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(54) Title: THERMOSETTING RESIN COMPOSITION SUITABLE FOR (RE)LINING

(57) Abstract: The present invention relates to a thermosetting, radically curable resin composition suitable for (re)lining comprising a.30 -70 wt.% of a methacrylate containing resin with a T_g of at least -5°C and at most 100°C , b.2.5 -20 wt.% of an unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and alkoxyated bisphenol A and/or alkoxyated bisphenol F building blocks as diol building blocks, c.1 -40 wt.% of at least one ethylenically unsaturated compound excluding benzyl methacrylate, which ethylenically unsaturated compound is able to copolymerize with (a), (b) and (d); d.5 -60 wt.% of benzyl methacrylate, the amounts are calculated as wt.% of the total weight of the compounds (a), (b), (c) and (d).



THERMOSETTING RESIN COMPOSITION SUITABLE FOR (RE)LINING

The present invention relates to a thermosetting, radically curable resin composition containing methacrylate containing resin and being suitable for (re)lining.

Such resin compositions are known from WO-A-2008077586. With the herein described resin compositions, a good balance of properties relevant for (re)lining applications can be achieved.

In general, in order to be applicable for relining, the cured, unreinforced and unfilled resin composition must be able to achieve an E-modulus of at least 2 GPa (measured according to ISO 527-2), the elongation at break must be higher than 2% (measured according to ISO 527-2) and the tensile strength needs to be at a high level and the viscosity of the uncured, unfilled and unreinforced resin composition must be between 300 and 1000 mPa.s (measured according to ISO 3219 at 23°C). However, for (re)lining of tubes or pipes which are under pressure in order to be able to transport for example drinking water, thus for (re)lining of pressurized tubes or pipes, the tube or pipe with the (re)liner needs to be designed to withstand an internal pressure higher than atmospheric pressure, which can be up to 8 bar. In view of this, there is a desire to further increase the elongation at break of the cured, unreinforced and unfilled resin composition to preferably 3% or more, however without sacrificing E modulus significantly.

Accordingly, the object of the present invention was to design a thermosetting resin composition which is suitable to be applied for (re)lining with increased elongation at break of the cured, unreinforced and unfilled resin composition, however without sacrificing E modulus significantly.

This object has surprisingly been achieved in that the resin composition comprises

- a. 30 - 70 wt.% of methacrylate containing resin with a T_g of at least -5°C and at most 100°C,
- b. 2.5 - 20 wt.% of unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and alkoxylated bisphenol A and/or alkoxylated bisphenol F building blocks as diol building blocks,
- c. 1 - 40 wt.% of ethylenically unsaturated compound, not being benzyl methacrylate, able to copolymerize with (a), (b) and (d);

d. 5 – 60 wt.% of benzyl methacrylate,
the amounts are calculated as wt.% of the total weight of the compounds (a), (b), (c)
and (d).

An additional advantage of the resin composition according to the
5 invention is that the tensile strength can even be further increased.

EP1762581A describes a curable resin composition useful in a lining
material; the curable resin composition comprises (A) urethane-modified epoxy
(meth)acrylate or unsaturated polyester and (B) monofunctional (meth)acrylate
monomer. JP2007 291179A also describes a curable resin composition useful to
10 provide a tubular lining material; the curable resin composition comprises unsaturated
polyester and a monofunctional (meth)acrylate monomer. WO2010/108939A describes
a curable vinyl ester resin composition comprising vinyl ester resin and, as reactive
diluent, methacrylate containing compound and an itaconate ester. These patent
publications at least do not describe the presence of benzyl methacrylate in the curable
15 resin composition.

As used herein, radically curable means that a network is formed via
a radical (co)polymerisation.

In the framework of the present invention, (re)lining is understood to
be the provision on the inside of a hollow object or system, such as a pipe system (for
20 example a sewage system, industrial line system or a transport line), a vessel, a tank
or a house sewer connection and the like, of a layer with a thickness of at least 2 mm,
but usually more than 3 mm and even up to 30 - 40 mm. The layer thickness of a
(re)lining is generally chosen to be thicker as the diameter of the hollow object
increases. The (re)lining generally has the object of contributing to the mechanical
25 strength and ensuring the resistance of the hollow object or system to chemicals,
corrosion, etc., as well as prevention of leaks. It should be noted that when a hollow
object or system is for the first time provided with a lining on the inside, this is referred
to as lining. Each subsequent time that a hollow object or system that is already
internally lined is provided again with a lining, this is called relining. The (re)lining
30 therefore refers to all situations where the lining is provided either for the first time or
for any subsequent time.

(Re)linings are clearly distinguished from so-called coating
applications, for which the layer thickness generally amounts to a maximum of 0.5 mm
and for which entirely different requirements are specified for the surface of the layer
35 (and for the adhesion to the substrate). As a rule a coating will, for example, have to

meet high requirements regarding surface quality and drying (in particular when being cured to the air), but will not contribute to the mechanical strength.

Thermosetting resin compositions harden by chemical reaction, often generating heat when they are formed, and cannot be melted or readily re-formed once hardened. The resin compositions are liquids at normal temperatures and pressures, so can be used to impregnate reinforcements, for instance fibrous reinforcements, especially glass fibers, and/or fillers may be present in the resin composition, but, when treated with suitable radical forming initiators, the various unsaturated compounds of the resin composition crosslink with each other via a free radical copolymerization mechanism to produce a hard, thermoset plastic mass (also referred to as structural part).

Preferably, the uncured, unreinforced and unfilled resin composition has a viscosity between 300 and 1000 mPa.s (measured according to ISO 3219 at 23 °C), more preferably between 300 and 800 mPa.s and even more preferably between 400 and 700 mPa.s.

The resin composition according to the invention comprises benzyl methacrylate in an amount of between 5 and 60 wt.%, preferably between 10 and 50 wt.% and more preferably between 15 and 45 wt.% (relative to the total weight of the compounds (a), (b), (c) and (d)).

Next to benzyl methacrylate, which is an ethylenically unsaturated compound able to copolymerize with (a) and (b), the resin composition according to the invention further comprises at least one other ethylenically unsaturated compound than benzyl methacrylate (compound(s) (c)), which ethylenically unsaturated compound(s) (c) is (are) able to copolymerize with (a) and (b) and preferably is (are) able to dilute (a) and (b). As used herein, compound(s) (c) is (are) able to dilute (a) and (b) means that mixing compound(s) (c) in an amount as present in the resin composition to a mixture of compounds (a) and (b) in amounts as present in the resin composition lowers the viscosity, at 23°C and atmospheric pressure, of such mixture of compounds (a) and (b).

The amount of ethylenically unsaturated compounds other than benzyl methacrylate and able to copolymerize with (a) and (b) and (d) (compound(s) (c)) is between 1 and 40 wt.%, preferably between 5 and 30 wt.% and more preferably between 10 and 25 wt.% (relative to the total weight of the compounds (a), (b), (c) and (d)).

Preferably, the resin composition comprises at least one methacrylate as compound (c). More preferably, compound (c) is a methacrylate or a mixture of

methacrylates.

More preferably, the resin composition comprises at least one polymethacrylate as compound (c). More preferably, compound (c) is a polymethacrylate or a mixture of polymethacrylates.

5 Even more preferably, the resin composition comprises at least one dimethacrylate as compound (c). More preferably, compound (c) is a dimethacrylate or a mixture of dimethacrylates. Preferably, the dimethacrylate is selected from the group consisting of 1,4-butanediol dimethacrylate, neopentylglycol dimethacrylate, PEG200 dimethacrylate, triethylene glycol dimethacrylate, tripropylene glycol dimethacrylate
10 and any mixtures thereof. More preferably, the dimethacrylate is selected from the group consisting of 1,4-butanediol dimethacrylate, PEG200 dimethacrylate and mixtures thereof. Even more preferably, the resin composition comprises 1,4-butanediol dimethacrylate as compound (c).

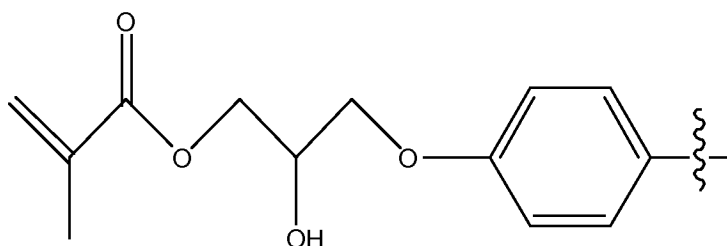
In a preferred embodiment of the invention, the resin composition
15 according to the invention comprises styrene in an amount less than 5 wt.%, more preferably in an amount less than 1 wt.% (relative to the total resin composition). Most preferably the resin composition is essentially styrene-free. Essentially free of styrene as used here means that the styrene concentration in the resin composition is lower than 0.01 wt% styrene (relative to the total resin composition).

20 The resin composition comprises at least one methacrylate containing resin with a glass transition temperature T_g of at least -5°C and preferably at most 100°C . The T_g is preferably at most 80°C and more preferably at most 60°C . Preferably, the resin composition comprises methacrylate containing resin with a T_g of at least 0°C , more preferably with a T_g of at least 5°C . Preferably, the resin
25 composition comprises methacrylate containing resin with a T_g of at least 5°C and at most 60°C . As used herein, the glass transition temperature T_g is $T_{g(\text{midpoint})}$ as determined using Differential Scanning Calorimetry (DSC) according to ISO11357 (edition 2009) with a heating rate of $5^{\circ}\text{C}/\text{min}$.

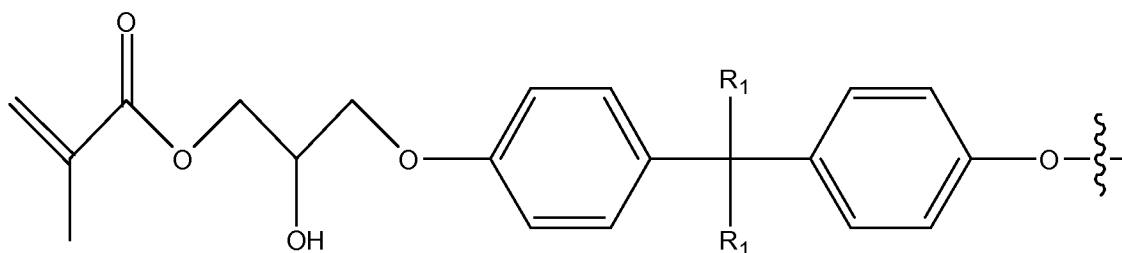
The amount of methacrylate containing resins with a T_g of at least
30 -5°C and at most 100°C , in the resin composition according to the invention is between 30 and 70 wt.% (relative to the total weight of the compounds (a), (b), (c) and (d)), preferably between 35 and 65 wt.% and more preferably between 40 and 60 wt.%.

Preferably, the resin composition comprises methacrylate containing resin (a) that further contains an ether group and a hydroxyl group. More preferably,
35 the methacrylate containing resin (a) present in the resin composition further contains

an ether group and a hydroxyl group. The methacrylate containing resin (a) that further contains an ether group and a hydroxyl group is preferably obtained by reaction of an epoxy oligomer or polymer with methacrylic acid or methacrylamide, preferably with methacrylic acid. The methacrylate containing resin (a) that further contains an ether group and a hydroxyl group preferably comprises a moiety with the following structure



More preferably, the methacrylate containing resin (a) that further contains an ether group and a hydroxyl group comprises a moiety with the following structure



in which R_1 is H or CH_3 , preferably CH_3 .

The resin composition according to the invention comprises at least one unsaturated polyester resin (b) comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and alkoxyated bisphenol A and/or alkoxyated bisphenol F building blocks as diol building blocks. The amount of unsaturated polyester resins (b) comprising fumaric acid building blocks and alkoxyated bisphenol A and/or alkoxyated bisphenol F building blocks in the resin composition according to the invention is between 2.5 and 20 wt.% (relative to the total weight of the compounds (a), (b), (c) and (d)), preferably between 4 and 15 wt.% and more preferably between 5 and 12.5 wt.%.

Preferably, the unsaturated polyester (b) comprises propoxylated bisphenol A and/or propoxylated bisphenol F building blocks as diol building blocks; more preferably, the unsaturated polyester (b) comprises propoxylated bisphenol A as diol building blocks. Preferably, the amount of fumaric acid building blocks and alkoxyated bisphenol A and alkoxyated bisphenol F in (b) is such that the molar amount of alkoxyated bisphenol A and alkoxyated bisphenol F in (b) relative to the molar amount of fumaric acid building blocks in (b) is from 4:1 up to and including 1:4.

Preferably, the unsaturated polyester resins (b) present in the resin composition according to the invention preferably has a molecular weight M_n of higher than 2000 Dalton, more preferably higher than 2500 Dalton and even more preferably higher than 3000 Dalton and lower than 15000 Dalton, more preferably lower than 12500 Dalton and even more preferably lower than 10000 Dalton. Preferably, the unsaturated polyester resins (b) present in the resin composition according to the invention preferably has a molecular weight M_n in the range from 2000 to 15000 Dalton, more preferably in the range from 2500 to 12500 Dalton and even more preferably in the range from 3000 to 10000 Dalton. As used herein, the molecular weight of the resin is determined in tetrahydrofuran using gel permeation chromatography according to ISO 13885-1 employing polystyrene standards and appropriate columns designed for the determination of the molecular weights. The unsaturated polyester resins (b) preferably has an acid value in the range from 2 to 80mg KOH/g resin, more preferably in the range from 5 to 70 mg KOH/g resin. As used herein, the acid value of the resin is determined titrimetrically according to ISO2114-2000. The unsaturated polyester resin preferably has a hydroxyl value of at least 47 mg KOH/g resin, more preferably at least 50 mg KOH/g resin and even more preferably at least 60 mg KOH/g resin. As used herein, the hydroxy value of the resin is determined titrimetrically according to ISO 4629-1978.

Preferably, the average molecular weight per reactive unsaturation (WPU) of the total amount of compounds (a), (b), (c) and (d) is higher than or equal to 190 and lower than or equal to 600.

In a preferred embodiment of the invention, the thermosetting resin composition comprises between 35 and 65 wt.% of compounds (a), between 4 and 15 wt.% of compounds (b), between 5 and 30 wt.% of compounds (c) and between 10 and 50 wt.% of benzyl methacrylate. In a more preferred embodiment of the invention, the resin composition comprises between 40 and 60 wt.% of compounds (a), between 5 and 12.5 wt.% of compounds (b), between 10 and 25 wt.% of compounds (c) and between 15 and 45 wt.% of benzyl methacrylate. Further details of compounds (a), (b), (c) and (d) and preferred compounds (a), (b), (c) and (d) are described above.

The resin composition according to the invention in addition optionally contains a filler in a weight ratio of 0.05:1 to 20:1, preferably in a weight ratio of 0.2:1 to 3:1, relative to the total weight of the compounds (a), (b), (c) and (d), the total of the weight percentages of the compounds (a), (b), (c) and (d) being 100. Suitable fillers are aluminium trihydrate, calcium carbonate, mica, microcrystalline silica, quartz powder,

barite and/or talc.

The resin composition according to the invention in addition optionally contains fibers. Examples of fibers are natural fibers, inorganic or organic fibers.

In order to obtain curing of the thermosetting resin composition according to the invention, a radical initiator (e) is added to the resin composition as described above. The radical initiator (e) is added to the resin composition in such an amount that the amount of radical initiator in the resin composition is between 0.00001-5 wt%. Preferably this quantity lies between 0.1 and 5 wt% (relative to the total resin composition).

The radical initiator (e), which is applied in the resin composition according to the invention, is as a rule chosen from initiators which are suitable for thermal curing (thermal initiators), light curing (photo-initiators) or room temperature curing by means of redox initiation (redox initiators). Thermal curing is understood to be curing of the resin composition by means of heat. In case the resin composition is applied for relining, the heat is originating from heated water or gas (such as for example steam) used to pressurize the (re)lining. Photo-initiation is understood to be curing using irradiation with light of a suitable wavelength (photo irradiation). This is also referred to as light cure. In case of relining, the light energy is generally supplied via lamps placed or moved forward in the hollow objects.

In one embodiment of the invention, the initiator is a photo-initiator. In this embodiment the resin composition preferably comprises a cleavage type photo-initiator, more preferably a α -hydroxy aryl ketone like for instance Irgacure 184, Irgacure 369, Darocure 1173 (Ciba) or acyl phosphine oxides like for instance Lucerine TPO, Lucerine TPO-L (BASF), Irgacure 819 (Ciba) or mixtures thereof. Even more preferably, the photoinitiator is an acyl phosphine oxide. The acyl phosphine oxide is a mono acyl phosphine oxide or a bis acyl phosphine oxide. Most preferably, the photo-initiator is a bis acyl phosphine oxide. A preferred bis acyl phosphine oxide is bis (2,4,6-trimethylbenzoyl) phenylphosphine oxide (Irgacure 819). The quantity of photo-initiator is preferably between 0.1 and 2 wt.%, more preferably between 0.2 and 1 wt.%.

In another embodiment of the invention, the initiator is a thermal initiator. Examples of suitable thermal initiators are azo compounds like azo isobutyronitril (AIBN) and derivatives thereof, and organic peroxides. The thermal initiator is preferably an organic peroxide, or a combination of two or more organic peroxides. Examples of suitable peroxides are, for instance, monoperoxy carbonates

(also referred to as monopercarbonates) (of the formula $-\text{OC}(\text{O})\text{OO}-$), peroxy dicarbonates (also referred to as dipercarbonate) (of the formula the formula $-\text{OC}(\text{O})\text{OOC}(\text{O})\text{O}-$), peroxyesters (also referred to as peresters) (of the formula $-\text{C}(\text{O})\text{OO}-$), diacylperoxides (of the formula $-\text{C}(\text{O})\text{OOC}(\text{O})-$), dialkylperoxides (of the formula $-\text{OO}-$), etc. The peroxides can also be oligomeric or polymeric in nature. An extensive series of examples of suitable peroxides can be found, for instance, in US 2002/0091214-A1, paragraph [0018]. The skilled person can easily obtain information about the peroxides and the precautions to be taken in handling the peroxides in the instructions as given by the peroxide producers. The thermal initiator is preferably selected from a perester, a perdicarbonate, a monopercarbonate or a mixture thereof.

In another embodiment of the invention, the initiator is a redox initiator. A preferred redox initiator is the combination of at least one transition metal compounds like for example Co, Cu, Mn, Fe compounds in combination with a hydroperoxide like for instance t-butyl hydroperoxide and cumenehydroperoxide, a perketal like for instance methyl ethyl ketone peroxide and acetylacetone peroxide, a perester like for instance t-butyl perbenzoate and a percarbonate, preferably in combination with an organic compound. The organic compound can be any organic compound that can be oxidized or reduced. Suitable examples are 1,2-dioxo compounds, 1,3-dioxo compounds, thiols, and N containing compounds like amides and amines. Preferably the organic compound is an N-containing compound. Examples of N-containing compounds are dimethylaniline, diethylaniline, dimethylparatoluidine, diethylhydroxylamine, N,N-diethylacetoacetamide, benzyl amine, p-toluidine, 2-(N-ethylanilino)ethanol, triethanol amine, triethyl amine and Jeffamines, like for example Jeffamine D-2000. Still another preferred redox initiator is the combination of an tertiary aromatic amine like N,N-dimethylaniline, N,N-diethylaniline, N,N-dimethylparatoluidine, N,N-diisopropyltoluidine with a peranhydride like for instance di benzoyl peroxide (BPO) or di lauroyl peroxide.

For relining thermal curing or photo curing is preferred.

The resin compositions according to the invention may contain one or more inhibitors. The inhibitor (f) of the resin composition of the invention can be any radical inhibitor known to the skilled man, preferably chosen from the group of phenolic compounds, stable radicals like galvinoxyl and N-oxyl based compounds and/or phenothiazines. Suitable examples of inhibitors that can be used in the resin compositions according to the invention are, for instance, 2-methoxyphenol,

4-methoxyphenol, 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butylphenol, 2,4,6-trimethylphenol, 2,4,6-tris-dimethylaminomethyl phenol, 4,4'-thio-bis(3-methyl-6-t-butylphenol), 4,4'-isopropylidene diphenol, 2,4-di-t-butylphenol, 6,6'-di-t-butyl-2,2'-methylene di-p-cresol, hydroquinone, 2-methylhydroquinone, 2-t-butylhydroquinone, 5 2,5-di-t-butylhydroquinone, 2,6-di-t-butylhydroquinone, 2,6-dimethylhydroquinone, 2,3,5-trimethylhydroquinone, catechol, 4-t-butylcatechol, 4,6-di-t-butylcatechol, benzoquinone, 2,3,5,6-tetrachloro-1,4-benzoquinone, methylbenzoquinone, 2,6-dimethylbenzoquinone, naphthoquinone, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine-4-ol (a compound also referred to as TEMPOL), 10 1-oxyl-2,2,6,6-tetramethylpiperidine-4-one (a compound also referred to as TEMPON), 1-oxyl-2,2,6,6-tetramethyl-4-carboxyl-piperidine (a compound also referred to as 4-carboxy-TEMPO), 1-oxyl-2,2,5,5-tetramethylpyrrolidine, 1-oxyl-2,2,5,5-tetramethyl-3-carboxylpyrrolidine (also called 3-carboxy-PROXYL), aluminium-N-nitrosophenyl hydroxylamine, diethylhydroxylamine, phenothiazine and/or derivatives or combinations 15 of any of these compounds.

Advantageously, the amount of inhibitor in the resin composition according to the invention is in the range of from 0.00001 to 5 % by weight, preferably from 0.0001 to 2 % by weight, more preferably, from 0.001 to 1 % by weight (relative to the total resin composition). The type and amount of inhibitor depends on the type of 20 curing. For example, in case of thermal curing 2,6-di-t-butyl-4-methylphenol and 2-methylhydroquinone are very suitable inhibitors.

The present invention also relates to a fiber mat comprising fibers impregnated with a resin composition as described above comprising compounds (a), (b), (c), (d) and (e).

25 The present invention further relates to a process for preparing a fiber reinforced composite article using a resin composition as described above comprising compounds (a), (b), (c), (d) and (e), wherein the process comprises mixing the compounds of said resin composition, impregnating fibers with this mixture and allowing the mixture to cure. In one embodiment, the fibers are present as a fiber mat, 30 preferably a glass or carbon fiber mat.

The invention also relates to the use of the resin composition according to the invention comprising compounds (a), (b), (c), (d) and (e) in a flexible, sleeve-shaped object for use in (re)lining. According to the invention the flexible, sleeve-shaped objects contain a supporting or reinforcing material that is impregnated 35 with the thermosetting, radically curable resin composition according to the invention,

at least one of the surfaces of the sleeve-shaped object being provided with a barrier layer that is impermeable to the resin composition.

The supporting or reinforcing material of which the flexible, sleeve-shaped object consists is for example a fibrous web or needle felt of glass fibers, silica
5 fibers, quartz fibers, carbon fibers, boron fibers, metal fibers, asbestos fibers, polyamide fibers (for example Kevlar® of Du Pont), polyester fibers, cotton fibers, silk fibers, polyethylene fibers and jute fibers. The person skilled in the art can readily determine the suitable fibers for a specific application or desired property of the structural element to be formed. Carbon fibers are used for example for applications in
10 which a low weight and a high rigidity are desirable.

The barrier layer that is impermeable to the curable resin composition and that is provided at least one of the surfaces of the sleeve-shaped object is a layer of polyethylene, polypropylene, polyamide etc.

The present invention also provides for a method for (re)lining a tube
15 or pipe, tank or vessel with a flexible, sleeve-shaped object as described above, where

- (a) the flexible, sleeve-shaped object is introduced into a tube, pipe, tank or vessel, and then
- (b) is pressurized therein with (i) a liquid or (ii) a gas, so that the flexible, sleeve-shaped object is forced against the inside of the wall of the tube,
20 the pipe, the tank or the vessel, and
- (c) the curable resin composition comprising compounds (a), (b), (c), (d) and a thermal initiator which resin composition is present in the flexible, sleeve-shaped object is cured thermally in the case of (i) or (ii), or by photo-irradiation in the case of (ii).

25 The material from which a pipe, tube, tank or vessel itself is made can be chosen from a large series of suitable materials, for example cement, concrete, sandstone, GFK, polymer concrete, metal, steel, PVC, etc.

The present invention also relates to cured (re)liners for objects, in particular pipes, tubes, tanks or vessels, obtained by curing a resin composition
30 according to the invention comprising compounds (a), (b), (c), (d) and (e). In case the resin composition comprises a thermal initiator, the curing is effected using thermal curing. In case the resin composition comprises a photo-initiator, the curing is effected using photo curing. In a preferred embodiment of the invention, the cured (re)liner is used at a pressure higher than atmospheric pressure.

35 Finally, the present invention relates to the use of resin composition

as described above in various applications such as for instance chemical anchoring, roofing, gel coats, containers, tanks, pipes, automotive parts, flooring, windmill blades, aviation, off shore applications. The present invention also relates to cured objects or structural parts obtained by mixing the compounds of a resin composition as described
5 above comprising compounds (a), (b), (c), (d) and (e).

The invention will now be elucidated further on the basis of a few examples, without however being limited to the compositions shown in the examples and comparative experiments.

The $T_{g(\text{midpoint})}$ is measured using DSC according to ISO11357 (edition
10 2009) with a heating rate of 5 °C/min. The test method for tensile testing (tensile strength, E-modulus, elongation at break) is according to ISO 527-2. The test method for viscosity measurement is according to ISO 3219 at 23°C.

Synthesis of resins

Resin A (methacrylate containing resin-compound (a) in the present application)

508 g epoxy resin with average mol mass of 350, 98 g diphenylol propane and 1.1g tetra butyl phosphonium bromide were heated up to 110°C. After
5 reaching exotherm, reaction was maintained at 115°C until EEW (epoxy equivalent weight) is approximately 330 g/epoxy. Thereafter, the mixture was cooled down to 110 °C, and 0.04 g inhibitor was added followed by 154 g methacrylic acid (dosing time 1 hr). Reaction was maintained until viscosity was 400 – 480 mPa.s (Cone & Plate at 125°C) and acid number was 10 – 16 mg KOH/g, WPU (average molecular weight per
10 reactive unsaturation) was 425. Finally when spec has reached resin A is cooled down to 80°C. The Tg of resin A is 12.6°C.

This solid resin A is then dissolved in 1,4-butanediol dimethacrylate (compound (c) in the present application) (for relative amounts see Table).

15 Resin B (unsaturated polyester- compound (b) in the present application)

Resin B, liquid at room temperature, was obtained by heating 913 g polyoxypropylene glycol bisphenol A, 87 g fumaric acid and 0.06 g hydroquinone within 2 hours to 210 °C with continuous stirring in a standard polycondensation reactor, use being made of a vacuum (to max. 0.1 bar): start of vacuum 1 hour after reaching 210
20 °C. The synthesis is ended at an acid number of < 20 mg KOH/g and a viscosity at 23 °C of < 4 dPa.s. The resin has a WPU of 1338.

This resin B is diluted with benzyl methacrylate (compound (d) in the present application) (for relative amounts see Table).

25 Resin C (methacrylate containing resin-compound (a) in the present application)

362 g epoxy resin with average mol mass of 350 is heated up to 100°C, continuously stirring using oxygen sparge and nitrogen blanket. At this temperature, 40 g of methacrylic acid, 0.1 g chromium chloride and 0.08 g hydrochinon are added. After 15 minutes everytime 3 x 40 g of methacrylic acid is added. Reaction
30 is maintained and synthesis is ended at an acid number < 5 mg KOH/g and EEW (epoxy equivalent weight of 5000 – 8000 g/epoxy. After reaching the end point the resin (having a WPU of 280); hereinafter referred to as resin C) is cooled down. The Tg of resin C is 0.2°C.

This solid resin C is then dissolved in 1,4-butanediol dimethacrylate
35 and PEG200DMA (both compound (c) in the present application) (for relative amounts

see Table).

Resin D (unsaturated polyester- compound (b) in the present application)

5 Resin D, liquid at room temperature, was obtained by heating 938 g polypropylene glycol bisphenol A, 89 g fumaric acid and 0.12 g hydroquinone within 2 hours to 210 °C with continuous stirring in a standard polycondensation reactor, use being made of a vacuum (to max. 0.1 bar): start of vacuum 1 hour after reaching 210 °C. The synthesis is ended at an acid number of < 20 mg KOH/g and a viscosity at 23 °C of < 4 dPa.s. The resin D has a WPU of 1338.

10

Example 1 and comparative experiments A-F

Formulations were prepared according to table 1 (amounts given are wt.%). The compounds were mixed at room temperature and the viscosities determined. Thereafter, in Comparative Experiments A-D and Example 1, the mixture
15 was cured at 60°C using 1% tert-butyl peroxybenzoate , 0.8% bis(4-tert-butylcyclohexyl) peroxydicarbonate and 1% of a 1% cobalt (II) 2-ethylhexanoate accelerator. In Comparative Experiments E and F, the mixture was cured at room temperature using 0.2% of a 10% solution of cobalt(II) octoate, 1.0% of a 10% solution of dimethyl aniline and 2.0% methylethylketon peroxide (Butanox M50) followed by a
20 postcure of 24 hours at 60 °C and 24 hours at 80 °C, according to the procedure according to WO-A-2008077586. After curing the tensile properties were determined. The following abbreviations are used:

1,4-BDDMA=1,4-butanediol dimethacrylate (molecular weight M_n 226) obtained from Aldrich,

25 BNMA= Benzyl methacrylate (molecular weight M_n 176) obtained from Aldrich.

PEG200DMA= polyethyleneglycol dimethacrylate (molecular weight M_n 330) obtained from Aldrich.

Table

Amount (in wt.%)	Comparative Experiment A	Comparative Experiment B	Comparative Experiment C	Comparative Experiment D	Example 1	Comp Ex E	Comp Ex F
Solid resin A (without reactive diluent)	50	43	40	43.7	43.7		
Solid resin B		4.3	10		7.7		
Solid resin C						59	59
Solid resin D						5	10
BDDMA	50	52.7	50	22.2	14.5	1	31
BNMA				34.1	34.1		
PEG200DMA						35	
Sum	100	100	100	100	100	100	100
Viscosity, 23°C (mPa.s)	911	550	688	233	431	602	856
WPU	179	175	184	244	232	207	185
EI at break [%]	1.5	1.8	1.5	1.1	4.6	2.8	1.5
E-mod [GPa]	3.2	3.1	3.0	3.5	2.7	3.0	3.6
Tensile Strength (MPa)	45	52	45	42	75	60	48

As the cured resin composition of Comparative Experiment E has an elongation at break of higher than 2%, an E-modulus of more than 2 GPa, a high tensile strength and as the viscosity of the uncured resin composition is between 300 and 1000 mPa.s, a resin composition according to the state of the art that is used in

5 Comparative Experiment E is suitable for being applied in (re)lining of tubes or pipes. However, for (re)lining of tubes or pipes which are under pressure, it would be beneficial to be able to increase the elongation at break, however without significantly sacrificing the E-modulus. As shown in Example 1, using the combination of compounds according to the invention surprisingly results in an increase of the

10 elongation at break without losing E-modulus too much, while the tensile strength is even increased.

Comparing Comparative Experiments A-D with Example 1 shows that the combination of compounds (a), (b), (c) and (d) as claimed is needed to obtain an increase of the elongation at break without significantly sacrificing the E-modulus and

15 further shows that the elongation at break can surprisingly be increased without significantly sacrificing the E-modulus:

Comparing Comparative Experiment B and C with Comparative Experiment A shows that adding resin B (compound (b)) to a mixture of compound (a) and (c) results in that the elongation at break remains the same or increases to a small

20 extent (+20%).

Comparing Comparative Experiment D with Comparative Experiment A shows that adding BNMA (compound (d)) to a mixture of compound (a) and (c) results in that the elongation at break decreases (-27%).

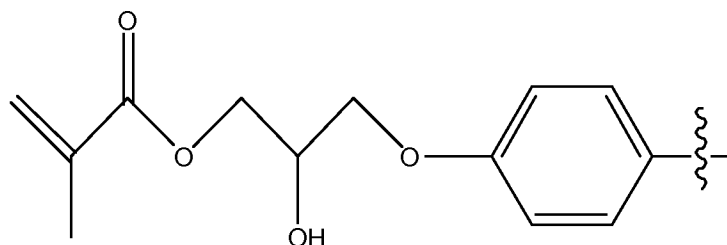
Very surprisingly when adding compound (b) and compound (d) to a

25 mixture of compound (a) and (c), the elongation at break remarkably increases (+155%) and without significantly sacrificing the E-modulus. The elongation at break increases to more than 3%, while the E modulus is maintained at a level higher than 2 GPa, even higher than 2.5 GPa. Furthermore, the tensile strength is even increased. As the elongation at break is higher than 3% and the E modulus is even higher than 2.5

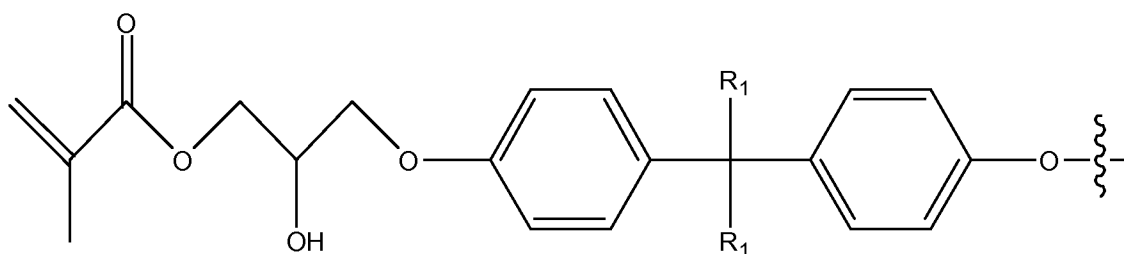
30 GPa, the resin composition is able to result in superior relining performance under high pressure.

CLAIMS

1. Thermosetting, radically curable resin composition suitable for (re)lining comprising
 - 5 a. 30 - 70 wt.% of a methacrylate containing resin with a T_g of at least -5°C and at most 100°C ,
 - b. 2.5 - 20 wt.% of an unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and alkoxyated bisphenol A and/or alkoxyated bisphenol F building blocks
 - 10 as diol building blocks,
 - c. 1 - 40 wt.% of at least one ethylenically unsaturated compound excluding benzyl methacrylate which ethylenically unsaturated compound is able to copolymerize with (a), (b) and (d);
 - d. 5 - 60 wt.% of benzyl methacrylate,
 - 15 the amounts are calculated as wt.% of the total weight of the compounds (a), (b), (c) and (d).
2. Thermosetting resin composition according to claim 1, wherein the resin composition comprises at least one dimethacrylate as compound (c).
3. Thermosetting resin composition according to claim 2, wherein the resin
- 20 composition comprises a dimethacrylate selected from 1,4-butanediol dimethacrylate, neopentylglycol dimethacrylate, PEG200 dimethacrylate, triethylene glycol dimethacrylate and/or tripropylene glycol dimethacrylate.
4. Thermosetting resin composition according to claim 2, wherein the dimethacrylate is selected from 1,4-butanediol dimethacrylate and/or PEG200
- 25 dimethacrylate.
5. Thermosetting resin composition according to anyone of the previous claims, wherein the resin composition comprises styrene in an amount lower than 0.01 wt.% (relative to the total resin composition).
6. Thermosetting resin composition according to anyone of the previous claims,
- 30 wherein the methacrylate containing resin (a) is obtained by reaction of an epoxy oligomer or polymer with methacrylic acid or methacrylamide, preferably with methacrylic acid.
7. Thermosetting resin composition according to anyone of the previous claims, wherein the methacrylate containing resin (a) is a resin comprising a moiety
- 35 with the following structure



8. Thermosetting resin composition according to anyone of the previous claims, wherein the methacrylate containing resin (a) is a resin comprising a moiety with the following structure



in which R_1 is H or CH_3 , preferably CH_3 .

9. Thermosetting resin composition according to anyone of the previous claims, wherein compound(s) (c) is (are) able to dilute (a) and (b).
10. Thermosetting resin composition according to anyone of the previous claims, wherein the unsaturated polyester (b) comprises propoxylated bisphenol A building blocks as diol building blocks.
11. Thermosetting resin composition according to anyone of the previous claims, wherein the resin composition comprises between 40 and 60 wt.% of compound (a), between 5 and 12.5 wt.% of compound (b), between 10 and 25 wt.% of compound (c) and between 15 and 45 wt.% of benzyl methacrylate (d).
12. Thermosetting resin composition according to anyone of the previous claims, wherein the resin composition further comprises radical initiator (e) in an amount of between 0.1 and 5 wt% (relative to the total resin composition) and the radical initiator is a photo-initiator or a thermal initiator or a redox initiator.
13. Fiber mat comprising fibers which fibers are impregnated with a resin composition according to claim 12.
14. Cured (re)liners obtained by curing a resin composition according to claim 12.
15. Use of a cured (re)liner according to claim 14 at a pressure higher than atmospheric pressure.
16. Use of a resin composition according to claim 12 in the field of chemical

anchoring, roofing, gelcoats, containers, tanks, pipes, automotive parts,
flooring, windmill blades, aviation, off shore applications.

17. Cured objects or structural parts obtained by mixing the compounds of a resin composition according to claim 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/053279

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C08L63/10	C08G59/14	C08G63/91
B29C51/00	B29C63/34	F16L55/16
D04H3/00	C08G59/17	
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) C08L C08F C08G F16L B29C F27D D04H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 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.
A	EP 1 762 581 A1 (YOSHIKA CORP [JP]) 14 March 2007 (2007-03-14) cited in the application paragraphs [0014] - [0017], [0019], [0038], [0039], [0043], [0044]; claims 1-15	1-17
A	----- JP 2007 291179 A (TOA GROUT KOGYO CO; JAPAN U PICA CO LTD) 8 November 2007 (2007-11-08) cited in the application examples 1-8	1-17
A	----- WO 2008/077586 A1 (DSM IP ASSETS BV [NL]; KLEIN NAGELVOORT JOANNA [NL]; BESTEN DEN CORNEL) 3 July 2008 (2008-07-03) cited in the application claims 1-29; table 1 ----- -/-	1-17
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 26 April 2013		Date of mailing of the international search report 06/05/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Madalinski, Maciej

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/053279

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/108939 A1 (DSM IP ASSETS BV [NL]; SZKUDLAREK MARIAN HENRYK [DE]; JANSEN JOHAN FRA) 30 September 2010 (2010-09-30) cited in the application table 1 -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/053279

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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