Effects of Diacrylate Monomers on the Bond Strength of Polymer Concrete to Wet Substrates

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ABSTRACT: The bond strengths of polymer concretes containing up to 15% (based on polymer resin) of diacrylate (DA) monomers were examined and compared with those without DA. A change occurring with the addition of DA monomers was an increase in the bond strength of polymer concrete to wet substrates. Zinc diacrylate (ZDA) and calcium diacrylate (CDA) were each used as an additive to monomers and resins [methyl methacrylate (MMA), polyester, and two kinds of epoxies]. The variables were amount of the DA monomers and surface conditions (wet or dry and smooth or rough). Bond strengths were measured by tension bond. ZDA was found to improve the bond strength of MMA and polyester, whereas CDA improved the bond strength of epoxies. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 991–1000, 2003

Key words: strength; monomers; additives; resins; polymer concrete (PC)

INTRODUCTION

Polymer concrete (PC) is a composite material produced from inorganic aggregates (such as sand, gravel, and fly ash) bonded together by a resin binder (or plastic glue) instead of the water and cement binder typically used in normal cement concrete.[1,2] Most PC has high strength in compression and flexure, provides excellent bonding properties, and is waterproof and resistant to corrosion.[3,4] PC will provide a longer, maintenance-free service life because the durability and physical properties are superior to those of Portland cement concrete. Also, PC is able to cure within 1 or 2 h. For these reasons, PC has been used to repair Portland cement concrete and overlay bridge decks, parking garage decks, industrial floors, and dams.[5–7] Recently, the ability to bond to a wet substrate is needed for some repairs. Unfortunately, normal polymer concrete does not bond well to wet surfaces. Diacrylate monomers offer the possibility of bonding polymer concrete to wet substrates and widen the application fields of polymer concrete repair.

The purpose of this study was to evaluate the change of the bond strength of the polymer concrete, using the commercial diacrylate monomers, to wet substrate.

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EXPERIMENTAL

Materials

Resins

Four different resins were used in making the polymer concrete overlays for bonding to wet substrates. Methyl methacrylate (MMA) and trimethylolpropane trimethacrylate (TMPTMA) were used to formulate MMA PC. MMA is a clear, volatile, very low viscosity liquid monomer. TMPTMA is a trifunctional crosslinking agent, which is used to increase the curing rate. Polyester PC was made from unsaturated polyester resin, a viscous liquid resin with a styrene monomer content of 43.9%. Two kinds of epoxy resins (A-type and B-type epoxies) were used in making epoxy PC. The epoxy resins were very viscous.

Initiators

Initiators are chemical compounds that decompose into free radicals that are responsible for the initiation of the polymerization process. The initiator used in MMA PC was benzoyl peroxide (BZP) in the form of 40% dispersion. The initiator used in polyester PC was methyl ethyl ketone peroxide (MEKP). In the case of A-type epoxy PC, an amine initiator was used. No initiator was used for B-type epoxy PC.

Promoters

Dimethyl-*para*-toluidine (DMPT) was the promoter used in MMA PC. Cobalt naphthenate (6% concentration) was the promoter used in polyester PC. An ac-

TABLE I
Mix Design for MMA-Based Polymer Concrete

Material	Proportions (parts by mass)
MMA monomer	13.1
TMPTMA (SR-350)	0.7
All–purpose sand	86.2
	Based on MMA monomer
Metallic monomer powder	5–15%
Dimethyl-*p*-toluidine (DMPT)	0.18%
Dibenzoyl peroxide (40% dispersion)	5%
Polymethyl methacrylate (PMMA)	3.0% of total sand

TABLE III
Mix Design for A-Type Epoxy Polymer Concrete

Material	Proportions (parts by mass)
A-type epoxy resin	5.5
Jeffamine (D-230)	1.8
Accelerator 399	1.1
Coarse aggregate (9.5 mm [3/8 in.])	55
All-purpose sand	27.5
Fly ash	9.2
	Based on A–type resin
Metallic monomer powder	5–15%

celerator was used in A-type epoxy PC, and EPI-CURE 3072 curing agent was used in B-type epoxy PC.

Monomers

Two monomers, zinc diacrylate (ZDA) and calcium diacrylate (CDA), were used in this study. They are white powders that do not readily dissolve in resins.

Aggregates

Fine and coarse aggregates, such as river sands and gravels, crushed sands, and stones recommended for ordinary cement concrete, are used for PC. However, very low moisture content, cleanness, and good quality are usually required for aggregates in the preparation of PC. The fine aggregate used throughout this study was all-purpose sand. It was oven-dried by the producer. The fineness modulus of sand was 2.35. The 9.5-mm ($\frac{3}{8}$-in.) coarse aggregate used in A-type epoxy PC was oven-dried for 24 h at 121.1°C (250°F).

Additives

Polymethyl methacrylate (PMMA) was used for MMA-base PC as a thickening agent. It is in the form of small solid particles. Fly ash was used as an additive for A-type epoxy PC.

Testing procedures

Mixing and casting

In principle, the mix design of PC typically uses an aggregate gradation to provide the lowest possible void volume that will require the minimum polymeric binder contents necessary to coat the aggregates and to fill the voids. In this study, the mix design was optimized for workability and strength without consideration of aggregate gradation because of the use of all-purpose sand.

ASTM C305 mixing was used as the standard mixing procedure for the mortar, using a planetary mixer. ASTM C305 mixing consists of a sequence of mixings that involve a total of 1.0 min at a paddle speed of 140 rpm, followed by a total of 1.5 min at a speed of 285 rpm.

MMA PC system. Basically, the resin-to-aggregate ratio was 13.8 : 86.2 by mass. The proportions of the components by mass are shown in Table I. The quantities of initiator and promoter were optimized by working and curing times and remained the same for this system. Diacrylate monomer powder contents were 0, 5, and 15% of MMA monomer.

Polyester PC system. The polyester resin-to-aggregate ratio was 2 : 8 by mass. Table II indicates the proportions of all components by mass used in the polyester PC system. The diacrylate monomer powder contents were 0, 5, and 15% of polyester resin.

A-type epoxy PC system. The binder formulation-to-graded aggregate ratio was 8.25 : 91.75 by mass. The

TABLE II
Mix Design for Polyester Polymer Concrete

Material	Proportions (parts by mass)
Polyester resin	20
All-purpose sand	80
	Based on polyester resin
Metallic monomer powder	5–15%
6% Cobalt–naphthenate	0.48%
MEKP	2.5%

TABLE IV
Mix Design for B-Type Epoxy Polymer Concrete

Material	Proportions (parts by mass)
B-type resin	11.35
EPI-CUPE 3072 curing agent	2.95
All-purpose sand	85.7
	Based on B-type resin
Metallic monomer powder	5–15%

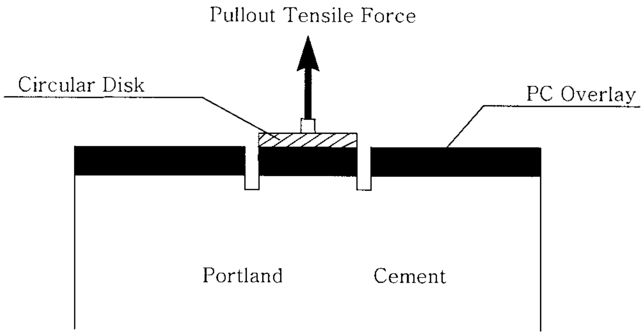

Figure 1 Pullout bond test.

proportions of the components by mass are shown in Table III.

B-type epoxy PC system. The B-type epoxy resin-to-aggregate ratio was 14.3 : 85.7 by mass. Table IV indicates the proportions of all components by mass used in the B-type epoxy PC system.

Substrate preparation

Portland cement concrete slabs had either a rough or smooth surface. The tensile bond strength of the concrete slabs was about 3.45 MPa (500 psi).

After sandblasting, the texture depth of concrete slabs was measured by Test Method Tex-436-A of The State Department of Highways and Public Transportation Materials and Tests Division using ASTM 20-30 silica sand. After a conversion table was prepared the mass of sand needed to fill the metal cylinder was determined, and then it was poured onto the test surface. The diameter of the sand patch at four or more equally spaced locations was measured and texture depth was calculated. Smooth slabs had texture depths ranging from 0.48 to 0.66 mm (0.019 to 0.026 in.); rough slabs had texture depths ranging from 0.84 to 1.24 mm (0.033 to 0.049 in.).

Bond strength test

There are no standard tests that are directly applicable to polymer concrete. Therefore, ASTM standards developed for cement-based materials were used as guidelines whenever applicable.[8]

Bond strength between PC and Portland cement concrete substrate was measured using the pullout test method[9] illustrated in Figure 1. Slabs were tested either wet or dry. Dry slabs were dried using a heater for about 10 min. Wet slabs had water ponded on the surface for 10 h, and just before application of the PC, the water was poured off and water was vacuumed from the surface. Polymer concrete overlays were placed to a thickness of about 12.5 mm ($\frac{1}{2}$ in.). The surface conditions were dry/smooth, dry/rough, wet/smooth, and wet/rough.

Circular grooves [102 mm (4 in.) diameter] were cored through the overlays and into the Portland cement concrete substrate. Circular steel disks were then bonded to the cleaned overlay at the cored locations using a strong epoxy resin. The disks were then pulled in direct tension to determine the type and magnitude of the bond failure.

RESULTS AND DISCUSSION

Modes of failure

Two different modes of failure were observed when testing for the tensile bond strength: (1) in the Portland cement concrete substrate and (2) at the interface of PC and Portland cement concrete (delamination-type failure). In overlay or repair applications, it is desirable to have failures occurring in the Portland cement concrete substrate rather than at the interface between the two materials because a Portland cement concrete mode of failure indicates that the strength between the PC and the Portland cement concrete substrate is higher than the strength of the Portland cement concrete substrate alone.

TABLE V
Tensile Bond Strength of MMA PC: Smooth Surfaces

Surface condition	DA type	Level of DA	Failure location	Tensile bond strength, MPa (psi)	Ratio of PC bond strength to concrete bond strength[a]
DRY		none	substrate	3.25 (471)	1.0+
	ZDA	5%	substrate	3.35 (486)	1.0+
	ZDA	15%	substrate	3.39 (491)	1.0+
	CDA	5%	substrate	3.44 (499)	1.0+
	CDA	15%	substrate	3.23 (469)	1.0+
WET		none	interface	1.45 (210)	0.43[b]
	ZDA	5%	interface	2.23 (323)	0.66[b]
	ZDA	15%	interface	2.50 (362)	0.74[b]
	CDA	5%	interface	1.71 (248)	0.51[b]
	CDA	15%	interface	1.90 (276)	0.56[b]

[a] If failure occurred in substrate, PC bond strength was greater than concrete bond strength; ratio given as 1.0+.
[b] Based on bond strength of concrete of 3.39 MPa (491 psi).

TABLE VI
Tensile Bond Strength of MMA PC: Rough Surfaces

Surface condition	DA type	Level of DA	Failure location	Tensile bond strength, MPa (psi)	Ratio of PC bond strength to concrete bond strength[a]
DRY		none	substrate	3.46 (502)	1.0+
	ZDA	5%	substrate	3.34 (484)	1.0+
	ZDA	15%	substrate	3.32 (481)	1.0+
	CDA	5%	substrate	3.38 (490)	1.0+
	CDA	15%	substrate	3.28 (476)	1.0+
WET		none	interface	1.72 (249)	0.50[b]
	ZDA	5%	interface	2.41 (349)	0.70[b]
	ZDA	15%	interface	2.56 (371)	0.75[b]
	CDA	5%	interface	2.04 (296)	0.60[b]
	CDA	15%	interface	1.99 (289)	0.58[b]

[a] If failure occurred in substrate, PC bond strength was greater than concrete bond strength; ratio given as 1.0+.
[b] Based on bond strength of concrete of 3.43 MPa (497 psi).

The modes of failure were dependent on the condition of surface used. As shown in Tables V–XII, the modes of failure for wet surface conditions were usually interface failures, except for the polyester PC system with ZDA (Tables VIII and IX). Even though the surface condition was rough and wet, the mode of failure in the case of the addition of ZDA was substrate failure. This type of failure indicates that ZDA increases the bond significantly for wet surfaces.

TABLE VII
Tensile Bond Strength of Polyester PC: Smooth Surfaces

Surface condition	DA type	Level of DA	Failure location	Tensile bond strength, MPa (psi)	Ratio of PC bond strength to concrete bond strength[a]
DRY		none	substrate	3.20 (464)	1.0+
	ZDA	5%	substrate	2.95 (428)	1.0+
	ZDA	15%	substrate	3.25 (471)	1.0+
	CDA	5%	substrate	3.35 (486)	1.0+
	CDA	15%	substrate	3.52 (511)	1.0+
WET		none	interface	1.54 (223)	0.46[b]
	ZDA	5%	80% interface	2.57 (373)	0.76[b]
	ZDA	15%	60% interface	2.68 (388)	0.79[b]
	CDA	5%	interface	1.20 (174)	0.36[b]
	CDA	15%	interface	1.17 (169)	0.34[b]

[a] If failure occurred in substrate, PC bond strength was greater than concrete bond strength; ratio given as 1.0+.
[b] Based on bond strength of concrete of 3.38 MPa (490 psi).

TABLE VIII
Tensile Bond Strength of Polyester PC: Rough Surfaces

Surface condition	DA type	Level of DA	Failure location	Tensile bond strength, MPa (psi)	Ratio of PC bond strength to concrete bond strength[a]
DRY		none	substrate	3.75 (544)	1.0+
	ZDA	5%	substrate	3.87 (562)	1.0+
	ZDA	15%	substrate	3.96 (574)	1.0+
	CDA	5%	substrate	3.75 (544)	1.0+
	CDA	15%	substrate	3.92 (569)	1.0+
WET		none	interface	3.60 (522)	0.95[b]
	ZDA	5%	substrate	3.72 (539)	1.0+
	ZDA	15%	substrate	3.95 (573)	1.0+
	CDA	5%	interface	1.55 (225)	0.41[b]
	CDA	15%	interface	1.15 (167)	0.30[b]

[a] If failure occurred in substrate, PC bond strength was greater than concrete bond strength; ratio given as 1.0+.
[b] Based on bond strength of concrete of 3.45 MPa (500 psi).

TABLE IX
Tensile Bond Strength of A-Type Epoxy PC: Smooth Surfaces

Surface condition	DA type	Level of DA	Failure location	Tensile Bond Strength, MPa (psi)	Ratio of PC bond strength to concrete bond strength[a]
Dry		none	substrate	3.30 (479)	1.0+
	ZDA	5%	substrate	3.10 (450)	1.0+
	ZDA	15%	substrate	3.30 (479)	1.0+
	CDA	5%	substrate	3.40 (493)	1.0+
	CDA	15%	substrate	3.50 (508)	1.0+
Wet		none	interface	2.40 (348)	0.71[b]
	ZDA	5%	interface	2.20 (319)	0.65[b]
	ZDA	15%	interface	2.90 (421)	0.86[b]
	CDA	5%	interface	2.60 (377)	0.77[b]
	CDA	15%	interface	2.80 (406)	0.83[b]

[a] If failure occurred in substrate, PC bond strength was greater than concrete bond strength; ratio given as 1.0+.
[b] Based on bond strength of concrete of 3.38 MPa (490 psi).

ZDA did not perform well with B-type epoxy resin. Even when the surface condition was rough and dry the mode of failure was at the interface, which indicates that ZDA has an adverse or no effect on B-type resin.

Bond strength

The bond strength between the PC overlays and Portland cement concrete substrate was found to be

TABLE X
Tensile Bond Strength of A-Type Epoxy PC: Rough Surfaces

Surface condition	DA type	Level of DA	Failure location	Tensile bond strength, MPa (psi)	Ratio of PC bond strength to concrete bond strength[a]
Dry		none	substrate	3.50 (508)	1.0+
	ZDA	5%	substrate	3.30 (479)	1.0+
	ZDA	15%	substrate	3.80 (551)	1.0+
	CDA	5%	substrate	3.70 (537)	1.0+
	CDA	15%	substrate	3.50 (508)	1.0+
Wet		none	interface	2.30 (334)	0.67[b]
	ZDA	5%	interface	2.40 (348)	0.70[b]
	ZDA	15%	interface	2.50 (363)	0.73[b]
	CDA	5%	interface	2.90 (421)	0.84[b]
	CDA	15%	interface	3.00 (435)	0.87[b]

[a] If failure occurred in substrate, PC bond strength was greater than concrete bond strength; ratio given as 1.0+.
[b] Based on bond strength of concrete of 3.45 MPa (500 psi).

TABLE XI
Tensile Bond Strength of B-Type Epoxy PC: Smooth Surfaces

Surface condition	DA type	Level of DA	Failure location	Tensile bond strength, MPa (psi)	Ratio of PC bond strength to concrete bond strength[a]
Dry		none	substrate	3.30 (479)	1.0+
	ZDA	5%	40% interface	2.61 (379)	0.77
	ZDA	15%	not hard enough	0.03 (5)	0.01[b]
	CDA	5%	substrate	3.47 (503)	1.0+
	CDA	15%	substrate	3.41 (495)	1.0+
Wet		none	interface	1.54 (223)	0.47[c]
	ZDA	5%	interface	0.90 (130)	0.27[c]
	ZDA	15%	not hard enough	0.03 (5)	0.01[b]
	CDA	5%	interface	1.80 (261)	0.53[c]
	CDA	15%	interface	1.95 (283)	0.58[c]

[a] If failure occurred in substrate, PC bond strength was greater than concrete bond strength; ratio given as 1.0+.
[b] After 7 days the PC was not cured (still soft).
[c] Based on bond strength of concrete of 3.31 MPa (480 psi).

TABLE XII
Tensile Bond Strength of B-Type Epoxy PC: Rough Surfaces

Surface condition	DA type	Level of DA	Failure location	Tensile bond strength, MPa (psi)	Ratio of PC bond strength to concrete bond strength[a]
Dry		none	substrate	3.55 (515)	1.0+
	ZDA	5%	20% interface	2.98 (432)	0.83
	ZDA	15%	not hard enough	0.03 (5)	0.01[b]
	CDA	5%	substrate	3.61 (523)	1.0+
	CDA	15%	substrate	3.65 (530)	1.0+
Wet		none	interface	2.00 (290)	0.6[c]
	ZDA	5%	interface	1.00 (145)	0.3[c]
	ZDA	15%	not hard enough	0.03 (5)	0.01[b]
	CDA	5%	interface	2.29 (332)	0.68[c]
	CDA	15%	interface	2.41 (350)	0.72[c]

[a] If failure occurred in substrate, PC bond strength was greater than concrete bond strength; ratio given as 1.0+.
[b] After 7 days the PC was not cured (still soft).
[c] Based on bond strength of concrete of 3.34 MPa (485 psi).

strongly dependent on the type of resin as well as the surface condition and the amount and type of DA monomer. As shown in Tables V–XII and Figures 2–9, the bond strength for dry surfaces with DA was greater than the tensile strength of concrete; the bond to wet surfaces with DA was usually increased compared to that of resin without DA.

In the case of MMA PC, the bond strength with DA, regardless of surface roughness, was greater than the tensile strength of concrete for dry surfaces. For smooth and wet surfaces, the bond strength with ZDA was increased about 60%, and the bond strength with CDA was increased about 25% based on the bond strength with no DA. For rough and wet surfaces, the bond strength with ZDA was increased about 45%, and the bond strength with CDA was increased about 20% based on the bond strength with no DA.

In the case of polyester PC, for a wet surface, a very significant increase of the bond strength with DA, regardless of surface roughness, was observed. For wet surfaces, however, the bond strength with CDA, regardless of surface roughness, was decreased compared to that of polyester resin with no DA.

In the case of the A-type epoxy PC system, the bond strength with DA, regardless of surface roughness, was greater than the tensile strength of concrete for dry surfaces. For smooth and wet surfaces, the bond strength with ZDA was increased about 10%, and the bond strength with CDA was increased about 10% based on the bond strength with no DA. For rough and wet surfaces, the bond strength with 15% ZDA was increased about 10%, and the bond strength with CDA was increased about 30% based on the bond strength with no DA.

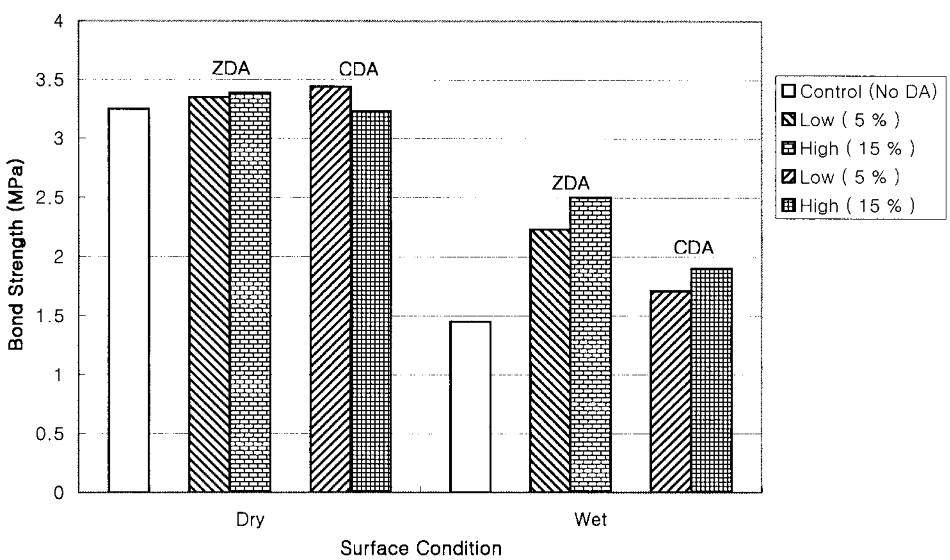

Figure 2 Comparison of the bond strengths of MMA PCs (smooth surface).

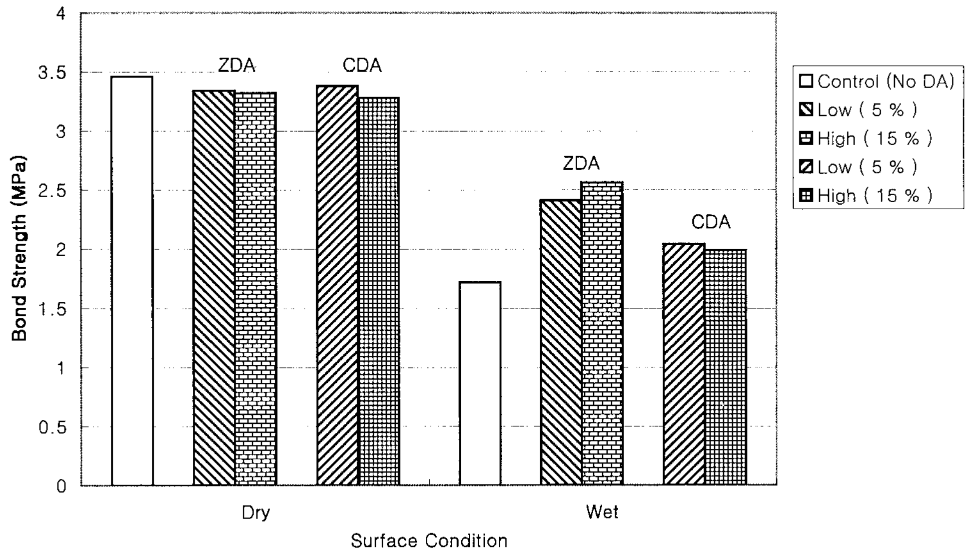

Figure 3 Comparison of the bond strengths of MMA PCs (rough surface).

In the case of the B-type epoxy PC system, the bond strength with CDA, regardless of surface roughness, was greater than the tensile strength of concrete for dry surfaces. The epoxy PC overlay with 15% ZDA, however, did not cure even after 7 days. The epoxy PC overlay with 5% ZDA required about 2 days to cure, which indicates that ZDA acted as an inhibitor. Regardless of the surface moisture condition, a decrease of the bond strength with 5% ZDA at both roughness surfaces was observed. For smooth and wet surfaces and for rough and wet surfaces, the bond strength with CDA was increased about 20% based on the bond strength with no DA.

CONCLUSIONS

The following conclusions can be drawn from the results of this study:

1. The bond strength for dry surfaces with diacrylate (DA) monomers was greater than the tensile strength of concrete; bonding to wet surfaces with DA was usually increased compared to resin without DA.
2. In the case of MMA PC, the bond strength with DA was greater than the tensile strength of concrete for dry surfaces. For wet surfaces, the bond strength with ZDA was increased about 50%, and the bond strength with CDA was increased about 25% based on the bond strength with no DA.
3. In the case of polyester PC, ZDA performed very well with polyester resin. For wet surfaces, a very significant increase of the bond strength with DA, regardless of surface roughness, was observed. For wet surfaces, however, the bond

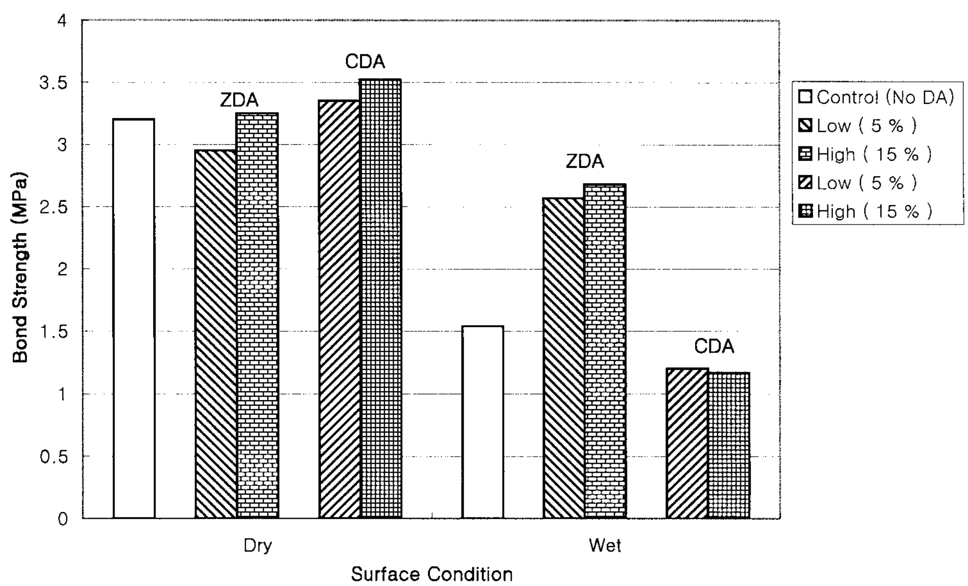

Figure 4 Comparison of the bond strengths of polyester PCs (smooth surface).

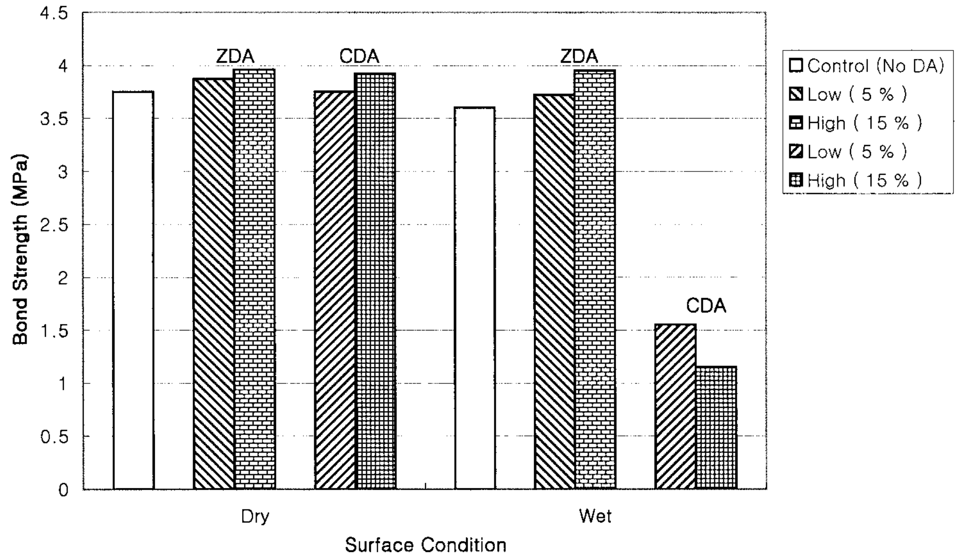

Figure 5 Comparison of the bond strengths of polyester PCs (rough surface).

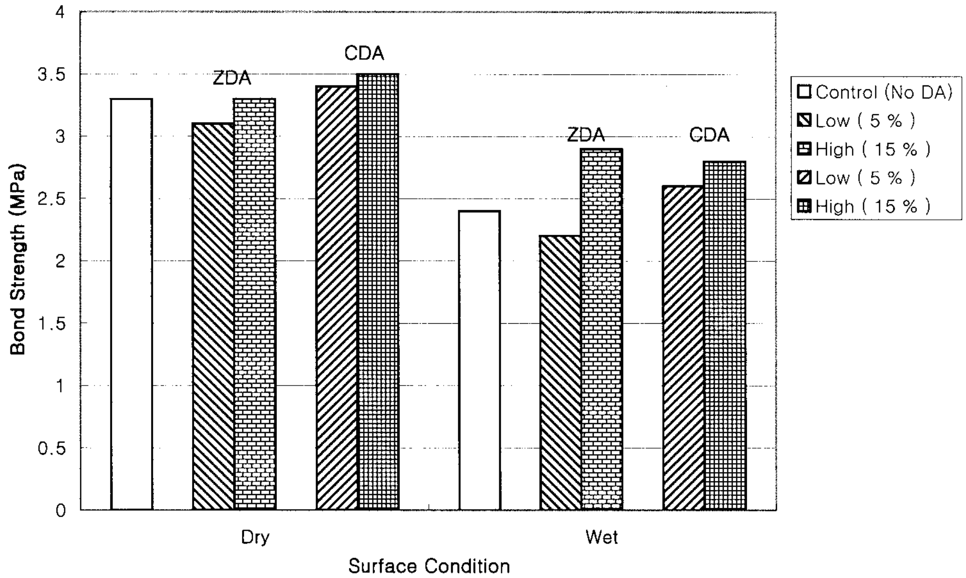

Figure 6 Comparison of the bond strengths of A-type epoxy PCs (smooth surface).

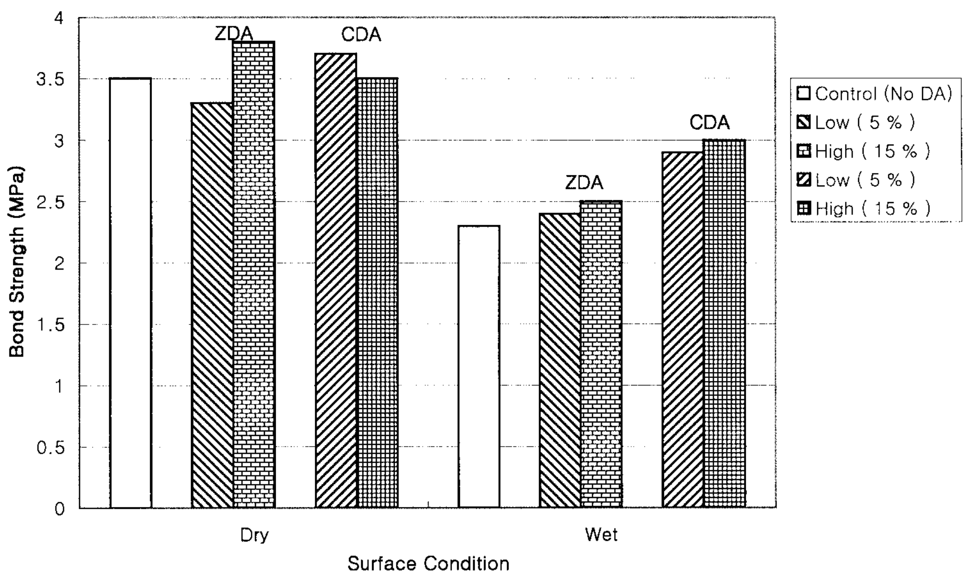

Figure 7 Comparison of the bond strengths of A-type epoxy PCs (rough surface).

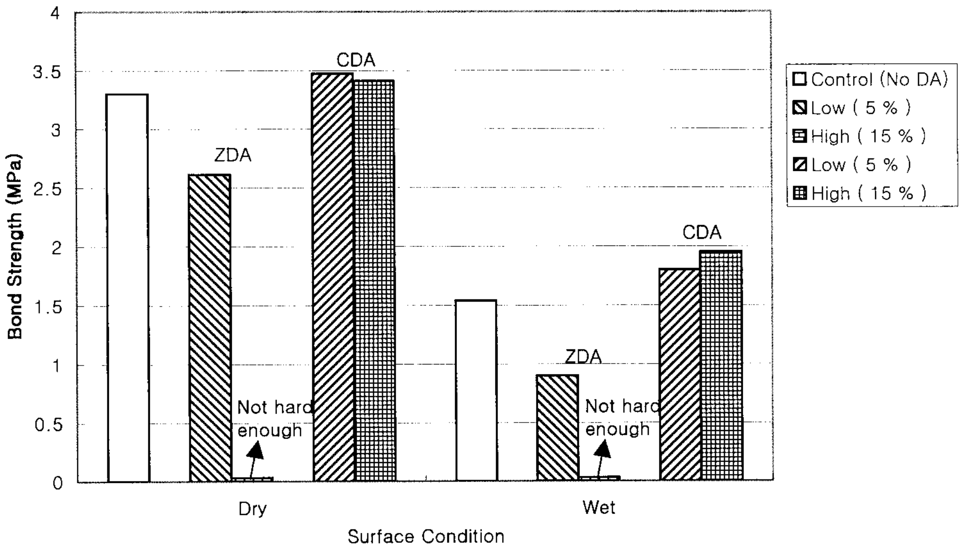

Figure 8 Comparison of the bond strengths of B-type epoxy PCs (smooth surface).

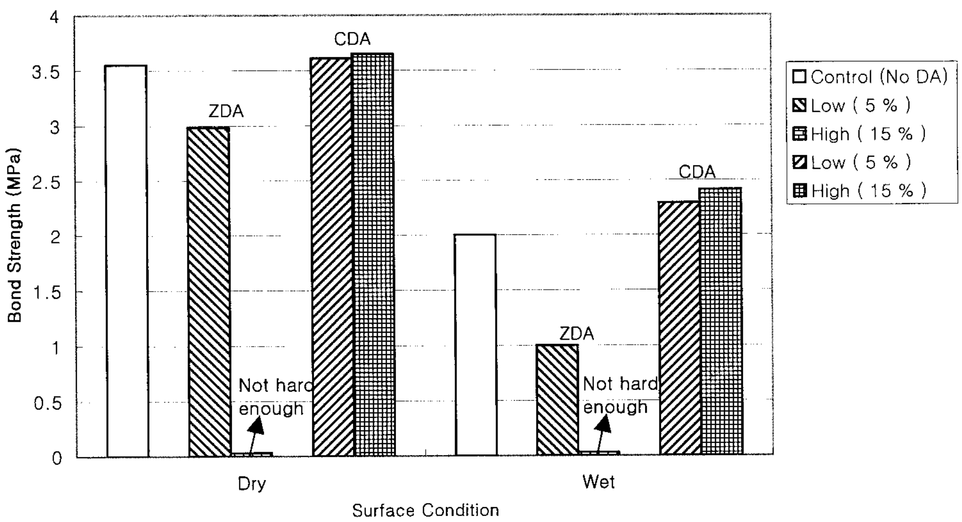

Figure 9 Comparison of the bond strengths of B-type epoxy PCs (rough surface).

strength with CDA, regardless of surface roughness, was decreased compared to that with no DA.

4. In the case of A-type epoxy PC, the bond strength with DA was greater than the tensile strength of concrete for dry surfaces. For wet surfaces, the bond strength with ZDA was increased about 10%, and the bond strength with CDA was increased about 20% based on the bond strength with no DA.
5. In the case of the B-type epoxy PC system, ZDA did not perform well with B-type epoxy resin. The epoxy PC overlay with 15% ZDA was not cured even after 7 days. The epoxy PC overlay with 5% ZDA required about 2 days to cure. Regardless of the surface condition, the decrease of the bond strength with 5% ZDA was observed. For smooth and wet surfaces and for rough and wet surfaces, the bond strength with CDA was increased about 20% based on the bond strength with no DA.

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