

DESCRIPTION

ROOM TEMPERATURE CURABLE RESIN COMPOSITION FOR PIPE RENEWAL

[0001]

Technical Field

The present invention relates to a room temperature curable resin composition for pipe renewal. More particularly, the present invention relates to a room temperature curable material for pipe renewal, which enables execution while ensuring sufficient working life in the execution field, and a method.

[0002]

Background Art

Pipe materials used for pipelines of waterwork and sewage system, crude oil, chemicals and city gas include, for example, concretes, steels, stainless steels, vinyl chlorides and ceramics. In the waterwork and sewage system, Hume concrete pipe is mainly used. However, physical damages occur during embedding for a long period and, particularly in the sewage work, corrosion, deterioration and cracks of an inner surface of a concrete pipe occur as a result of generation of a sulfurous acid gas attendant upon the decomposition of pollutants by sulfur reducing bacteria and generation of a sulfuric acid ions by sulfur oxidizing bacteria, thus leading to problems such as joint shift, differential settlement, and immersion of ground water and the

earth. Therefore, necessity of renewal of an existing pipe has increased. However, electric installation, gas fitting and waterwork are also embedded in the road in which sewage pipes are embedded, and thus making it difficult to renew the sewage pipe by an open-cut method. Since the open-cut work which required a long period causes traffic hindrance, a method capable of conducting without open-cutting has been needed.

[0003]

As means for meeting these requirements, for example, there are disclosed a method in which a cylindrical fiber material impregnated with a mixture obtained by adding a thixotropic agent to a thermosetting resin such as a vinyl ester resin or an unsaturated polyester resin is inserted into a tube, followed by pressure bonding and further curing with hot water or hot air (Japanese Examined Patent (Kokoku) No. 1-15374) and a method in which a tubular composite material obtained by impregnating a glass mat or a glass cloth with an unsaturated polyester resin or a vinyl ester resin, followed by thickening is used and ultraviolet rays or visible rays are used as curing means (Japanese Unexamined Patent Publication (Kokai) No. 11-210981). Thus, it became possible to efficiently repair the sewage pipe without open-cutting. However, curing with hot water or hot air requires a large-scaled heating apparatus such as boiler car, while curing with ultraviolet rays or visible rays requires a special lamp. In both cases, there was a problem that

tremendous energy or a special facility is required.

In order to solve the above problems, a method of conducting pipe renewal work by curing at room temperature has also been proposed. However, the method had a problem that a room temperature curable material for pipe renewal is cured before completion of work and sufficient strength cannot be exhibited after curing at room temperature when a working life is increased to 12 hours or more. It was impossible to prepare a curing system which has working life of 12 hours or more at room temperature and can exhibit sufficient strength after curing at room temperature.

[0004]

Disclosure of the Invention

Problems to be Solved by the Invention

Under these circumstances, an object of the present invention is to provide a room temperature curable resin composition for pipe renewal of a curing system which has working life of 12 hours or more at room temperature and can exhibit sufficient strength after curing at room temperature in a method of curing at room temperature without requiring tremendous energy or special facility, and a stable method using the same.

[0005]

Means for Solving the Problems

According to the present invention, the above object was achieved by the development of:

(1) A room temperature curable resin composition for pipe renewal, comprising 100 parts by weight of a radical polymerizable resin composition comprising (A) 40 to 95% by weight of a vinyl ester and/or an unsaturated polyester, and (B) 5 to 60% by weight of a radical polymerizable unsaturated monomer, and

(C) 0.05 to 0.25 part by weight of trimethylhydroquinone, (D) 0.1 to 5.0 parts by weight of a cobalt metal salt, and (E) 0.1 to 5.0 parts by weight of an organic peroxide catalyst containing at least an alkylperoxy ester added thereto;

(2) The room temperature curable resin composition for pipe renewal according to (1), wherein the alkylperoxy ester described in the component (E) is a tertiary butyl perbenzoate;

(3) A room temperature curable material for pipe renewal, comprising the room temperature curable resin composition for pipe renewal according to (1) or (2), and a fiber layered material (F) impregnated with the room temperature curable resin composition for pipe renewal;

(4) The room temperature curable material for pipe renewal according to (3), wherein the fiber layered material (F) is a nonwoven fabric and/or a cloth made of at least one or more kinds of fibers selected from a glass fiber, a polyester fiber, an aramid fiber, a carbon fiber and a basalt fiber, and the shape

is one or more shapes selected from a sheet shape, a roll shape, a tubular shape and a cylindrical shape;

(5) The room temperature curable material for pipe renewal according to (4), which has a cylindrical shape, one end portion of a cylindrical base material is closed;

(6) A method which comprises curing the sheet-shaped or tubular room temperature curable material for pipe renewal according to (4) in a state of being applied to the portion where repair inside an embedded pipe is required; and

(7) A method which comprises inserting the room temperature curable material for pipe renewal according to (5) into an embedded pipe while reversing, and curing the room temperature curable material in a state of being pressure bonded with air.

[0006]

Embodiments of the Invention

The vinyl ester used in the present invention is usually a compound having a polymerizable unsaturated bond produced by a ring-opening reaction of a compound having a glycidyl group (epoxy group) with a carboxyl group of a compound having a polymerizable unsaturated bond, such as acrylic acid, and is described in "Polyester Resin Handbook" (published by THE NIKKAN KOGYO SHIMBUN, LTD. on 1988) or "Coating Material Glossary" (published by Japan Society of Colour Material on 1993).

[0007]

The vinyl ester used in the present invention is produced by a known method and is obtained by reacting a bisphenol type or novolak type epoxy resin with an unsaturated monobasic acid, for example, acrylic acid or methacrylic acid.

Examples of the epoxy resin as the raw material include bisphenol A diglycidyl ether and a high-molecular weight homologue thereof; novolak type poly glycidyl ethers; and aliphatic glycidyl ethers such as 1,6-hexanediol diglycidyl ether.

Examples of the unsaturated monobasic acid as the raw material include acrylic acid and methacrylic acid. Examples of the acid other than the unsaturated monobasic acid include saturated dibasic acids such as adipic acid, sebacic acid and dimer acid.

[0008]

The unsaturated polyester used in the present invention is obtained by an esterification reaction of a polybasic acid with a polyalcohol and is described in, for example, "Polyester Resin Handbook" (published by THE NIKKAN KOGYO SHIMBUN, LTD. on 1988) or "Coating Material Glossary" (edited by Japan Society of Colour Material on 1993).

[0009]

Examples of the polybasic acid include an unsaturated dibasic acid and a saturated dibasic acid. These polybasic acids are not particularly limited and the unsaturated dibasic acid

includes, for example, maleic acid, maleic anhydride, fumaric acid, itaconic acid and itaconic anhydride. These unsaturated dibasic acids may be used alone, or two or more kinds of thereof may be used in combination. Examples of the saturated dibasic acid include aromatic dibasic acids and halogenated saturated 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 anhydride, 4,4'-biphenyldicarboxylic acid, or dialkyl esters thereof. These saturated dibasic acids may be used alone, or two or more kinds thereof may be used in combination.

[0010]

Examples of the polyalcohol component used in the present invention include, but are not limited to, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, cyclohexane-1,4-dimethanol, an ethylene oxide adduct of bisphenol A, and a propylene oxide adduct of bisphenol A. These polyalcohol components may be used alone, or two or more kinds thereof may be used in combination.

[0011]

The unsaturated polyester used in the present invention include known unsaturated polyesters such as ortho-, iso-, tere- and bisphenol-type unsaturated polyesters, and it is also possible to use those modified with a dicyclopentadiene-type compound as long as the effects of the present invention are not impaired. As the method for modification with a dicyclopentadiene-type compound, various known methods can be used and the method includes, for example, a method in which a maleic acid addition product (cydecanol monomaleate) is obtained using dicyclopentadiene and a dicyclopentadiene skeleton is introduced by using the same as a monobasic acid.

[0012]

The radical polymerizable unsaturated monomer used in the present invention is used as a diluent monomer of a vinyl ester resin and an unsaturated polyester resin. The radical polymerizable unsaturated monomer is not particularly limited as long as it is a monomer having a radical polymerizable unsaturated group and includes, for example, styrene-type monomers such as styrene, chlorostyrene, vinyltoluene and divinylbenzene; (meth)acrylic acid esters such as (meth)ethyl acrylate, (meth)methyl 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 and

tetrahydrofuryl (meth)acrylate; (meth)acrylic acid amides such as (meth)acrylic acid amide and (meth)acrylic acid N,N-dimethylamide; (meth)acryloyl-type monomers such as (meth)acrylic acid anilide; unsaturated dicarboxylic acid diesters such as diethyl citraconate; monomaleimide compound such as N-phenylmaleimide; and N-(meth)acryloylphthalimide.

[0013]

In the present invention, a (meth)acrylic acid ester compound having two or more (meth)acryloyl groups in the molecule, and dienes may also be used, and known (meth)acrylic acid ester compound and dienes can be used. Specific examples of the (meth)acrylic acid ester compound having two or more (meth)acryloyl groups in the molecule include 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, while specific examples of dienes include butadiene, 2,3-dimethylbutadiene, isoprene and chloroprene.

[0014]

The radical polymerizable unsaturated monomer used in the present invention is important so as to decrease viscosity of the resin and to improve hardness, strength, weatherability, water resistance and abrasion resistance, and is used in the amount of 5 to 60% by weight, and preferably 10 to 50% by weight, based on the radical polymerizable resin composition of the

present invention. It is not preferred because workability and impregnating ability deteriorate are reduced due to high viscosity when the content of the radical polymerizable unsaturated monomer is less than 5% by weight. It is not also preferred because various physical properties are inferior when the content is more than 60% by weight.

In the present invention, it is effective to increase the acid value of the resin composition by adding an acidic compound so as to increase the working life.

A known acidic compound can be used as the acidic compound and includes, for example, unsaturated monobasic acids such as (meth)acrylic acid; and unsaturated dibasic acids such as maleic acid, fumaric acid and itaconic acid.

Alternatively, a saturated polyester and an unsaturated polyester having a high acid value may also be added.

The acid value of the resin containing them added therein is from about 10 to 60 KOHmg/g.

[0015]

A known trimethylhydroquinone is used in the present invention. The amount of trimethylhydroquinone is used so that the resultant product exhibits the working life of 15 hours or more at room temperature and surely exhibits predetermined strength after curing, and is from 0.05 to 0.25 part by weight, and preferably from 0.06 to 0.2 part by weight, based on 100 parts by weight of the vinyl ester resin and/or

the unsaturated polyester resin. It is not preferred because it becomes difficult to ensure the working life of 15 hours at room temperature when the amount of trimethylhydroquinone is less than 0.05 part, and also curing deficiency may occur when the amount is more than 0.25 part by weight.

[0016]

Examples of the cobalt metal salt used in the present invention include, but are not limited to, cobalt naphthenate, cobalt octylate and cobalt hydroxide. Of these cobalt metal salts, cobalt naphthenate and cobalt octylate are preferred. The additive amount is from 0.1 to 5.0 part by weight, and preferably from 0.1 to 3.0 part by weight, based on 100 parts by weight of the vinyl ester resin and/or the unsaturated polyester resin. It is not preferred because curing deficiency may occur when the additive amount of the cobalt metal salt is 0.1 part by weight or less. It is not also preferred because it becomes impossible to ensure the working life when the additive amount is 5.0 parts by weight or more.

[0017]

The organic peroxide catalyst used in the present invention must contain an alkylperoxy ester. Examples of the alkylperoxy ester used in the present invention include, but are not limited to, cumyl peroxyneodecanoate, 1,1,3,3-tetramethylbutyl peroxyneodecanoate, 1-cyclohexyl-1-methylethyl peroxyneodecanoate, t-hexyl peroxyneodecanoate, t-butyl

peroxyneodecanoate, 1,1,3,3-tetramethylbutyl
peroxy-2-ethylhexanoate,
2,5-dimethyl-2,5-di(2-ethylhexanolperoxy)hexane, t-hexyl
peroxy-2-ethylhexanoate, t-butyl peroxyisobutyrate, t-hexyl
peroxyisopropylmonocarbonate, t-butylperoxymaleic acid,
t-butyl peroxy-3,5,5-trimethylhexanoate, t-butyl
peroxylaurate, t-butyl peroxybenzoate,
2,5-di-methyl-2,5-di(benzoylperoxy)hexane, t-butyl
peroxyacetate and t-peroxybenzoate. Of these alkylperoxy
esters, t-peroxybenzoate is particularly preferred.

[0018]

The organic peroxide catalyst other than the alkylperoxy
ester used in the present invention is classified into known
ketone peroxide, peroxyketal, hydroperoxide, diallyl peroxide,
diacyl peroxide and peroxydicarbonate, and azo compounds are
also effective. Specifically, 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-isopropylhydr
o peroxide, t-butyl hydroperoxide, dicumyl peroxide, dicumyl
hydroperoxide, acetyl peroxide,
bis(4-t-butylcyclohexyl)peroxydicarbonate, diisopropyl
peroxydicarbonate, isobutyl peroxide, 3,3,5-trimethylhexanoyl
peroxide, lauryl peroxide azobisisobutyronitrile and
azobiscarbonamide can be used. Examples of particularly

effective one to be used in combination with the alkylperoxy ester include p-methane hydroperoxide, diisopropylbenzene hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, cumen hydroperoxide and t-butyl hydroperoxide which are classified into hydroperoxide.

[0019]

The additive amount of the organic peroxide catalyst containing at least alkylperoxy ester used in the present invention is from 0.1 to 5.0 parts by weight based on 100 parts by weight of the vinyl ester resin and/or the unsaturated polyester resin, and also the amount of the alkylperoxy ester component is from 0.1 to 5.0 parts by weight, and preferably from 0.2 to 3.0 parts by weight, based on 100 parts by weight of the vinyl ester resin and/or the unsaturated polyester resin. It is not preferred because curing deficiency may occur when the amount of the organic peroxide catalyst containing the alkylperoxy ester is 0.1 part by weight or less. It is not also preferred because the working life cannot be ensured when the amount is 5.0 parts by weight.

[0020]

In the present invention, an inorganic or organic filler can also be added. As the inorganic filler, for example, known inorganic fillers such as aluminum hydroxide, calcium carbonate, talc, clay, glass power, silica, barium sulfate, titanium oxide and cement can be used. When flame retardancy is imparted to

a curable prepreg composition, aluminum hydroxide is effective. It is also possible to use two or more kinds of these inorganic fillers in combination, and the amount to be used is from 0 to 200 parts by weight, and preferably from 0 to 100 parts by weight, based on 100 parts by weight of the vinyl ester resin and/or the unsaturated polyester resin. When the amount of the inorganic filler is more than 200 parts by weight, workability is reduced because of too high viscosity, and also bubbles are likely to remain and the strength decreases. In the present invention, thixotropy may be imparted by a known method. The known method includes, for example, a method of adding a thixotropic agent such as a silica powder (aerosil type), a mica powder or a calcium carbonate powder in the amount of 0.1 to 50 parts by weight based on 100 parts by weight of the vinyl ester resin and/or the unsaturated polyester resin.

[0021]

It is possible to use, as an organic filler or polymer, those which are also effective as a low constrictive agent, for example, known polystyrene, polyvinyl acetate, polymethyl methacrylate, polyethylene, polyvinylidene chloride microballoon and polyacrylonitrile microballoon. When used as the low constrictive agent, the amount is from 0 to 200 parts by weight, and preferably from 0 to 50 parts by weight, based on 100 parts by weight of the vinyl ester resin and/or the unsaturated polyester resin. In addition, in the present

invention, a pigment can be used. There is no particular limitation of the kind of the pigment, and an organic pigment or an inorganic pigment can be used. The amount of the pigment is 20 parts by weight at most, and preferably 10 parts by weight, based on 100 parts by weight of the vinyl ester resin and/or the unsaturated polyester resin.

[0022]

In the present invention, waxes may be blended for the purpose of improving drying property. Known waxes can be used without any limitation and, for example, petroleum waxes (paraffin wax, microcrystalline, etc.), plant waxes (candelilla wax, rice wax, Japan tallow, etc.), animal waxes (beeswax, spermaceti, etc.), mineral wax (montan wax, etc.) and synthetic waxes (polyethylene wax, amide wax, etc.) can be used. More specifically, a paraffin wax having a melting point of about 20°C to 80°C, and BYK-S-750, BYK-S-740, BYK-LP-S6665 (manufactured by BYK-Chemie) are exemplified and waxes each having a different melting point may also be used in combination. The amount of waxes to be blended is preferably from 0.1 part by mass to 5.0 part by mass based on 100 parts by mass of the vinyl ester resin and/or the unsaturated polyester resin.

[0023]

The shape of the fiber layered material in the present invention includes sheet shape, roll shape, tubular shape and cylindrical shape. The fiber-reinforced material for

reinforcing these fiber layered materials includes an organic fiber and/or an inorganic fiber and, for example, it is possible to use known roving, cloth, mat, and nonwoven fabric made of fibers such as glass fiber, polyester fiber, aramid fiber, carbon fiber, basalt fiber (basalt fiber), amide fiber, high-density polyethylene fiber, polyethylene terephthalate fiber, vinylon fiber, polyester fiber, amide fiber, metal fiber and ceramic fiber. As a matter of course, two or more kinds of these fibers may also be used in combination. In the present invention, glass fiber and organic fiber are particularly preferred in these reinforcing materials, and cloth-shaped and mat-shaped ones are preferred taking workability into consideration. Under the atmosphere where a corrosive gas is generated, an acid-resistant glass fiber is preferably used as the glass fiber.

[0024]

The method of coating an inner surface of a tubular molded article with a curable material of the present invention includes the following method. For example, a film is provided on an inner surface of a cylindrical body made of the material and a light irradiator is provided in the cylindrical body, and also both ends of the cylindrical body is closed and the cylindrical body is inserted into the tubular molded article and the cylindrical body is blown up by blowing air, thereby adhering the cylindrical body to the inner surface of the tubular molded article inner surface, and then the material is cured at room

temperature. After curing, the film may be optionally removed. Alternatively, the material can be cured at room temperature by employing a method in which a film is provided outside a cylindrical body and the cylindrical body is inserted in a tubular molded article while inverting the rear and front surfaces (see, for example, Japanese Unexamined Patent Publication (Kokai) No. 5-138738 and Japanese Unexamined Patent Publication (Kokai) No. 8-1779). In order to locally repairing an inner surface of a tubular molded article, a resin-impregnated sheet of the present invention is directly applied to the localized part or wound around the outside of a rubber sleeve and then applied to the part to be repaired. The rubber sleeve is blown up by compressed air thereby performing pressure bonding, and then the sheet is cured at room temperature.

[0025]

Examples of the tube which can be coated or repaired in the present invention include concrete fume tube, steel tube, stainless steel tube, vinyl chloride tube, ceramic tube, knuckle type tube (culvert), and shaft tube such as manhole, while examples of the sewage pipe include main tube, branch tube and lateral tube. In the case of a vinyl chloride tube or ceramic tube having poor adhesion, it is effective to coat or repair by providing one primer layer between the tube and a tubular body.

[0026]

Examples

The contents of the present invention will be described in detail below by way of the following Examples and Comparative Examples. In the respective Examples, parts and percentages are by weight.

[0027]

Synthesis Example 1 (Synthesis of vinyl ester VE-1)

In a reactor equipped with a stirrer, a reflux condenser, a gas introducing tube and a thermometer, 189 parts of EPIKOTE 828 (epoxy resin manufactured by Yuka-Shell Epoxy Co. Ltd.: epoxy equivalent 189): 1 equivalent (189 g), 57 parts (0.5 equivalent) of bisphenol A and 0.5 part of triethylamine were charged and reacted under a nitrogen atmosphere at 150°C for 2 hours. After the completion of the reaction, the reaction solution was cooled to 90°C, and then 43.1 parts of methacrylic acid, 0.5 part of tetradecyldimethylbenzylammonium chloride, 0.05 part of hydroquinone and 147 parts of styrene were charged. The mixture was reacted at 90°C for 20 hours while blowing air and the reaction was terminated when an acid value became 10 mgKOH/g. Styrene (294 parts) was added to obtain a bisphenol A-type vinyl ester resin (VE-1) having a viscosity of 1.5 Pa·s at 25°C and a solid content of 60% by weight.

Synthesis Example 2 (Synthesis of unsaturated polyester PE-1)

In a reactor equipped with a stirrer, a reflux condenser, a gas introducing tube and a thermometer, 100 mol of maleic anhydride and 100 mol of propylene glycol were charged and reacted at 210°C according to a conventional method until an acid value became 215 mgKOH/g. After the completion of the reaction, to the resultant unsaturated polyester, 0.01 part of hydroquinone and 25 parts of a styrene monomer were added to obtain an unsaturated polyester resin (PE-1) having a viscosity of 0.4 Pa·s at 25°C, a solid content of 80% and an acid value of 172 mgKOH/mg.

Synthesis Example 3 (Synthesis of unsaturated polyester PE-2)

In a four-necked flask equipped with a thermometer, a stirrer, an inert gas introducing tube and a reflux condenser, 60 mol of isophthalic acid, 50 mol of 1,2-propanediol and 50 mol of neopentyl glycol were charged and heated to 190°C under a nitrogen gas flow while heating with stirring, and then esterified by gradually heating to 215°C. When an acid value became 9.5 mgKOH/g, cooling was started, 40 mol of maleic anhydride was charged at 120°C and an esterification reaction was conducted at a temperature from 150°C to 210°C according to a conventional procedure. Cooling was started when an acid value became 9.8 mgKOH/g to produce an unsaturated polyester. After the reaction, 0.015 part of hydroquinone was added to 100 parts by weight of the resultant unsaturated polyester and, after

cooling to 120°C, 65 parts of a styrene monomer was added to obtain an unsaturated polyester resin (PE-2) having a viscosity of 1.3 Pa·s at 25°C, a solid content of 60% and an acid value of 6 mgKOH/mg.

[0028]

Preparation of resins (Examples 1 to 9 and Comparative Examples 1 to 10)

Radical polymerizable resins were prepared by mixing components at each mixing ratio shown in Table 1 and Table 2. A polymerization inhibitor such as trimethylhydroquinone was added and then dissolved by appropriately heating. Unit of the amount of each component in Table 1 and Table 2 is part.

[0029]

The resin compositions of Examples 1 to 9 and Comparative Examples 1 to 10 were subjected to various evaluations. The evaluations were conducted by the following procedures.

[0030]

<Stability>

Each (80 g) of the resin compositions prepared in Examples 1 to 9 and Comparative Examples 1 to 10 was charged in a 100 cc screw bottle and stored under the atmosphere at 23°C, and then the time until fluidity disappeared was measured. Rating described in the table is as follows.

B: Fluidity suited for use is maintained for 12 hours to 18 hours.

A: Fluidity suited for use is maintained for 18 hours to 24 hours.

C: Fluidity suited for use is 12 hours or less.

D: Fluidity suited for use is maintained for too long time, for example, 24 hours or more.

<Surface hardness>

Using each of the resin compositions prepared in Examples 1 to 9 and Comparative Examples 1 to 10, FRP was produced and allowed to stand under the atmosphere at 23°C for 48 hours, and then surface hardness was measured by a Barcol hardness tester defined in JIS K 6911(1995). FRP was composed of a surfacing mat, a #450 chopped strand mat (3 ply) and a surfacing mat, and had a thickness of about 3 mm and a glass content of 28 to 33%.

<Bending strength>

Using each of the resin compositions prepared in Examples 1 to 9 and Comparative Examples 1 to 10, FRP was produced and allowed to stand under the atmosphere at 23°C for 96 hours. Then, FRP was appropriately cut and a bending strength was measured in accordance with JIS K 7171(1994). FRP was composed of Sontara #8001 (manufactured by Japan Vilene Company) (2 ply) and had a thickness of about 3 mm

<Molding test>

Using each of the resin compositions prepared in Examples 1 to 9 and Comparative Examples 1 to 10, Sontara #8001 (manufactured by Japan Vilene Company) (2 ply) was impregnated on a PET film under the atmosphere at 23°C. After impregnation, a cylindrical product was obtained by coating with a PET film again and one end portion was closed. The cylindrical product was inserted into concrete fume tube having an inner diameter of 250 mm and then pressure bonded by introducing compressed air (0.1 MPa) from an open end part. After 3 days, cutting was conducted and a hardness of the cured article surface was measured by a Barcol hardness tester defined in JIS K 6911(1995).

[0031]

Curing can be conducted under the atmosphere at a temperature of 20 to 80°C. It is known that the storage time increases by storing a resin composition under the atmosphere at a temperature of 23°C or lower, at which able to maintain fluidity suited for use for 18 to 24 hours while storing under the atmosphere at a temperature of 23°C. It is known that a resin composition, capable of maintaining fluidity suited for use for 18 to 24 hours while storing under the atmosphere at a temperature of 23°C, having surface hardness of the resin composition reaching to the value of 20 to 30 after 48 hours, is cured at the temperature of 23°C or higher. Namely, using each of the resin compositions prepared in Examples 1 to 9, Sontara #8001 (manufactured by Japan Vilene Company) (2 ply) is

impregnated on a PET film, followed by storage under the atmosphere at a temperature of 0 to 25°C for 20 to 48 hours, thus making it possible to cure under the atmosphere at a temperature of 23 to 35°C. Alternately, using each of the resin compositions prepared in Examples 1 to 9, Sontara #8001 (manufactured by Japan Vilene Company) (2 ply) is impregnated on a PET film, followed by storage under the atmosphere at a temperature of 20 to 35°C for 20 to 48 hours, thus making it possible to cure under the atmosphere at a temperature of 25 to 120°C.

[0032]

Table 1: Examples

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
VE-1	100	100	100	100	100	95	80		100
PE-1						5	20	80	
PE-2								20	
Amount of monomer	40	40	40	40	40	39	36	36	40
VE:PE	100:0	100:0	100:0	100:0	100:0	93:7	75:25	0:100	100:0
Cobalt naphthenate	0.5	0.5	2.0	4.0		0.5	3.0	3.0	2.0
Cobalt octylate					0.4				
TMHQ	0.05	0.1	0.2	0.25	0.1	0.2	0.1	0.1	0.1
CHP	0.3	0.4	0.6	3.2	0.4	0.9	0.6	1.5	0.0
TBPB	1.2	1.6	2.4	0.8	1.6	0.1	2.4	1.5	2.0
CHP:TBPB	2:8	2:8	2:8	8:2	2:8	9:1	2:8	5:5	0:10
Stability	B	B	B	B	B	A	A	B	B
Surface hardness	20	21	21	21	22	33	34	25	24
Flexural strength (MPa)	38	31	33	33	32	40	41	36	38
Hardness of molded article	21	21	20	21	22	31	35	27	26

TMHQ: Trimethylhydroquinone

HQ: Hydroquinone

MHQ: Methylhydroquinone

TBC: t-butylcatechol

CHP: Cumen hydroperoxide

TBPB: t-butyl peroxybenzoate

[0033]

Table 2: Comparative Examples

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
VE-1	100	100	100	100	100
PE-1					
PE-2					
Amount of monomer	40	40	40	40	40
VE:PE	100:0	100:0	100:0	100:0	100:0
Cobalt naphthenate	2.0	2.0	2.0	2.0	
Cobalt octylate					0.5
TMHQ					0.1
HQ	0.1				
TBHQ		0.1			
MHQ			0.1		
TBC				0.1	
CHP	0.4	0.4	0.4	0.4	1.0
TBPB	1.6	1.6	1.6	1.6	0
CHP:TBPB	2:8	2:8	2:8	2:8	10:0
Stability	D	D	D	D	B
Surface hardness	Impossible to measure	Impossible to measure	Impossible to measure	Impossible to measure	5
Flexural strength (MPa)	Impossible to measure	Impossible to measure	Impossible to measure	Impossible to measure	0
Hardness of molded article	Impossible to measure	Impossible to measure	Impossible to measure	Impossible to measure	2

TMHQ: Trimethylhydroquinone

HQ: Hydroquinone

MHQ: Methylhydroquinone

TBC: t-butylcatechol

CHP: Cumen hydroperoxide

TBPB: t-butyl peroxybenzoate

[0034]

Table 3: Comparative Examples

	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10
VE-1			100	100	100
PE-1	100				
PE-2		100			
Amount of monomer	20	40	40	40	40
VE:PE	0:100	0:100	100:0	100:0	100:0
Cobalt naphthenate	2.0	2.0	4.0		2.0
Cobalt octylate					
TMHQ	0.1	0.1	0.3	0.1	0.2
CHP	0.8	0.7	3.2		
TBPB	0.2	0.3	0.8		
CHP:TBPB	8:2	7:3	8:2		
DMA				2.0	
BPO				2.0	
MEKPO					2.0
Stability	D	C	D	C	B
Surface hardness	Impossible to measure	21	Impossible to measure	0	0
Flexural strength (MPa)	Impossible to measure	32	Impossible to measure	0	0
Hardness of molded article	Impossible to measure	22	Impossible to measure	0	0

TMHQ: Trimethylhydroquinone

HQ: Hydroquinone

TBHQ: t-butylhydroquinone

MHQ: Methylhydroquinone

TBC: t-butylcatechol

CHP: Cumen hydroperoxide

TBPB: t-butyl peroxybenzoate

DMA: Dimethylaniline

BPO: Benzoyl peroxide (50%)

MEKPO: Methyl ethyl ketone peroxide (55%)

Effects of the Invention

It became apparent that the room temperature curable resin composition for pipe renewal of the present invention has sufficient working time and is curable without heating or irradiation with energy rays, thus making it possible to exhibit sufficient strength.

CLAIMS

1. A room temperature curable resin composition for pipe renewal, comprising 100 parts by weight of a radical polymerizable resin composition comprising:

(A) 40 to 95% by weight of a vinyl ester and/or an unsaturated polyester, and

(B) 5 to 60% by weight of a radical polymerizable unsaturated monomer, and

(C) 0.05 to 0.25 part by weight of trimethylhydroquinone,

(D) 0.1 to 5.0 parts by weight of a cobalt metal salt, and

(E) 0.1 to 5.0 parts by weight of an organic peroxide catalyst containing at least an alkylperoxy ester added thereto.

2. The room temperature curable resin composition for pipe renewal according to claim 1, wherein the alkylperoxy ester described in the component (E) is a tertiary butyl perbenzoate.

3. A room temperature curable material for pipe renewal, comprising the room temperature curable resin composition for pipe renewal according to claim 1 or 2, and a fiber layered material (F) impregnated with the room temperature curable resin composition for pipe renewal.

4. The room temperature curable material for pipe renewal according to claim 3, wherein the fiber layered material (F) is a nonwoven fabric and/or a cloth made of at least one or more kinds of fibers selected from a glass fiber, a polyester fiber, an aramid fiber, a carbon fiber and a basalt fiber, and the shape is one or more shapes selected from a sheet shape, a roll shape, a tubular shape and a cylindrical shape.

5. The room temperature curable material for pipe renewal according to claim 4, which has a cylindrical shape, one end portion of a cylindrical base material is closed.

6. A method which comprises curing the sheet-shaped or tubular room temperature curable material for pipe renewal according to claim 4 in a state of being applied to the portion where repair inside an embedded pipe is required.

7. A method which comprises inserting the room temperature curable material for pipe renewal according to claim 5 into an embedded pipe while reversing, and curing the room temperature curable material in a state of being pressure bonded with air.

8. A method which comprises pulling the room temperature curable material for pipe renewal according to claim 5 into an embedded pipe, and curing the room temperature curable material

in a state of being pressure bonded with air.