

RADICALLY POLYMERIZABLE RESIN COMPOSITION AND CURED PRODUCT THEREOF

BACKGROUND

5 [Technical Field]

[0001]

The present invention relates to a radically polymerizable resin composition and a cured product thereof.

This application claims priority under Japanese Patent Application No. 2019-235910
10 filed on December 26, 2019, the contents of which are incorporated herein by reference.

[Background Technology]

[0002]

When polymerization is carried out by using common liquid vinyl monomers, large shrinkage occurs. The shrinkage causes strain problems when the vinyl monomers are
15 used in industrial products. Therefore, it is important to produce a resin having a small shrinkage rate of polymerization.

[0003]

Radically polymerizable resin compositions, such as unsaturated polyester resins and vinyl ester resins (epoxy acrylates), also generally shrink during curing. Since
20 “styrene” and “methyl methacrylate”, which are monomers shown in Table 1 of Non-Patent Document 1, are often used as monomers, unsaturated polyester resins in general compositions undergo volume shrinkage of about 8 to 12%, and vinyl ester resins undergo volume shrinkage of about 8 to 10%.

The values are also much larger than the 3 to 6% volumetric shrinkage found in typical epoxy resins. This has prevented the use of unsaturated polyester resins or vinyl ester resins in this industrial applications, as well as in other industries and applications.

[0004]

5 As a method for solving this problem, Patent Document 1 discloses that by using polystyrene beads as a low-shrinkage material, the man-hours of manufacturing or the manufacturing time can be reduced, and a low-shrinkage unsaturated polyester resin composition having excellent small shrinkage, dimensional stability, and surface smoothness can be manufactured.

10 [0005]

Further, Patent Document 2 discloses that by adding an A-B type block copolymer with an unsaturated polyester resin composition, a low-shrinkage unsaturated polyester resin composition capable of producing a molded product having low shrinkage at the time of curing and excellent heat resistance can be obtained.

15 [0006]

Further, Patent Document 3 discloses that by mixing an A-B type block copolymer (vinyl acetate-styrene type) composed of A and B segments with fine particles of silicic acid, a low shrinkage unsaturated polyester resin composition having a large low shrinkage effect and high water resistance can be obtained when molding at room
20 temperature or at medium temperature.

[0007]

In addition, a concrete, what is called “expandable concrete”, is obtained by mixed an expansive additive into a conventional hydraulic curable composition (containing cement such as Portland cement). According to the Japanese JIS standard, it is said that
25 the expandable concrete is cured in water for 7 days to form a hydrate of the expansive

additive and expands to use the increased volume of the hydrate, but the expansion effect in air is not recognized.

[Prior Art Documents]

Patent Documents

5 [0008]

[Patent Document 1] Japanese Patent Application Laid-Open No. Hei 11-315198

[Patent Document 2] Japanese Patent No. 2794802

[Patent Document 3] Japanese Patent Application Laid-Open No. Hei 05-222282

[Non-Patent Documents]

10 [0009]

[Non-patent Document 1] Takeshi Endo, Whether volume shrinkage during polymerization is inevitable, Polymer, Vol. 27, February issue (1978), pages 108 to 111.

SUMMARY

15 [Problems to Be Solved by the Invention]

[0010]

In the conventional radically polymerizable resin composition, a thermoplastic resin such as polystyrene is used alone, or two or more kinds of block copolymers are used to produce a resin having a low shrinkage rate. They mostly function as "shrinkage preventive materials".

20

In addition, these resin compositions are based on the idea of offsetting the thermal expansion of the thermoplastic resin due to the heat generated by curing and the curing shrinkage of the unsaturated polyester resin, and are often limited to applications such as sheet molding compounds (SMC) and bulk molding compounds (BMC) in which heat

25 molding is performed in the middle temperature range or higher.

[0011]

It is an object of the present invention to provide a radically polymerizable resin composition having a small shrinkage ratio by incorporating an expansive additive rather than the shrinkage preventing material, thereby expanding the resin composition as a whole at a constant ratio when the resin composition is cured, and then stabilizing the resin composition, without being limited to a molding method, a working temperature, an application, etc.

It is another object of the present invention to provide a cured product which does not cause deterioration in strength after molding.

10 [Means for Solving Problems]

[0012]

That is, the present invention is represented by the following [1] to [13].

[1] A radically polymerizable resin composition, comprising a radically polymerizable compound (A), an expansive additive (B), a radical polymerization initiator (C) and an aggregate (I); and

not comprising free water,

wherein the aggregate (I) comprises bonding water.

[2] The radically polymerizable resin composition according to [1],

wherein an amount of the aggregate (I) is 5 to 500 parts by mass with respect to 100

20 parts by mass of the radically polymerizable compound (A).

[3] The radically polymerizable resin composition according to [1] or [2],

wherein the radically polymerizable compound (A) comprises a vinyl ester resin and a radically polymerizable monomer.

[4] The radically polymerizable resin composition according to any one of [1] to [3], wherein the expansive additive (B) comprises at least one kind selected from the group consisting of lime and calcium sulfo aluminate.

[5] The radically polymerizable resin composition according to any one of [1] to [4],
5 wherein the radical polymerization initiator (C) is a hydroperoxide (ROOH).

[6] The radically polymerizable resin composition according to any one of [1] to [5] further comprising a metal-containing compound (D) and a thiol compound (E).

[7] The radically polymerizable resin composition according to any one of [1] to [6], wherein an amount of the expansive additive (B) is 0.3 parts by mass to 30 parts by mass
10 with respect to 100 parts by mass of the radically polymerizable compound (A).

[8] The radically polymerizable resin composition according to any one of [1] to [7], wherein an amount of the radical polymerization initiator (C) is 0.1 parts by mass to 10 parts by mass with respect to 100 parts by mass of the radically polymerizable compound (A).

[9] A cured product of the radically polymerizable resin composition described in
15 any one of [1] to [8].

[10] The cured product according to [9], wherein the rate of change in the length of the cured product is 0 to 1000×10^{-6} after 3000 hours from curing.

[11] A method of producing a radically polymerizable resin composition, the
20 method comprises

a mixing step of mixing a radically polymerizable compound (A), an expansive additive (B), a radical polymerization initiator (C) and an aggregate (I), wherein the aggregate (I) comprises bonding water.

[12] The method of producing the radically polymerizable resin composition
25 according to [11],

wherein the method does not include the step of adding water.

[13] The radically polymerizable resin composition is obtained by using the method of producing the radically polymerizable resin composition described in [11] or [12],

wherein the radically polymerizable resin composition comprises a radically
5 polymerizable compound (A), an expansive additive (B), a radical polymerization initiator (C) and an aggregate (I).

[0013]

[Effect of the Invention]

10 [0014]

According to the present invention, it is possible to provide a radically
polymerizable resin composition capable of suppressing shrinkage while maintaining
strength by adding an appropriate amount of an expansive additive to the radically
polymerizable resin composition, which causes curing shrinkage by decreasing free
15 volume of liquid components when the resin composition is cured, and to provide a cured
product of the radically polymerizable resin composition.

DETAILED DESCRIPTION OF DRAWINGS

[0015]

20 FIG. 1 is a graph showing the results of Examples 1 to 3 and Comparative Examples
1 to 3.

FIG. 2 is a graph showing the results of Example 4 and Comparative Example 4.

DETAILED DESCRIPTION OF THE EMBODIMENTS

25 [0016]

The present invention will now be described in detail.

[0017]

(Radically Polymerizable Resin Composition)

The radically polymerizable resin composition comprises a radically polymerizable
5 compound (A), an expansive additive (B), a radical polymerization initiator (C), and an
aggregate (I), and does not contain free water. The aggregate (I) contains bonding water.
Here, the term “bonding water” is a concept to be distinguished from free water. As
described in “Method of Measuring Water Content” below, a bonding water content is
calculated from the weight change rate (decrease rate) from 95°C to 105°C in the TG/DTA
10 experiment. Examples of the bonding water include crystal water contained in the
aggregate (I) and adsorbed water strongly adsorbed on the internal micropores and
surfaces of the aggregate (I). The term “free water” includes, for example, water added
in a step of adding water in a step of manufacturing a radically polymerizable resin
composition. “The radically polymerizable resin composition does not contain free
15 water, and the aggregate (I) contains bonding water.” means a radically polymerizable
resin composition obtained by a production method without a step of adding water.
Preferably, the radical polymerizable resin composition is obtained by a manufacturing
method which does not include a step of pretreating the aggregate (I) under a dry
condition described later, and does not include a step of adding water. For example,
20 aggregate (I) which is usually available in the market can be used as it is. Alternatively,
the aggregate (I) may be pretreated to preserve the aggregate (I) at a constant temperature
and humidity for a constant time in order to stabilize the amount of the bonding water
contained in the aggregate (I). Since the content of the bonding water contained in the
aggregate (I) can be confirmed by the measurement method described later, the
25 temperature, humidity, and treatment time can be appropriately determined depending on

the type of aggregate (I) to be used and the water content of the aggregate (I) at the time of obtaining.

[0018]

<Radical Polymerizable Compound (A)>

5 The radically polymerizable resin composition uses a radically polymerizable compound (A) as a base material. In the present invention, the radical polymerizable compound (A) refers to a compound having an ethylenically unsaturated group in the molecule and undergoing a polymerization reaction by a radical.

Examples of the radically polymerizable compound (A) include a vinyl ester resin
10 (epoxy (meth) acrylate resin), an unsaturated polyester resin, a polyester (meth) acrylate resin, a urethane (meth) acrylate resin, a (meth) acrylate resin, a radically polymerizable unsaturated monomer, and a mixture of the above-mentioned resins and a radically polymerizable unsaturated monomer. Among them, one or more kinds selected from a vinyl ester resin, an unsaturated polyester resin, and a mixture of these resins and a
15 radically polymerizable unsaturated monomer are preferable. Among them, a vinyl ester resin is more preferable. In this specification, “(meth) acrylate” means “acrylate or methacrylate”.

[0019]

[Vinyl Ester Resin]

20 The vinyl ester resin may be obtained by reacting an epoxy resin with an unsaturated monobasic acid.

[0020]

Examples of the epoxy resin include bisphenol-type epoxy resin, biphenyl type epoxy resin, novolak type epoxy resin, trisphenol methane type epoxy resin,

aralkyldiphenol type epoxy resin, naphthalene type epoxy resin, aliphatic type epoxy resin and the like. These may be used alone or in combination.

[0021]

Examples of the bisphenol-type epoxy resin include those obtained by reacting
5 bisphenols with epichlorohydrin and/or methyl epichlorohydrin, and those obtained by reacting glycidyl ether of bisphenol A with a condensate of the bisphenols with epichlorohydrin and/or methyl epichlorohydrin. Examples of the bisphenols include bisphenol A, bisphenol F, bisphenol S, tetrabromobisphenol A and the like.

Examples of the biphenyl type epoxy resin include those obtained by reacting
10 biphenol with epichlorohydrin and/or methyl epichlorohydrin.

[0022]

Examples of the novolak type epoxy resin include those obtained by reacting phenol novolak or cresol novolak with epichlorohydrin and/or methyl epichlorohydrin.

Examples of the trisphenolmethane-type epoxy resin include those obtained by
15 reacting trisphenolmethane, triscresol methane with epichlorohydrin and/or methyl epichlorohydrin.

Examples of the aralkyldiphenol-type epoxy resin include those obtained by reacting aralkylphenol with epichlorohydrin and/or methyl epichlorohydrin.

[0023]

20 Examples of the naphthalene type epoxy resin include those obtained by reacting dihydroxynaphthalene with epichlorohydrin and/or methyl epichlorohydrin.

[0024]

Examples of the aliphatic epoxy type resin include an alicyclic type epoxy resin, an alicyclic diol diglycidyl ether type epoxy resin, an aliphatic diol diglycidyl ether type
25 epoxy resin, a poly (oxyalkylene) glycol diglycidyl ether type epoxy resin and the like.

[0025]

Examples of the alicyclic type epoxy resin include an alicyclic diepoxy acetal, an alicyclic diepoxy adipate, and an alicyclic diepoxy carboxylate.

Specific examples of the alicyclic diol diglycidyl ether include diglycidyl ethers of alicyclic diols having 3 to 20 carbons (preferably 6 to 12 carbon atoms, more preferably 7 to 10 carbon atoms), such as cyclohexane dimethanol diglycidyl ether, dicyclopentenyl dialcohol diglycidyl ether, diglycidyl ether of hydrogenated bisphenol A, and dihydroxyterpene diglycidyl ether. A commercial product of cyclohexanedimethanol diglycidyl ether is "Denacol EX -216 L" of Nagase ChemteX Corporation.

[0026]

Specific examples of aliphatic diol diglycidyl ethers include, for example, diglycidyl ethers of aliphatic diols having 2 to 20 carbons (preferably 4 to 12 carbon atoms, more preferably 4 to 8 carbon atoms, and particularly preferably 4 to 6 carbon atoms), such as 1,6-hexanediol diglycidyl ether, 1,4-butanediol diglycidyl ether, ethylene glycol diglycidyl ether, and propylene glycol diglycidyl ether. Among these, commercial products of 1,6-hexanediol diglycidyl ether include "Denacol EX -212 L" of Nagase ChemteX Co., Ltd., "SR -16 H" or "SR -16 HL" of Sakamoto Pharmaceutical Industry Co., Ltd., and "Epogose (registered trademark) HD" of Yokkaichi Synthetic Co., Ltd. In addition, a commercial product of 1, 4-butanediol diglycidyl ether is "Denacol EX -214 L" of Nagase ChemteX Co., Ltd.

[0027]

Specific examples of the poly (oxyalkylene) glycol diglycidyl ether include, for example, diethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, tripropylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, poly (tetramethylene) glycol diglycidyl ether, and the like.

[0028]

Preferred examples of aliphatic epoxy resins include 1, 6-hexanediol diglycidyl ether, polyethylene glycol diglycidyl ether, poly (tetramethylene) glycol diglycidyl ether, and the like. Among them, those having a number-average molecular weight of 150 to 1000 are more preferable.

[0029]

The epoxy resin may be a diglycidyl ester such as a dimer acid diglycidyl ester or a hexahydrophthalic acid diglycidyl ester. The epoxy resin includes an epoxy resin having an oxazolidone ring obtained by reacting the epoxy resin with a diisocyanate. Specific examples of epoxy resins having an oxazolidone ring include ARALDITE (registered trademark) AER 4152 made by Asahi Kasei Epoxy Co., Ltd.

[0030]

Examples of the unsaturated monobasic acid include (meth) acrylic acid, crotonic acid, cinnamic acid and the like. A product obtained by reacting a compound having one hydroxy group and one or more (meth) acryloyl groups with a polybasic acid anhydride may be used. In this specification, “(meth) acrylic acid” means one or both of “acrylic acid and methacrylic acid” and “(meth) acryloyl group” means one or both of “acryloyl group and methacryloyl group”.

The polybasic acid is used to increase the molecular weight of the epoxy resin, and can be used in a known manner. Examples of the polybasic acid include succinic acid, glutaric acid, adipic acid, sebacic acid, phthalic acid, fumaric acid, maleic acid, itaconic acid, tetrahydrophthalic acid, hexahydrophthalic acid, dimer acid, ethylene glycol 2 mol maleic anhydride adduct, polyethylene glycol 2 mol maleic anhydride adduct, propylene glycol 2 mol maleic anhydride adduct, polypropylene glycol 2 mol maleic anhydride adduct, dodecane diacid, tridecane diacid, octadecane diacid, 1, 16 - (6-ethylhexadecane)

dicarboxylic acid, 1, 12 - (6-ethyldodecane) dicarboxylic acid, and carboxyl-terminated butadiene-acrylonitrile copolymer (trade name: Hycar CTBN).

[0031]

[Unsaturated Polyester Resin]

5 The unsaturated polyester resin may be obtained by esterifying a dibasic acid component containing an unsaturated dibasic acid and, if necessary, a saturated dibasic acid with a polyhydric alcohol component.

Examples of the unsaturated dibasic acid include maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, and the like, which may be used alone or
10 in combination of two or more kinds.

Examples of the saturated dibasic acid include, for example, aliphatic dibasic acids such as adipic acid, sebacic acid, azelaic acid, and isosebacic acid; aromatic dibasic acids such as phthalic acid, phthalic anhydride, halogenated phthalic anhydride, isophthalic acid, terephthalic acid, tetrachlorophthalic acid, tetrachlorophthalic anhydride, dimer acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 2,3-naphthalenedicarboxylic acid, 2,3-naphthalenedicarboxylic acid anhydride, 4,4'-biphenyldicarboxylic acid, and dialkyl esters thereof; and halogenated saturated dibasic acids. These saturated dibasic acids may be used alone or in combination of two or
15 more.

20 [0032]

The polyhydric alcohol is not particularly limited, and examples of the polyhydric alcohol include dihydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 2-methyl -1, 3-propanediol, 2-methyl -1, 4-butanediol, 2, 2-dimethyl -1, 3-propanediol, 2, 2, 4-trimethyl -1, 3-pentanediol, 2-ethyl -2
25 butanediol, 2, 2-dimethyl -1, 3-propanediol, 2, 2, 4-trimethyl -1, 3-pentanediol, 2-ethyl -2

butyl -1, 3-propanediol, 3-methyl -1, 5-pentanediol, diethylene glycol, triethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, 1, 2-cyclohexane glycol, 1, 3-cyclohexane glycol, 1, 4-cyclohexane glycol, 1,4-cyclohexanedimethanol, paraxylene glycol, bicyclohexyl -4, 4 '-diol, 2,6-decalin glycol, and 2,7-decalin glycol;

5 dihydric alcohols such as adducts of dihydric phenols represented by hydrogenated bisphenol A, cyclohexanedimethanol, bisphenol A, bisphenol F, bisphenol S, tetrabromobisphenol A and the like with alkylene oxides represented by propylene oxide or ethylene oxide; and

trivalent or higher alcohols such as 1,2,3,4-tetrahydroxybutane, glycerin,
10 trimethylolpropane and pentaerythritol.

[0033]

The unsaturated polyester may be modified with a dicyclopentadiene-based compound to the extent that the effect of the present invention is not impaired. Examples of the method of modifying the unsaturated polyester by the dicyclopentadiene-based
15 compound include a known method such as a method of obtaining an addition product (cidecanol monomaleate) of a dicyclopentadiene and a maleic acid, and introducing a dicyclopentadiene skeleton by using, as a single basic acid, the resulting addition product.

Oxidative polymerization (air curing) groups such as allyl groups or benzyl groups can be introduced into the vinyl ester resin or unsaturated polyester resin used in the
20 present invention. The introduction method is not particularly limited. Examples of the introduction method include a method of addition of a polymer containing an oxidation polymerization group; a method of condensation of a compound having a hydroxyl group and an allyl ether group; and a method of addition of a reaction product which is obtained by reacting allyl glycidyl ether or 2, 6-diglycidyl phenyl allyl ether with a compound
25 having a hydroxyl group and an allyl ether group and with an acid anhydride.

The oxidative polymerization (air curing) in the present invention refers to crosslinking accompanied by formation and decomposition of a peroxide by oxidation of a methylene bond between an ether bond and a double bond, which is found in, for example, an allyl ether group.

5 [0034]

[Polyester (Meth) Acrylate Resin, Urethane (Meth) Acrylate Resin, and (Meth) Acrylate Resin]

Examples of the polyester (meth) acrylate resin in the present invention include a polyester obtained by reacting a polycarboxylic acid with a polyhydric alcohol,
10 specifically a resin obtained by reacting (meth) acrylic acid with hydroxyl groups at both ends of polyethylene terephthalate or the like.

Examples of the urethane (meth) acrylate resin include a resin obtained by reacting (meth) acrylic acid with hydroxyl groups or isocyanate groups at both ends of a polyurethane obtained by reacting an isocyanate with a polyhydric alcohol.

15 Examples of the (meth) acrylate resin include a poly (meth) acrylic resin having one or more substituents selected from a hydroxyl group, an isocyanate group, a carboxy group and an epoxy group; and a resin obtained by reacting a (meth) acrylic ester having a hydroxyl group with the substituents of a polymer which is obtained by polymerization of the (meth) acrylate and the monomer having one or more substituents selected from a
20 hydroxyl group, an isocyanate group, a carboxy group and an epoxy group.

[0035]

[Radically Polymerizable Unsaturated Monomer]

In the present invention, a radically polymerizable unsaturated monomer can be used as the radically polymerizable compound (A).

The radically polymerizable unsaturated monomer may be used alone, but is preferably used as a mixture of the radically polymerizable unsaturated monomer and at least one of the vinyl ester resin and the unsaturated polyester resin.

The radically polymerizable unsaturated monomer is not particularly limited, but preferably has a vinyl group or a (meth) acryloyl group.

Specific examples of the monomer having the vinyl group include styrene, p-chlorostyrene, vinyltoluene, α -methylstyrene, dichlorostyrene, divinylbenzene, tert-butylstyrene, vinyl acetate, diallyl phthalate, triallyl isocyanurate and the like.

[0036]

Specific examples of monomers having (meth) acryloyl groups include (meth) acrylate esters and the like. Examples of the (meth) acrylate esters include methyl (meth) acrylate, ethyl (meth) acrylate, n-butyl (meth) acrylate, iso-butyl (meth) acrylate, tert-butyl (meth) acrylate, 2-ethylhexyl (meth) acrylate, lauryl (meth) acrylate, cyclohexyl (meth) acrylate, benzyl (meth) acrylate, stearyl (meth) acrylate, tridecyl (meth) acrylate, cyclohexyl (meth) acrylate, dicyclopentanyl (meth) acrylate, dicyclopentenyl (meth) acrylate, dicyclopentenylloxyethyl (meth) acrylate, phenoxyethyl methacrylate, 2-hydroxyethyl methacrylate, ethylene glycol monomethyl ether (meth) acrylate, ethylene glycol monoethyl ether (meth) acrylate, ethylene glycol monobutyl ether (meth) acrylate, ethylene glycol monohexyl ether (meth) acrylate, ethylene glycol mono-2-ethylhexyl ether (meth) acrylate, diethylene glycol monomethyl ether (meth) acrylate, diethylene glycol monoethyl ether (meth) acrylate, diethylene glycol monobutyl ether (meth) acrylate, diethylene glycol monohexyl ether (meth) acrylate, diethylene glycol mono-2-ethylhexyl ether (meth) acrylate, neopentyl glycol di (meth) acrylate, PTMG dimethacrylate, 1,3-butylene glycol di (meth) acrylate, 1,6-hexanediol di (meth) acrylate, neopentyl glycol di (meth) acrylate, 2-hydroxy -1, 3-dimethacryloxypropane, 2,2-bis [4- (methacryloyl

ethoxy) phenyl] propane, 2,2-bis [4- (methacryloxy-diethoxy) phenyl] propane, 2,2-bis [4- (methacryloxy-polyethoxy) phenyl] propane, tetraethylene glycol diacrylate, bisphenol AEO-modified (n = 2) diacrylate, isocyanuric acid EO-modified (n = 3) diacrylate, pentaerythritol diacrylate monostearate, dicyclopentenyl acrylate, dicyclopentenyl oxyethyl acrylate, tricyclodecanyl (meth) acrylate, tris (2-hydroxyethyl) isocyanuryl acrylate, and the like.

[0037]

Further, examples of the polyfunctional (meth) acrylate ester include alkanediol di (meth) acrylates such as ethylene glycol di (meth) acrylate, 1,2-propylene glycol di (meth) acrylate, 1,3-butylene glycol di (meth) acrylate, 1,4-butylene glycol di (meth) acrylate, neopentyl glycol di (meth) acrylate, 1,6-hexanediol di (meth) acrylate, and the like; polyoxyalkylene glycol di (meth) acrylates such as diethylene glycol di (meth) acrylate, dipropylene glycol di (meth) acrylate, triethylene glycol (meth) acrylate, tetraethylene glycol di (meth) acrylate, polyethylene glycol (meth) acrylate; trimethylolpropane di (meth) acrylate, glycerol di (meth) acrylate, pentaerythritol di (meth) acrylate, trimethylolpropane tri (meth) acrylate, glycerol tri (meth) acrylate, pentaerythritol tri (meth) acrylate, pentaerythritol tetra (meth) acrylate, dipentaerythritol hexa (meth) acrylate, and the like.

[0038]

Further, the following compounds may be used as the radically polymerizable unsaturated monomer. Examples thereof include divinylbenzene, diallyl phthalate, triallyl phthalate, triallyl cyanurate, triallyl isocyanurate, allyl (meth) acrylate, diallyl fumarate, allyl methacrylate, vinyl benzyl butyl ether, vinyl benzyl hexyl ether, vinyl benzyl octyl ether, vinyl benzyl (2-ethylhexyl) ether, vinyl benzyl (β -methoxymethyl) ether, vinyl benzyl (n-butoxypropyl) ether, vinyl benzyl cyclohexyl ether, vinyl benzyl (β -

phenoxyethyl) ether, vinyl benzyl dicyclopentenyl ether, vinyl benzyl dicyclopentenyl oxyethyl ether, vinyl benzyl dicyclopentenyl methyl ether, and divinylbenzyl ether.

In addition to the above, dicyclopentenyl (meth) acrylate, dicyclopentenyl oxyethyl (meth) acrylate and the like can be used.

5 These may be used alone or in combination of two or more species.

[0039]

The radically polymerizable unsaturated monomer can be used to reduce the viscosity of the radically polymerizable resin composition of the present invention and to improve the hardness, strength, chemical resistance, water resistance, etc., however, if the
10 content of the radically polymerizable unsaturated monomer is too high, it may lead to deterioration of the cured product and environmental pollution. Therefore, the content of the radically polymerizable unsaturated monomer is preferably 90% by mass or less in the radically polymerizable compound (A).

[0040]

15 In the radical polymerizable compound (A), the catalyst or the polymerization inhibitor which are used in the steps of synthesizing a vinyl ester resin, an unsaturated polyester resin, a polyester (meth) acrylate resin, a urethane (meth) acrylate resin, and a (meth) acrylate resin may remain in the reaction system. Examples of the catalyst include a compound containing tertiary nitrogen such as triethylamine, pyridine derivative,
20 imidazole derivative, and the like; an amine salt such as tetramethylammonium chloride and triethylamine and the like; a phosphorus compound such as trimethylphosphine, triphenylphosphine and the like.

Examples of the polymerization inhibitor include hydroquinone, methyl hydroquinone, phenothiazine and the like.

When the catalyst or the polymerization inhibitor remains in the radically polymerizable compound (A), the amount thereof is preferably 0.001 to 2 parts by mass with respect to 100 parts by mass of a total amount of the vinyl ester resin and the unsaturated polyester resin.

5 [0041]

The content of the radically polymerizable compound (A) in the radically polymerizable resin composition of the present invention is preferably 10 to 99.9% by mass, more preferably 15 to 80% by mass, still more preferably 20 to 60% by mass, and the most preferably 25 to 40% by mass. When the content of the radical polymerizable
10 compound (A) in the radical polymerizable resin composition is within the above range, the hardness of the cured product is further improved.

[0042]

<Expansive Additive (B)>

The expansive additive (B) used in the present invention may be any expansive
15 additive as long as the expansive additive (B) is generally used as an expansive additive for concrete and satisfies the Japanese Industrial Standard JIS A 6202 "Expansive Additive for Concrete". Specially, an expansive additive from which calcium hydroxide or ettringite may be formed by a hydration reaction may be used. Preferable expansive additives include (1) an expansive additive containing free quicklime as an active
20 component (quicklime-based expansive additive), (2) an expansive additive containing calcium sulfoaluminate as an active component (ettringite-based expansive additive), and (3) a quicklime/ettringite composite expansive additive.

[0043]

Specific examples of quicklime-based expansive additives include Taiheiyo Hyper Expan-K, Taiheiyo Hyper Expan-M, Taiheiyo Expan-K, Taiheiyo Expan-M, and Taiheiyo N-EX made by Taiheiyo Materials Corporation.

Specific examples of the ettringite-based expansive additive include Denca CSA #
 5 10 and Denca CSA # 20 made by Denca.

Specific examples of the quicklime/ettringite composite expansive additive include Denka Power CSA Type S, Denka Power CSA Type R, and Denka Power CSA Type T made by Denka Company Limited.

[0044]

10 The amount of the expansive additive (B) of the present invention is preferably 0.3 to 30 parts by mass, more preferably 0.5 to 25 parts by mass, still more preferably 0.7 to 20 parts by mass, and most preferably 1 to 16 parts by mass with respect to 100 parts by mass of the radically polymerizable compound (A). When the amount of the expansive additive (B) is 30 parts by mass or less, the expansion rate does not exceed the elongation
 15 amount of the resin when the radically polymerizable resin composition is cured. On the other hand, when the amount is 0.3 parts by mass or more, it is impossible that the expansion performance with respect to the radical polymerizable compound (A) does not appear. These expansive additives (B) may be used alone or may be used by mixing two or more kinds.

20 [0045]

<Radical Polymerization Initiator (C)>

The radically polymerizable resin composition contains a radical polymerization initiator (C) as a curing agent. Examples of the radical polymerization initiator (C) include a thermal radical polymerization initiator (C-1) and a photoradical polymerization

initiator (C-2). Among them, a thermal radical polymerization initiator (C-1) is preferable.

Examples of the thermal radical polymerization initiator (C-1) include an organic peroxide-based radical polymerization initiator such as a diacylperoxide-based radical polymerization initiator such as benzoyl peroxide; a peroxyester system such as tert-butyl peroxybenzoate; a hydroperoxide system-based radical polymerization initiator such as cumene hydroperoxide (CHP), diisopropylbenzene hydroperoxide, tert-butyl hydroperoxide, and paramentane hydroperoxide; a dialkyl peroxide-based radical polymerization initiator such as dicumyl peroxide; a ketone peroxide-based radical polymerization initiator such as methylethyl ketone peroxide and acetylacetone peroxide; a peroxyketal system; an alkyl perester-based radical polymerization initiator; a percarbonate-based radical polymerization initiator, and the like. Among them, the hydroperoxide-based organic peroxide (RCOOH) (also referred to simply as hydroperoxides (RCOOH)) are preferable; and among them, cumene hydroperoxides (CHP) such as PERCUMYL (registered trademark) H-80 produced by Nichiyu Corporation, and the like are more preferable.

[0046]

Examples of the photoradical polymerization initiator (C-2) include benzoin ethers such as benzoin alkyl ethers; benzophenones such as benzophenone, benzyl, methyl orthobenzoyl benzoate; acetophenone such as benzyl dimethyl ketal, 2,2-diethoxyacetophenone, 2-hydroxy -2 methylpropiophenone, 4-isopropyl -2 hydroxy -2 methylpropiophenone, 1,1-dichloroacetophenone; and thioxanthone such as 2-chlorothioxanthone, 2-methylthioxanthone, and 2-isopropylthioxanthone.

[0047]

Examples of the photoradical polymerization initiator (C-2) having photosensitivity in the range from ultraviolet light to visible light include known initiators such as acetophenone, benzyl ketal and (bis) acylphosphine oxide. Specific examples of the photoradical polymerization initiator (C2) include Irgacure -1700 (Ciba Specialty Chemicals Co., Ltd.) which is a product name and is obtained by mixing 2-hydroxy -2-methyl -1-phenylpropane -1-one (product name: Darocur 1173, manufactured by Ciba Specialty Chemicals Co., Ltd.) and bis (2, 6-dimethoxybenzoyl) -2, 4, 4-trimethylpentylphosphine oxide (Ciba Specialty Chemicals Co., Ltd.) at a ratio of 75%/25%; Irgacure 1800, a 75%/25% mixture of 1-hydroxycyclohexyl phenyl ketone (product name: Irgacure 184, manufactured by Ciba Specialty Chemicals Co., Ltd.) and bis (2, 6-dimethoxybenzoyl) -2, 4, 4-trimethylpentylphosphine oxide (manufactured by Ciba Specialty Chemicals Co., Ltd.), Irgacure 1850, a 50%/50% mixture thereof; bis (2,4,6-trimethylbenzoyl) phenylphosphine oxide (product name: Irgacure 819, manufactured by Ciba Specialty Chemicals Co., Ltd.); 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (product name: Lucirin TPO, manufactured by BASF Co., Ltd.); Darocur 4265, which is a trade name and is a 50%/50% mixture of 2-hydroxy -2-methyl -1-phenylpropane -1-one (Product name: Darocur 1173, manufactured by Ciba Specialty Chemicals Co., Ltd.) and 2, 4, 6-trimethylbenzoyldiphenylphosphine oxide (Product name: Lucirin TPO, manufactured by BASF Co., Ltd.).

[0048]

Examples of the photoradical polymerization initiator (C-2) having photosensitivity in the visible light region include camphorquinone, benzyl trimethyl benzoyl diphenylphosphin oxide, methylthioxanthone, dicyclopentadiethyltitanium-di (pentafluorophenyl) and the like.

These radical polymerization initiators (C) may be used alone or used by mixing two or more of them. For the purpose of assisting main reaction of the thermosetting and photocuring reactions, the other reaction may be incorporated. Further, the thermal radical polymerization initiator (C-1) and the photoradical polymerization initiator (C-2) may be used together as necessary.

[0049]

Depending on the molding conditions, the radical polymerization initiators (C) may be used in a composite form such as a composite of an organic peroxide and dye system, a composite of a diphenyliodine salt and dye system, a composite of an imidazole and keto compound, a composite of a hexaallylbiimidazole compound and hydrogen donating compound, a composite of a mercaptobenzothiazole and thiopyrium salt, a composite of a metal arene and cyanine dye, a composite of a hexaallylbiimidazole and radical generator, and the like.

[0050]

When the radical polymerizable resin composition of the present invention contains a radical polymerization initiator (C), the amount thereof is preferably 0.1 to 10 parts by mass, more preferably 0.5 to 8 parts by mass, still more preferably 0.5 to 5 parts by mass, with respect to 100 parts by mass of the radical polymerizable compound (A).

[0051]

<Metal-Containing Compound (D)>

In the radically polymerizable resin composition, one or more kinds of metal-containing compounds (D) selected from a metal soap (D-1) and a metal complex (D-2) having a β -diketone skeleton may be used as a curing accelerator. The metal soap (D-1) in the present invention refers to a salt of a long-chain fatty acid or an organic acid other than a long-chain fatty acid and a metal element other than potassium and sodium. The

metal complex (D-2) having a β -diketone skeleton in the present invention refers to a complex in which a compound having a structure which has one carbon atom between two carbonyl groups is coordinated to a metal element.

[0052]

5 The amount of the metal-containing compound (D) in the radically polymerizable resin composition in terms of the metal component is preferably 0.0001 to 5 parts by mass, more preferably 0.001 to 4 parts by mass, and still more preferably 0.005 to 3 parts by mass with respect to 100 parts by mass of the radically polymerizable compound (A).
When the amount of the metal-containing compound (D) in terms of the metal component
10 is within the above range, curing proceeds rapidly even in water and a wet atmosphere.

[0053]

[Metal Soap (D-1)]

The long-chain fatty acid in the metal soap (D-1) is not particularly limited, but for example, a fatty acid having 6 to 30 carbon atoms is preferable. Specific examples of the
15 long-chain fatty acid preferably include linear fatty acids or cyclic saturated fatty acids such as heptanoic acid, octanoic acid such as 2-ethylhexanoic acid, nonanoic acid, decanoic acid, neodecanoic acid, undecanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, eicosanoic acid, docosanoic acid, tetracosanoic acid, hexacosanoic acid, octacosanoic acid, triacontanoic acid, naphthenic acid; and
20 unsaturated fatty acids such as oleic acid, linoleic acid, and linolenic acid.

Rosinic acid, flaxseed oil fatty acid, soybean oil fatty acid, tall oil acid, and the like can also be used.

[0054]

The organic acid other than the long-chain fatty acid in the metal soap (D-1) is not particularly limited, but a weak acid compound having a carboxy group, a hydroxy group and an enol group and soluble in an organic solvent is preferable.

Examples of the compound having a carboxy group include a carboxylic acid such as formic acid, acetic acid, oxalic acid, and the like; a hydroxy acid such as citric acid, bile acid, sugar acid, 12-hydroxystearic acid, hydroxycinnamic acid, folic acid, and the like; amino acids such as alanine, arginine, and the like; an aromatic acid such as benzoic acid, phthalic acid, and the like.

Examples of the compound having the hydroxy group and the enol group include ascorbic acid, α acid, imide acid, erythorbic acid, croconic acid, kojic acid, squalic acid, sulfinic acid, taichoic acid, dehydroacetic acid, delta acid, uric acid, hydroxamic acid, humic acid, fulvic acid, phosphonic acid, and the like.

Among these, long-chain fatty acids are preferable; chain or cyclic saturated fatty acids having 6 to 16 carbon atoms or unsaturated fatty acids having 6 to 16 carbon atoms are more preferable; octanoic acid, 2-ethylhexanoic acid and naphthenic acid are still more preferable. Among them, 2-ethylhexanoic acid and naphthenic acid are preferable.

[0055]

The metal elements constituting the metal soap (D-1) include Groups 1 to 2 metal elements such as lithium, magnesium, calcium and barium (however, potassium and sodium are excluded), Groups 3 to 12 metal elements such as titanium, zirconium, vanadium, manganese, iron, ruthenium, cobalt, rhodium, nickel, palladium, platinum, copper, silver, gold and zinc; Groups 13 to 14 metal elements such as aluminum, indium, tin and lead; rare earth metal elements such as neodymium and cerium; bismuth; and the like.

In the present invention, Groups 2 to 12 metal elements are preferred; zirconium, barium, vanadium, manganese, iron, cobalt, copper, titanium, bismuth, calcium, lead, tin, and zinc are more preferred; zirconium, manganese, iron, cobalt, copper, titanium, bismuth, calcium, lead, tin, and zinc are still more preferred; and zirconium, manganese, cobalt, bismuth, and calcium are most preferred.

[0056]

Specific examples of the metal soap (D-1) preferably include zirconium octylate, manganese octylate, cobalt octylate, bismuth octylate, calcium octylate, zinc octylate, vanadium octylate, lead octylate, tin octylate, cobalt naphthenate, copper naphthenate, barium naphthenate, bismuth naphthenate, calcium naphthenate, lead naphthenate, and tin naphthenate, and more preferably zirconium octylate octylate, manganese octylate, cobalt octylate, bismuth octylate, calcium octylate, lead octylate, tin octylate, bismuth naphthenate, calcium naphthenate, lead naphthenate, and tin naphthenate. Among them, manganese octylate and cobalt octylate are more preferable. Specific examples of the cobalt octylate include hexoate cobalt (cobalt amount in the entire product: 8% by mass, molecular weight: 345.34) produced by Toei Corporation. Specific examples of manganese octylate include hexoate manganese (manganese amount in the total amount of the product: 8% by mass, molecular weight: 341.35) produced by Toei Chemical Industries, Ltd.

[0057]

[Metal Complex with β -Diketone Skeleton (D-2)]

A metal complex (D-2) having a β -diketone skeleton, hereinafter, also referred to as a “metal complex (D-2)”. Examples of the metal complex (D-2) include a complex formed from acetylacetone, ethyl acetoacetate, benzoylacetone, or the like and a metal.

Further, these metal complexes (D-2) exhibit the same function as the metal soap (D-1).

As the metal element constituting the metal complex (D-2), a metal element similar to the metal soap (D-1) can be used.

[0058]

Specific examples of the metal complex (D-2) preferably include zirconium
5 acetylacetonate, vanadium acetylacetonate, cobalt acetylacetonate, titanium
acetylacetonate, titanium dibutoxybis (acetylacetonate), iron acetylacetonate, and
acetoacetate ethyl ester cobalt. Further, zirconium acetylacetonate, titanium
acetylacetonate, and titanium dibutoxybis (acetylacetonate) are more preferable.

[0059]

10 <Thiol Compounds (E)>

The radically polymerizable resin composition may contain one or more thiol
compounds (E) selected from a secondary thiol compound (E-1) and a tertiary thiol
compound (E-2). In the present invention, it is supposed that the thiol compound (E) has
a function as a curing accelerator and also has a function of coordinating to the vicinity of
15 the metal of the metal-containing compound (D) and preventing the deactivation of the
metal by water.

The thiol compound (E) used in the present invention is not particularly limited as
long as the compound has at least one mercapto group bonded to a secondary or tertiary
carbon atom in the molecule (hereinafter, each of them may be referred to as a “secondary
20 mercapto group” or a “tertiary mercapto group”), but from the viewpoint of rapidly
advancing curing even in water and preventing the metal of the metal-containing
compound (D) from being deactivated by water, a polyfunctional thiol which is a
compound having at least two secondary or tertiary mercapto groups in the molecule is
preferable, and among them, a bifunctional thiol which is a compound having two

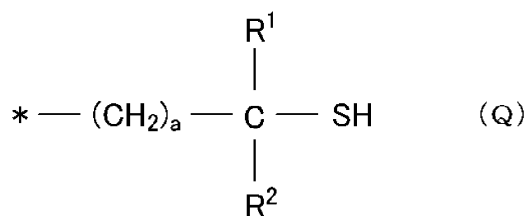
secondary or tertiary mercapto groups in the molecule is preferable. The secondary thiol compound (E-1) is more preferable to the tertiary thiol compound (E-2).

Here, “polyfunctional thiol” means a thiol compound having two or more mercapto groups as functional groups, and “bifunctional thiol” means a thiol compound having two
 5 mercapto groups as functional groups.

[0060]

There is no particular restriction on the compound having two or more secondary or tertiary mercapto groups in the molecule, but, for example, a compound having at least one structure represented by formula (Q) and having two or more secondary or tertiary
 10 mercapto groups in the molecule is preferable, wherein the mercapto groups in the structure represented by formula (Q) is included among the two or more secondary or tertiary mercapto groups.

[0061]



15 [0062]

(In the formula (Q), R¹ is a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, or an aromatic group having 6 to 18 carbon atoms; R² is an alkyl group having 1 to 10 carbon atoms or an aromatic group having 6 to 18 carbon atoms; * is linked to any organic group; and “a” is an integer of 0 to 2.)

20 [0063]

[Secondary Thiol Compound (E-1)]

When the thiol compound (E) having a structure represented by formula (Q) is a secondary thiol compound (E-1), specific examples thereof include 3-mercaptopropionic acid, di (1-mercaptopropyl) 3-mercaptopthalate, di (2-mercaptopropyl) phthalate, di (3-mercaptopropyl) phthalate, ethylene glycol bis (3-mercaptopropionate), propylene glycol bis (3-mercaptopropionate), diethylene glycol bis (3-mercaptopropionate), butanediol bis (3-mercaptopropionate), octanediol bis (3-mercaptopropionate), trimethylolpropantris (3-mercaptopropionate), trimethylolpropantris (3-mercaptopropionate), pentaerythritol tetrakis (3-mercaptopropionate), dipentaerythritol hexakis (3-mercaptopropionate), ethylene glycol bis (2-mercaptopropionate), propylene glycol bis (2-mercaptopropionate), diethylene glycol bis (2-mercaptopropionate), butanediol bis (2-mercaptopropionate), octanediol bis (2-mercaptopropionate), trimethylolpropantris (2-mercaptopropionate), pentaerythritol tetrakis (2-mercaptopropionate), dipentaerythritol hexakis (2-mercaptopropionate), ethylene glycol bis (4-mercaptopropionate), diethylene glycol bis (4-mercaptopropionate), butanediol bis (4-mercaptopropionate), octanediol bis (4-mercaptopropionate), trimethylolpropantris (4-mercaptopropionate), pentaerythritol tetrakis (4-mercaptopropionate), dipentaerythritol hexakis (4-mercaptopropionate), ethylene glycol bis (3-mercaptopropionate), propylene glycol bis (3-mercaptopropionate), diethylene glycol bis (3-mercaptopropionate), butanediol bis (3-mercaptopropionate), octanediol bis (3-mercaptopropionate), trimethylolpropantris (3-mercaptopropionate), pentaerythritol tetrakis (3-mercaptopropionate), dipentaerythritol hexakis (3-mercaptopropionate), hydrogenated bisphenol A bis (3-mercaptopropionate), bisphenol A dihydroxyethyl ether -3- mercaptopropionate, 4,4'-(9-fluorenylidene) bis (2-phenoxyethyl (3-mercaptopropionate)), ethylene glycol bis (3-mercaptopropionate -3- phenylpropionate), propylene glycol bis (3-mercaptopropionate -3- phenylpropionate), diethylene glycol bis (3-mercaptopropionate -3- phenylpropionate), butanediol bis (3-mercaptopropionate -3- phenylpropionate), octanediol bis (3-mercaptopropionate -3- phenylpropionate),

trimethylolpropantris (3-mercapto -3- phenylpropionate), tris -2- (3-mercapto -3- phenylpropionate) ethyl isocyanurate, pentaerythritol tetrakis (3-mercapto -3- phenylpropionate), dipentaerythritol hexakis (3-mercapto -3- phenylpropionate), and the like.

5 [0064]

Among the secondary thiol compounds (E-1), commercially available compounds having two or more secondary mercapto groups in the molecule include 1, 4-bis (3- mercaptobutyryloxy) butane (KarenzMT (registered trademark) BD1, manufactured by Showa Denko K.K.), pentaerythritol tetrakis (3-mercaptobutyrate) (KarenzMT (registered trademark) PE1, manufactured by Showa Denko K.K.), 1, 3, 5-tris [2- (3- mercaptobutyryloxyethyl) -1, 3, 5-triazine -2, 4, 6 (1H, 3H, 5H) -trione (KarenzMT (registered trademark) NR1, manufactured by Showa Denko K.K.), trimethylolethantris (3-mercaptobutyrate) (made by Showa Denko K.K., TEMB), trimethylolpropantris (3- mercaptobutyrate) (TPMB manufactured by Showa Denko K.K.) and the like, and it is preferable to use one or more of these compounds. Among them, 1, 4-bis (3- mercaptobutyryloxy) butane (KarenzMT (registered trademark) BD1, manufactured by Showa Denko K.K.) is preferable.

[0065]

[Tertiary Thiol Compound (E-2)]

20 When the thiol compound (E) having a structure represented by formula (Q) is a tertiary thiol compound (E-2), specific examples thereof include di (2-mercaptoisobutyl) phthalate, ethylene glycol bis (2-mercaptoisobutyrate), propylene glycol bis (2- mercaptoisobutyrate), diethylene glycol bis (2-mercaptoisobutyrate), butanediol bis (2- mercaptoisobutyrate), octanediol bis (2-mercaptoisobutyrate), trimethylolethantris (2- mercaptoisobutyrate), trimethylolpropantris (2-mercaptoisobutyrate), pentaerythritol

25

tetrakis (2-mercaptoisobutyrate), dipentaerythritol hexakis (2-mercaptoisobutyrate), di (3-mercapto -3- methylbutyl) phthalate, ethylene glycol bis (3-mercapto -3- methylbutyrate), propylene glycol bis (3-mercapto -3- methylbutyrate), diethylene glycol bis (3-mercapto -3- methylbutyrate), butanediol bis (3-mercapto -3- methylbutyrate), octanediol bis (3-mercapto -3- methylbutyrate), trimethylolethantris (3-mercapto -3- methylbutyrate), trimethylolpropantris (3-mercapto -3- methylbutyrate), pentaerythritol tetrakis (3-mercapto -3- methylbutyrate), dipentaerythritol hexakis (3-mercapto -3- methylbutyrate).

[0066]

The total amount of the thiol compounds (E) in the radically polymerizable resin composition of the present invention is preferably 0.01 to 10 parts by mass, more preferably 0.1 to 7 parts by mass, still more preferably 0.1 to 5 parts by mass, most preferably 0.2 to 4 parts by mass with respect to 100 parts by mass of the radically polymerizable compound (A). When the amount of the thiol compound (E) is 0.01 parts by mass or more, the curing function can be sufficiently obtained, and when the amount of the thiol compound (F) is 10 parts by mass or less, the curing proceeds rapidly.

[0067]

Further, the total molar ratio of the thiol compound (E) to the metal component of the metal-containing compound (D) $[(E) / (D)]$ is preferably 0.1 to 15; in one aspect of the invention, more preferably 0.3 to 10, still more preferably 0.6 to 8, most preferably 0.8 to 5, particularly more preferably 0.5 to 15; in another aspect of the invention, more preferably 1 to 12, still more preferably 1.5 to 10, and most preferably 2 to 9. When the molar ratio $[(E) / (D)]$ is 0.1 or more, the thiol compound (E) can be sufficiently coordinated to the vicinity of the metal of the metal-containing compound (D), and when the molar ratio is 15 or less, the balance between the production cost and the effect is improved.

[0068]

One kind of the thiol compound (E) may be used alone, or two or more kinds may be used together. When the secondary thiol compound (E-1) and the tertiary thiol compound (E-2) are used together, the molar ratio of the secondary thiol compound (E-1) and the tertiary thiol compound (E-2) [(E-1) / (E-2)] is preferably 0.001 to 1000, and more preferably 1 to 10. When the molar ratio [(F-1) / (F-2)] is within the above range, the metal-containing compound (A) and the thiol compound (E) are stabilized in the radically polymerizable resin composition, and the disulfide compound due to the bonding between the thiol compounds (E) is not generated as a by-product. From the viewpoint of preserving the radical polymerizable resin composition in a stable state of the metal-containing compound (D) and the thiol compound (E), it is preferable to use a secondary thiol compound (E-1) or a tertiary thiol compound (E-2) alone.

[0069]

<Curing Accelerator (F)>

The radically polymerizable resin composition may contain a curing accelerator (F) other than a metal-containing compound (D) and a thiol compound (E) for the purpose of improving curability.

Examples of the curing accelerator (F) other than the metal-containing compound (D) and the thiol compound (E) include amines. Specific examples of the amines include aniline; N, N-substituted aniline such as N, N-dimethylaniline, N, N-diethylaniline, p-toluidine, N, N-dimethyl-p-toluidine, N, N-bis (2-hydroxyethyl) -p-toluidine, 4- (N, N-dimethylamino) benzaldehyde, 4- [N, N-bis (2-hydroxyethyl) amino] benzaldehyde, 4- (N-methyl-N-hydroxyethylamino) benzaldehyde, N, N-bis (2-hydroxypropyl) -p-toluidine, N-ethyl-m-toluidine, triethanolamine, m-toluidine, diethylenetriamine, pyridine,

phenylmorpholine, piperidine, N, N-bis (hydroxyethyl) aniline, diethanolaniline, and the like; N, N-substituted p-toluidine; 4- (N, N-substituted amino) benzaldehyde; and the like.

When the radically polymerizable resin composition of the present invention contains a curing accelerator (F), the amount thereof is preferably 0.01 to 10 parts by mass, more preferably 0.05 to 5 parts by mass, and still more preferably 0.1 to 3 parts by mass with respect to 100 parts by mass of the radically polymerizable compound (A).

[0070]

<Polymerization Inhibitor (G)>

The radically polymerizable resin composition may contain a polymerization inhibitor from the viewpoint of suppressing excessive polymerization of the radically polymerizable compound (A) and controlling the reaction rate.

Examples of the polymerization inhibitor include known ones such as hydroquinone, methyl hydroquinone, phenothiazine, catechol and 4-tert-butyl catechol.

[0071]

<Curing Retarder (H)>

The radically polymerizable resin composition may contain a curing retarder for the purpose of delaying curing of the radically polymerizable compound (A). Examples of the curing retarder include free radical curing retarders, such as TEMPO derivatives such as 2, 2, 6, 6-tetramethylpiperidine-1-oxyl free radical (TEMPO), 4-hydroxy -2, 2, 6, 6-tetramethylpiperidine-1-oxyl free radical (4H-TEMPO), and 4-oxo -2, 2, 6, 6-tetramethylpiperidine-1-oxyl free radical (4-Oxo-TEMPO). Among these, 4-hydroxy -2, 2, 6, 6-tetramethylpiperidine -1-oxyl free radical (4H-TEMPO) is preferable from the viewpoint of cost and ease of handling.

When the radically polymerizable resin composition contains a polymerization inhibitor and a curing retarder, each amounts thereof is preferably 0.0001 to 10 parts by

mass, and more preferably 0.001 to 1 part by mass with respect to 100 parts by mass of the radically polymerizable compound (A).

[0072]

<Aggregate (I)>

5 The radically polymerizable resin composition contains an aggregate (I). The aggregate (I) contains bonding water. The water content of the bonding water of the aggregate (I) is not particularly limited, but is preferably 0.10 mass% or more, more preferably 0.20 mass% or more, still more preferably 0.30 mass% or more, and most preferably 0.40 mass% or more. The water content of the bonding water of the aggregate
10 (I) is preferably 5.0 mass% or less, more preferably 2.5 mass% or less, still more preferably 1.5 mass% or less, and most preferably 1.0 mass% or less. The water content of the bonding water of the aggregate (I) is not particularly limited, but is preferably 0.2 parts by mass or more, more preferably 0.5 parts by mass or more, still more preferably 1.0 parts by mass or more, and most preferably 1.5 parts by mass or more, with respect to
15 100 parts by mass of the radical polymerizable compound (A). The water content of the bonding water of the aggregate (I) is preferably 7 parts by mass or less, more preferably 5 parts by mass or less, more preferably 2.5 parts by mass or less, and most preferably 2.0 parts by mass or less, with respect to 100 parts by mass of the radically polymerizable compound (A). The method for measuring the water content of the bonding water of the
20 aggregate (I) is as described in the Examples.

The aggregate (I) is not particularly limited and can be used in mortar or concrete. Examples of the aggregate include, but are not limited to, calcium carbonate, crushed stone, sandstone, cryolite, marble, quartz, limestone, silica sand, silica stone, river sand, and the like. However, cement is not included in the aggregate (I). From the

viewpoint of weight reduction, lightweight aggregates such as sintered shale, silicate-based balloon, and non-silicate-based balloon perlite can also be used.

[0073]

The radically polymerizable resin composition of the present invention preferably
5 contains substantially no cement. The term “contains substantially no cement” means
containing 3 mass% or less, preferably 2 mass% or less, more preferably 1 mass% or less,
and still more preferably 0.5 mass% or less, based on the radically polymerizable resin
composition.

[0074]

10 Here, as the cement, Portland cement, other mixed cement, superspeed hardening
cement or the like can be used without any particular limitation. As the Portland cement,
various Portland cements such as low heat Portland cement, moderate heat Portland
cement, ordinary Portland cement, early-strength Portland cement, super early-strength
Portland cement, sulfate resistance Portland cement, and the like can be used. Examples
15 of the mixed cements include blast furnace cement, fly ash cement, silica cement and the
like.

[0075]

Calcium carbonate functions as a constitutional pigment which is transparent in the
coating film and which does not hide the surface to be coated (base material surface), and
20 has functions such as filling recessed parts and reducing coating cost. Examples of the
calcium carbonate on the market include TM -2 (manufactured by Yuko Mining Co.,
Ltd.).

Since the calcium carbonate has a specific particle size distribution, is excellent in
dispersibility, and is porous; the specific gravity of the aggregate itself can be reduced to
25 make it difficult to drip, and the film-forming property can be improved.

[0076]

Examples of silicic acid balloons include shirasu balloons, perlite, glass (silica) balloons, fly ash balloons and the like. Examples of the non-silicic acid balloons include alumina balloons, zirconia balloons, carbon balloons, and the like.

5 [0077]

The amount of the aggregate in the composition of the present invention is not particularly limited, but is 5 to 500 parts by mass, preferably 10 to 450 parts by mass with respect to 100 parts by mass of the radically polymerizable compound (A). In particular, when the amount of the aggregate is 5 parts by mass or more, practical fluidity can be
10 secured. When the amount of the aggregate is 500 parts by mass or less, the adhesion amount of the trowel is reduced and the deterioration of workability can be prevented.

[0078]

<Fiber (J)>

The radically polymerizable composition of the present invention may optionally
15 contain fibers. Specific examples of fibers used in the present invention include glass fibers, carbon fibers, vinylon fibers, nylon fibers, aramid fibers, polyolefin fibers, acrylic fibers, polyester fibers such as polyethylene terephthalate fibers, cellulose fibers and metal fibers such as steel fibers, and ceramic fibers such as alumina fibers. Among them, for example, polyolefin fibers can be used as the thixotropic agent. The thixotropic agent is
20 blended for the purpose of imparting thixotropic properties.

[0079]

The polyolefin fibers which are currently commercially available include polyethylene-based products such as Kemibesto (registered trademark) FDSS -2 (average fiber length 0.6 mm), Kemibesto (registered trademark) FDSS -5 (average fiber length 0.1
25 mm), Kemibesto (registered trademark) FDSS -25 (average fiber length 0.6 mm,

hydrophilized product), and Kemibesto (registered trademark) FDSS -50 (average fiber length 0.1 mm, hydrophilized product), all of which are manufactured by Mitsui Petrochemical Industries, Ltd.

[0080]

5 The carbon fiber is not particularly limited, and any of the known carbon fibers can be used. Examples of the carbon fiber include polyacrylonitrile-based (PAN-based) carbon fibers, rayon-based carbon fibers, pitch-based carbon fibers, and the like. The carbon fibers may be used individually or in a mixture of two or more. In view of low cost and good mechanical properties, it is preferable to use PAN-based carbon fibers.

10 Such carbon fibers are available commercially. As the carbon fiber, carbon fiber reinforced plastic (CFRP) may be used.

[0081]

 The diameter of the carbon fiber is preferably 3 to 15 μm , more preferably 5 to 10 μm . The length of the carbon fiber is usually 5 to 100 mm. In the present invention,

15 carbon fibers may be cut to 10.0 mm to 100.0 mm, and may be further cut to 12.5 mm to 50.0 mm.

[0082]

 These fibers are preferably used in the form of a fiber structure, a biaxial mesh, a triaxial mesh or the like, wherein the fiber structure is selected from, for example, plain

20 weave, satin weave, nonwoven fabric, mat, roving, chop, knitting, braid, and composite structures thereof. For example, the fiber structure can be used by impregnating the fiber structure with a radically polymerizable composition, and in some cases prepolymerizing the fiber structure to prepreg the fiber structure.

 For example, as the mesh, a biaxial mesh or a triaxial mesh may be used. Both of

25 the length (mesh size) of one side of the square of the biaxial mesh and the length (mesh

size) of one side of the equilateral triangle of the triaxial mesh are preferably 5 mm or more and more preferably 10 to 20 mm. By using a biaxial mesh or a triaxial mesh, it is possible to obtain a curable material for preventing concrete flaking which is lightweight and excellent in economical efficiency, workability and durability.

5 These fibers are preferably used for reinforcing coating film performance such as concrete flaking prevention property and FRP waterproof property, or for manufacturing FRP molded products.

In applications such as concrete flaking prevention, among the fibers, glass fibers, cellulose fibers and the like having excellent transparency are preferable from the
10 viewpoint that the deterioration state of the base material can be visually inspected from the outside.

[0083]

The amount of such fibers is preferably 0.3 to 200 parts by mass, more preferably 0.5 to 100 parts by mass, and still more preferably 1.0 to 50 parts by mass with respect to
15 100 parts by mass of the radically polymerizable compound (A).

[0084]

<Water Reducing Agent (K)>

The radically polymerizable resin composition may optionally contain a usable water reducing agent (K) capable of imparting water reducing properties. As the water
20 reducing agent, a known water reducing agent used for concrete such as a liquid or powder water reducing agent, an AE water reducing agent, a high-performance water reducing agent, and a high-performance AE water reducing agent can be used without limitation.

The polycarboxylic acid-based water reducing agent can suppress the deterioration of the fluidity of the concrete due to the addition of the aluminosilicate having the

swellability described above, and is also suitable from the viewpoint of improving the workability by maintaining good fluidity.

As the water reducing agent, a known water reducing agent used for concrete such as a liquid or powdery water reducing agent, an AE water reducing agent, a high-
5 performance water reducing agent, and a high-performance AE water reducing agent can be used without limitation.

The water reducing agent is preferably contained in 0.1 to 3.0 % by mass of the radically polymerizable resin composition.

[0085]

10 [Solvent]

The radically polymerizable resin composition of the present invention may optionally be blended with a solvent. Examples of solvents that can be blended include aromatic hydrocarbon solvents such as toluene and xylene; ester solvents such as ethyl acetate, butyl acetate, amyl acetate and cellosolve acetate; ketone-based solvents such as
15 methyl ethyl ketone, methyl isobutyl ketone, and diisobutyl ketone. These solvents may be used in the manufacture of polymers.

[0086]

[Polyisocyanate Compound]

The radically polymerizable resin composition may contain a polyisocyanate
20 compound. The polyisocyanate compound reacts with the hydroxyl group of the radical polymerizable compound (A) to form a cured coating film.

The polyisocyanate compound contains two or more isocyanate groups in the molecule, and the isocyanate groups may be blocked by a blocking agent or the like.

Examples of the polyisocyanate compound not blocked by the blocking agent
25 include aliphatic diisocyanates such as lysine diisocyanate, hexamethylene diisocyanate,

trimethylhexane diisocyanate and the like; cyclic aliphatic diisocyanates such as hydrogenated xylylene diisocyanate, isophorone diisocyanate, methylcyclohexane -2, 4 (or 2, 6) -diisocyanate, 4, 4' -methylenebis (cyclohexyl isocyanate), 1, 3- (isocyanatomethyl) cyclohexane; aromatic diisocyanates such as tolylene diisocyanate, xylylene diisocyanate, 5 diphenylmethane diisocyanate; trivalent or higher polyisocyanates such as lysine triisocyanates. Examples of the polyisocyanate compound not blocked by the blocking agent also include adducts of these polyisocyanates with polyhydric alcohols, low molecular weight polyester resins, water, or the like; cyclized polymers of the diisocyanates (for example, isocyanurate); biuret type adducts, and the like. Among 10 them, isocyanurate of hexamethylene diisocyanate is preferable.

These polyisocyanate compounds may be used alone or in combination of two or more.

[0087]

When the radically polymerizable resin composition contains a polyisocyanate 15 compound, the amount thereof is preferably 0.1 to 50 parts by mass, more preferably 1 to 30 parts by mass, and still more preferably 2 to 20 parts by mass with respect to 100 parts by mass of the radically polymerizable compound (A).

[0088]

The blocked polyisocyanate compound is obtained by blocking an isocyanate group 20 of the polyisocyanate compound with a blocking agent.

Examples of blocking agents include a phenolic compound such as phenol, cresol, xylenol or the like; epsilon-caprolactam; lactams such as δ -valerolactam, γ -butyrolactam, and β -propiolactam; alcoholic systems such as methanol, ethanol, n-propyl or isopropyl alcohol, n-, iso- or tert-butyl alcohol, ethylene glycol monomethyl ether, ethylene glycol 25 monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether,

diethylene glycol monoethyl ether, propylene glycol monomethyl ether, benzyl alcohol; oximes such as formamidoxime, acetaldoxime, acetoxime, methylethylketoxime, diacetylmonoxime, benzophenone oxime, cyclohexane oxime; active methylene such as dimethyl malonate, diethyl malonate, ethyl acetoacetate, methyl acetoacetate, and acetylacetone. The isocyanate group of the polyisocyanate can be easily blocked by mixing the polyisocyanate with the blocking agent.

[0089]

When the polyisocyanate compound is an unblocked polyisocyanate compound, the radical polymerizable compound (A) in the radical polymerizable resin composition of the present invention and the polyisocyanate compound are mixed to cause reactions between the two compounds, so that it is preferable to separate the radical polymerizable compound (A) and the polyisocyanate compound before use and to mix them when use.

A curing catalyst can be used for reacting the radical polymerizable compound (A) with the polyisocyanate compound. Examples of suitable curing catalysts include organometallic catalysts such as tin octylate, dibutyltin di (2-ethylhexanoate), dioctyltin di (2-ethylhexanoate), dioctyltin diacetate, dibutyltin dilaurate, dibutyltin oxide, dioctyltin oxide, and lead 2-ethylhexanoate.

When the radically polymerizable resin composition contains the curing catalyst, the amount thereof is preferably 0.01 to 5 parts by mass, more preferably 0.05 to 4 parts by mass with respect to 100 parts by mass of the radically polymerizable compound (A).

[0090]

<Other Components>

The radically polymerizable resin composition of the present invention may contain components other than the above components, as long as the components do not particularly hinder the strength development and acid resistance of the cured product.

Examples of the components that can be contained include hydraulic inorganic materials such as calcium sulfate and pozzolan materials; admixtures that can be used for mortar or concrete that can impart properties such as setting adjustment, hardening acceleration, hardening delay, thickening, water retention, defoaming, water repellency, and waterproofing; and admixtures that can be used for mortar or concrete such as fibers made of materials such as metals, polymers, carbon; pigments; extenders; foams; and clay minerals such as zeolites; and the like.

[0091]

<Method for Producing Radically Polymerizable Resin Composition>

10 The method for producing the radically polymerizable resin composition of the present invention is not particularly limited, and a method known in the art can be used. The method includes a mixing step of mixing a radical polymerizable compound (A), an expansive additive (B), a radical polymerization initiator (C) and an aggregate (I). The aggregate (I) contains bonding water. For example, the radically polymerizable resin
15 composition can be produced by mixing the radically polymerizable compound (A) with the metal-containing compound (D) as necessary, and further mixing the radically polymerizable compound (A) with a radical polymerization initiator (C), an expansive additive (B), and, an aggregate (I). The method of producing the radically polymerizable resin composition preferably does not include a step of adding water. When water is
20 added, free water is contained in the radically polymerizable resin composition, and the compressive strength of the cured product of the radically polymerizable resin composition is deteriorated. However, the bonding water contained in the raw material such as aggregate (I) has little influence on the compressive strength of the cured product unlike the added free water.

One embodiment of a method for producing a radically polymerizable resin composition of the present invention comprises a step (S1) of mixing a radically polymerizable compound (A) with a metal-containing compound (D) as necessary to obtain a resin product, a step (S2) of mixing a radical polymerization initiator (C) with the obtained resin product to obtain a curable resin product, and a step (S3) of mixing the obtained curable resin product an expansive additive (B) to obtain a radically polymerizable resin composition.

[0092]

In the step (S1) of obtaining the resin product (sometimes simply referred to as the “Step (S1)”), a polymerization inhibitor (G), a curing retarder (H), a thiol compound (E) or the like may be mixed as necessary in addition to mixing the metal-containing compound (D) with the radically polymerizable compound (A).

In the step (S3) (sometimes referred to simply as “Step (S3)”) of obtaining the radically polymerizable resin composition, the curable resin product obtained in the step (S2) (sometimes referred to simply as “Step (S2)”) of obtaining the curable resin product may be mixed with an aggregate (I), a water reducing agent (K), a fiber (J), or the like, as necessary, in addition to mixing an expansive additive (B). Specific examples of the aggregate (I) include, for example, early-strength Portland cement, N 90 silica sand , calcium carbonate TM -2, N 50 silica sand, N 40 silica sand, and the like.

[0093]

The radically polymerizable resin composition thus produced can be cured at room temperature and is excellent in workability, early strength development and curability. Since the radically polymerizable resin composition contains the expansive additive (B), the shrinkage rate at the time of curing is small, and the expansion rate of the cured product can be made larger than 0 in some conditions.

[0094]

<Cured Product of Radically Polymerizable Resin Composition>

The cured product of the radically polymerizable resin composition is obtained by curing the radically polymerizable resin composition.

- 5 The rate of change in the length of the cured product is not particularly limited and can be adjusted by each component of the radically polymerizable resin composition used. For example, the rate of change in the length of the cured product is preferably 0 to 1000×10^{-6} after 3000 hours from curing.

[0095]

- 10 [Method for Curing Radically Polymerizable Resin Composition]

- When the radically polymerizable resin composition of the present invention contains a thermal radical polymerization initiator (C-1), one example of a curing method of the radically polymerizable resin composition of the present invention include a curing method in which the radically polymerizable resin composition of the present invention is applied to the surface of a base material and cured at room temperature. For example, the radically polymerizable resin composition of the present invention is used as a cross section repairing material of a structure composed of inorganic substances. Since the radically polymerizable resin composition of the present invention contains an expansive additive (B), the cured product thus obtained does not largely shrink as in the prior art even after a certain time elapses.
- 15
- 20

Examples of the base material include concrete, asphalt concrete, mortar, brick, wood, metal; thermosetting resins such as phenol resin, epoxy resin, melamine resin, urea resin, unsaturated polyester resin, vinyl ester resin, alkyd resin, polyurethane, polyimide; and thermoplastic resins such as polyethylene, polypropylene, polyvinyl chloride,

polystyrene, polyvinyl acetate, polyurethane, Teflon (registered trademark), ABS resin, AS resin, acrylic resin, and the like.

[0096]

When the radically polymerizable resin composition of the present invention contains a photo-radical polymerization initiator (C-2), as the photo-curing timing, a method in which the radically polymerizable resin composition is applied to a base material and then photo-cured, or a method in which the radically polymerizable resin composition is pre-polymerized (also referred to as B-staged or pre-pregulated) to form a sheet, and the sheet is stuck to the base material and then photo-cured, may be used.

[0097]

As the light source, any light source having a spectral distribution in the photosensitive wavelength region of the photo-radical polymerization initiator (C-2) may be used, for example, a solar light, an ultraviolet lamp, a near-infrared lamp, a sodium lamp, a halogen lamp, a fluorescent lamp, a metal halide lamp, an LED, and the like may be used. It is also possible to use different wavelengths necessary for prepolymerization and polymerization by using two or more kinds of photoradical polymerization initiators (C-2) in combination, to use a wavelength-cut filter as a light source, or to use a specific wavelength of an LED. The wavelength used for the prepolymerization is desirably a long wavelength having a low energy level, and the degree of polymerization can be easily controlled, especially when near-infrared light is used. In the present invention, ultraviolet light (ultraviolet ray) refers to a light beam having a wavelength of 280 to 380 nm, visible light (visible ray) refers to a light beam having a wavelength of 380 to 780 nm, and near infrared light (near infrared ray) refers to a light beam having a wavelength of 780 to 1200 nm. The irradiation time of the lamp required for the prepolymerization cannot be generally defined because the effective wavelength range of the light source, the

output, the irradiation distance, the thickness of the composition, and the like may affect the irradiation time, however, the irradiation time may be, for example, 0.01 hours or more, preferably 0.05 hours or more.

5 EXAMPLES

[0098]

Although the present invention will be described in more detail with reference to the following examples, the present invention is not limited in any way by the examples.

[0099]

10 <Method for Measuring Curing Shrinkage>

The shrinkage/expansion rate (rate of change: negative is shrinkage, positive is expansion) after curing of a cured product of the radically polymerizable resin composition of the present invention was measured in accordance with Japanese Standard JIS A 1129 -3 (dial gauge method). The molding (cured product) was made by referring to Annex A of Japanese Standard JIS A 1129. Formwork for the test piece of 40 × 40 × 160 mm defined in Japanese standard JIS R 5201 was used. The test piece of the cured product was molded according to the method of making the test piece for strength test prescribed in 10 of JIS R 5201, and after molding, the test piece was left as a mold and was left standing (cured) in a room at a temperature of 23°C ± 2 °C and at a humidity of 50%, and was removed from the mold about 24 hours after molding. Then, the measurement was started under the conditions indicated in 4.3 of JIS A 1129 -3 using the instrument indicated in 3 of JIS A 1129 -3 (starting time is set to 0.).

[0100]

Amount of change (Negative: Shrinkage, Positive: Expansion) = Length of long side at elapsed time - Length (160 mm) of long side at start (time is set to 0.) (1)

[0101]

Rate of change (Negative: Shrinkage, Positive: Expansion) = Amount of change /
Length (160 mm) of long side at start (time is set to 0.) (2)

[0102]

5 The raw materials used for producing each of the radically polymerizable resin
compositions in the examples and comparative Examples are shown as follows.

[0103]

<Radical Polymerizable Compound (A)>

(Synthesis Example 1)

10 [Synthesis of Radically Polymerizable Compounds (A-1)]

In a 4-neck separable flask of 1 L capacity equipped with a stirrer, a reflux
condenser, a gas introduction tube and a thermometer, 150.4 g of AER -2603 (bisphenol A
type epoxy resin manufactured by Asahi Kasei: epoxy equivalent 189), 188.4 g of SR -16
H (1, 6-hexanediol diglycidyl ether manufactured by Sakamoto Pharmaceutical Industries,
15 Ltd.), 0.255 g of methyl hydroquinone and 1.5 g of DMP -30 (2, 4, 6-tris
(dimethylaminomethyl) phenol manufactured by Tokyo Kasei Kogyo Co., Ltd.) were
added, and then it was heated to 110°C. After the temperature was raised to 110°C, 172
g of methacrylic acid (manufactured by Mitsubishi Rayon Co., Ltd.) was added dropwise
over about 30 minutes and reaction was carried out for about 4 hours. When the acid
20 value became 10 mg KOH/g, the reaction was completed to obtain a vinyl ester
compound.

Then, 256.3 g of dicyclopentenylloxyethyl methacrylate (FA-512 MT manufactured
by Hitachi Chemical Co., Ltd.) and 85.4 g of dicyclopentanyl methacrylate (FA-513 M
manufactured by Hitachi Chemical Co., Ltd.) were added as the radically polymerizable
25 unsaturated monomer to obtain a non-styrene radical polymerizable compound (A-1)

having a viscosity at 25°C of 280 mPa · s and an ester compound component ratio of 60 % by mass.

[0104]

<Expansive Additive (B)>

5 As quicklime/etringite composite-based expansive additive, Denka Power CSA Type S made by Denka was used.

[0105]

<Radical Polymerization Initiator (C)>

As the thermal radical polymerization initiator (C -1), cumene hydroperoxide
10 (CHP), PERCUMYL (registered trademark) H -80 manufactured by Nichiyu Co., Ltd., was used.

. [0106]

<Metal-Containing Compound (D)>

As a metallic soap (D-1), manganese octylate (HEXOATE,MANGANESE,
15 manufactured by Toei Kako Co., Ltd., contains 8 % by mass manganese in the entire product, molecular weight 341.35) was used.

[0107]

<Thiol Compounds (E)>

As the secondary thiol compound (E-1), a bifunctional secondary thiol, Karenz MT
20 (registered trademark) BD1 (1, 4-bis (3-mercaptobutyryloxy) butane, molecular weight 299.43, manufactured by Showa Denko K.K.), was used.

[0108]

<Polymerization Inhibitor (G)>

Tertiary butyl catechol was used.

25 [0109]

<Curing Retarder (H)>

4-H-TEMPO was used.

[0110]

<Aggregate (I)>

5 N 90 Silica sand

Calcium carbonate TM -2

Perlite FL-0

N 50 Silica sand

N 40 Silica sand

10 N 70 Silica sand

[0111]

<Fiber (J)>

Kemibesto (registered trademark) FDSS -5

Multibranched polyolefin fibers manufactured by Mitsui Petrochemical Industries,

15 Ltd.

[0112]

<Epoxy Resin>

Bond E 208 S (Main Agent)

Bond E 208 S (Curing agent)

20 [0113]

(Example 1)

"Preparation of Radically Polymerizable Resin Compositions"

(1) Step (S1):

A resin product was prepared by mixing a metal-containing compound (D), a thiol
25 compound (E), a polymerization inhibitor (G), and a curing retarder (H) with the radically

polymerizable compound (A-1) obtained in Synthesis Example 1 at the blending amount shown in Table 1.

(2) Step (S2):

The curable resin product was prepared by mixing the resin product obtained in step
5 (S1) with the radical polymerization initiator (C) at the blending amount shown in Table 1.

(3) Step (S3):

The radically polymerizable resin composition of the present embodiment was
obtained by mixing the curable resin product obtained in Step (S2) with the expansive
additive (B), the aggregate (I), and the fiber (J) in the components and the blending
10 amounts shown in Table 1.

[0114]

The mixing conditions for each step are as follows.

Stirrer: HOMOGENIZING DISPER Model 2.5 (made by Primus)

Stirring speed: 3000 to 5000 rpm

15 Temperature: 25°C

[0115]

“Preparation of Cured Product of Radically Polymerizable Resin Compositions”

The radically polymerizable resin composition thus obtained was injected into a 40
× 40 × 160 mm mold, and the mold was cured by standing (curing) in a room at a
20 temperature of 23°C ± 2°C and at a humidity of 50%, and was removed from the mold
about 24 hours after molding. A cured product of the radically polymerizable resin
composition of the present example was obtained.

[0116]

“Evaluation of Shrinkage and Expansion Properties of Cured Products”

Shrinkage and expansion properties of the cured product of the radically polymerizable resin composition was evaluated by the above evaluation method. The results are shown in Table 2 and Fig. 1.

[0117]

5 (Example 2)

A radically polymerizable resin composition was obtained in the same manner as in Example 1, except that 8.0 g of expansive additive (B) were used. Cured product of the radically polymerizable resin composition was prepared by the same method as in Example 1. Then, the shrinkage and expansion properties of the cured product were
10 evaluated in the same manner as in Example 1. The results are shown in Table 2 and FIG. 1.

[0118]

(Example 3)

A radically polymerizable resin composition was obtained in the same manner as in
15 Example 1, except that 12.0 g of expansive additive (B) were used. Cured product of the radically polymerizable resin composition was prepared by the same method as in Example 1. Then, the shrinkage and expansion properties of the cured product were evaluated in the same manner as in Example 1. The results are shown in Table 2 and FIG. 1.

20 [0119]

“Compressive Strength Test”

The cured product prepared in Example 3 was tested for compressive strength, and the results are shown in Table 3.

The test pieces used for compressive strength were prepared in accordance with
25 Japanese JIS A 1138 (How to make concrete in a laboratory.) and Japanese JIS A 1132

(How to make test pieces for concrete strength test), and the time required to remove the mold from the mold was set to 24 hours using a mold of ϕ 5 cm x 10 cm.

The compressive strength of the fabricated specimens was measured using an Amsler type concrete compressive strength tester (CCM -1000 kNI, manufactured by Shimadzu Corporation) in accordance with Japanese JIS A 1108 (Compressive strength test method of concrete). The age of the wood is shown in Table 3.

[0120]

(Comparative Example 1)

A radically polymerizable resin composition was obtained in the same manner as in Example 1, except that expansive additive (B) were not used. Cured product of the radically polymerizable resin composition was prepared by the same method as in Example 3. Then, the shrinkage and expansion properties of the cured product were evaluated in the same manner as in Example 1. The results are shown in Table 2 and FIG. 1. The compressive strength was tested in the same manner as in Example 3, and the results are shown in Table 3.

[0121]

(Comparative Example 2)

An epoxy resin composition was obtained in the same manner as in Example 1 except that Bond E 208 S (main agent) and Bond E 208 S (curing agent) (manufactured by Konishi Co., Ltd.; product name: epoxy resin for civil engineering and construction; main agent: bisphenol A type epoxy resin; curing agent: mixture of modified polyamidoamine and polyamidoamine.), which are epoxy resins, were used instead of the radically polymerizable compound (A-1). A cured product of the epoxy resin composition was prepared in the same manner as in Example 1. Then, shrinkage and expansion property of each cured product was evaluated in the same manner as in Example 1. The results

are shown in Table 2 and Figure 1. The compressive strength was tested in the same manner as in Example 3, and the results are shown in Table 3.

[0122]

(Comparative Example 3)

- 5 An epoxy resin composition was obtained in the same manner as in Comparative Example 2 except that the expansive additive (B) was not used. A cured product of the epoxy composition was prepared by the same method as in Comparative Example 1. Then, the shrinkage and expansion property of each cured products was evaluated in the same manner as in Example 1. The results are shown in Table 2 and Figure 1. The
- 10 compressive strength was tested in the same manner as in Example 3, and the results are shown in Table 3.

[0123]

[Table 1]

[Table 1]

Unit (g)		Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Resin product	Radically polymerizable compound(A)	98.35	98.35	98.35	98.35		
	Metal-containing compound(D)	1	1	1	1		
	Thiol compound(E)	0.5	0.5	0.5	0.5		
	Polymerization inhibitor(G)	0.05	0.05	0.05	0.05		
	Retarder(H)	0.1	0.1	0.1	0.1		
Epoxy Resin	Main agent					66	66
	Curing agent					33	33
Expansive additive (B)		4	8	12	0	12	0
Radical polymerization initiator(C)	C-1	2	2	2	2		
	N90 Silica sand	60	60	60	60	45	45
	Calcium Carbonate TM-2	60	60	60	60	45	45
	Perlite No. FL-0	8	8	8	8	6	6
	N50 Silica sand	180	180	180	180	135	135
Aggregate(I)	N40 Silica sand	40	40	40	40	30	30
	N70 Silica sand	50	50	50	50	37.5	37.5
	Fiber(J)	2	2	2	2	0	0
Kemibestro®FDSS-5							

[0124]

[Table 2]

	Elapsed Time (Hours)	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Amount of change * (μm)	500	-41	2	45	-58	-159	-164
	1000	-31	22	77	-64	-155	-164
	1500	-24	34	94	-68	-143	-165
	2000	-21	43	105	-72	-133	-164
	2500	-19	49	114	-75	-130	-165
	3000	-17	55	120	-78	-131	-164
Rate of change ** ($\times 10^{-6}$)	3500	-16	57	126	-80	-130	-164
	500	-256	13	281	-363	-994	-1025
	1000	-194	138	481	-400	-969	-1025
	1500	-150	213	588	-425	-894	-1031
	2000	-131	269	656	-450	-831	-1025
	2500	-119	306	713	-469	-813	-1031
	3000	-106	344	750	-488	-819	-1025
	3500	-100	356	788	-500	-813	-1025

* Reference length 160 mm. A positive number is the amount increased by expansion, and a negative number is the amount decreased by contraction.

** Change/Reference Length "

[0125]

[Table 3]

Unit:N/mm ²	Elapsed Time														
	75 Min	2 Hrs	3 Hrs	4 Hrs	5 Hrs	6 Hrs	15 Hrs	1 d	2 d	3 d	7d	14 d	28 d	60 d	90 d
Example 3	11.6	28.8	39.8	46.5	50.1	52.6	63.5	66.8	73.3	75.6	80.1	83.4	83.1	83.0	83.8
Comparative Example 1	12.1	30.8	41.1	47.2	51.9	53.8	64.5	64.5	66.3	66.5	67.0	66.7	68.4	68.2	69.1
Comparative Example 2	-	-	-	-	-	-	-	23.2	27.4	27.9	30.3	36.8	48.4	49.2	50.1
Comparative Example 3	-	-	-	-	-	-	-	22.4	28.4	26.9	31.7	35.9	49.1	50.8	47.3

[0126]

(Example 4)

A radically polymerizable resin composition was obtained in the same manner as in Example 3 except that the aggregate (I) shown in Table 4 was used. A cured product of the radically polymerizable resin composition was prepared by the same method as in Example 1. Then, the shrinkage and expansion property of each cured product was evaluated in the same manner as in Example 1. The results are shown in Table 4 and Figure 2. The compressive strength was tested in the same manner as in Example 3, and the results at 24 hours and 672 hours are shown in Table 4.

The water contents of the aggregate (I) and the fiber (J) used in Example 4 were measured before mixing the aggregate (I) and the fiber (J) with the resin product. The results are shown in Table 4.

[0127]

“Method for measuring water content”

For the aggregate (I) and the fiber (J) mixed with the radically polymerizable resin composition of the present invention, the content of water contained in the aggregate and the fiber was measured by the following method.

(1) A total of 20 mg of aggregate and fiber mixed at a mass ratio similar to that of the aggregate (I) and the fiber (J) shown in Table 4 was measured and set in TG/DTA (TA 7000 Series, simultaneous thermogravimetry / differential Thermal Analysis , STA 7200 RV, manufactured by Hitachi High-Tech Science Co., Ltd.).

(2) The apparatus was operated at a temperature rising speed of 10°C/min from 30°C to 105°C and held at 105°C for 60 min.

(3) Weight change rate (decrease rate) from 95°C to 105°C was calculated.

[0128]

[Table 4]

Unit (g)			Example 4	Comparative Example 4	Comparative Example 5
Resin product	Radically Polymerizable compound(A)	A-1	98.35	98.35	98.35
	Metal-Containing compound(D)	D-1	1.00	1.00	1.00
	Thiol compound(E)	E-1	0.50	0.50	0.50
	Polymerization inhibitor(G)	Tertiary butyl catechol	0.05	0.05	0.05
Radical polymerization initiator©	Retarder(H)	4-H-TEMPO	0.10	0.10	0.10
	Radical polymerization initiator©	C-1	2.00	2.00	2.00
	Water	after-added free water			5.00
	Expansive additive (B)	Denka Power CSA Type S	12.00	12.00	12.00
Aggregate(I)		N90 Silica sand	50.0	50.0	50.0
		Calcium Carbonate TM-2	60.0	60.0	60.0
		Perlite No. FL-0	6.0	6.0	6.0
		N50 Silica sand	180.0	180.0	180.0
		N40 Silica sand	40.0	40.0	40.0
Fiber(J)		N70 Silica sand	50.0	50.0	50.0
		Kemibesto®FDSS-5	2.00	2.00	2.00
	Weight decrease rate (%) of aggregate (I) + fiber (J)		0.41	0.00	0.00
	Weight (parts by mass) of aggregate (I) + fiber (J)		388.0	388.0	388.0
	Water content (weight loss) of aggregate (I) + fiber (J)		1.59	0.00	0.00
	Evaluation of compressive strength at 24 hours (N/mm ²)		52.9	53.8	2.8
	Evaluation of compressive strength at 672 hours(N/mm ²)		66.4	68.4	14.0

[0129]

(Comparative Example 4)

The radically polymerizable resin composition was obtained in the same manner as in Example 4 except that the aggregate (I) of Example 4 was dried under the following absolute dry condition. A cured product of the radically polymerizable resin composition was prepared by the same method as in Example 1. Then, the shrinkage and expansion properties of the respective cured products were evaluated in the same manner as in Example 1. The results are shown in Table 4 and Figure 2. The compressive strength was tested in the same manner as in Example 3, and the results at 24 hours and 672 hours are shown in Table 4.

The water content of the aggregate (I) used in Comparative Example 4 was measured before mixing with the resin product in the same manner as in Example 4. The results are shown in Table 4.

[0130]

"Absolute dry condition"

The following procedure was applied to the aggregate prior to mixing with the radically polymerizable resin composition in order to create an absolute dry aggregate in which the water contained in the aggregate was completely evaporated.

(1) 400 g of aggregate was put into an aluminum tray, thinly leveled, and dried in an oven at 105°C.

(2) After 48 hours, they were removed from the oven and used.

[0131]

(Comparative Example 5)

A radically polymerizable resin composition was obtained in the same manner as in Comparative Example 4 except that 5.00 g of water was added after the aggregate (I) was

mixed with the resin product. A cured product of the radically polymerizable resin composition was prepared by the same method as in Example 1. Compressive strength tests at 24 hours and 672 hours were conducted in the same manner as in Example 3, and the results are shown in Table 4.

5 Regarding the aggregate (I) used in Comparative Example 5, the content of water contained in the aggregate was measured before mixing with the resin product in the same manner as in Example 4. The results are shown in Table 4.

[0132]

(Discussion)

10 From the results of Table 2 and FIG. 1, it was found that according to the radically polymerizable resin composition of the present invention having the expansive additive (B), the shrinkage rate during curing was significantly suppressed in Example 1, and the cured product of Examples 2 and 3 expanded from the reference length (160 mm) after curing for 24 hours from the start of curing.

15 [0133]

The cured product of the radically polymerizable resin composition of Example 3 exhibited an expansion amount (expansion rate) of + 40 μm ($+ 250 \times 10^{-6}$) to + 131 μm ($+ 819 \times 10^{-6}$).

20 However, since the radically polymerizable resin composition of Comparative Example 1 did not contain the expansive additive (B), a shrinkage amount (shrinkage rate) of -48 μm (-300×10^{-6}) to -80 μm (-500×10^{-6}) was observed for the cured product.

Further, in Comparative Example 2 using the epoxy resin composition, although the expansive additive (B) was included, a large shrinkage amount similar to that in Comparative Example 3 which did not include the expansive additive (B) was observed.

25 [0134]

According to the results of Table 4 and FIG. 2, in Comparative Example 4 in which the water content of the aggregate (I) pretreated under the absolute dry condition was 0.00 g, a shrinkage rate of -250×10^{-6} to -350×10^{-6}) was observed for the cured product, rather than expansion. In Comparative Example 5 in which the aggregate (I) was mixed with the resin product and water was added, the compressive strength of the cured product was deteriorated as compared with Comparative Example 4 and Example 1.

CLAIMS

1. A radically polymerizable resin composition, comprising
a radically polymerizable compound (A),
an expansive additive (B),
5 a radical polymerization initiator (C) and
an aggregate (I); and
not comprising free water,
wherein the aggregate (I) comprises bonding water.
- 10 2. The radically polymerizable resin composition according to claim 1,
wherein an amount of the aggregate (I) is 5 to 500 parts by mass with respect to 100
parts by mass of the radically polymerizable compound (A).
3. The radically polymerizable resin composition according to claim 1,
15 wherein the radically polymerizable compound (A) comprises a vinyl ester resin and
a radically polymerizable monomer.
4. The radically polymerizable resin composition according to any one of claims 1 to
3,
20 wherein said expansive additive (B) comprises at least one selected from the group
consisting of lime and calcium sulfo aluminate.
5. The radically polymerizable resin composition according to any one of claims 1 to
4, wherein the radical polymerization initiator (C) is a hydroperoxide (ROOH).

6. The radically polymerizable resin composition according to any one of claims 1 to 5, further comprising a metal-containing compound (D) and a thiol compound (E).

7. The radically polymerizable resin composition according to any one claims 1 to 6,
5 wherein an amount of the expansive additive (B) is 0.3 to 30 parts by mass with respect to 100 parts by mass of the radically polymerizable compound (A).

8. The radically polymerizable resin composition according to any one of claims 1 to 7, wherein an amount of the radical polymerization initiator (C) is 0.1 to 10 parts by mass
10 with respect to 100 parts by mass of the radically polymerizable compound (A).

9. A cured product of the radically polymerizable resin composition according to any one of claims 1 to 8.

15 10. The cured product according to claim 9, wherein the rate of change in the length of the cured product is 0 to 1000×10^{-6} after 3000 hours from curing.

11. A method of producing a radically polymerizable resin composition, the method comprises

20 a mixing step of mixing a radically polymerizable compound (A), an expansive additive (B), a radical polymerization initiator (C) and an aggregate (I), wherein the aggregate (I) comprises bonding water.

12 The method of producing a radically polymerizable resin composition according
25 to claim 11,

wherein the method does not comprise a step of adding water.

13. A radical polymerizable resin composition obtained by using the method of producing a radical polymerizable resin composition according to claim 11 or claim 12,

5 wherein the radically polymerizable resin composition comprises a radically polymerizable compound (A), an expansive additive (B), a radical polymerization initiator (C) and an aggregate (I).