellent mechanical properties for pipe repair when cured in a liner. The results for elasticity (Youngs-modulus), ring stiffness and deflection clearly indicate that the composition provides properties fully satisfactory for e.g. sewer pipe renovation. Moreover, the resin-composition showed good adhesion to
5 plastic (PVC) and cast iron, and had a low percentage of shrinkage during curing; the volume shrinkage was typically below 5%.

The invention provides a curable and polymerizable resin-composition having a low shrinkage and a good adhesion to plastic and steel. Moreover, it is possible to adjust and control peak
10 exotherm temperature during the curing process, typically between 110 and 230 °C, so undesired overheating can be avoided.

The tested resin compositions according to the invention have after curing proven to have a satisfactory tensile strength, elasticity and adequate temperature resistance.
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