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(54) **METHOD FOR REPAIRING AND REINFORCING EXISTING CONCRETE STRUCTURE AND RESIN**

(57) The present invention relates to repair and reinforcement of existing concrete structures such as bridge footings and buildings. The repairing and reinforcing method of the present invention is characterized by applying a reinforcement fiber sheet material having a resin content of 15% by weight or less to the surface of the existing concrete structure while being impregnated with a resin having a viscosity within a range of 2.5-300 poise and a curing time within a range of 1-24 hours, and curing the resin. According to this method, existing concrete structures can be repaired and reinforced easily in a short time without being influenced by temperature conditions on execution, while providing concrete structures with high strength.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a method of repairing and reinforcing existing concrete structures such as bridge footings, bridges, and pillars of building structures.

[0002] This application is based on Japanese Patent Application No. Hei 10-144249 filed in Japan, the content of which is incorporated herein by reference.

10 BACKGROUND ART

[0003] As the method of repairing and reinforcing existing concrete structures such as bridge footings, for example, there has been known a method of casting an epoxy resin into the space between a steel plate and concrete and curing the epoxy resin, thereby bonding them. A method of impregnating a reinforcement fiber sheet material with an epoxy resin and applying the reinforcement fiber sheet material to the surface of an existing concrete structure has attracted special interest recently, and actual results have increased gradually. This method has such art advantage that haulage of heavy weights such as steel plate, assembling operation, and welding operation are not required as compared with a method of using a steel plate.

15 **[0004]** However, the epoxy resin used exclusively in impregnation of the reinforcement fiber sheet material had the following problems. That is, several days are required to cure the epoxy resin, thereby securing sufficient strength even at normal temperature. Furthermore, when using no special heating means at low temperature such as 5°C or lower, curing hardly proceeds, thereby to drastically lengthen a term of works.

[0005] To solve these problems of the epoxy resin, there has been suggested a method of using, as an impregnating resin, a radically polymerizable resin capable of curing even at low temperature such as about 5°C, particularly cryogenic temperature such as about -10°C, because of its high curing rate (e.g. Japanese Patent Publication (A) Nos. Hei 9-184304, Hei 9-184305 and Hei 10-7750.)

20 **[0006]** A means of using the radically polymerizable resin as the impregnating resin exerts excellent reinforcing effect when using in combination with a reinforcement fiber sheet material in the form suited for a radically polymerizable resin. However, when using in combination with reinforcement fiber sheet materials developed by using, as the impregnating resin, an epoxy resin which has widely been used at present, for example, reinforcement fiber sheet materials prepared by unidirectionally arranging reinforcement fibers on a substrate sheet through an adhesive layer (Japanese Patent Publication (A) Nos. Hei 3-224901, Hei 3-222734 and Hei 5-32804) and reinforcement fiber sheet materials prepared by impregnating reinforcement fibers with a small amount (15% by weight or less) of a resin (Japanese Patent Publication (A) Nos. Hei 7-34677 and Hei 7-228714), the curing in the vicinity of the reinforcement fibers does not proceed sufficiently because of a difference in method of reacting the resin, resulting in poor repairing and reinforcing effect.

DISCLOSURE OF THE INVENTION

40 **[0007]** To solve the problems described above, the present inventors have intensively studied and found that, by using an additional impregnating resin having a viscosity and a curing time within a specific range, a sufficient reinforcing effect can be exerted even when using a reinforcement fiber sheet material whose resin content is 15% by weight or less, which was developed by using an epoxy resin as an impregnating resin. Thus, the present invention has been accomplished.

45 **[0008]** That is, a first gist of the present invention lies in a method of repairing and reinforcing an existing concrete structure, which comprises applying a reinforcement fiber sheet material having a resin content of 15% by weight or less to the surface of the existing concrete structure while being impregnated with a resin having a viscosity within a range of 2.5-300 poise and a curing time within a range of 1-24 hours, and curing the resin.

[0009] A second gist of the present invention lies in a method of repairing and reinforcing an existing concrete structure, which comprises applying a reinforcement fiber sheet material having a resin content of 15% by weight or less to the surface of the existing concrete structure, impregnating the reinforcement fiber sheet with a resin having a viscosity within a range of 2.5-300 poise and a curing time within a range of 1-24 hours, and curing the resin.

50 **[0010]** In the present invention, a resin (resin having a viscosity within a range of 2.5-300 poise and a curing time within a range of 1-24 hours), with which the reinforcement fiber sheet material is impregnated subsequently, is referred to as an additional impregnating resin.

55 **[0011]** The additional impregnating resin is particularly preferably a radically polymerizable resin having a viscosity within a range of 10-100 poise and a curing time within a range of 2-12 hours, which corresponds to a third gist of the present invention.

[0012] According to the present invention, even when using a reinforcement fiber sheet material having a resin content of 15% by weight or less, which was developed by using an epoxy resin as an impregnating resin used widely to repair and reinforce existing concrete structures, the curing can be carried out very easily in a comparatively short time within a day without depending on the temperature conditions. The execution can be conducted even at low temperature and an excellent reinforcing effect is exerted.

BEST MODE FOR CARRYING OUT THE INVENTION

(Reinforcement fiber sheet material - Resin)

[0013] In the method of repairing and reinforcing an existing concrete structure of the present invention, a reinforcement fiber sheet material comprising reinforcement fibers and a resin whose content is limited to 15% by weight, which is preferably used in a repairing and reinforcing method using an epoxy resin as an impregnating resin, is used.

[0014] The resin constituting the reinforcement fiber sheet material may impregnate with the reinforcement fibers of the sheet material. Alternatively, the resin may be in the form of an adhesive layer for bonding arranged reinforcement fibers or woven reinforced fibers with a release paper or a substrate sheet.

[0015] In the present invention, the resin constituting the reinforcement fiber sheet material may be either of an uncured thermosetting resin and a polymerized thermoplastic resin and is not specifically limited, but an epoxy resin containing no curing agent is generally used. As a matter of course, the reinforcement fiber sheet material may be a reinforcement fiber sheet material which was specially produced by fitting to the resin (additional impregnating resin) with which the reinforcing resin material is impregnated subsequently. When using, as the additional impregnating resin, a radically polymerizable monomer such as acrylate or methacrylate, a resin having a solubility parameter (SP) value within a range of 17-28 (MPa)^{1/2}, which is described hereinafter, is preferably used as the resin constituting the reinforcement fiber material.

[0016] It is necessary that the amount of the matrix resin constituting the reinforcement fiber sheet material is 15% by weight or less. When the amount of the resin exceeds 15% by weight, poor curing of the additional impregnating resin and deterioration of physical properties of the cured article are caused, which is not preferable. On the other hand, when the amount of the resin constituting the reinforcement fiber sheet material is 7% by weight or less, sufficient curability and sufficient strength of the cured article are obtained, which is particularly preferable, even in case the resin constituting the reinforcement fiber sheet material is different from the resin which with the reinforcement fiber sheet material is impregnated subsequently, for example, the resin constituting the reinforcement fiber sheet material is an epoxy resin and the reinforcement fiber sheet material is subsequently impregnated with a radically polymerizable resin. The amount of the resin constituting the reinforcement fiber sheet material is preferably 1% by weight or more because handling properties of the reinforcement fiber sheet material largely vary depending on the amount of the resin. The resin constituting the reinforcement fiber sheet material is preferably an uncured resin, or cured resin having enough rigidity to conform to the place having a curvature where the reinforcement fiber sheet material is applied, or a cured resin having a shape suited for the place, so that the reinforcement fiber sheet material can be applied to the existing concrete structures having a curvature. As a matter of course, when using the uncured resin, the shelf life at normal temperature is preferably long.

(Reinforcement fiber sheet material - Reinforcement fibers)

[0017] Preferable examples of the reinforcement fibers constituting the reinforcement fiber sheet material in the present invention are fibers, which are generally used as reinforcement fibers, such as carbon fibers, aramid fibers, and glass fibers. Among these fibers, carbon fibers are preferable.

[0018] The reinforcement fibers are preferably high-strength carbon fibers having a tensile strength of 4000 MPa or more when utilizing a strength, and more preferably high-elasticity carbon fibers having an elasticity of 250 GPa or more when utilizing an elastic modulus.

[0019] When using carbon fibers as the reinforcement fibers of the reinforcement fiber sheet material and using a radically polymerizable resin as the resin for subsequent impregnation, it is particularly preferable to use carbon fibers using, as a sizing agent, a compound having a radically polymerizable functional group at at least one terminal in view of attainment of the strength of the cured article.

(Reinforcement fiber sheet material - Reinforcing form)

[0020] In the present invention, the reinforcing form in the reinforcement fiber sheet material is not specifically limited, but includes unidirectional arrangement of the reinforcement fibers, or production of sheet from a woven fabric made of the reinforcement fibers. In view of the repairing and reinforcing effect, the weight of the reinforcement fibers

is preferably 150 g/m² or more.

[0021] As the form used preferably as the reinforcement fiber sheet material used in the present invention, for example, the following forms (1) to (3): (1) a reinforcement fiber sheet material produced by unidirectionally arranging reinforcement fibers or weaving the reinforcement fibers to form a reinforcement fiber woven fabric, forming the reinforcement fiber woven fabric into a sheet having a weight of reinforcement fibers of 150 g/m², and impregnating the sheet with a resin described above, (2) a reinforcement fiber sheet material produced by laminating a glass fiber fabric on at least one surface of the reinforcement fiber sheet material (1), and (3) a reinforcement fiber sheet material produced by unidirectionally arranging reinforcement fibers on a substrate sheet through an adhesive layer are preferable as described in Japanese Patent Application (A) Nos. Hei 3-224901, Hei 3-222734, Hei 5-32804, Hei 7-34677, and Hei 7-228714.

[0022] As the substrate sheet, for example, glass fiber woven fabric, glass scrim cloth, glass fiber paper, glass fiber nonwoven fabric, and nonwoven fabrics made of fibers of various polymers such as polyamide and polyphenylene sulfide are used.

[0023] The adhesive may be those capable of temporarily bonding reinforcement fibers on a substrate and is preferably made of a resin having good compatibility with a matrix resin of the reinforcement fiber sheet material. For example, when the matrix resin is an epoxy resin, an epoxy adhesive is preferable.

[0024] As a matter of course, the reinforcement fiber sheet material used in the present invention is not limited to the above reinforcement fiber sheet material and, for example, there can be applied those obtained by unidirectionally arranging reinforcement fibers or weaving the reinforcement fibers, coating with a resin constituting the reinforcement fiber sheet material in a linear or dot form, thereby retaining the form, or those obtained by further laminating a substrate sheet thereon.

(Additional impregnating resin)

[0025] In the present invention, the reinforcement fiber sheet material is impregnated with a curable resin on or after application of it on the surface of an existing structure. In the present invention, it is necessary to use a resin having a viscosity within a range of 2.5-300 poise and a curing time within a range of 1-24 hours as the additional impregnating resin in order to enhance the repairing and reinforcing effect by using the above reinforcement fiber sheet material.

[0026] The viscosity of the resin used for impregnation is a viscosity measured at the execution temperature using a B type viscometer, or a viscosity measured before adding an organic peroxide which serves as a polymerization initiator in case the resin used for impregnation is a radically polymerizable resin. When the viscosity of the resin exceeds 300 poise, it becomes difficult to impregnate the reinforcement fiber sheet material with the resin. On the other hand, when the viscosity is less than 2.5 poise, the reinforcement fibers are liable to move during the impregnation and curing process of the resin, thereby lowering the reinforcing effect in a combination with the reinforcement fiber sheet material. The lower limit of preferable viscosity is 10 poise, while the upper limit thereof is 100 poise.

[0027] As used herein, the term "curing time" refers to a time from the beginning of the curing of the resin to the point of time where a tacky feel on touch with fingers disappears. When using a resin having the curing time of one hour or less, sufficient strength is hardly attained. When using a resin whose curing time exceeds 24 hours, the resin is not suited for the purpose of the present invention because of its too long curing time.

[0028] The lower limit of the curing time is more preferably 2 hour or more, while the upper limit is more preferably 12 hours or more, and most preferably 8 hours or less.

[0029] The resin may be a resin which satisfies the requirements of the viscosity and curing time. A thermosetting resin is preferable and a cold curing resin is particularly preferable. A radically polymerizable resin is particularly preferable in view of the low-temperature curability, and a radically polymerizable resin composed of a radically polymerizable monomer or oligomer having a methacryloyl group or an acryloyl group as a reactive group at terminal is particularly preferable in view of balance between the curability and attainment of physical properties of the cured article.

[0030] The composition may be a composition containing a monomer having a terminal reactive group other than the methacryloyl or a cryloyl group, for example, styrene as far as it satisfies the requirements of the viscosity and curing time.

[0031] Examples of the radically polymerizable monomer include acrylate, for example, methyl acrylate and ethyl acrylate, methacrylate, for example, methyl methacrylate, 2-ethylhexyl methacrylate, hydroxyethyl methacrylate, and tetrahydrofurfuryl methacrylate, styrene, vinyltoluene, divinylbenzene, and acrylonitrile, and these monomers can be used alone or in combination according to the purposes. Among these monomers, acrylate and methacrylate are particularly preferable in view of the curability and attainment of the strength.

[0032] Since the radically polymerizable monomer in the present invention is preferably a monomer which is compatible with a resin adhered to the reinforcement fiber sheet to some extent, a radically polymerizable monomer having a solubility parameter (SP) value within a range of 17-22 (MPa)^{1/2} is particularly preferable.

[0033] The SP value of the radically polymerizable monomer can be calculated by the equation: $SP = \Sigma (Wn/100SPn)$ [Wn: weight percentage of n monomer, SPn: SP value of n monomer].

[0034] Examples of the radically polymerizable oligomer include, but are not limited to, polyester poly(meth)acrylate obtained by introducing an acryloyl group or a methacryloyl group into terminal of an oligomer, which is obtained by reacting a polybasic acid such as phthalic acid or adipic acid with a polyhydric alcohol such as ethylene glycol or butanediol, by the reaction with acrylic acid or methacrylic acid; allyl group-containing polyester(meth)acrylate obtained by reacting a polybasic acid, a polyhydric alcohol, an allyl group-containing alcohol such as pentaerythritol triallyl ether or trimethylolpropane diallyl ether, and a (meth)acrylate; allyl group-containing polyester obtained by reacting a polybasic acid, a polyhydric alcohol, and an allyl group-containing alcohol; epoxy poly(meth)acrylate obtained by reacting an epoxy resin with a (meth)acrylate; and urethane poly(meth)acrylate obtained by reacting a polyol, a polyisocyanate, and a hydroxyl group-containing (meth)acrylate.

[0035] The molecular weight of the radically polymerizable oligomer used in the present invention is not specifically limited, but is more preferably 10000 or less in terms of a number-average molecular weight in view of the curability at low temperature.

[0036] As a matter of course, an elastomer component having a reactive functional group at terminal, as a reactive oligomer, can be added to provide high toughness and durability with the cured article.

[0037] The mixing ratio of the monomer to the oligomer in the impregnating resin used in the present invention is not specifically limited as far as it satisfies limitation of the viscosity and curing time of the composition.

[0038] Examples of an initiator used for initiating the polymerization of these radically polymerizable monomers and oligomers include commonly used curing agents, for example, redox catalysts prepared by using a peroxide in combination with a curing accelerator such as metal soap or tertiary amine. The combination is selected so that the curing time becomes one hour or more and 24 hours or less, preferably 12 hours or less.

[0039] For the purpose of adjusting the viscosity of the composition and improving high toughness and durability of the cured article, a polymer is added in place of or in addition to the oligomer as the impregnating resin. Preferable polymers include, but are not limited to, elastomer polymers such as acrylic polymer, acrylonitrile-butadiene rubber, acrylic rubber, styrene block polymer, and urethane elastomer. The amount of the polymer is not specifically limited as far as it satisfies limitation of the viscosity and curing time of the composition, but is preferably 50% by weight or less in most cases.

[0040] It is preferable to contain a radically-polymerizable monomer and a non-reactive polymer as a principal component because the viscosity of the resin can be properly controlled.

[0041] It is more preferable to contain a radically polymerizable monomer, a radically polymerizable oligomer having a number-average molecular weight of 10000 or less and a non-reactive polymer as a principal component because the reactivity and viscosity of the resin can be properly controlled.

[0042] The radically polymerizable resin in the present invention can be incorporated with agents capable of imparting thixotropy, agents capable of imparting air-curability, coupling agents, polymerization inhibitors and colorants according to the purposes, in addition to the monomers, oligomers, polymers and curing agent components described above.

[0043] Examples of the agent capable of imparting thixotropy include, but are not limited to, finely powdered silica such as "AEROSIL 200" manufactured by Nippon Aerosil Co., Ltd., "NIPSEAL LP" manufactured by Nippon Silica Industries Co., Ltd.; finely powdered calcium carbonate such as "HAKUENKA CC" manufactured by Shiraishi Calcium Co., Ltd. and "NANOX 25" manufactured by Maruo Calcium Co., Ltd.; and powdered organic matter such as "DISPARLON 305" manufactured by Kusumoto Chemical Company. The amount of thereof is 10% by weight or less, and usually 5% by weight or less.

[0044] Typical examples of the agent capable of imparting the air-curability include higher fatty acids such as paraffin wax represented by n-paraffin, polyethylene wax, and stearic acid. Commercially available compounds having an air drying function, for example, monoepoxy compound such as glycidyl methacrylate or allyl glycidyl ether, acrylic acid derivative of dicyclopentadiene, and "RIPOXY AC-201" manufactured by Showa Highpolymer Chemicals Co., Ltd. can be used alone or in combination. The amount of the agent capable of imparting the air-curability is preferably within a range of 0.1-10% by weight based on the resin for impregnation. When the amount is less than 0.1% by weight, sufficient air-curability can not be obtained. On the other hand, when the amount exceeds 10% by weight, the physical properties of the cured article are liable to be lowered. When using higher fatty acid such as paraffin wax, the amount is particularly preferably within a range of 0.1-5% by weight based on the resin for impregnation.

[0045] The resin used in the present invention can be optionally mixed with coupling agents, for example, silane coupling agent such as γ -methacryloxypropyltrimethoxysilane, titanate coupling agent, zirconate coupling agent, and organoaluminum coupling agent alone or in combination. The amount is preferably within a range of 0.5-5 parts by weight based on 100 parts by weight of the resin for impregnation.

[0046] The resin used in the present invention is preferably incorporated with a sufficient amount of polymerization inhibitors to secure the stability during the circulation. If necessary, colorants, pigments and defoamers can be added.

[0047] In the present invention, the amount of the additional impregnating resin, with which the reinforcement fiber

material is impregnated, maybe an enough amount to form a composite wherein the reinforcement fiber sheet and additional impregnating resin are integrated with each other after impregnation, but is not specifically limited.

(Execution procedure of repair and reinforcement)

[0048] The execution procedure for repair and reinforcement of the existing concrete structure in the present invention will be described.

[0049] In the present invention, the repair and reinforcement of the existing concrete structure can be carried out by applying the reinforcement fiber sheet material described above to the surface of an existing concrete structure while impregnating the reinforcement fiber sheet material with a resin, or applying the reinforcement fiber sheet material to the surface of the existing concrete structure and impregnating with the resin, and curing the resin. In this case, the place where the reinforcement fiber sheet material is applied may be previously coated with an impregnating resin before applying the reinforcement fiber sheet material.

[0050] It is preferable to previously repair the surface of the existing concrete structure, on which the reinforcement fiber sheet material is applied, by smoothly grinding unevenness, difference in level, defect portions, and cracks using a grinder, or filled them with putty or pour in view of the improvement in application strength.

[0051] It is preferable that the surface of the existing concrete structure, on which the reinforcement fiber sheet material is applied, is optionally coated with an adequate amount of a primer resin using a known means such as a roller brush or spray after removal of the unevenness, and then the resin is cured. The primer resin is preferably the same resin as the impregnating resin used to apply the reinforcement fiber sheet material is applied subsequently. The primer resin having lower viscosity is more preferable in view of the adhesion with concrete and workability, and the primer resin is preferably a composition which is cured more rapidly, that is, a composition which is cured in about one hour. Such a primer resin mixed with a curing agent and a curing accelerator immediately before use.

[0052] Examples of the acrylic primer resin which can be used in the present invention include, but are not limited to, "ACRYSYRUP DR-80" manufactured by Mitsubishi Rayon Co., Ltd.

[0053] In the method of the present invention, the impregnating resin is mixed with the curing agent and curing accelerator immediately before use so as to obtain a predetermined curing time.

[0054] More preferable repairing and reinforcing method of the present invention includes, for example, a method of coating the surface of an existing concrete structure, on which a primer resin is coated, with the above additional impregnating resin, applying a reinforcement fiber sheet material thereon, further coating with the additional impregnating resin, impregnating the reinforcement fiber sheet material with the additional impregnating resin while pushing out an air contained in the sheet using a deaeration roller, and allowing to stand, thereby curing the reinforcement fiber sheet material.

[0055] According to the purposes, a repairing and reinforcing layer can also be formed by laminating plural reinforcement fiber sheet materials while changing the fiber direction.

[0056] Finally, the reinforcement fiber sheet material can be optionally coated with paint or mortar, as a matter of course.

EXAMPLES

[0057] The present invention will be described in detail by way of examples.

(Example 1)

(Synthesis of oligomer 1)

[0058] In a vessel equipped with a stirrer, a temperature controller and a condenser, 148 parts by weight of phthalic anhydride, 1227 parts by weight of methyl methacrylate, 230 parts by weight of pentaerythritol triallyl ether ("P-30M", manufactured by Daiso Co., Ltd.), 3.8 parts by weight of dimethylaminoethyl methacrylate and 0.38 parts by weight of hydroquinone monomethyl ether were charged, and then the mixture was reacted at the reaction temperature of 85°C for three hours to obtain a resin solution containing an allyl group-containing carboxylic acid. Furthermore, 1943 parts by weight of a bisphenol A epoxy resin ("EPIKOTE 1004", manufactured by Yuka Shell Epoxy Co., Ltd.), 86 parts by weight of methacrylic acid, 40 parts by weight of dimethylaminoethyl methacrylate, 2 parts by weight of hydroquinone monomethyl ether and 1227 parts by weight of methyl methacrylate were added and the reaction was conducted until the acid value became 8 (mgKOH/g) or less by heating the reaction temperature to 90°C to obtain an oligomer 1 containing 50% by weight of methyl methacrylate. The number-average molecular weight of the composition obtained after removing the monomer component from the resulting oligomer 1 was 2000.

(Preparation of impregnating resin)

[0059] To 100 parts by weight of a mixture (viscosity is 10 poise at 25°C) of methyl methacrylate (SP value: 18) and an oligomer in a weight ratio of 1:1, 1 part by weight of n-paraffin as the component capable of imparting air-cura-
 5 bility, 1 part by weight of γ -methacryloxypropyltrimethoxysilane as the silane coupling agent, 1 part by weight of cumene hydroperoxide as the initiator and 1 part by weight of cobalt naphtenate as the curing accelerator were added.

(Production of reinforcement fiber sheet material)

[0060] Carbon fibers ("TR50", manufactured by Mitsubishi Rayon Co., Ltd.) (Tensile strength: 4900 Mpa) coated with a sizing agent, an epoxy ester ("3002M", manufactured by Kyoei Fats and Oils Chemical Industries Co., Ltd.) containing a bisphenol A derivative having a methacrylic group at terminal as a principal component were unidirectionally arranged so that the weight of carbon fibers per 1 m² became 300 g, and then impregnated with an epoxy resin composition ("base resin for #350", manufactured by Mitsubishi Rayon Co., Ltd., SP value: 23) containing no curing agent
 15 in an amount of 15 g per 1 m². Then, SCRIM CLOTH (manufactured by Nittobo) having a thickness of 25 μ m as the substrate was laminated thereon to obtain a reinforcement fiber sheet 1.

(Impregnation with resin / Curing)

[0061] The reinforcement fiber sheet 1 was impregnated with the above impregnating resin in the resin amount of about 400 g per 1 m², and then allowed to stand in an atmosphere at 25°C, thereby curing the resin. After two hours, tack of the surface disappeared and the resin was cured.

[0062] Test samples for tensile test were made from the cured reinforcement fiber sheet material and the tensile strength in the direction of carbon fibers was measured. The average tensile strength of the composite was 4100 MPa calculated based on 100% carbon fibers.
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[0063] The surface of a concrete sample based on JIS (Japanese Industrial Standards)-A-1132 was coated with an acrylic primer resin ("ACRYSYRUP DR-80", manufactured by Mitsubishi Rayon Co., Ltd.) at 25°C using a brush in the amount of 200 g per 1 m², and then the reinforcement fiber sheet material 1 was applied to the surface of the concrete sample in the same manner as described above. After aging for one day, the bonding test to the concrete was carried
 30 out in accordance with JIS-A-6909. As a result, the strength was 2.4 MPa and the fracture mode corresponded to material fracture in concrete.

(Example 2)

[0064] In the same manner as in Example 1, except that the above oligomer 1 and an epoxy oligomer ("EPOXY ESTER 3000M", manufactured by KyoeiSha Kagaku Co., Ltd., hereinafter referred to as an oligomer 2) were used in combination as the oligomer and each proportion of the respective components was changed as shown in Table 1, the operation was conducted. The evaluation results are shown in Table 1.

(Example 3)

[0065] In the same manner as in Example 2, except that the amount of the curing accelerator was reduced to half, the operation was conducted. The evaluation results are shown in Table 1.

(Example 4)

(Synthesis of oligomer 3)

[0066] In a vessel equipped with a stirrer, a temperature controller and a condenser, 583 parts by weight of a bisphenol A epoxy resin "EPIKOTE 1004", manufactured by Yuka Shell Epoxy Co., Ltd.), 43 parts by weight of acrylic acid, 6.2 parts by weight of dimethylaminoethyl methacrylate, 0.62 parts by weight of hydroquinone monomethyl ether and 633 parts by weight of methyl methacrylate were charged, and then the mixture was reacted at the reaction temperature of 90°C until the acid value became 5 (mgKOH/g) or less to obtain an oligomer 3 containing 50% by weight of methyl methacrylate. The number-average molecular weight of the composition obtained after removing the monomer component from the resulting oligomer 3 was 2300.
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(Preparation of impregnating resin)

5 **[0067]** In the same manner as in Example 1, except that an oligomer 3 was used as the oligomer component in place of the oligomer 1 and each proportion of the respective components was changed as shown in Table 1, the operation was conducted. The evaluation results are shown in Table 1.

(Example 5)

10 **[0068]** In the same manner as in Example 1, except that an acrylic resin ("DIANAL BR-83", manufactured by Mitsubishi Rayon Co., Ltd.) was used in place of the oligomer 1 and each amount of the respective components was changed as shown in Table 1, the operation was conducted. The evaluation results are shown in Table 1.

(Example 6)

15 **[0069]** In the same manner as in Example 5, except that the amount of the curing accelerator was reduced to half, the operation was conducted. The evaluation results are shown in Table 1.

(Comparative Example 1)

20 **[0070]** The monomer component and oligomer component were mixed in the proportion shown in Table 1 to prepare a resin composition whose viscosity is 2 poise at 25°C and the same operation was conducted in the same manner as in Example 1. The evaluation results are shown in Table 1. The curability of the impregnating resin was excellent and the adhesion with concrete was good, but the tensile strength of the composite was poor such as 3720 MPa.

25 (Examples 7 and 8)

[0071] Using the same impregnating resin as in Comparative Example 1, a test was conducted by changing the temperature, at which a sample is made, to 5 and -10°C, respectively.

30 **[0072]** In this case, the amount of the curing accelerator was changed as shown in Table 1 so that the curing time became five hours. The viscosity of this composition was 15 poise at 5°C, and 45 poise at -10°C.

[0073] The results are shown in Table 1. With the decrease of the temperature at which a test piece is made, the viscosity of the resin increased, thus attaining sufficient tensile strength.

(Comparative Example 2)

35 **[0074]** The curing agent of the resin composition used in Comparative Example 1 was changed and the resin composition was prepared so that the curing time became 30 minutes. The evaluation results are shown in Table 1. The tensile strength of the composite further decreased.

40 (Comparative Example 3)

[0075] We made a trial of mixing the monomer component and polymer component in the proportion shown in Table 1 to prepare a resin composition having a viscosity of 400 poise at 25°C and carrying out the same test. However, it was difficult to carry out an operation of impregnating a reinforcement fiber sheet with a resin so that the subsequent evaluation could not be carried out.

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Table 1

		Examples										Comp. Examples		
		1	2	3	4	5	6	7	8			1	2	3
Composition	Monomer	MMA	50	42.5	42.5	15	15					50	50	50
		2EHA				15								50
		PEGA						15	15			15	15	
	SP value	18	18	18	17	18	18	19.2	19.2	19.2	19.2	19.2	19.2	18
	Oligomer or copolymer	O1	50	42.5	42.5			35	35	35	35	35	35	
		O2		15	15									
		O3												
		PI				70								
	Curing agent	CHPO	1	1	1	1	1	1	1	1	1	1	1	1
	Accelerating agent	BPO											2	
Resin properties	Others	NC	1	1	0.5	1	1	0.5	1	2	0.5			1
		DMPT											1	
		n-P	1	1	1	1	1	1	1	1	1	1	1	1
		γMX	1	1	1	1	1	1	1	1	1	1	1	1
		25°C	10	30	30	70	100	100	100		2			400
	Viscosity (poise)							15					15	
		5°C												
		-10°C							45					
	Curing time (hour)	25°C	2	2	5	3	3	6			5			2
		5°C						5					0.5	
Evaluation results	Tensile strength (MPa)													
	Surface tack	4100	4170	4310	4250	4150	4210	4280	4250	3720	3410			
	Adhesion with concrete	2.4	2.4	2.5	2.4	2.4	2.5	2.4	2.3	2.5	2.4			
		Fracture in interior of concrete										Not evaluated		

[0076] Abbreviations in Table 1 denote the following substances, respectively.

MMA: methyl methacrylate

2-EHA: 2-ethylhexyl acrylate

PEGA: phenoxyethylene glycol acrylate

CHPO: cumene hydroperoxide

BPO: benzoyl peroxide

NC: cobalt naphthenate

DMPT: N,N-dimethyl-p-toluidine

n-P: n-paraffin

γ MX: γ -methacryloxypropyltrimethoxysilane

O1: oligomer 1

O2: oligomer 2, epoxy oligomer ("EPOXY ESTER 3000M", manufactured by KyoeiSha Kagaku Co., Ltd.)

O3: oligomer 3

P1: acrylic resin ("DIANAL BR-83", manufactured by Mitsubishi Rayon Co., Ltd.)

15 (Comparative Example 4)

[0077] 60 Parts by weight of a bisphenol A epoxy resin "EPIKOTE 828", manufactured by Yuka Shell Epoxy Co., Ltd.), 40 parts by weight of trimethylolpropane triglycidyl ether ("ADEKA GLYCEROL ED-505", manufactured by Asahi Denka Kogyo K.K.) and 45 parts by weight of an aliphatic polyamide curing agent ("ANCAMINE 2021", manufactured by ACI Japan Co.) were mixed to prepare a cold curable epoxy resin composition. The viscosity of this composition was 50 poise at 25°C.

[0078] The reinforcement fiber sheet used in Example 1 was impregnated with this epoxy resin composition to make a test piece of the composite. The tackiness of the resin disappeared after allowing to stand for 12 hours, but seven days were required to attain sufficient strength and elasticity. The tensile strength evaluated after seven days was 4200 MPa.

[0079] We made a trial of carrying out the same test at 5°C, but gave up because the resin could not be cured.

(Example 9)

[0080] In the same manner as in Example 1, except that 100 parts by weight of a vinyl ester resin (RIPOXY R-840" manufactured by Showa Highpolymer Chemicals Co., Ltd., viscosity at 25°C: 25 poise, SP value: 19) as the impregnating resin, 1 part by weight of a curing catalyst ("CH", manufactured by Showa Highpolymer Chemicals Co., Ltd.) and 0.3 parts by weight of cobalt naphthenate as the curing accelerator, the operation was conducted. The curing time was three hours at 25°C. The surface tack disappeared at all after six hours have passed since the impregnation of the reinforcement fiber sheet material with the resin, and the tensile strength of the composite was 4020 MPa.

(Example 10)

[0081] In the same manner as in Example 9, except that 2 parts by weight of methylethyl peroxide as the curing agent and 1 part by weight of cobalt naphthenate as the curing accelerator were used relative to 100 parts by weight of the resin, the operation was conducted. The curing time was one hour at 25°C, and the tensile strength of the composite obtained after six hours was 3000 MPa.

(Example 11)

[0082] In the same manner as in Example 7, except that a n-butyl acrylate oligomer having a number-average molecular weight of 6000, which has a methacryl group at one terminal, was used in place of phenoxyethylene glycol acrylate, the test was conducted. The viscosity of this resin was 5 poise at 5°C.

[0083] After six hours, the tackiness of the surface of the sample thus obtained disappeared and the low-temperature curability was also good. The tensile strength of the composite was 4100 MPa and the fracture mode in the adhesion test corresponded to material fracture of concrete.

(Example 12)

[0084] In the same manner as in Example 1, except that "CONWOOD NET ON5050" (weight of 7 g/m²) manufactured by Nisseki Pallet System Co., Ltd. was used in place of "SCRIM CLOTH" manufactured by Nittobo, a reinforcement fiber sheet 2 was made. In the same manner as in Example 3, a combination of this reinforcement fiber sheet material and the resin used in Example 3 was operated. The resulting composite attained sufficient tensile strength

such as 4300 MPa.

(Example 13)

- 5 **[0085]** In the same manner as in Example 1, except that high-elasticity carbon fibers having an elastic modulus of 392 Gpa ("HR40" manufactured by Mitsubishi Rayon Co., Ltd., tensile strength: 4610 MPa) were used as the carbon fibers and the resin composition used in Example 3 was used as the resin composition, a resin composition was obtained and the tensile strength of the composite was evaluated. The resulting composite attained sufficient strength such as 4050 MPa.

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(Example 14)

- 15 **[0086]** In the same manner as in Example 1, except that "FOLKA SHEET FTS-C1-30" (SP value of used resin: 23) manufactured by Tonen Co., Ltd. in the form where reinforcement fibers are unidirectionally arranged on a substrate sheet through an adhesive layer was used as the reinforcement fiber sheet and the resin used in Example 3 was used as the impregnating resin, a resin composition was obtained and the tensile strength of the composite was evaluated. The resulting composite attained sufficient strength such as 4300 MPa.

INDUSTRIAL APPLICABILITY

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[0087] According to the present invention, existing concrete structures such as bridge footings and buildings can be repaired and reinforced easily in a short time without being influenced by temperature conditions on execution, while providing concrete structures with high strength. In particular, existing reinforcement fiber sheet materials can be effectively used.

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Claims

1. A method of repairing and reinforcing an existing concrete structure, which comprises applying a reinforcement fiber sheet material having a resin content of 15% by weight or less to the surface of the existing concrete structure while being impregnated with a resin having a viscosity within a range of 2.5-300 poise and a curing time within a range of 1-24 hours, and curing the resin.
2. A method of repairing and reinforcing an existing concrete structure, which comprises applying a reinforcement fiber sheet material having a resin content of 15% by weight or less to the surface of the existing concrete structure, impregnating the reinforcement fiber sheet with a resin having a viscosity within a range of 2.5-300 poise and a curing time within a range of 1-24 hours, and curing the resin.
3. The method of repairing and reinforcing an existing concrete structure according to claim 1 or 2, wherein a weight of reinforcement fibers of the reinforcement fiber sheet material is 150 g/m² or more.
4. The method of repairing and reinforcing an existing concrete structure according to claim 1 or 2, wherein the reinforcement fiber sheet material is a reinforcement fiber sheet material prepared by impregnating arranged reinforcement fibers or a reinforcement fiber woven fabric with a resin.
5. The method of repairing and reinforcing an existing concrete structure according to claim 1 or 2, wherein the reinforcement fiber sheet material is a reinforcement fiber sheet material prepared by impregnating arranged reinforcement fibers or a reinforcement fiber woven fabric with a resin and laminating a glass fiber fabric on at least one surface.
6. The method of repairing and reinforcing an existing concrete structure according to claim 1 or 2, wherein the reinforcement fiber sheet material is a reinforcement fiber sheet material prepared by unidirectionally arranging reinforcement fibers on a substrate sheet through an adhesive layer.
7. The method of repairing and reinforcing an existing concrete structure according to claim 1 or 2, wherein the resin content of the reinforcement fiber sheet material is 7% by weight or less.
8. The method of repairing and reinforcing an existing concrete structure according to claim 1 or 2, wherein the reinforcement fibers constituting the reinforcement fiber sheet material are high-strength carbon fibers having a tensile

strength of 4000 MPa or more.

- 5 9. The method of repairing and reinforcing an existing concrete structure according to claim 1 or 2, wherein the reinforcement fibers constituting the reinforcement fiber sheet material are high-elasticity carbon fibers having an elasticity modulus of 250 GPa or more.
- 10 10. The method of repairing and reinforcing an existing concrete structure according to claim 1 or 2, wherein the carbon fibers constituting the reinforcement fiber sheet material are carbon fibers coated with a compound having a radically polymerizable functional group at at least one terminal group.
- 11 11. The method of repairing and reinforcing an existing concrete structure according to claim 1 or 2, wherein a solubility parameter (SP) value of the resin constituting the reinforcement fiber sheet material is within a range of 17-28 (MPa)^{1/2}.
- 15 12. A radically polymerizable resin having a viscosity within a range of 10-100 poise and a curing time within a range of 2-12 hours.
- 20 13. A radically polymerizable resin comprising a component having a methacryloyl group or an acryloyl group at terminal, which has a viscosity within a range of 10-100 poise and a curing time within a range of 1-8 hours.
- 25 14. The resin according to claim 12 or 13, comprising a radically polymerizable monomer and a radically polymerizable oligomer having a number-average molecular weight of 10000 or less as a principal component.
- 30 15. The resin according to claim 12 or 13, comprising a radically polymerizable monomer and a non-reactive polymer as a principal component.
- 35 16. The resin according to claim 12 or 13, comprising a radically polymerizable monomer, a radically polymerizable oligomer having a number-average molecular weight of 1000 or less and a non-reactive polymer as a principal component.
- 40 17. The resin according to claim 12 or 13, wherein a solubility parameter (SP) value of the radically polymerizable monomer component is within a range of 17-22 (MPa)^{1/2}.
- 45 18. The resin according to claim 12 or 13, which contains 0.1-5% by weight of a component capable of imparting air curability.
- 50 19. The method of repairing and reinforcing an existing concrete structure according to claim 1, wherein an additional impregnating resin, with which the reinforcement fiber sheet material is impregnated while being applied to the surface of the concrete structure, is a resin of claim 12 or 13.
- 55 20. The method of repairing and reinforcing an existing concrete structure according to claim 2, wherein an additional impregnating resin, with which the reinforcement fiber sheet material applied to the surface of the concrete structure is impregnated, is a resin of claim 12 or 13.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/02756

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁶ E04G23/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁶ E04G23/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1999 Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 10-88820, A (Mitsubishi Chemical Corp., Dainippon Shikizai Kogyo K.K.), 7 April, 1998 (07. 04. 98) Full text	1-4, 7, 12, 13, 19, 20
Y	Full text (Family: none)	5, 6, 8-11, 14-18
Y	JP, 10-7750, A (Nippon NSC K.K.), 13 January, 1998 (13. 01. 98), Full text ; Fig. 1	1-11, 19, 20
X	Full text (Family: none)	12-18
Y	JP, 9-221919, A (Mitsubishi Rayon Co., Ltd.), 26 August, 1997 (26. 08. 97), Full text	1-11, 19, 20
X	Full text (Family: none)	12-18
Y	JP, 9-184305, A (Mitsubishi Rayon Co., Ltd.), 15 July, 1997 (15. 07. 97), Full text	1-11, 19, 20
X	Full text (Family: none)	12-18
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search 23 August, 1999 (23. 08. 99)		Date of mailing of the international search report 7 September, 1999 (07. 09. 99)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 5-32804, A (Tonen Corp.), 9 February, 1993 (09. 02. 93), Full text ; Figs. 1 to 8 (Family: none)	1-11, 19, 20
Y	JP, 7-34677, A (Mitsubishi Chemical Corp.), 3 February, 1995 (03. 02. 95), Full text (Family: none)	1-11, 19, 20
Y	JP, 8-158665, A (Sho-Bond Corp., Toray Industries, Inc.), 18 June, 1996 (18. 06. 96), Full text & GB, 2295637, A1 & AU, 2494995, A1	12-18

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