

DESCRIPTION

RESIN COMPOSITION FOR REPAIRING PIPE CULVERT, MATERIAL FOR REPAIRING PIPE CULVERT, AND METHOD FOR REPAIRING EXISTING PIPE CULVERT

TECHNICAL FIELD

[0001] This invention relates to a resin composition for repairing a pipe culvert, a material for repairing a pipe culvert, and a method for repairing an existing pipe culvert.

BACKGROUND ART

[0002] Existing pipe culverts such as gas pipes, water pipes, sewer pipes, and agricultural water pipes are repaired by using a material for repairing a pipe culvert which is obtained by impregnating a fiber base material with a thermosetting resin composition including an unsaturated polyester resin, drawing the material to the predetermined position inside the pipe culvert, and then thermally curing the material by bringing it into contact with a heat medium such as hot water or steam.

[0003] With such a repair method, it is necessary to extend as much as possible the storage period of the thermosetting resin composition at a low temperature so as to prevent the composition from curing before the material for repairing a pipe culvert is drawn to the predetermined position.

Meanwhile, in order to shorten the operation period as much as

possible, it is necessary that the curing, once it is started, be rapidly completed at a comparatively low temperature.

[0004] In recent years, vinyl ester resins which excel in toughness and corrosion resistance have been used as thermosetting resins for repairing existing pipe culverts (see, for example, Patent Document 1). However, a problem associated with vinyl ester resins is that the storage period thereof is shorter than that of unsaturated polyester resins, and therefore gelling occurs within an interval of time after the impregnation and before the repair material is drawn to the predetermined position. Accordingly, it is desirable to extend the storage period and also ensure rapid curing of thermosetting resin compositions including a vinyl ester resin.

[0005] Patent Document 1: Japanese Patent Application laid-open No. 2011-133036

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0006] With the foregoing in view, it is an objective of the present invention to provide a resin composition for repairing a pipe culvert that ensures both extended storage life and rapid curing.

SOLUTION TO THE PROBLEM

[0007] Thus, the present invention is disclosed in the following items [1] to [9].

[1] A resin composition for repairing a pipe culvert, including: (A) a vinyl ester resin composition; (B) a urethane (meth)acrylate composition; (C) an unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more; and (D) a curing agent including cumene hydroperoxide and t-butyl peroxybenzoate.

[2] The resin composition for repairing a pipe culvert according to item [1], wherein in (D) the curing agent including cumene hydroperoxide and t-butyl peroxybenzoate, the mass ratio of cumene hydroperoxide and t-butyl peroxybenzoate is 5 : 95 to 40 : 60.

[3] The resin composition for repairing a pipe culvert according to item [1] or [2], wherein (C) the unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more is contained at 0.5 part by mass to 10 parts by mass per a total of 100 parts by mass of (A) the vinyl ester resin composition and (B) the urethane (meth)acrylate composition.

[4] The resin composition for repairing a pipe culvert according to item [1] or [2], wherein the total amount of (D) the curing agent including cumene hydroperoxide and t-butyl peroxybenzoate is 0.5 part by mass to 5 parts by mass per a total of 100 parts by mass of (A) the vinyl ester resin composition, (B) the urethane (meth)acrylate composition, and

(C) the unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more.

[5] The resin composition for repairing a pipe culvert according to any one of items [1] to [4], wherein a vinyl ester resin contained in (A) the vinyl ester resin composition is one or more of vinyl ester resins selected from a group consisting of a bisphenol vinyl ester resin, a novolac vinyl ester resin, and a brominated vinyl ester resin with a weight-average molecular weight of 500 to 6000.

[6] The resin composition for repairing a pipe culvert according to any one of items [1] to [5], wherein a urethane (meth)acrylate contained in (B) the urethane (meth)acrylate composition is a urethane (meth)acrylate resin with a weight-average molecular weight of 2000 to 8000 which is obtained by reacting an isocyanate compound having at least two isocyanate groups in a molecule, one or more (meth)acrylic compounds selected from the group consisting of 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate, polyethylene glycol, and a polyether polyol and/or an adipate-based polyester polyol.

[7] A material for repairing a pipe culvert in which the resin composition for repairing a pipe culvert according to any one of items [1] to [6] is impregnated in a fiber base material.

[8] The material for repairing a pipe culvert according to item [7], wherein the fiber base material consists of glass fibers.

[9] A method for repairing an existing pipe culvert, the method including drawing the material for repairing a pipe culvert according to item [7] or [8], in an uncured state, into the pipe culvert or inserting the material into the pipe culvert, while reversing an inner surface side and an outer surface side, and then thermally curing the material for repairing a pipe culvert.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0008] The present invention can provide a resin composition for repairing a pipe culvert that ensures both extended storage life and rapid curing.

DESCRIPTION OF EMBODIMENTS

[0009] The present invention is explained hereinbelow in greater detail.

The resin composition for repairing a pipe culvert in accordance with the present invention, includes as the necessary components: (A) a vinyl ester resin composition (also referred to hereinbelow as component (A)); (B) a urethane (meth)acrylate composition (also referred to hereinbelow as component (B)); (C) an unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more

(also referred to hereinbelow as component (C)); and (D) a curing agent including cumene hydroperoxide and t-butyl peroxybenzoate (also referred to hereinbelow as component (D)).

The values of weight-average molecular weight of the various resins described hereinbelow are calculated by using gel permeation chromatography (GPC), performing measurements under the following conditions, and recalculating for polystyrene. The weight-average molecular weight is calculated by taking a period from a GPC rise time to 30 min as a calculation range.

Device: a high-speed device GPC SYSTEM-21 manufactured by Showa Denko K.K.

Column: Shodex (trademark) KF-802+KF-802 manufactured by Showa Denko K.K.

Oven temperature: 40°C

Eluent: tetrahydrofuran

Sample concentration: 0.2 mass%

Flow velocity: 1 ml/min

Detector: differential refractometer

[0010] [(A) Vinyl ester resin composition]

(A) The vinyl ester resin composition which is used in accordance with the present invention is obtained by dissolving a vinyl ester resin in a radical polymerizable monomer, the vinyl ester resin being obtained by a reaction of a compound having an epoxy group and a carboxyl compound

including an ethylenic unsaturated group, such as (meth)acrylic acid. Such vinyl ester resins are described, for example, in "Polyester Resin Handbook" (published in 1988 by NITTO KOGYO SHIMBUNSHA) or "Paints Glossary" (published in 1993 by Japan Society of Color Material). Here, "(meth)acrylic" indicates one or two of methacrylic and acrylic.

The weight-average molecular weight of the vinyl ester resin is preferably 500 to 6000, more preferably 1000 to 5000. Where the weight-average molecular weight of the vinyl ester resin is equal to or higher than 500, a strength which enables practical use is obtained, and where the weight-average molecular weight is equal to or less than 6000, the desirable operability and storage stability are obtained.

[0011] The vinyl ester resin is not particularly limited and can be manufactured by a well-known method. More specifically, for example, it is an epoxy (meth)acrylate obtained by reacting a (meth)acrylic acid with an epoxy resin.

Examples of the epoxy resin include a bisphenol A epoxy resin, a bisphenol F epoxy resin, a phenol novolac epoxy resin, a cresol novolac epoxy resin, and an aliphatic glycidyl ether such as 1,6-hexanediol diglycidyl ether. Those epoxy resins may be used individually or in combinations of two or more thereof. Among them, from the standpoint of toughness during curing of the resin composition for repairing a pipe culvert, bisphenol A epoxy resins, novolac epoxy resins, and

bromine compounds thereof are preferred. From the standpoint of imparting flexibility to the cured product of the resin composition for repairing a pipe culvert, an epoxy resin modified by a saturated dibasic acid such as adipic acid, sebacic acid, and dimer acids may be used.

From the standpoint of operability and storage stability and also strength and toughness of the cured product, it is preferred that the vinyl ester resin contained in (A) the vinyl ester resin composition be one or more of vinyl ester resins selected from a group consisting of a bisphenol vinyl ester resin, a novolac vinyl ester resin, and a brominated vinyl ester resin with a weight-average molecular weight of 500 to 6000.

[0012] The radical polymerizable monomer is not be particularly limited, and conventionally well-known monomers can be used. Examples of the radical polymerizable monomer include styrene, styrene derivatives substituted with an alkyl group, a nitro group, a cyano group, an amide group, a halogen group, or an ester-containing group, and styrene-based monomers such as vinyl toluene and divinyl benzene; dienes such as butadiene, 2,3-dimethyl butadiene, isoprene, and chloroprene; (meth)acrylic acid esters such as ethyl (meth)acrylate, methyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, dodecyl (meth)acrylate, cyclopentyl (meth)acrylate, cyclohexyl

(meth)acrylate, tetrahydrofuryl (meth)acrylate, acetoacetoxyethyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, and phenoxyethyl (meth)acrylate; (meth)acrylamides such as (meth)acrylamide and N, N-dimethylamide (meth)acrylate; vinyl compounds such as (meth)acrylic acid anilides; unsaturated dicarboxylic acid diesters such as diethyl citraconate; monomaleimide compounds such as N-phenyl maleimide; and N-(meth)acryloyl phthalimide. Also can be used is a (meth)acrylic acid ester compound having two or more (meth)acryloyl groups in a molecule, such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, and 1,6-hexanediol di(meth)acrylate. Those radical polymerizable monomers may be used individually or in combinations of two or more thereof. Among them, from the standpoint of operability, cost, and curability, styrene is preferred.

[0013] The content of the radical polymerizable monomer in (A) the vinyl ester resin composition is preferably 20 mass% to 60 mass%, more preferably 30 mass% to 50 mass%. Where the content of the radical polymerizable monomer is 20 mass% or more, operability is improved without raising the resin viscosity. Meanwhile, where the content of the radical polymerizable monomer is 60 mass% or less, a cured product with a more desirable toughness is obtained.

[0014] [(B) Urethane (meth)acrylate composition]

(B) The urethane (meth)acrylate composition which is used in accordance with the present invention is obtained by dissolving a urethane (meth)acrylate in a radical polymerizable monomer.

[0015] The urethane (meth)acrylate is obtained by reacting an isocyanate compound having at least two isocyanate groups in a molecule, a (meth)acrylic compound having at least one hydroxyl group in a molecule, and a polyol compound. The polyol compound is preferably, for example, polyethylene glycol, a polyether polyol and/or an adipate-based polyester polyol.

[0016] The isocyanate compound having at least two isocyanate groups in a molecule is not particularly limited, and the conventional well-known compounds can be used. Examples of such isocyanate compounds include diphenylmethane diisocyanate, 2,4-tolylene diisocyanate and an isomer thereof, hexamethylene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, and triphenylmethane triisocyanate. Those cyanate compounds may be used individually or in combinations of two or more thereof. Among those isocyanate compounds, diphenylmethane diisocyanate, which excels in reactivity and is barely hazardous to humans, is preferred.

The amount of the isocyanate compound which is to be used is preferably 5 mass% to 90 mass%, more preferably 10 mass% to 50 mass% in the total starting material of the urethane (meth)acrylate. Where the amount of the isocyanate compound

which is to be used is 5 mass% or more, a cured product having a more desirable strength is obtained. Meanwhile, where the amount of the isocyanate compound which is to be used is 90 mass% or less, a cured product having a more desirable flexibility is obtained.

[0017] The (meth)acrylic compound having at least one hydroxyl group in a molecule is not particularly limited and the conventional well-known compounds can be used. Examples of such (meth)acrylic compounds include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, tris(hydroxyethyl)isocyanuric acid di(meth)acrylate, and pentaerythritol tri(meth)acrylate. Those (meth) acrylic compounds may be used individually or in combinations of two or more thereof. Among those (meth)acrylic compounds, from the standpoint of cost and safety, 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate are preferred.

The amount of the (meth)acrylic compound which is to be used is preferably 5 mass% to 90 mass%, more preferably 10 mass% to 50 mass% in the total starting material for the urethane (meth)acrylate. Where the amount of the (meth)acrylic compound which is to be used is 5 mass% or more, a cured product with a more desirable strength is obtained,

and where the amount is 90 mass% or less, a cured product with a more desirable flexibility is obtained.

[0018] The polyethylene glycol is not particularly limited, but it is preferred that the polyethylene glycol have a weight-average molecular weight of 200 to 2000, more preferably 400 to 1500. Where the weight-average molecular weight of the polyethylene glycol is 200 or more, a urethane (meth)acrylate compound having more desirable viscosity and physical properties is obtained. Meanwhile, where the weight-average molecular weight of the polyethylene glycol is 2000 or less, the weight-average molecular weight of the urethane (meth)acrylate can be suppressed to 8000 or less and more desirable compatibility with the vinyl ester resin can be obtained.

The amount of the polyethylene glycol which is to be used is preferably 0.1 mass% to 90 mass%, more preferably 5 mass% to 50 mass% in the total starting material for the urethane (meth)acrylate. Where the amount of the polyethylene glycol which is to be used is 0.1 mass% or more, more desirable compatibility with the vinyl ester resin is obtained, and where the amount is 90 mass% or less, a cured product having a more desirable resistance to water is obtained.

[0019] The polyether polyol is not particularly limited, but it is preferred that the polyether polyol have a weight-average molecular weight of 500 to 1500, more preferably 800 to 1200. Where the weight-average molecular weight of the

polyether polyol is 500 or more, a urethane (meth)acrylate compound having more desirable viscosity and physical properties is obtained. Where the weight-average molecular weight of the polyether polyol is 1500 or less, the weight-average molecular weight of the urethane (meth)acrylate can be suppressed to 8000 or less and more desirable compatibility with the vinyl ester resin can be obtained.

Where the polyether polyol is used, the amount thereof which is to be used is preferably 5 mass% to 90 mass%, more preferably 20 mass% to 60 mass% in the total starting material for the urethane (meth)acrylate. Where the amount of the polyether polyol which is to be used is 5 mass% or more, a cured product having a more desirable flexibility is obtained, and where the amount is 90 mass% or less, more desirable compatibility with the vinyl ester resin is obtained.

[0020] The adipate-based polyester polyol is a polyester of adipic acid and a polyol. This polyester polyol is not particularly limited, but it is preferred that the adipate-based polyester polyol have a weight-average molecular weight of 600 to 3000, more preferably 800 to 2500. Where the weight-average molecular weight of the adipate-based polyester polyol is 600 or more, a urethane (meth)acrylate compound having more desirable viscosity and physical properties is obtained. Where the weight-average molecular weight is 3000 or less, the weight-average molecular weight of the urethane (meth)acrylate can be suppressed to 8000 or less and more

desirable compatibility with the vinyl ester resin can be obtained.

Where the adipate-based polyester polyol is used, the amount thereof which is to be used is preferably 0.1 mass% to 90 mass%, more preferably 5 mass% to 50 mass% in the total starting material for the urethane (meth)acrylate. Where the amount of the adipate-based polyester polyol which is to be used is 0.1 mass% or more, more desirable compatibility with the vinyl ester resin is obtained and where the amount is 90 mass% or less, a cured product having a more desirable water resistance is obtained.

[0021] A method for manufacturing the urethane (meth)acrylate is not particularly limited, and the urethane (meth)acrylate can be manufactured by a well-known method using the abovementioned components. For example, the urethane (meth)acrylate can be manufactured by mixing and reacting an isocyanate compound having at least two isocyanate groups in a molecule with polyethylene glycol to generate a prepolymer including an end isocyanate group, and then blending and reacting a (meth)acrylic compound having at least one hydroxyl group in a molecule with the prepolymer. In the abovementioned reaction, a catalyst such as dibutyltin laurate, tertiary amines, and phosphonates can be added. Where a catalyst is used, the amount thereof is preferably 0.0001 part by mass to 1 part by mass, more preferably 0.001 part by mass to 0.5 part by mass per a total of 100 parts by

mass of the starting material for the urethane (meth)acrylate. Where the amount of the catalyst which is to be used is 0.0001 part by mass or more, the reaction is easily advanced, and where the amount of the catalyst is 1 part of mass or less, the reaction is easy to control.

[0022] In the abovementioned reaction, the reaction temperature is preferably 40°C to 120°C. The reaction time is preferably 1 hour to 24 hours. Where the reaction temperature is 40°C or higher and the reaction time is 1 hour or longer, the reaction advances sufficiently and the desired urethane (meth)acrylate is obtained. Meanwhile, from the standpoint of cost and reaction control, it is preferred that the reaction temperature be 120°C or lower or the reaction time be 24 hours or shorter.

The urethane (meth)acrylate thus obtained preferably has a weight-average molecular weight of 2000 to 8000, more preferably 3000 to 6500. With the urethane (meth)acrylate having the weight-average molecular weight within this range, excellent compatibility with the vinyl ester resin is attained. Therefore, when a resin composition is manufactured using those resins, no phase separation of the vinyl ester resin and urethane (meth)acrylate takes place during storage. Therefore, such a resin composition provides a transparent cured product.

In particular, from the standpoint of cost, safety and ability to obtain a transparent cured product, it is preferred that the urethane (meth)acrylate to be included in (B) the urethane (meth)acrylate composition be a urethane (meth)acrylate resin with a weight-average molecular weight of 2000 to 8000 which is obtained by reacting an isocyanate compound having at least two isocyanate groups in a molecule, one or more (meth)acrylic compounds selected from the group consisting of 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate, polyethylene glycol, and a polyether polyol and/or adipate-based polyester polyol.

[0023] The radical polymerizable monomer which is used for dissolving the urethane (meth)acrylate is not particularly limited, and the conventional well-known radical polymerizable monomers can be used. Examples of the radical polymerizable monomer are the same as those described in reference to (A) the vinyl ester resin composition.

The content of the radical polymerizable monomer in (B) the urethane (meth)acrylate composition is preferably 20 mass% to 60 mass%, more preferably 30 mass% to 50 mass%. Where the content of the radical polymerizable monomer is 20 mass% or more, the decrease in operability caused by the increase in resin viscosity is suppressed. Meanwhile, where the content of the radical polymerizable monomer is 60 mass% or less, a cured product having a more desirable toughness is obtained.

[0024] (A) The vinyl ester resin composition is preferably contained at 50 parts by mass to 90 parts by mass, more preferably 60 parts by mass to 80 parts by mass per a total of 100 parts by mass of component (A) and component (B). Where the content of (A) the vinyl ester resin composition is 50 parts by mass or more, strength and corrosion resistance of the cured product are increased. Meanwhile, where the content of (A) the vinyl ester resin composition is 90 parts by mass or less, the cured product is improved in toughness.

[0025] [(C) Unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more]

(C) The unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more which is used in accordance with the present invention is obtained by dissolving an unsaturated polyester resin in a radical polymerizable monomer, the unsaturated polyester resin being obtained by esterification of a polyhydric alcohol, an unsaturated polyvalent acid component, and an optional saturated polyvalent acid component. The acid value of the unsaturated polyester resin can be adjusted by the molar ratio of the polyhydric alcohol and the unsaturated polyvalent acid component and the optional saturated polyvalent acid component. The acid value of the unsaturated polyester resin composition is 90 KOHmg/g or more, preferably 90 KOHmg/g to 300 KOHmg/g. The acid value in the present invention is the number of milligrams of potassium hydroxide required for the

titration performed with a potassium hydroxide solution as stipulated by JIS K6901. (C) The unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more is added preferably at 0.5 part by mass to 10 parts by mass, more preferably 4 parts by mass to 6 parts by mass per a total of 100 parts by mass of (A) the vinyl ester resin composition and (B) the urethane (meth)acrylate composition. Where the amount added of (C) the unsaturated polyester resin composition is 0.5 part by mass or more, a sufficient usability time can be ensured, and where the amount added of (C) the unsaturated polyester resin composition is 10 parts by mass or less, curing defects and decrease in strength can be prevented.

[0026] Examples of the polyhydric alcohol to be used as the starting material for the unsaturated polyester resin include ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol), 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 2-methyl-1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 2,4-diethyl-1,5-pentanediol, 1,6-hexanediol, 2-ethyl-1,3-hexanediol, 2,5-dimethyl-2,5-hexanediol, 1,2-octanediol, 1,2-nonanediol, 1,4-cyclohexanediol, 1,8-octanediol, 1,9-nonanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, and 1,4-cyclohexanedimethanol. Other examples include commercial dihydric alcohols such as propylene oxide adducts or ethylene oxide adducts such as

bisphenol A, bisphenol F, and bisphenol S, 2,2-di(4-hydroxycyclohexyl)propane {hydrogenated bisphenol A}, polyethylene glycol, and polypropylene glycol. Other examples include commercial polyhydric alcohols such as glycerin, trimethylolethane, trimethylolpropane, pentaerythritol, and dipentaerythritol. These polyhydric alcohols may be used individually or in combinations of two or more thereof.

[0027] Examples of the unsaturated polyvalent acid component to be used as the starting material for the unsaturated polyester resin include α,β -unsaturated polyvalent carboxylic acids and reactive derivatives thereof. Examples of the α,β -unsaturated polyvalent carboxylic acids include maleic acid, fumaric acid, itaconic acid, citraconic acid, and chloromaleic acid. Examples of the reactive derivative thereof include acid anhydrides such as maleic anhydride, itaconic anhydride, and chloromaleic anhydride, and lower alkyl esters of the unsaturated polyvalent carboxylic acids. Those unsaturated polyvalent acid components may be used individually or in combinations of two or more thereof. Among them, from the standpoint of cost of starting materials and copolymerization with styrene, it is preferred that (anhydrous) maleic acid and fumaric acid be used.

[0028] Examples of the saturated polyvalent acid component used as a starting material for the unsaturated polyester resin include succinic acid, adipic acid, sebacic acid,

tetrahydrophthalic acid, endomethylene tetrahydrophthalic acid, and hexahydrophthalic acid (1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid). Examples of aromatic polycarboxylic acids include orthophthalic acid, isophthalic acid, terephthalic acid, naphthalenedicarboxylic acid, trimellitic acid, and pyromellitic acid, and also chlorendic acid (HET acid) and a halogenated phthalic acid such as tetrabromophthalic acid. Other examples include acid anhydrides such as phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, endomethylene tetrahydrophthalic anhydride, succinic anhydride, chlorendic anhydride, trimellitic anhydride, and pyromellitic anhydride, and lower alkyl esters such as dimethylorthophthalate, dimethylisophthalate, and dimethylterephthalate. Those saturated polyvalent acid components may be used individually or in combinations of two or more thereof.

The unsaturated polyester resin obtained in this manner has a weight-average molecular weight preferably of 200 to 3000, and more preferably of 350 to 2000. The unsaturated polyester resin having a weight-average molecular weight within this range is preferred from the standpoint of obtaining the desired acid value.

[0029] The method for manufacturing the unsaturated polyester resin is not particularly limited, and the resin can be manufactured by a well-known method using the

abovementioned components. The reaction is performed under a condition according to which a temperature is 100°C to 230°C in the flow of an inactive gas such as nitrogen and the esterification is carried out under increased or reduced pressure to the required stage. In the esterification reaction, an esterification catalyst can be used, as necessary. Examples of well-known esterification catalysts include organic compounds of titanium, for example, tetraisopropyltitanate and titanium acetylacetonate; organic salts of zinc, for example, zinc acetate; tin compounds, for example, dibutyltin oxide; and inorganic compounds of antimony, for example, antimony trioxide.

[0030] The radical polymerizable monomer which is used for dissolving the unsaturated polyester resin is not particularly limited, and the conventional well-known radical polymerizable monomers can be used. Examples of the radical polymerizable monomer are the same as those described in reference to (A) the vinyl ester resin composition.

The content of the radical polymerizable monomer in (C) the unsaturated polyester resin composition is preferably 5 mass% to 60 mass%, more preferably 10 mass% to 40 mass%. Where the content of the radical polymerizable monomer is 5 mass% or more, the decrease in operability caused by the increase in resin viscosity is suppressed. Meanwhile, where the content of the radical polymerizable monomer is 60 mass%

or less, a cured product having a more desirable toughness is obtained.

[0031] The resin composition for repairing a pipe culvert in accordance with the present invention, which is preferred from the standpoint of strength, toughness, and corrosion resistance of the cured product, includes components (A) to (C) at the following ratios:

(A) the vinyl ester resin composition including 30 mass% to 50 mass% of a radical polymerizable monomer and using a vinyl ester resin having a weight-average molecular weight of 1000 to 5000 is contained at 60 mass% to 80 mass% with respect to a total of 100 mass% of component (A) and component (B);

the urethane (meth)acrylate composition including 30 mass% to 50 mass% of a radical polymerizable monomer and using an urethane (meth)acrylate having a weight-average molecular weight of 3000 to 6500 is contained at 20 mass% to 40 mass% with respect to a total of 100 mass% of component (A) and component (B); and

the unsaturated polyester resin composition (C) including 10 mass% to 40 mass% of a radical polymerizable monomer and using an unsaturated polyester resin having a weight-average molecular weight of 1000 to 2000 is contained at 0.5 mass% to 10 mass% with respect to a total of 100 mass% of component (A) and component (B).

Further, where the radical polymerizable monomers are included, from the standpoint of extending the storage period

and ensuring rapid curing, it is preferred that a mass ratio of the resin included in component (A) and the resin included in component (B) be 1 : 1 to 9 : 1 and a mass ratio of the resins contained in component (A) and component (B) to the resin contained in component (C) be 100 : 4 to 100 : 12.

[0032] [(D) Curing agent]

(D) The curing agent used in accordance with the present invention includes cumene hydroperoxide and t-butyl peroxybenzoate as the necessary components. A mass ratio of cumene hydroperoxide and t-butyl peroxybenzoate included in (D) the curing agent is preferably 5 : 95 to 40 : 60, more preferably 10 : 20 to 30 : 70. At such a mass ratio, both the curability and the usability time are improved and good operability is attained. Commercial curing agents of such properties are available, an example thereof being 328E manufactured by Kayaku Akzo Corp. (cumene hydroperoxide 10 mass% to 15 mass%, t-butyl peroxybenzoate 50 mass% to 55 mass%, and ethyl acetoacetate 30 mass% to 35 mass%). (D) The curing agent including cumene hydroperoxide and t-butyl peroxybenzoate is added preferably at 0.5 part by mass to 5 parts by mass, more preferably 0.8 part by mass to 3.0 parts by mass per a total of 100 parts by mass of component (A), component (B) and component (C). Where the amount added of (D) the curing agent is 0.5 part by mass or more, more desirable curability is obtained, and where the amount added

is 5 parts by mass or less, a cost-efficient cured product having more desirable physical properties is obtained.

Cumene hydroperoxide and t-butyl peroxybenzoate, which are the components of (D) the curing agent, are necessary components, and where either one of them is not added, it is difficult to obtain extended storage period and ensure rapid curing.

[0033] Within a range in which the effect of the present invention is not impaired, the aforementioned curing agent may be used together with the following well-known curing agents: methyl ethyl ketone peroxide, t-butyl perbenzoate, benzoyl peroxide, dicumyl peroxide, diisopropyl peroxide, di-t-butyl peroxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexyne-3, 3-isopropyl hydroperoxide, t-butyl hydroperoxide, dicumyl hydroperoxide, acetyl peroxide, bis(4-t-butylcyclohexyl) peroxydicarbonate, diisopropyl peroxydicarbonate, isobutyl peroxide, 3,3,5-trimethylhexanoyl peroxide, lauryl peroxide, azobisisobutyronitrile, and azobiscarbonamide.

[0034] A curing accelerator, an auxiliary curing accelerator, a polymerization inhibitor, a thixotropic agent, an inorganic filler, and a crosslinkable monomer and the like can be added, as desired, to the resin composition for repairing a pipe culvert in accordance with the present invention.

Examples of the curing accelerator include cobalt octoate, cobalt naphthenate, and cobalt acetylacetate. Among them, cobalt octoate and cobalt naphthenate are preferred. By adding the curing accelerator, it is possible to further increase the curing rate. Where the curing accelerator is added, the amount added thereof is preferably 0.1 part by mass to 1.0 part by mass, more preferably 0.2 part by mass to 0.5 part by mass per a total of 100 parts by mass of component (A), component (B) and component (C) in the resin composition for repairing a pipe culvert.

[0035] Examples of the auxiliary curing accelerator include methyl acetoacetate, ethyl acetoacetate, propyl acetoacetate, butyl acetoacetate, acetylacetone, N,N-dimethylacetoacetamide, N,N-diethylacetoacetamide, aniline, 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, N,N-substituted-p-toluidine, and 4-(N,N-disubstituted amino)benzaldehyde. Among them, ethyl acetoacetate and N,N-dimethylaniline are preferred. By adding the auxiliary curing accelerator, the curing rate can be improved further. Where

the auxiliary curing accelerator is added, the added amount thereof is preferably 0.01 part by mass to 0.1 part by mass, more preferably 0.02 part by mass to 0.05 part by mass per a total of 100 parts by mass of component (A), component (B) and component (C) in the resin composition for repairing a pipe culvert.

[0036] Examples of the polymerization inhibitor include t-butylhydroquinone, butylhydroxytoluene, hydroquinone, trihydrobenzene, benzoquinone, P-benzoquinone, methylhydroquinone, trimethylhydroquinone, hydroquinone monomethyl ether, catechol, t-butylcatechol, and 2,6-di-t-butyl-4-methylphenol. By adding the polymerization inhibitor, it is possible to improve the storage stability. Where the polymerization inhibitor is added, the added amount thereof is preferably 0.001 part by mass to 0.1 part by mass, more preferably 0.005 part by mass to 0.05 part by mass per a total of 100 parts by mass of component (A), component (B) and component (C) in the resin composition for repairing a pipe culvert.

[0037] Examples of the thixotropic agent include silica and organic amides. By adding the thixotropic agent, it is possible to suppress the movement of the resin after impregnation of fibers and ensuring the uniform thickness of the cured product. Where the thixotropic agent is added, the added amount thereof is preferably 0.5 part by mass to 5 part by mass, more preferably 1 part by mass to 4 part by mass per

a total of 100 parts by mass of component (A), component (B) and component (C) in the resin composition for repairing a pipe culvert.

[0038] Examples of the inorganic filler include calcium carbonate and aluminum hydroxide. By adding the inorganic filler, it is possible to increase the strength of the molded article and reduce the curing shrinkage. Where the inorganic filler is added, the added amount thereof is preferably 50 parts by mass to 90 parts by mass, more preferably 10 parts by mass to 50 parts by mass per a total of 100 parts by mass of component (A), component (B) and component (C) in the resin composition for repairing a pipe culvert.

[0039] Examples of the crosslinkable monomer include: including aromatic divinyl compounds, which are radical polymerizable compounds having two or more C=C bonds, for example, divinylbenzene; (meth)acrylic acid ester compounds having two or more (meth)acryloyl groups in a molecule, such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, and 1,6-hexanediol di(meth)acrylate; and unsaturated dicarboxylic acid diesters such as diethyl citraconate. By adding the crosslinkable monomer, it is possible to increase the mechanical strength. Where the crosslinkable monomer is added, the added amount thereof is preferably 0.5 part by mass to 20 parts by mass, more preferably 2 parts by mass to 10 parts by mass per a

total of 100 parts by mass of component (A), component (B) and component (C) in the resin composition for repairing a pipe culvert.

[0040] The resin composition for repairing a pipe culvert in accordance with the present invention can be obtained by mixing components (A) to (D) and optional components. The mixing method is not particularly limited, and the well-known conventional methods can be used. For example, the components can be charged all together or sequentially and mixed using a device such as a three-one motor, a high-shear mixer, a planetary mixer, a bead mill, and a three-roll mill. The material for repairing a pipe culvert in accordance with the present invention can be obtained by impregnating a fiber base material with the resin composition for repairing a pipe culvert which is obtained in the above-described manner.

Woven or nonwoven fabric constituted by fibers such as glass fibers and polyester fibers can be used as the fiber base material to be impregnated with the resin composition for repairing a pipe culvert in accordance with the present invention. Among them, from the standpoint of toughness and corrosion resistance of the molded article, glass fibers are preferred.

[0041] A conventional well-known method can be used for repairing an existing pipe culvert by using the material for repairing a pipe culvert in accordance with the present invention. For example, a method may be used by which the

material for repairing a pipe culvert is drawn, in an uncured state thereof, into the pipe culvert or inserted into the pipe culvert, while reversing an inner surface side and an outer surface side, and the material for repairing a pipe culvert is then thermally cured by contact with a thermal medium such as steam.

EXAMPLES

[0042] The present invention will be described hereinbelow in greater detail by examples thereof, but the invention is not limited to the examples.

The values of weight-average molecular weight of various resins described hereinbelow are calculated by using gel permeation chromatography (GPC), performing measurements under the following conditions, and recalculating for polystyrene. The weight-average molecular weight is calculated by taking a period from a GPC rise time to 30 min as a calculation range.

Device: a high-speed device GPC SYSTEM-21 manufactured by Showa Denko K.K.

Column: Shodex (trademark) KF-802+KF-802 manufactured by Showa Denko K.K.

Oven temperature: 40°C

Eluent: tetrahydrofuran

Sample concentration: 0.2 mass%

Flow velocity: 1 ml/min

Detector: differential refractometer

The acid value of the vinyl ester resin is calculated from the number of milligrams of potassium hydroxide required for the titration performed with a potassium hydroxide solution as stipulated by JIS K0070. The acid value of the unsaturated polyester resin is calculated from the number of milligrams of potassium hydroxide required for the titration performed with a potassium hydroxide solution as stipulated by JIS K6901.

[0043] <Preparation of vinyl ester resin composition>

A total of 189 parts by mass of Epikote (trademark) 828 (epoxy resin, epoxy equivalent 189, manufactured by Yuka Shell K.K.), 57 parts by mass (0.5 equivalent) of bisphenol A, and 0.5 part by mass of triethylamine were charged into a reaction vessel equipped with a stirrer, a reflux cooler, a gas introducing tube, and a thermometer, and a reaction was conducted for 2 hours at 150°C under a nitrogen atmosphere. After the reaction end, the reaction product was cooled to 90°C, 43.1 parts by mass of methacrylic acid, 0.5 part by mass of tetradecyldimethylbenzyl ammonium chloride, 0.5 part by mass of hydroquinone, and 147 parts by mass of styrene were added thereto, a reaction was further conducted for 20 hours at 90°C while blowing air into the reaction vessel, the reaction was ended when the acid value became 10 mgKOH/g, and a vinyl ester resin was obtained. A total of 294 parts by mass of styrene was then added to the vinyl ester resin, and a

bisphenol A vinyl ester resin composition (VE-1) with a vinyl ester resin content of 60 mass% was obtained. The weight-average molecular weight of the vinyl ester resin was 2520.

[0044] <Preparation of urethane methacrylate composition>

A total of 935 parts by mass of Millionate MT-F (diphenylmethane diisocyanate, molecular weight of 250, manufactured by Nippon Polyurethane Industry Co., Ltd.), 1322 parts by mass of Actocol (trademark) D-1000 (polyether polyol, molecular weight of 1010, manufactured by Mitsui Chemicals, Inc.), 324 parts by mass of PEG600 (polyethylene glycol, molecular weight of 578, manufactured by Toho Chemical Industry Co., Ltd.), 0.9 part by mass of K-NOX BHT (2,6-di-tertiary-butyl-4-cresol, manufactured by Degussa Co.), 0.2 part by mass of KS-1260, (dibutyltin dilaurate, manufactured by Kyodo Chemical Co., Ltd.), and 1349 parts by mass of styrene were charged into a reaction vessel equipped with a stirrer, a reflux cooler, a gas introducing tube, and a thermometer, and a reaction was conducted for 1 hour at 80°C under stirring. Then, 566 parts by mass of Light Ester HOP (hydroxypropyl methacrylate, molecular weight of 144, manufactured by Kyoeisha Chemical Co., Ltd.) was dropwise added to the reaction product over 1 h under stirring, and a reaction was conducted under stirring for 2 hours after the completion of dropwise addition to yield a urethane methacrylate resin composition (UMA-1). The content of urethane methacrylate in the urethane methacrylate composition was 70 mass%. The

weight-average molecular weight of the urethane methacrylate was 5160.

[0045] <Preparation of unsaturated polyester resin composition>

A total of 981 parts by mass (10 mole) of maleic anhydride, 152 parts by mass (2 mole) of propylene glycol, 1393 parts by mass (6.5 mole) of trimethylolpropane diallyl ester, 1.2 part by mass of methylhydroquinone, and 0.1 part by mass of 5% copper naphthenate were charged into a reaction vessel equipped with a stirrer, a reflux cooler, a gas introducing tube, and a thermometer, an esterification reaction was conducted for 2 hours at 120°C under a nitrogen atmosphere, the reaction product was cooled when the acid value became 215 KOHmg/g, and an unsaturated polyester resin was obtained. Then, 590 parts by mass of styrene and 75 parts by mass of ethanol were added to the unsaturated polyester resin, and an unsaturated polyester resin composition (UPE-1) with an unsaturated polyester resin content of 80 mass% was obtained. The weight-average molecular weight of the unsaturated polyester resin was 393.

[0046] <Preparation of resin compositions for repairing a pipe culvert>

(Examples 1 to 5 and Comparative Examples 1 to 5)

Resin compositions for repairing a pipe culvert were prepared by using the components listed in Tables 1 and 2 at

the compounding ratios presented in the tables. The units of the amounts of components in Tables 1 and 2 are parts by mass.

[0047] <Evaluation>

(Storage period at a low temperature)

A total of 100 parts by mass of a resin composition for repairing a pipe culvert was weighed into a plastic container with a capacity of 150 cc, and the container was put into a thermostatic water tank maintained at 20°C. The interval of time from the start of mixing till the resin composition for repairing a pipe culvert loses flowability was taken as a usability time. The results are presented in Tables 1 and 2. Where the usability time was 48 hours or longer, it was determined that the composition has a sufficient storage period at a low temperature.

(Operability and rapid curing ability)

The curability was measured by a test tube method. More specifically, the resin composition for repairing a pipe culvert was placed into a test tube, a thermocouple was inserted therein, and the test tube was put into a thermostatic water tank maintained at 70°C. The time required for the temperature of the resin composition for repairing a pipe culvert to reach 75°C from 55°C was taken as a gelling time, and the time required to reach a maximum exothermic temperature from 55°C was taken as a curing time. The results are presented in Tables 1 and 2. Where the time required for

gelling was 5 minutes to 10 minutes and the time required for curing was 7 minutes to 15 minutes, it was determined that both the operability and the rapid curing ability are attained.

[0048]

Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5
Vinyl ester resin composition (A)	VE-1	70	70	70	70	70
Urethane (meth)acrylate composition (B)	UMA-1	30	30	30	30	30
Unsaturated polyester resin composition (C)	UPE-1	4	5	4	10	10
Curing accelerator	N-Co	0.5	0.5	0.5	0.5	0.5
Auxiliary curing accelerator	DMA	0.05	0.05	0.05	0.05	0.05
Polymerization inhibitor	BHT	0.02	0.02	0.2	0.02	0.02
Curing agent (D)	CHP	—	—	0.21	—	—
	TBPB	—	—	0.79	—	—
	328E	1.5	1.5	—	2.5	3.0
Evaluation	Usability time at 20°C (Hr)	≥48	≥60	≥60	≥48	≥48
	Gelling time at 70°C (min)	5.8	7.2	6.5	9.1	7.9
	Curing time at 70°C (min)	9.1	11.3	10.2	14.4	12.6

[0049]

Table 2

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Vinyl ester resin composition (A)	VE-1	70	70	70	70	70

Urethane (meth)acrylate composition (B)	UMA-1	30	30	30	30	30
Unsaturated polyester resin composition (C)	UPE-1	4	4	4	4	0
Curing accelerator	N-Co	0.5	0.5	0.5	0.5	0.5
Auxiliary curing accelerator	DMA	0.05	0.05	0.05	0.05	0.05
Polymerization inhibitor	BHT	0.02	0.02	0.02	0.02	0.02
Curing agent (D)	CHP	1	3	—	—	—
	TBPB	—	—	1	3	—
	328E	—	—	—	—	1.5
Evaluation	Usability time at 20°C (Hr)	≤24	≤24	≥60	≥60	≤24
	Gelling time at 70°C (min)	2.4	1.8	34.9	12.8	1.4
	Curing time at 70°C (min)	8.3	9.4	41.7	16.9	3.1

[0050] In Tables 1 and 2, N-Co is cobalt naphthenate, DMA is N,N-dimethylacetoacetamide, BHT is 2,6-di-tertiary-butyl-4-cresol, CHP is cumene hydroperoxide, TBPB is t-butyl peroxybenzoate, and 328E (cumene hydroperoxide 10 mass% to 15 mass%, t-butyl peroxybenzoate 50 mass% to 55 mass%, and ethyl acetoacetate 30 mass% to 35 mass%) is a curing agent manufactured by Kayaku Akzo Corp.

[0051] The present international application claims priority from Japanese Patent Application No. 2013-216966, filed on October 18, 2013, the entire contents of which are incorporated herein by reference.

CLAIMS

1. A resin composition for repairing a pipe culvert, comprising: (A) a vinyl ester resin composition; (B) a urethane (meth)acrylate composition; (C) an unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more; and (D) a curing agent including cumene hydroperoxide and t-butyl peroxybenzoate.
2. The resin composition for repairing a pipe culvert of claim 1, wherein in (D) the curing agent including cumene hydroperoxide and t-butyl peroxybenzoate, the mass ratio of cumene hydroperoxide and t-butyl peroxybenzoate is 5 : 95 to 40 : 60.
3. The resin composition for repairing a pipe culvert of claim 1 or 2, wherein (C) the unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more is contained at 0.5 part by mass to 10 parts by mass per a total of 100 parts by mass of (A) the vinyl ester resin composition and (B) the urethane (meth)acrylate composition.
4. The resin composition for repairing a pipe culvert of any one of claims 1 to 3, wherein the total amount of (D) the curing agent including cumene hydroperoxide and t-butyl peroxybenzoate is 0.5 part by mass to 5 parts by mass per a total of 100 parts by mass of (A) the vinyl ester resin

composition, (B) the urethane (meth)acrylate composition, and (C) the unsaturated polyester resin composition having an acid value of 90 KOHmg/g or more.

5. The resin composition for repairing a pipe culvert of any one of claims 1 to 4, wherein a vinyl ester resin contained in (A) the vinyl ester resin composition is one or more of vinyl ester resins selected from a group consisting of a bisphenol vinyl ester resin, a novolac vinyl ester resin, and a brominated vinyl ester resin with a weight-average molecular weight of 500 to 6000.

6. The resin composition for repairing a pipe culvert of any one of claims 1 to 5, wherein a urethane (meth)acrylate contained in (B) the urethane (meth)acrylate composition is a urethane (meth)acrylate resin with a weight-average molecular weight of 2000 to 8000 which is obtained by reacting an isocyanate compound having at least two isocyanate groups in a molecule, one or more (meth)acrylic compounds selected from the group consisting of 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate, polyethylene glycol, and a polyether polyol and/or an adipate-based polyester polyol.

7. A material for repairing a pipe culvert in which the resin composition for repairing a pipe culvert of any one of claims 1 to 6 is impregnated in a fiber base material.

8. The material for repairing a pipe culvert of claim 7, wherein the fiber base material consists of glass fibers.

9. A method for repairing an existing pipe culvert, the method comprising drawing the material for repairing a pipe culvert of claim 7 or 8, in an uncured state, into the pipe culvert or inserting the material into the pipe culvert, while reversing an inner surface side and an outer surface side, and then thermally curing the material for repairing a pipe culvert.