DURABLE INTEGRATION FRESH CONCRETE TO EXISTING CONCRETE USING EPOXY RESIN ADHESIVE

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ABSTRACT**:** In order to prolong service life of deteriorated structures, The authors have developed a rehabilitation method, i.e., durable integration using epoxy resin adhesives such as thin steel fiber reinforced concrete pavement on orthotropic steel decks and thin bonded overlay on existing concrete pavement. The above-mentioned rehabilitation method is new technology characterized by integrating fresh concrete with existing structures using epoxy resin adhesives. The influence of each ingredient, which composes the epoxy resin adhesives used for durable integration on compressive strength, was checked first, and the influence of each ingredient on hydration reactions was investigated by X-ray diffraction. Furthermore, the degree of deterioration by fatigue in water-soaked state, by exposure to both high temperature and low temperature was checked.

KEYWORDS: ingredients of epoxy resin adhesives, fresh concrete, durable integration
(space)

1. INTRODUCTION

In Japan, many infrastructures constructed in the high-growth period of postwar are deteriorating and the time for repair, reinforcement, and updating has come around. However, with an aged society and with fewer children come social structure changes, so that available capacity of investment and reconstruction for infrastructures is declining. Renewal and maintenance technology has to meet new social needs, economical efficiency and being environment-friendly. The authors have developed rehabilitation technology that combines fresh concrete into the existing structure by using epoxy resin adhesives. This new rehabilitation technology is used for improving fatigue durability of welded parts in existing orthotropic steel decks and constructing thin overlay bonded on existing concrete apron pavement in the case of uneven settlement encounters where the surface slope must be corrected.

With regard to fatigue damage of orthotropic steel decks, in the intersection zone of transverse ribs and longitudinal ribs, the welded zone of longitudinal ribs and deck plates and the welded zone of vertical stiffeners etc. many fatigue cracks are detected. Since the fatigue cracks originating in the root of the welded zone may rarely penetrate the steel deck plates thoroughly, road surfaces cave in and there is worry that vehicles may be involved in a traffic accident. In the SFRC pavement on orthotropic steel decks damaged by fatigue cracks, epoxy resin adhesives about 1.0mm thick

($1.4 kg/mm^2$) are applied to the orthotropic steel decks after removing exiting asphalt pavement, then 50mm or 75mm in thickness steel fiber reinforcement concrete (SFRC) pavement is placed. The thickness of SFRC depends on the structure of damaged orthotropic steel decks. The SFRC pavement can suppress local deformation and reduce local stress in the steel deck plates due to the durable integration with exiting orthotropic steel decks. This rehabilitation method was adopted in Shonan-Ohashi Bridge, Ohira Viaduct and Metropolitan Expressway.

Since an airport is generally constructed on an offshore filled area or on a high banking structure fill in Japan, the foundation conditions are so bad that concrete apron pavement tends to settle unevenly in many cases. Most of the concrete apron pavement chiefly consists of plain concrete, therefore, main rehabilitation method has been limited to “reconstruction” that means to place new concrete after removing the existing pavement. However, National Institute for Land and Infrastructure Management in cooperation with three private corporations executed research on bonded concrete overlay method for applying it to rehabilitation of concrete apron pavement and confirmed that the bonded concrete overlay method which used shot blasting as a surface treatment of existing concrete and applying epoxy resin adhesives to the treated surface was effective.

The authors have proposed the above-mentioned rehabilitation method by durable integration fresh concrete using epoxy resin adhesives to meet new social needs that were not during construction time. Authors have also clarified the integration mechanism between epoxy resin adhesives and fresh concrete, factors that influence a degree of integration and various types of strength on integrated specimens in order to expand the scope of the rehabilitation method. In this study authors will report the influence of ingredients in epoxy resin adhesive on cement hydration, a degree of deterioration by fatigue in water-soaked state, by exposure to both high temperature and low temperature which should be solved.

2. INGREDIENTS IN EPOXY RESIN ADHESIVE

An epoxy resin is a general term for the compound which contains two or more epoxide (oxiran) in one molecule, therefore, epoxy resin adhesives are epoxy resins in which denatured hardening agents and sub-materials are added and adjusted. The main features of the hardening agents used for epoxy resin adhesives and an example of typical sub-materials are summarized in Table 1and Table 2, respectively. With regard to the civil engineering field, integration technology using epoxy resin adhesives is used in precast concrete block method, construction joints, steel plates bonding method and CFRP bonding method. Moreover, as hardening agents used in this field, it is almost the case in which poly amine type or combined poly amine type with poly-thiol (mercaptan) type is applied within the author’s research.

Table 1 Classification of hardening agents used for epoxy resin adhesives

Classification	Characteristics
Polyamine type curing agents	Aliphatic polyamine：The reaction is fast and heat generation is remarkable. Durable to water and organic solvent. Good adhesion.
	Polyamide：Long pot life and low cost
	Epoxy adducted polyamine：High viscosity (useful to viscosity control).
	Mannich-modified polyamine：Good to low temperature curing.
	Poly-thiol：Good to low temperature curing. Polymer network structures are looser than those of poly-amine. High water absorption. Low durability to water.
Catalysts	Tertiary amine：Catalyst of Poly-amine and Poly-amide amine.
	Imidazole：Reacts as hardener and as catalyst of anhydride curing agents.

Table 2 Sub-materials for typical epoxy resin

Classification	
Additives to give functions	Fillers, Coupling agents, Thixotropic agents, Electro conductive agents, Diluents etc.
Others	Pigments, Dyestuff

Table 3 Ingredients that compose the adhesives for examination

Ingredients	No.	Materials	Content/Details
Base resins	1	None	Reference (W／C＝40%、c／s＝2.0)
	2	Base Resin A	Low viscosity epoxy resin
	3	Reactive diluents	Epoxy resin. reactive diluents
	4	Base Resin B	Middle viscosity epoxy resin
	5	Rubber modified resin	Rubber modified epoxy resin Toughening additive
	6	Silane coupling agent	Uniting organic material and inorganic material
	7	accelerator	Accelerating the reaction rate
Hardening agents	8	Amine A	Hydrophobic amine(hydrophobicA)
	9	Amine B	Hydrophilic amine(hydrophilic)
	10	Amine C	Hydrophobic amine(hydrophobicB)
	11	Amine D	High-viscosity hardener. Polyamide
	12	Polyamine A	Standard curing agent-MXDA
	13	Polyamine B	Mannich-modified MXDA
	14	Polyamine C	Hardener.(Delayed type)
	15	Polyamine D	Hardener.(Standard type)
	16	Polyamine E	Hardener.(Rapid type)
	17	Petroleum resin	Ratio adjustment agent
	18	Dyestuff	Blue pigments

Tg：The glass metastasis point(degree)

MXDA：Meta-xylenediamine

3. SUMMARY OF EXPERIMENTS

3.1 Influence of ingredients in epoxy resin adhesive on compressive strength of mortar

In execution of thin bonded concrete overlay, epoxy resin adhesive in unhardening state is applied to existing concrete, and then fresh concrete is placed for about an hour. Therefore, ingredients composing epoxy resin adhesive, i.e., base resins and hardening agents may mix with fresh concrete and affect cement hydration. In order to check whether ingredients composing epoxy resin adhesive are appropriate for integration of fresh concrete or not, compressive strength of mortar, which seemed to detect sensitively the influence of ingredients in epoxy resin adhesive on cement hydration, was measured. Since these experiments are basic study, ordinary Portland cement was used as the most general material. Two cylindrical specimens measuring 50mm in diameter and 100mm in height were made from mortar to which each ingredient in epoxy resin adhesive was added by 1% of mass of cement.

The ingredients for the object of examination are shown in Table.3, where two kinds of typical base resin and supplementary material, four kinds of typical amine and five kinds of typical polyamine as a hardening agent, further petroleum resin and dye were tested. In the mix proportion of cement mortar, water content was 226 kg/m^3, water-cement ratio was 0.4 and sand-cement ratio was 2.0. The top surface of specimens was sealed with poly seal immediately after fabrication and was cured at 20 degrees in Centigrade. The compressive strength of the specimens was measured at the age of 7 days according to JIS A 1108. In order to examine the influence of ingredients in epoxy resin adhesive on cement hydration, both unsound hardening mortar (No.13) and mortar from standard specimens including no epoxy resin (No.1) were analyzed by X-ray diffraction or by thermal differential test. In the X-ray diffraction analysis, $Ca(OH)_2$ as cement hydrates and C_3S as cement un-hydrates were targeted.

3.2 Durability

With regard to durability, taking into account the influence of water, a degree of deterioration by fatigue and by exposure to high temperature was checked. Further, a degree of deterioration by exposure to low temperature was also checked. The epoxy resin type adhesive A of which ingredients were optimized based on examination for the foregoing paragraph was used in comparison with epoxy resin type adhesive B which includes poly-thiol and is generally used in the civil engineering field. The performance of epoxy resin type adhesives, the specification and the mix proportion of concrete are shown in Table 4-6, respectively. Mix proportion of exiting concrete and overlay concrete were the same, then

Table 4 Characteristics of epoxy adhesive

Item	Test method	epoxy adhesive	
		A	B
Hardened density (g/cm^3)	JIS K 7112	1.41	1.35
Working time (min.)	-	73	>40
Compressive strength (N/mm^2)	JIS K 7208	79.1	>70
Compressive modulus (N/mm^2)	JIS K7208	3060	>1500
Bending strength (N/mm^2)	JIS K 7203	65.5	>40
Shear strength (N/mm^2)	JIS K 6850	14.9	>13
Bonding strength (N/mm^2)	JHS 412	2.9	—

Type A of epoxy adhesive means the test results.
Type B of epoxy adhesive means the value of standard.

Table 5 Specification of overlay concrete

Maximum Size of aggregate	20 mm
Specified bending strength	5.0 N/mm^2
Required average bending strength	5.85 N/mm^2
Slump	6.5±1.5 cm
Air content	4.5±1.5 %

Table 6 Mix proportion of overlay concrete

W/C	s/a (%)	Content of material (kg/m^3)				
		W	C	S1	S2	G
0.47	44.4	157	334	472	325	1030

high-early-strength portland cement and crushed limestone aggregate were used taking into account execution of rehabilitation.

3.2.1 Fatigue test in water-soaked state

It seemed that the rip off between existing concrete and overlay concrete is caused by combined shear stress and tensile stress due to drying shrinkage of concrete or temperature difference in the section, however, mostly by normal stress acting at end of slab. Tensile fatigue testing apparatus which can take into account the influence of water was newly devised by the authors as shown in Pphoto.1. Tensile

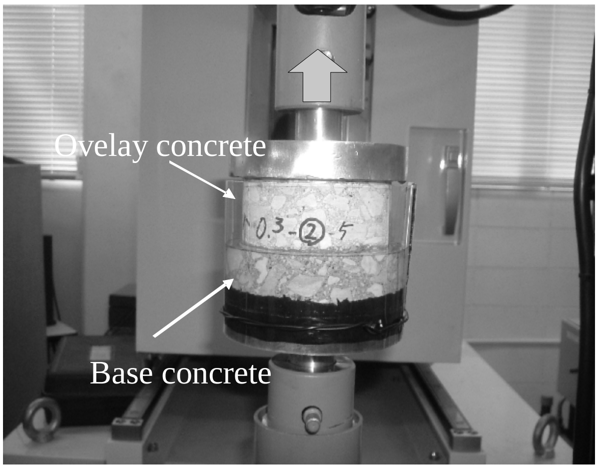

Photo. 1 Fatigue Tensile test in water-soaked state

Table 7 Condition of cyclic tensile test in wet condition

Helz of loading(Hz)	10
Type of loading	Sign wave
Stress of loading	1.1~1.3N/mm^2 from FEM
Times of loading	Max2,000,000
Temperature	Room temp.

fatigue test was conducted on the conditions shown in Table 7. The size of the tensile fatigue test specimen was a cylindrical specimen measuring 100mm in diameter and 100mm in total height as existing concrete is 50 mm in height and overlay concrete is 50mm in height. To fabricate the cylindrical specimen, the epoxy resin type adhesive A was applied to the surface of existing concrete cut with concrete cutter, then overlay concrete was placed. The quantity of epoxy resin was changed from 0 kg/m^2 to 4.2kg/m^2. Maximum stresses loaded were set to 1.1-1.3N/mm^2. The above values were maximum stresses due to drying shrinkage and temperature difference in thin bonded overlay concrete, which were calculated by FEM software Pave-3D. Water level at interface between exiting concrete and overlay concrete set the tensile fatigue test specimen to severest conditions.

3.2.2 Exposure to high temperature in water-soaked state

The same size specimen as tensile fatigue test was stored in water at 50 degrees in Centigrade for 12 weeks, then direct tensile strength was measured in order to confirm durability against exposure to high temperature in water-soaked state. The temperature at 50 degrees in Centigrade was maximum value measured in concrete apron pavement. The epoxy resin type adhesive A and B were used. Direct tensile strength was measured in dry state at 20 degrees in Centigrade with a tensile fatigue testing apparatus. Loading rate for 1 minute was 0.4N/mm^2.

3.2.3 Exposure to low temperature

The same size specimen as tensile fatigue test was cured in sealed state for 28 days after overlaying and was stored at -20 degrees in Centigrade for 12 weeks, then direct tensile strength was measured in order to confirm durability against exposure to low temperature. The epoxy resin type adhesive A was used and the quantity was changed from 0.3kg/m^2 to 4.2kg/m^2.

Moreover, test for resistance of concrete to freezing and thawing according to JIS A 1148, direct tensile test in dry state after 90, 180 and 300 cycles of freezing and thawing and tensile fatigue test in water-soaked state after 300 cycles of freezing and thawing were conducted. In specimen for the above tests, the epoxy resin type adhesive A or B was applied to existing concrete measuring 100mm in width, 50mm in height and 400mm in length, as shown in Fig 1, then overlay concrete was placed to be 100mm in height. The quantity of epoxy resin type was 0.7kg/m^2 or 0 kg/m^2. Monolithic prism was also fabricated. All prism specimens were cured in sealed state for 14 days after fabricating. In the direct tensile test and tensile fatigue test after freezing and thawing in water-soaked state, prism specimens measuring 100mm in width and 80mm in height cut from the concrete prism in Fig.1 were measured. In tensile fatigue test after freezing and thawing in water-soaked state, water level at interface between exiting concrete and overlay concrete was set up, applied stress was set up to 0.8N/mm^2 equivalent to 50% of target tensile strength, then loading was repeated up to 2 million cycles at the frequency of 10Hz.

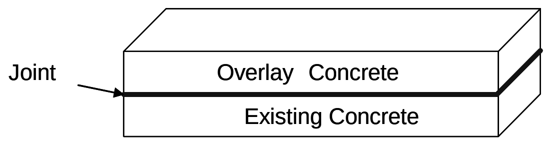

Fig.1 Concrete specimen for freezing and thawing test

4.EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Influence of ingredients in epoxy resin adhesive on cement hydration

Compressive strength of mortar to which each ingredient of base resins or hardening agents in epoxy resin adhesive was added by 1% of mass of cement was shown in Fig.2.

With regard to base resins such as epoxy resin base resins (No.2,4), silane coupling agent (No.6) and hardening agent (No.7), the compressive strength ranged from 16 to 18 N/mm^2 and was almost the same. The change in appearance of hardened specimens, such as color tone change, was small.

When reactive type (No.3) in agents adjusting viscosity (No.3 and No.5) was used, the compressive strength was almost same as that of standard

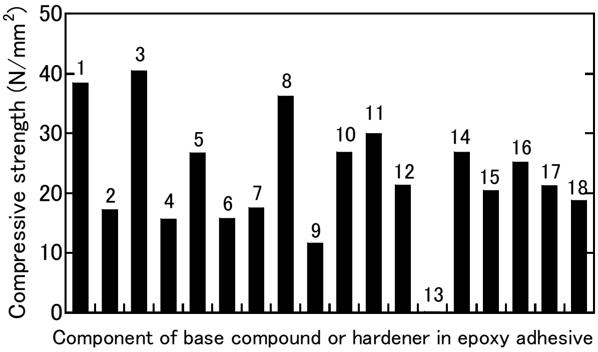

Fig. 2 Compressive strength of cement mortar

Table 8 Influence of hardening agent used for epoxy resin on fresh concrete

Element		Features
Base resins	Epoxy Base Silane coupling agents accelerator	The influence is small.
	Speed of hardner	The material with an early reaction enlarges strength.
Harden-ing agents	Hardening agents	The hydrophilic curing agents are not suitable. For they absorb the moisture which is needed for concrete curing.
	Polyamine	Some types of polyamines interferes the cement curing. So the selection of polyamines is important.
	Petroleum resin、Dyestuff	The influence is small.

specimen including no epoxy resin. Since this reactive type is characterized by short time to affect cement hydration because of its low molecule and fast reaction, this reactive type did not affect the compressive strength.

With regard to amine types (No.8-11), when hydrophobic hardening agent (No.9) was used, the compressive strength became lowest and fell to about 0.5 of average compressive strength of other types. In addition to strength reduction, the appearance of hardened specimens was darkish. Since hydrophobic material deprived cement mortar of water when it was mixed in cement mortar, it was estimated that the compressive strength of cement mortar decreased. If this phenomenon occurs in the vicinity of the interface between exiting concrete and overlay concrete, bond strength at the interface decreases. Therefore, hydrophobic hardening agent is inappropriate for ingredients of epoxy resin adhesives to be used in integration fresh concrete with existing structures. In addition, the cause of strength reduction and the analysis of a reaction process are the subject for a future study.

With regard to poly amine types (No.12-17), when Mannich-modefied MXDA was used, the compressive strength nearly equal to zero and the appearance of hardened specimens was darkish, further unsound hardening occurred. These phenomena are estimated to be due to interference in cement hydration. When a poly amine type is used as a hardening agent, prudent selection of poly amine type of which influence on cement hydration should be checked in advance is needed. When petroleum resin or dyestuff was used, the compressive strength decreased in comparison with that of standard specimen including no epoxy resin. However, the strength reduction rate of petroleum resin or dyestuff was almost the same as that of other hardening agent, in addition the change in appearance of hardened specimens was small. It can be considered that these materials did not affect cement hydration seriously.
The influence of each ingredient in epoxy resin adhesive on cement hydration is summarized in Table 8. Compound of epoxy resin adhesive can be conducted on the base of the qualitative influence in Table 8, however, quantitative influence of each ingredient of epoxy resin adhesive should be checked each time in advance.

In order to check whether interference in cement hydration might be occur by a specific ingredient or not, both unsound hardening mortar (No.13) including Mannich-modefied MXDA and mortar from standard specimens (No.1) including no epoxy resin were analyzed by X-ray diffraction or by thermal differential test. The X-ray diffraction results including specially magnified detail drawings showing diffraction degrees within range of 30 to 40 and of 45 to 55 are in Fig.3. A peak indicating $Ca(OH)_2$ was recognized in referential specimens (No.1), while a sharp peak indicating C_3S and no peak indicating $Ca(OH)_2$ was recognized in unsound hardening mortar (No.13). Further as shown in Fig.4, in the thermal differential test a endothermic peak by decomposition in $Ca(OH)_2$ in the vicinity of 450 degrees in Centigrade was recognized in No.1, while almost no endothermic peak was recognized in No.13. It is confirmed, accordingly, that interference in cement hydration was caused in No.13.

4.2 Fatigue test results in water-soaked state

Fatigue test results in water-soaked state were shown in Table 9. When the epoxy resin type adhesive A of which ingredients were optimized was used and the quantity of applying epoxy resin adhesive to specimens were changed in wide range of 0.3 to 4.2kg/m^3, fatigue failure has not been recognized in the specimens under repeated loading up to 2 million cycles. On the other hand fatigue failure has been recognized extremely in its early stage when no epoxy resin type adhesive was applied to test specimens. In past trial execution of thin bonded concrete overlay, rip off between existing concrete and overlay concrete was recognized when no epoxy

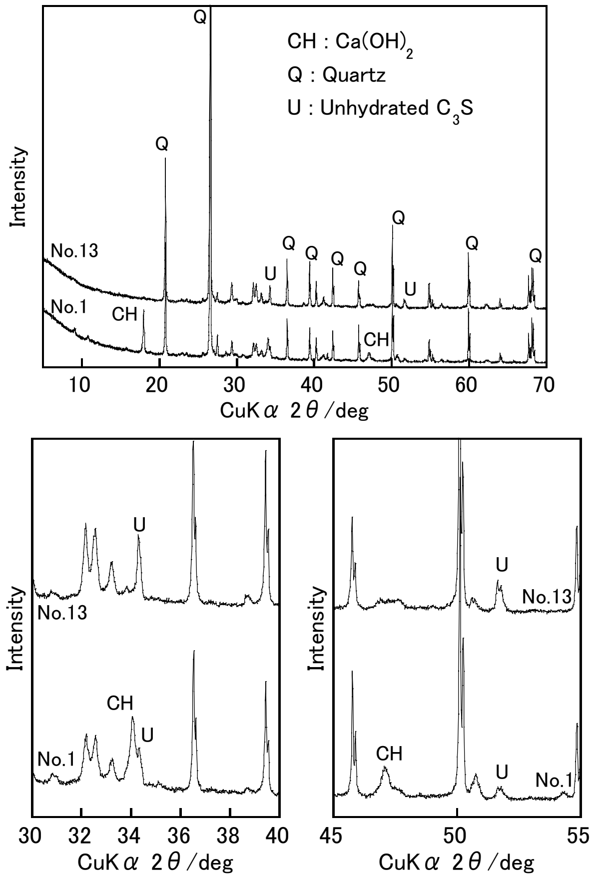

Fig. 3 X-ray diffraction of cement mortar

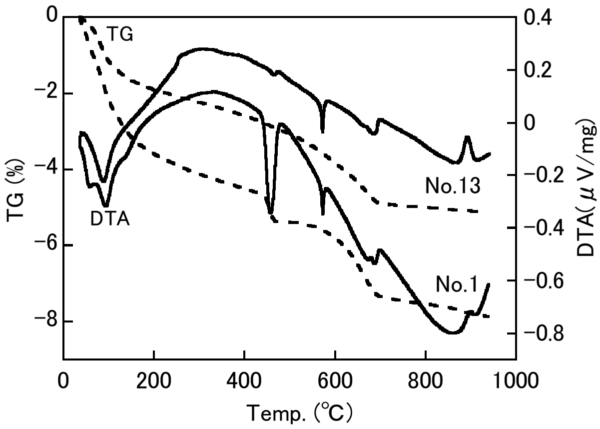

Fig. 4 TG and DTA curve of cement mortar

Table 9 Test results of fatigue test in water soaked state

Epoxy adhesive (kg/m^2)	Tensile stress (N/mm^2)	Number of loading	Failure mode
0.0	1.1	20,855	Interface
0.3	1.3	2,000,000	No
0.4	1.3	2,000,000	No
0.5	1.3	2,000,000	No
0.6	1.3	2,000,000	No
0.7	1.3	2,000,000	No
2.8	1.3	2,000,000	No
4.2	1.3	2,000,000	No

Photo.2 Specimen after Exam(B).

resin type adhesive was applied to existing concrete, and it seemed that the above phenomenon could be reproduced in this fatigue test. It is confirmed that resistance to fatigue in water-soaked state was enhanced by using specially tuned epoxy resin adhesive.

4.3 Exposure results to high temperature in water-soaked state

Results of direct tensile strength after exposure to 50 degrees in Centigrade in water-soaked state were shown in Fig.5. The direct tensile strength of specimens to which epoxy resin type adhesive A was applied decreased slightly in comparison with that before the exposure, however, it is confirmed that the direct tensile strength met the target value of 1.6 N/mm^2 fully in any quantity of applying epoxy resin adhesive. Fractured section in any specimen existed inside the existing concrete or the overlay concrete. On the other hand, before the exposure the direct tensile strength of specimens to which epoxy resin type adhesive B was applied was almost the same as that of epoxy resin type adhesive A, however the direct tensile strength of specimens after exposure to 50 degrees in Centigrade decreased extremely. The test specimen of direct tensile strength after the

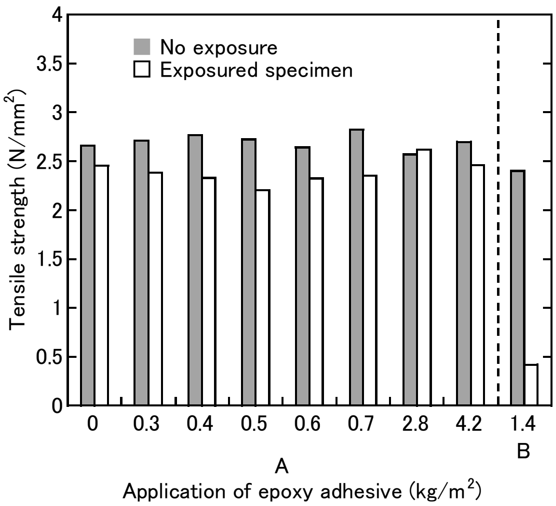

Fig.5 Tensile strength after 50℃ water-exposure

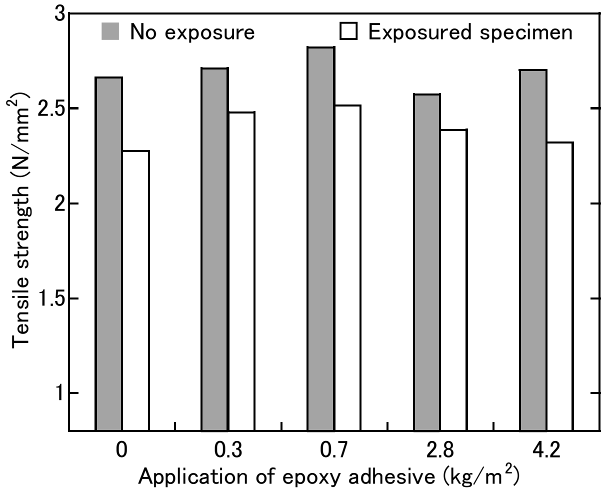

Fig.6 Tensile strength after -20℃ exposure

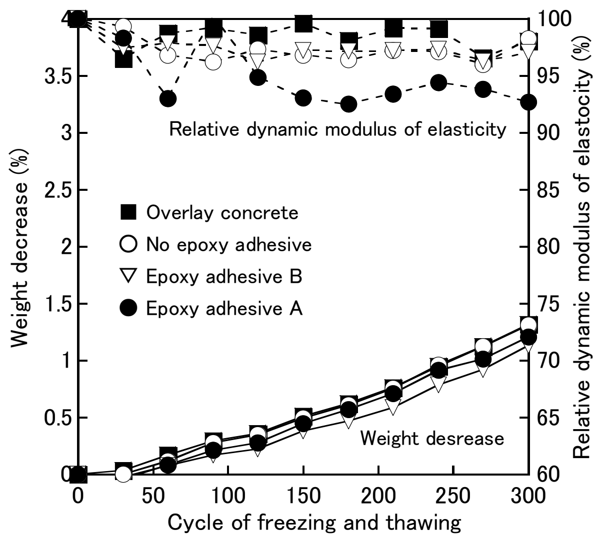

Fig.7 Test results of freezing and thawing test

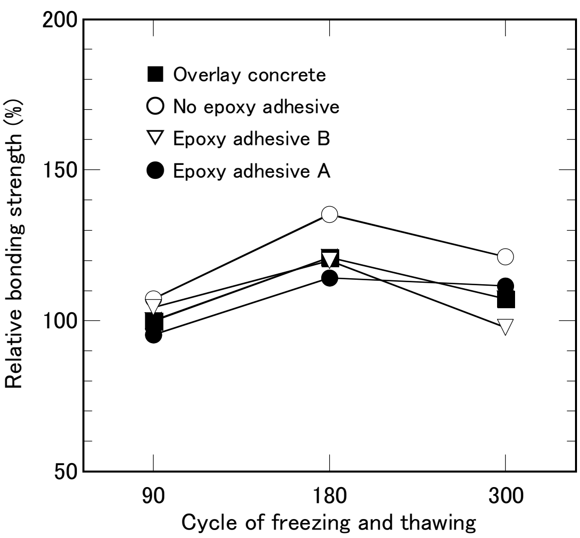

Fig.8 Relative tensile strength after freezing and thawing test

exposure was shown in Photo.2, swelling phenomenon of epoxy resin adhesive was recognized and the test specimen fractured inside the epoxy resin adhesive. Since the epoxy resin type adhesive B includes poly-thiol (mercaptan) and the branching and cross-linking structure of the poly-thiol is looser than that of poly amine type, it has been reported that the resistance to water and solvent, and water tightness are inferior to that of poly amine type. In integration fresh concrete with existing members, the abovementioned inferior performance of the poly-thiol was revealed.

4.4 Exposure results to low temperature

The comparison between direct tensile strength after exposure to –20 degrees in Centigrade for 12 weeks and that before the exposure was shown in Fig.6. Regardless of the quantity of applying epoxy resin adhesive to specimens, there was no significant difference in the direct tensile strength after the exposure. The direct tensile strength after the exposure decreased slightly in comparison with that before the exposure, however, fractured section in any specimen existed inside the existing concrete and the direct tensile strength met the target value of 1.6 N/mm^2 fully. It is confirmed that after exposure to the low temperature deterioration of the epoxy resin adhesive and bond strength at the interface did not occur, further the integration fresh concrete with existing members was maintained satisfactory.

Change in relative dynamic modulus of elasticity and mass of specimens in freezing and thawing test are shown in Fig.7. There was no significant difference in relative dynamic modulus of elasticity of any specimen, further the relative dynamic modulus of elasticity of specimens to which epoxy resin adhesive was not applied did not decrease. The ratio of direct tensile strength after 90, 180 and 300 cycles to that before the test is indicated in Fig.8. The strength reduction after the test did not appear,

Table 10 Test results of fatigue tensile in water-soaked state

Specimen	Number of fatigue failure	Failure mode or part at bonding strength test after freezing and thawing
Epoxy adhesive A	>2000000	Existing concrete
Epoxy adhesive B	155139	Interface of adhesive and overlay concrete
No adhesive	647319	Interface of Existing concrete and overlay concrete

while the specimens to which no epoxy resin adhesive was applied fractured at the interface between exiting concrete and overlay concrete and the specimens to which epoxy resin type B adhesive was applied fractured at the interface between epoxy resin adhesive and overlay concrete. The influence of existence of water and its freezing did not appear in the direct tensile strength, however there is any possibility of above factors affected the interface between exiting concrete and overlay concrete or epoxy resin type adhesive B in itself.

Fatigue test results of direct tensile strength in water-soaked state after 300 cycles of freezing and thawing are shown in Table 10. In the already described direct tensile strength exiting concrete of specimen to which epoxy resin type A adhesive was applied was fractured, however, the same type specimens were not fractured in the fatigue test. On the other hand specimens to which epoxy resin type B adhesive or no epoxy resin adhesive was applied were fractured during the fatigue test. Since epoxy resin type B includes poly-thiol and the resistance to water of the poly-thiol is inferior to that of poly amine type, mentioned already, it is estimated that specimens to which epoxy resin type B was applied was fractured at an early stage of the fatigue test. It confirmed also that specimens to which epoxy resin type A was applied had excellent integration fresh concrete with existing structures when they were exposed to low temperature or freezing and thawing.

5. CONCLUSION

In the problem to be solved for the time being, authors studied influence of ingredients in epoxy resin adhesive on cement hydration, a degree of deterioration by fatigue in water-soaked state, by exposure to both high temperature and low temperature. The following findings were revealed by this study.

(1) In hardening agent of amine types, there is a high probability that hydrophobic hardening agent deprives cement mortar of water, therefore, hydrophobic hardening agent is inappropriate for ingredient of epoxy resin adhesives to be used in integration fresh concrete with existing concrete.

(2) In hardening agent of poly amine types, there is a probability that some ingredients, especially Mannich-modefied MXDA affect cement hydration, therefore, prudent selection of poly amine type of which influence on cement hydration should be checked in advance is needed.

(3) When the optimized epoxy resin type adhesive was used, fatigue failure has not been recognized in fatigue test in water-soaked state under repeated loading up to 2 million cycles.

(4) After exposure to 50 degrees in Centigrade in water-soaked state, direct tensile strength of specimens to which the optimized epoxy resin type adhesive was applied decreased slightly in comparison with that before the exposure, however met the target value of 1.6 N/mm^2 fully. Further fractured section in any specimen existed inside the existing concrete or the overlay concrete.

(5) After exposure to –20 degrees in Centigrade for 12 weeks or freezing and thawing test, direct tensile strength of specimens to which the optimized epoxy resin type adhesive was applied did not decrease significantly and met the target value of 1.6 N/mm^2 fully. Further fractured section in any specimen existed inside the existing concrete or the overlay concrete.

(6) With regard to epoxy resin type adhesive including poly-thiol, swelling phenomenon was recognized after exposure to 50 degrees in Centigrade in water-soaked state and remarkable deterioration occurred. In addition specimens were fractured at an early stage during fatigue test of direct tensile strength in water-soaked state after 300 cycles of freezing and thawing. Abovementioned phenomenon conform well to the reports that the branching and cross-linking structure of the poly-thiol is looser than that of poly amine type, therefore, the resistance of poly-thiol to water is inferior to that of poly amine type.

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