CLAIMS

1. The epoxy resin composition , comprising at least the following components [A], [B] and [C]: [A]: An epoxy resin from bisphenol-A and epichlorphydrin ; [B]: fine particles containing mineral fillers and inorganic pigments and insoluble in the epoxy resin; [C]: A curing agent.
2. The epoxy resin composition as claimed in claim 1, wherein the composition can be cured at high humidity, low temperatures and underwater conditions.
3. The epoxy resin composition as claimed in claim 1, wherein the shelf life of the composition can be 20 to 30 mins
4. The epoxy resin composition as claimed in claim 1, wherein the gel time of the composition is around 30 mins.
5. The epoxy resin composition as claimed in claim 1, wherein the composition can be hardened in 3 to 4 hours in the temperature range of 25 to 35 °C.
6. The epoxy resin composition as claimed in claim 1, wherein said epoxy resin from bisphenol-A and epichlorphydrin has an epoxy equivalent of 184-190 g/eq..
7. The epoxy resin composition as claimed in claim 1, wherein said curing agent is a modified cycloaliphatic amine with amine value of 280-320.
8. The epoxy resin composition as claimed in claim 1, wherein the viscosity of said epoxy resin composition of (A)+(B)+(C) is 100 to 5,000 poises at 30 degree C.
9. The epoxy resin composition as claimed in claim 1, wherein the composition ratio by weight of the said epoxy resin [A], fine particles [B] and curing agent [C] is such that:
   [A]/[C] = from 100/30 to 100/80 and
   [A]/[B] = from 100/50 to 100/100.
10. A FRP system, comprising prime coat, undercoat, a sheet of reinforcing fibers and a topcoat.
11. A FRP system, comprising the few layers (2 t0 10 layers) of the system as claimed in claim 10.
12. A prime coat, comprising epoxy resin composition as claimed in claim 1.
13. A undercoat, comprising epoxy resin composition as claimed in claim 1.
14. A topcoat, comprising epoxy resin composition as claimed in claim 1.

15. An epoxy resin composition according to claim 1, wherein the tensile strength will be 62 MPa or more when it is tested according to BS 2782.
16. An epoxy resin composition according to claim 1, wherein the tensile modulus will be 3800MPa or more when it is tested according to BS 2782.
17. An epoxy resin composition according to claim 1, wherein the compressive strength will be 75 MPa or more when it is tested according to ASTM D695.
18. An epoxy resin composition according to claim 1, wherein the compressive modulus will be 1900 MPa or more when it is tested according to ASTM D695.
19. An epoxy resin composition according to claim 1, wherein the adhesion pull-off strength to concrete substrate will be 2.4 MPa or more when it is tested according to ASTM D4541.
20. An FRP system according to claim 10 using carbon fiber sheet, wherein the tensile strength of the carbon fiber in the system will be 2000MPa or more when it is tested according to ASTM D3039M.
21. An FRP system according to claim 10 using carbon fiber sheet, wherein the tensile modulus of the carbon fiber in the system will be 200 GPa or more when it is tested according to ASTM D3039M.
22. An FRP system according to claim 10 using carbon fiber sheet, wherein the overlapping length for the join will be from 100mm to 150mm.

DESCRIPTION

TECHNICAL FIELD

The present invention relates to an epoxy resin composition for fiber reinforced plastics (abbreviated to FRP in this specification), a FRP system that can be cured at high humidity, low temperatures and underwater conditions with good mechanical strength, good chemical resistance and excellent heat resistance and a method for wrapping of concrete elements using the FRP system for strengthening and repair of marine concrete structure.

BACKGROUND ART

Fiber Reinforced Plastic (FRP) products were first used to reinforce concrete structures in the mid 1950s. Today, these FRP products take the form of bars, cables, 2-D and 3-D grids, sheet materials, plates, etc. FRP products may achieve the same or better reinforcement objective of commonly used metallic products such as steel reinforcing bars, prestressing tendons, and bonded plates. Concrete members can benefit from the following features of FRP reinforcement: light weight, high specific strength and modulus, durability, corrosion resistance, chemical and environmental resistance, electromagnetic permeability, and impact resistance.

The class of FRP composite materials is defined as a polymer matrix, whether thermosetting (e.g. polyester, vinyl ester, epoxy, phenolic) or thermoplastic (e.g., nylon, PET) which is reinforced by fibers (e.g., aramid, carbon, glass). The performance of any composite depends on the materials of which the composite is made, the arrangement of the primary load-bearing portion of the composite (reinforcing fibers), and the interaction between the materials (fibers and matrix). The major factors affecting the physical performance of the FRP matrix composite are fiber mechanical properties, fiber orientation, length, shape and composition of the fibers, the mechanical properties of the resin matrix, and the adhesion of the bond between the fibers and the matrix.

The roles of the polymer matrix are to transfer stresses between the reinforcing fibers and the surrounding structure and to protect the fibers from environmental and mechanical damage. This is analogous to the important role of concrete in a reinforced-concrete structure. For this to occur, an excellent degree of adhesion to the surfaces involved must be achieved and sustained. The principal requirements for the polymer matrix are that:

- It should exhibit adequate adhesion to the materials involved (e.g: concrete and FRP).
- It should exhibit good moisture resistance and resistance to creep.
- It should possess gap-filling properties, be thixotropic, and be suitable for application to vertical and overhead surfaces.
- It should not be sensitive to the alkaline nature of concrete and its potential effect on the durability of joints.
- It should not be unduly sensitive to variations in the quality or moisture content of prepared surfaces.
- The working characteristics of the material should enable an adequate joint quality to be achieved with respect to mixing, application and curing.

Since epoxy resins after curing are excellent in mechanical properties, electrical properties, and adhesive properties, they are widely used in the fields, for example, of sealants for electronic materials, paints, coating materials, and adhesives. Further, epoxy resins are important as matrix resins for FRP. Particularly, when carbon fibers are used as reinforcing fibers for FRP, epoxy resins are preferably used since they are excellent in adhesion to carbon fibers. FRP composites made up of carbon fibers and epoxy resin are used in wide range of applications ranging from general-purpose use in fishing rods, golf club shafts, etc. to the use in airplanes and also in a variety of civil engineering applications with both reinforced and prestressed concrete. But most of the applications is in dry conditions. There are no systems specially developed for the humid conditions or underwater application.

SUMMARY OF THE INVENTION

The present invention provides an epoxy resin composition suitable as a matrix for fiber reinforcement of concrete structure under marine condition. Under this condition the epoxy resin can be applied in 30 mins and hardened in 3 to 4 hours.

By using the epoxy resin composition for FRP of the present invention, a FRP system which can be cured at high humidity, low temperatures and underwater conditions can be obtained for strengthening and repair of marine concrete structure.

The invention also provides a FRP system with good mechanical strength, good chemical resistance and excellent heat resistance.

DISCLOSURE OF THE INVENTION

To carry out repair work on marine structures, one main problem would be time. As the rapid changes in water level in the tidal zones are at their maximum at every 6 hours, the entire repair process would have to be kept within this time frame. This includes the preparation of epoxy and application of primer coat, topcoat, fiber sheet and finishing coat on the structures. Hence, we need to formulate the special epoxy resin composition which would fit the criteria.

The first subject matter of the present invention resides in an epoxy resin composition for FRP, characterized in that it comprises (A) an epoxy resin from bisphenol-A and epichlorphydrin, (B) fine particles containing mineral fillers and inorganic pigments, and (C) a curing agent. The gel-time measured by the below-described method is 30 mins and the surface touch-free time is about 110 to 130 mins.

Method for measuring gel-time

Knowing the time taken for an epoxy to gel after mixing is important. Too short a time will make the repair task a difficult one. Too long a time would also be a problem as it would delay the touch-dry time and hardening time.
Immediately after stirring thoroughly with a wooden stick, determine the time at which a soft, gelatinous mass forms in the centre of the mixture by probing with a glass stick every 2 minutes, starting 8 minutes after mixing.

The second subject matter resides in a system comprising a sheet of reinforcing fibers impregnated with the above epoxy resin composition for FRP.

Further the third subject matter resides in an epoxy resin composition for FRP, characterized in that when the epoxy composition is tested according to BS 2782: Methods of Testing for Plastics Part 3, Mechanical Properties, Methods 320A to 320F: Tensile Strength, Elongation and Elastic Modulus, the tensile strength is 62 MPa or more, the E modulus is 3800MPa or more and elongation is about 2%.

Best Mode for Carrying Out the Invention

As the component (A) of the epoxy resin composition for FRP of the present invention, those which are generally on the market can be used. The epoxy equivalent, the molecular weight, and the state at normal temperatures of the component (A) are not particularly restricted. Herein, “epoxy equivalent” in the present invention means the number of grams of the resin containing epoxy groups in an amount of 1 gram equivalent.

As typical ones from bisphenol-A and epichlorphydrin having an epoxy equivalent weight of 184-190 g/eq is a liquid at normal temperatures, NPEL-128 manufactured by Nan Yan Plastics Corporation, Taiwan and GELR-128 manufactured by Guangzhou Epoxy Base Electronic Corporation, China can be mentioned by way of example.

As the component (B) of the epoxy resin composition for FRP of the present invention, fine particles containing mineral fillers and inorganic pigments are used. Any mineral

fillers and inorganic pigments for normal coating and paint which are insoluble in epoxy resin can be used. As typical fillers, calcium carbonate with the particle size smaller than 0.075mm can be mentioned by way of example. As typical pigment, TiO^2, Iron Oxide and etc can be mentioned by way of example.

As the component (C) of the epoxy resin composition of FRP of the present invention, a modified cycloaliphatic amine curing agent that is able to cure with epoxy resin at high humidity, low temperatures and underwater conditions can be used. As typical ones having an Amine Value of 280-320 is a liquid at normal temperatures, Sunmide I965 manufactured by Sanwa Chemical (S) Pte Ltd, Singapore can be mentioned by way of example.

The formulation ratio of the components in the epoxy resin composition for FRP of the present invention is not particularly restricted so long as the composition satisfies the above conditions. If the component (D) is not contained, the formulation ratio [(A)/(C)] of the component (A) and the component (C) is preferably in the range of from 100/45 to 100/55 by weight.

A sheet of reinforcing fibers is impregnated with the epoxy resin composition for FRP of the present invention to make them integrated, thereby forming a plate after hardening.

The reinforcing fibers used in the present invention are not particularly restricted and use is made of carbon fibers, glass fibers, aramid fibers, boron fibers, steel fibers, etc. singly or in combination. Among others, carbon fibers are particularly preferably used since the mechanical properties after hardening are good.

As the carbon fibers, any of PAN precursor carbon fibers and pitch precursor carbon fibers can be used. Further, as the carbon fibers, various carbon fibers different in strength and elastic modulus can be selected and used according to the purpose.

In the present invention, the sheetlike product wherein reinforcing fibers are arranged in one direction, the fabric wherein reinforcing fibers are woven, the nonwoven fabric made up of reinforcing fibers, the tow of reinforcing fibers, and the like are simply referred to as a sheet of reinforcing fibers.

The method for impregnating reinforcing fibers with the epoxy resin composition for FRP of the present invention is not particularly restricted. For wrapping of concrete elements under marine condition, the following procedures may be followed.

1. Grind the sharp corners down to a radius in excess of 10mm.

2. Remove the deteriorated surface of the concrete (weathering, laitance, oil, paint, coatings, chipped mortar and other surface contaminants) using a hand grinder until a hard surface is obtained.

3. Apply the primer uniformly over the prepared surface using a brush.

4. After the primer is dried, mix the resin and hardener for a period of approximately 2-3 minutes. Immediately after mixing, apply the undercoat of resin to the prepared surface.

5. The carbon sheet should be cut into the appropriate lengths, according to the installation plan, using scissors or a cutter in advance of the installation. Immediately after applying resin to the work area, the pre-cut carbon sheet should be applied to the same area.

6. In order to gain the proper impregnation of the carbon sheet, the sheet should be rolled using an impregnation roller in a direction parallel to the fibers in the carbon sheet.

7. After the impregnation of the undercoat of resin, the topcoat of resin should be applied in the same manner to the carbon sheet.

8. In the case of two or more plys applications the application of the second ply should not be initiated until the first ply has reasonably hardened (usually next day). Then follow the same procedure as the above steps, undercoat, carbon sheet, impregnation, topcoat.

EXAMPLES

Herein below, the present invention is described more specifically with reference to Examples.

Abbreviations for compounds, and the test methods in the Examples are as follows.

Component (A)

NPEL-128: a liquid resin, which is manufactured from bisphenol-A and epichlorohydrin by Nan Ya Plastics Corporation.

Component (C)

I-965: a modified cycloaliphatic amine curing agent, Sunmide I-965, manufactured by Sanwa Chemical (S) Pte Ltd.

Uniweb F657: a sheet of unidirectionally oriented continuous carbon filaments held in position by a lightweight, open mesh, glass scrim, Uniweb F657 (carbon fiber weight: 300 g/m^2), manufactured by Fortafil Fibers, INC.

Measurement of Set-To-Touch Time

In accordance with ASTM D1640-95, to determine set-to-touch time, lightly touch the test film with the tip of a clean finger and immediately place the fingertip against a piece

of clean, clear glass. Observe if any of the coating is transferred to the glass. The film is wet-to-touch when it still shows a tacky condition, but none of it adheres to the finger.

Measurement of Dry-Hard time

In accordance with ASTM D1640-95, with the end of the thumb resting on the test film and the forefinger supporting the test panel, exert a maximum downward pressure (without twisting) of the thumb on the film. Lightly polish the contacted area with a soft cloth. The film is considered dry-hard when any mark left by the thumb is completely removed by the polishing operation.

Measurement of Tensile Strength, Elongation and Elastic Modulus of Epoxy Resin

BS 2728: Part 3, Method E was followed for determination of the strength properties of hardened epoxy resin. The dimension of test specimens was 220 mm X 150 mm. No end pieces were used for the testing.

Measurement of Compressive Strength and Elastic Modulus of Epoxy Resin

ASTM D695 -02a was followed for determination of the compressive strength and elastic modulus of epoxy resin. The test specimens were in the form a right prism with the size of 12.7 by 12.7 by 50.8 mm.

Measurement of Adhesive Strength of Epoxy Resin to Concrete

ASTM D4541-02 was followed for determination of the pull-off adhesive strength of epoxy resin to concrete substrate. The size of the metal plates used is 100 X 100 mm.
Measurement of Tensile Strength, Elongation and Elastic Modulus of FRP Composites

ASTM D3039M-93 was followed for determination of the tensile strength, elongation and elastic modulus of FRP composites. The testing specimens were cut to strips with the size of 15 X 230 mm.

Measurement of Flexural Strength of Concrete Beams Wrapped with FRP Composites

BS 1881: Part 118:1983 described a method for the determination of the flexural strength of test specimens of hardened concrete by means of a constant moment in the central zone using a two-point (or third-point) loading. All test specimens were of the preferred dimensions 150 by 150 by 750 mm.

Example 1 for Epoxy Resin Product

Epoxy resin sample having the formulation (the values indicate parts by weight) shown in Table 1 was coated to a release paper to a thickness of 1.5mm for tensile testing and cast in the prism moulds of 12.7 by 12.7 by 50.8mm for compressive testing after curing in air for 7 days.

Table 1 Example

Component (A): NPEL-128	100
Component (C): I-965	55
Set-to-Touch Time	124 mins
Dry-Hard Time	150 mins
Tensile Strength	62 MPa
E-Modulus	3826MPa
Compressive Strength	75 MPa
E-Modulus	1913 MPa
Adhesion Strength to Concrete	2.45 MPa (concrete failure)

Example 2 for FRP Composite

The first coat of epoxy resin with the formulation (the values indicate parts by weight) shown in Table 1 was coated to a release paper and then a piece of carbon fiber sheet (Uniweb F657) was placed on the epoxy resin composition to allow them to be impregnated with the epoxy resin composition with the rolling action of a metal roller on it. A second layer of epoxy with the same formulation was applied on the top of the Uniweb G657 sheet and followed by the action of rolling once again to ensure proper immersion of the fiber sheet in the epoxy resin composition. After curing in air for 7 days the sheet was cut to strips of dimension of 15 X 230mm along the direction of the length of the sheet for tensile, elongation and E-Modulus testing.

Table 2 Example

Tensile Strength of Composite	513 MPa
Tensile Strength of Carbon Fiber in the Composite	2024 MPa
Elongation of Composite	0.99%
E-Modulus of Composite	48543 MPa

Example 3 Concrete Beam wrapped with FRP Composite

Nine pieces of concrete beams with the dimensions of 150 X150 X750 were prepared with Grade 40 concrete. 3 beams were tested for flexural strength as control and the rest 6 beams were wrapped with FRP composite for strengthening by 1 or 2 ply (3 beams for 1 ply of FRP wrapping and 3 beams for 2 ply of FRP wrapping respectively). The sharp corners of the beams were ground down to a radius in excess of 10 mm and then the loose particles on the beam surface (weathering, laitance, oil, paint, coatings, chipped mortar and other surface contaminants) were removed using a hand grinder until an even surface is obtained. The primer coat with the formulation as shown in Table 1 was uniformly

applied over the prepared surface using a brush. After the primer is dried, the first coat of epoxy resin with the same formulation as for primer coat is applied to the prepared surface. The carbon fibre sheet is then cut into the appropriate size and placed on the first coat of epoxy resin. In order to gain the proper impregnation of the carbon sheet, the sheet should be rolled using am impregnation roller in a direction parallel to the fibers in the carbon fiber sheet. After the impregnation of the undercoat of resin, the topcoat of resin with the same formulation should be applied in the same manner to the carbon sheet. In the case of 2-ply applications, the application of the second ply should not be initiated until the first ply has hardened. Then the same procedure as the above steps should be followed.

Table 3 Example of concrete beams wrapped with FRP composite

Beam	Flexural Strength (MPa)	Comparison (%)
Control	4.6	100
1 ply FRP wrapped	11.6	252
2 ply FRP wrapped	16.0	348