Effects of Metallic Monomer Powders on the Mechanical Properties of Hardened Polyester and Acrylic Polymer Concrete

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ABSTRACT: To investigate the effects of three metallic monomer powders on polyester- and acrylic-hardened polymer concretes, polymer concretes incorporating different levels of these materials were investigated for the properties of hardened polymer concrete. The mix design was made and optimized for workability and strength, depending on the resin viscosity, the intended use, and the additional quantities of these polymeric materials. The investigated properties included the compressive strength, flexural strength, and bond strength of hardened polymer concrete. It was concluded that these polymeric materials offer the possibility of improving the properties of polyester- and acrylic-hardened polymer concretes. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3106–3113, 2006

Key words: monomers; strength

INTRODUCTION

For many applications, polymer concrete (PC) is designed not only for high compressive strength but also for high flexural strength. Higher strengths will allow designers to reduce the thickness of load-bearing elements, thus making them lighter for easier transportation and installation.

There are several previous studies involved in enhancing compressive strengths for PC. It has been shown by several researchers that silane coupling agents have a significant effect on the compressive strength of polyester PC.[1–4] Fontana[1] reported that the compressive strength of polyester PC with silane coupling agents was 16–24% higher than that of equivalent samples without silane. It is believed that the use of silane coupling agents promotes adhesion between resin and silica aggregates, thus increasing the strength of the composites. However, silane coupling agents are very expensive, and for the best results, the aggregate should be pretreated with the coupling agents.

It has been reported by researchers[1,5] that the fiber reinforcement of PC offers the possibility of improving the flexural strength of polyester PC. For methyl methacrylate (MMA) based PC, trimethylolpropane trimethacrylate (TMPTMA), a crosslinking agent, has been used to improve the flexural strength.

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Metallic monomer powders, products of S-Company (Houston, TX), contain a metallic element and acrylic functional groups in their molecular structures. From the viewpoint of chemistry, these metallic monomers have a tendency to act as a crosslinking agent in polymerization to make the polymer matrix much stronger, thus improving the strength of PC. In addition, metallic elements in molecules will possibly have an effect on the adhesion between resin and aggregates or steel used in concrete.[6]

The purpose of this study was to evaluate the mechanical properties of hardened polyester and acrylic PC with commercial metallic monomer powders.

EXPERIMENTAL

Materials

As polymeric binders themselves cannot set or harden, initiators and promoters are selected and added to the polymeric binders. The working life and curing time (or hardening time) of PC can be controlled by the suitable selection of the types and contents of the initiators and promoters. Two types of PC were employed in this research.[6]

Resins or liquid monomers

Two different resins were used in making the PC. MMA and TMPTMA were used to formulate MMA PC. MMA is a clear, volatile, very low viscosity liquid monomer.[7,8] TMPTMA is a trifunctional crosslinking agent, which is used to increase the curing rate. Also,

TABLE I
Mix Design for MMA PC

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	0–15%
DMPT	0.18%
Dibenzoyl peroxide (40% dispersion)	5%
PMMA	3.0% of total sand

polyester PC was made from unsaturated polyester resin,[9] a viscous liquid resin with a styrene monomer content of 43.9.

Initiators

Two types of initiator were used in this research. The initiator used in MMA PC was benzoyl peroxide in the form of a 40% dispersion, and the initiator used in polyester PC was methyl ethyl ketone peroxide (MEKP).

Promoters

Also, two promoters were used. Dimethyl-*para*-toluidine (DMPT) was the promoter used in MMA PC, and cobalt naphthenate (6% concentration) was the promoter used in polyester PC.

Metallic monomer powders

Three metallic monomer powders were used in this study: zinc diacrylate (ZDA), zinc dimethacrylate (ZMA), and calcium diacrylate (CDA). They are white powders that do not readily dissolve in resins or monomers.

Aggregates

The aggregate used throughout this study was all-purpose sand. The sand was free of asphalt, dirt, and other organic materials. It was oven-dried by the manufacturer. The moisture content of the sand was 0.02%. The fineness modulus of the sand was 2.35.

Additives

In this study, poly(methyl methacrylate) (PMMA) was used for MMA PC as a thickening agent. It is a white substance in the form of small, solid particles. PMMA served as a thickening agent, making the freshly mixed PC more cohesive and workable. It also resulted in a skin on the PC surface soon after placement, which reduced the evaporation of the MMA monomer and minimized the danger of fire.[10]

Mix design

The mix design was optimized for workability and strength without consideration of aggregate gradation because of the use of all-purpose sand.[6]

MMA PC system

The MMA resin-to-aggregate ratio was 13.8:86.2 by mass. The proportions of the components by mass are shown in Table I. The concentrations of the metallic monomer powder were 0–15% of the MMA monomer by weight. In this research, the same amounts of the initiator and promoter were used to optimize the working and curing times.

Polyester PC system

The polyester resin-to-aggregate ratio was 2:8 by mass. The metallic monomer powder concentrations were 0–20% of the polyester resin. Table II indicates the proportions of all the components by mass used in the polyester PC system.

Experimental program

There are no standard tests that are directly applicable to PC.[2,6,11] Therefore, ASTM standards developed for cement-based materials were used as guidelines whenever applicable.

Compressive strength

Methods for determining the compressive strength were adapted from ASTM C 116-90 and ASTM C 579-91.[12] The test method was varied from the MMA-based PC to the polyester PC system.

PC system The compressive strength of MMA PC was measured at room temperature with ASTM C 116-90 ("Compressive Strength of Concrete Using Portions of

TABLE II
Mix Design for Polyester PC

Material	Proportions (parts by mass)
Polyester resin	20
All-purpose sand	80
	Based on polyester resin
Metallic monomer powder	0–20%
6% cobalt naphthenate	0.48%
MEKP	2.5%

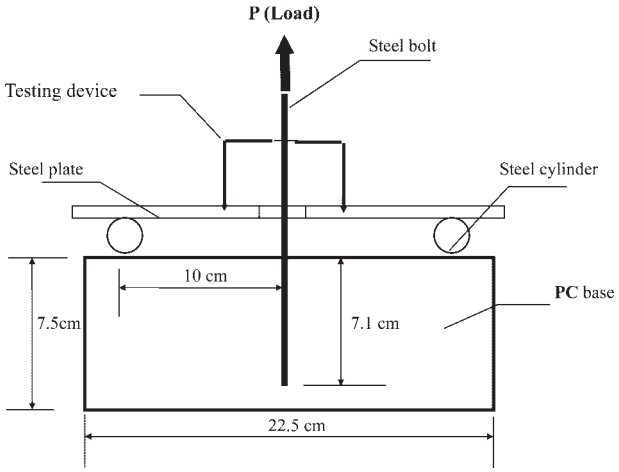

Figure 1 Tensile bond strength test arrangement.

Beams Broken in Flexure"). The beam was 2 in. × 2 in. × 12 in. and was cast in molds fabricated from polyethylene. The length of the broken portions of beams selected for the compressive test was at least 2 in. greater than the width, and the specimens were free of cracks, chipped surfaces, and other obvious defects. For bearing, two bosses were welded to a bearing plate to keep the plate in alignment so that the upper plate was placed directly over the lower plate. The width between the side guide supports was 3 in. to ensure the free expansion of the specimen under loading.

Polyester PC system The test for the compressive strength of polyester PC at room temperature was adapted from ASTM C 579-91 ("Standard Test Method for Compressive Strength of Chemical-Resistant Mortars, Grouts, Monolithic Surfacing and Polymer Concretes"). Specimens were 2-in. cubes and were cast in molds fabricated from metal. The compressive strengths were measured at an age of 7 days.

Flexural strength

The test for the flexural strength of the MMA PC and the polyester PC at room temperature was adapted from ASTM C 580-93 ["Standard Test Method for Flexural Strength and Modulus of Elasticity of Chemical Resistant Mortars, Grouts, Monolithic Surfacing and Polymer Concretes (Using Simple Beam with Center-Point Loading)"].[12] However, different specimen sizes were used in the different PC systems.

PC system

Specimens, 2-in. × 2-in. × 12-in. beams, were tested in flexure with center-point loading. The beams were cast in molds fabricated from polyethylene. The depth-to-span ratio of the specimens was 2 : 9. Beams were loaded at a constant rate of 0.02 in./min until failure occurred. The flexural strengths were measured at an age of 3 days.

Polyester PC system

Specimens, 1-in. × 1-in. × 12-in. beams, were tested in flexure with center-point loading. The beams were cast in molds fabricated from metal. The depth-to-span ratio of the specimens was 1:9. Beams were loaded at a constant rate of 0.05 in./min until failure occurred. The flexural strengths were measured at an age of 7 days.

Bond strength

The bond strength between PC and a steel rod was determined with the following procedure developed by the Construction Materials Research Group. The test specimens were made with a 3/4-in.-diameter steel bolt cast in the center of the specimens, as shown in Figure 1. The specimens were 9 in. × 9 in. × 3 in. The head of each steel bolt was cut, and the surface was wiped with a dry cloth. The surface of each bolt was very smooth. The total length of the bolts was 6 in., and the length of the bolt embedded in the specimens was about 2.8 in.

To avoid excess forces acting on the specimen, a steel plate with a circular hole at the center and two steel rods were used to bear forces generated by the pulling-out operation, as shown in Figure 1.

RESULTS AND DISCUSSION

MMA-based PC system

Compressive strength

The compressive strengths of MMA PCs incorporating different levels of the metallic monomers are given in

TABLE III
Influence of Metallic Monomers on the Compressive Strength for MMA-Based PC

Metallic monomer	Metallic monomer content based on resins (wt %)	Compressive strength	
		At 3 days [MPa (psi)]	At 7 days [MPa (psi)]
Control	0.0	58.0 (8408)	58.1 (8420)
ZDA	2.5	60.3 (8746)	—
	5.0	61.5 (8916)	76.4 (11075)
	7.5	64.8 (9393)	—
ZMA	2.5	62.0 (8989)	—
	5.0	53.3 (7726)	60.5 (8779)
	7.5	35.8 (5188)	—
CDA	5.0	62.0 (8985)	64.4 (9346)
	7.5	62.4 (9050)	—
	10.0	64.1 (9290)	—
	15.0	64.3 (9325)	—

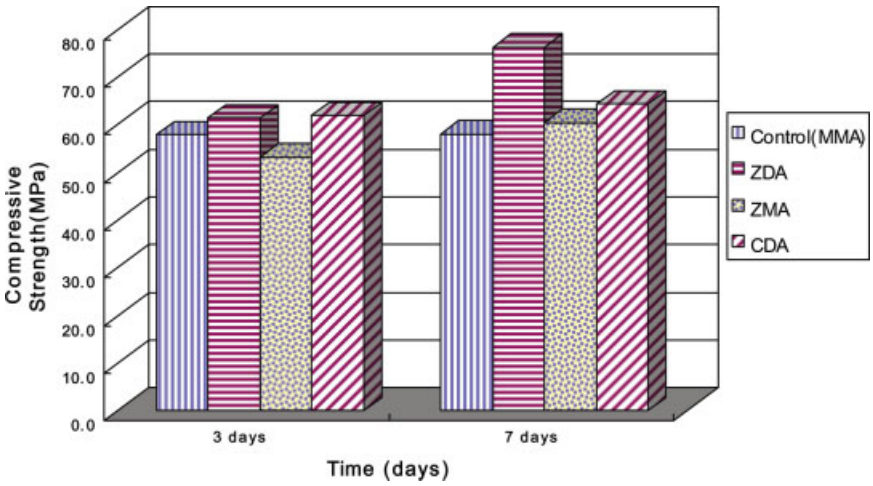

Figure 2 Compressive strength versus time for MMA-based PC with 5.0 wt % metallic monomer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table III. In general, ZDA and CDA had a positive effect on the compressive strength of MMA-based PC. For instance, 7.5 wt % ZDA and 15.0 wt % CDA gave approximately 11.7 and 10.9% improvements over the control, respectively. On the other hand, ZDA improved the compressive strength more than CDA at low additions. However, ZMA did not work very well in MMA-based PC. The difference in the compressive strengths for the three metallic monomers may be related to their different solubilities. None of the three metallic monomers completely dissolved in the MMA monomer, and they behaved differently. The ZDA and CDA powder coagulated and formed small solid particles when mixed with the MMA monomer. However, the ZMA powder was dispersed in the MMA monomer by mechanical stirring. Because the solution of the MMA monomer with ZMA was not stable, the ZMA precipitated as very finely divided particles from the solution in 30–40 min. Vibrating the specimens caused this fine precipitant of ZMA to rise to the top surface of the specimens, resulting in concentrated powder deposits, which in turn caused the compressive strength to vary greatly for different specimens.

The compressive strength of the MMA-based PC that incorporated the metallic monomers increased with time, as shown in Figure 2. The compressive strength for the batch with 5.0 wt % ZDA increased by 24.2% from 61.5 to 76.4 MPa (8916 to 11,075 psi) for 3 and 7 days, respectively. For the batch with 5.0 wt % ZMA, the compressive strength increased by 13.6% from 53.3 to 60.5 MPa (7726 to 8779 psi) for 3 and 7 days, respectively. For the batch with 5.0 wt % CDA, the compressive strength increased by 4.0% from 62.0 to 64.4 MPa (8985 to 9346 psi) for 3 and 7 days, respectively. The compressive strength for the control was, however, almost the same between 3 and 7 days: 58.0 and 58.1 MPa (8408 and 8420 psi), respectively. Therefore, significant increases in the compressive strength for batches with the metallic monomers were expected to be obtained only after a longer curing time. For the batch with 5.0 wt % ZDA, for instance, increases in the compressive strength were found to be 6 and 31.5% over the control for 3 and 7 days, respectively. The slow strength gain for batches with ZDA and ZMA, which was related to the longer curing time discussed previously, indicated that ZDA and ZMA acted as retarders in this system.

Flexural strength

The influence of the metallic monomers on the flexural strength of MMA-based PC is presented in Table IV. Generally, different metallic monomers had different effects on the flexural strength. In addition, these ef-

TABLE IV
Influence of Metallic Monomers on the Flexural Strength for MMA-Based PC

Metallic monomer	Metallic monomer content based on resins (wt %)	Flexural strength	
		At 3 days [MPa (psi)]	At 7 days [MPa (psi)]
Control	0.0	16.2 (2345)	16.3 (2370)
ZDA	2.5	16.2 (2350)	—
	5.0	17.0 (2462)	20.6 (2989)
	7.5	16.5 (2400)	—
ZMA	2.5	20.4 (2957)	—
	5.0	14.8 (2150)	16.4 (2375)
	7.5	11.3 (1635)	—
CDA	5.0	17.1 (2479)	17.6 (2558)
	7.5	17.7 (2567)	—
	10.0	18.7 (2706)	—
	15.0	19.7 (2855)	—

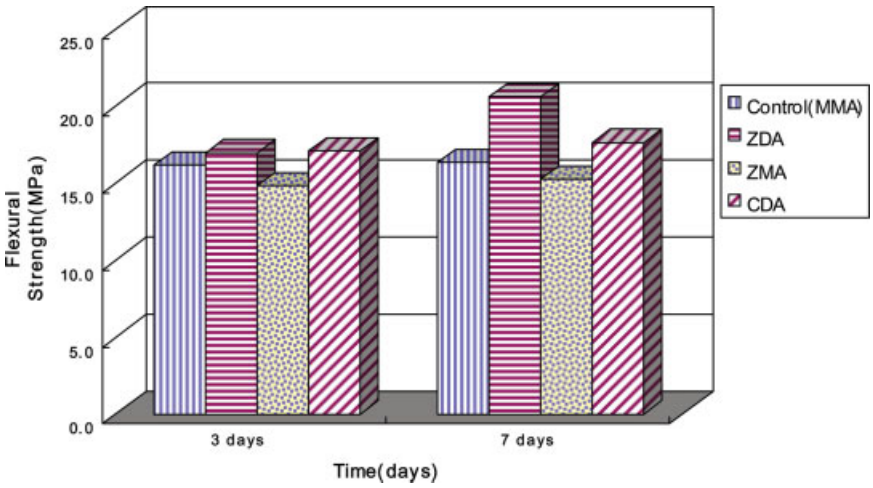

Figure 3 Flexural strength versus time for MMA-based PC with 5.0 wt % metallic monomer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fects were related to the curing times of the specimens. For short curing times, the improvement in the flexural strength was lower than that for longer curing times.

At an age of 3 days, a maximum improvement of 5.0% over the control was obtained when the ZDA concentration was 5.0% of the resins. However, the flexural strength was not further increased when the ZDA concentration exceeded 5.0% of the resins. For the batches with ZMA, the flexural strength decreased with increasing ZMA. ZMA did not improve the flexural strength in comparison with the control. Although an improvement of about 26% was obtained with the addition of ZMA, this value was not representative. Incomplete mixing indicated by concentrated ZMA deposits present on the top surface of the specimens caused the flexural strength of the specimens to vary greatly. Unlike the zinc monomers (ZDA and ZMA), CDA had a positive effect on the flexural strength of PC. The flexural strength increased with increasing CDA. A 21.7% improvement over the control was obtained at an age of 3 days when the CDA concentration was 15.0% of the resins.

Figure 3 illustrates that the flexural strengths increased with time. The flexural strength for the batch with 5.0% ZDA increased by 21.4% from 17.0 to 20.6 MPa (2462 to 2989 psi) for 3 and 7 days, respectively. For the batch with 5.0% ZDA, the flexural strength increased by 10.5% from 14.8 to 16.4 MPa (from 2150 to 2375 psi) for 3 and 7 days, respectively. For 5.0% CDA modified MMA-based PC, the flexural strength increased by 3.2% from 17.1 to 17.6 MPa (from 2479 to 2558 psi) for 3 and 7 days, respectively. For the control, the flexural strength varied slightly between 3 and 7 days: 16.2 and 16.3 MPa (2345 and 2370 psi), respectively. Therefore, a high increase in the flexural strength for batches with the metallic monomers was expected to be obtained after longer curing times. Again, it could be seen that the batches with zinc monomers had a slower flexural strength gain than the control and the batch with CDA.

On the basis of the compressive and flexural strength testing results, it is suggested that the addition of zinc may have delayed the strength gain of MMA-based PC, and a postthermal cure after a 24-h room-temperature cure may be necessary to achieve high early strength.

Bond strength

The addition of 5.0 wt % metallic monomer to MMA-based PC was used to evaluate the effect of these monomers on the bond strength between PC and a steel rod. The test was performed at an age of 14 days. The results are given in Table V. All three metallic monomers significantly improved the bond strength. Increases of 56, 27, and 36% in the bond strength over the control were obtained for additions of ZDA, ZMA, and CDA, respectively. The significant improvement in the bond strength indicates that these metallic monomers offer better opportunity for MMA-based PC to be used as a repair material. As in the other tests,

TABLE V
Summary of the Bond Strength in MMA-Based PC with 5.0% Metallic Monomer

Specimen	Ultimate load [kN (lb)]	Average bond strength [MPa (psi)]	Failure zone
ZDA–PC	31.6 (7100)	7.3 (1062)	Interface
ZMA–PC	25.4 (5700)	6.0 (863)	Interface
CDA–PC	27.1 (6100)	6.4 (925)	Interface
Control	20.0 (4500)	4.7 (680)	Interface

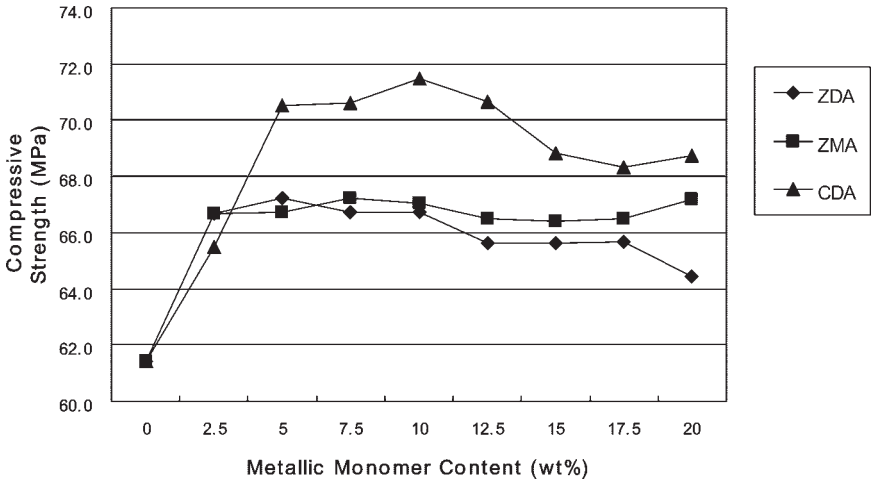

Figure 4 Influence of the metallic monomer on the compressive strength of polyester PC.

ZDA performed best among the three metallic monomers for bond strength in MMA-based PC.

Maintaining a vertical alignment of the steel rod in the specimens was crucial to the test. The test values and failure modes were significantly changed when the steel rod was not vertically cast in the specimens. The typical failure zone occurred at the interface between the PC base and the steel rod. After the steel rod was pulled out, a hole was left in the specimen without any damage around the hole. In this test, the values were discarded when the failure zone did not occur at the interface.

Polyester PC system

Compressive strength

The influence of the metallic monomers on the compressive strength of polyester PCs incorporating different levels of the metallic monomers is shown in Figure 4. In general, all three metallic monomers increased the compressive strength. Basically, ZDA and ZMA behaved similarly. At low contents, the compressive strength was increased with increasing levels of ZDA and ZMA up to a certain amount. A maximum increase of approximately 10% in the compressive strength could be obtained over the control when the concentrations of ZDA and ZMA ranged from 5.0 to 7.5% of the resin. CDA performed better than ZDA and ZMA. For instance, the compressive strength was increased by 15% over the control for 5.0% calcium. The maximum increase in the compressive strength was obtained when the CDA concentration was around 10% of the resin, above which the compressive strength tended to decrease. The difference in the effects on the compressive strength for the three metallic monomers was related to their different soluble behaviors in the polyester resin. ZMA and ZDA had better solubility in the polyester resin but less effect on the compressive strength of polyester PC in comparison with CDA. In other words, the good solubility of the metallic monomers improved the compressive strength. Although CDA did not dissolve well in polyester, it significantly enhanced the compressive strength of polyester PC.

Flexural strength

Figure 5 schematically shows the influence of the metallic monomers on the flexural strength of polyester PC. Generally, the addition of the metallic monomers to polyester PC led to a considerable improvement in the flexural strength, except that they behaved in a different manner. For the batches with ZDA or ZMA, the flexural strength was increased with increasing levels. The flexural strength increased faster at low concentrations of ZDA and ZMA than at higher concentrations. The maximum increase in the flexural strength was found to be about 20% over the control when the ZDA or ZMA concentration was 20% of the resin. Unlike ZDA or ZMA, CDA enhanced the flexural strength in a different manner. At low concentrations, the flexural strength increased with increasing levels. The maximum increase in the flexural strength was obtained when its concentration was around 10% of the resin, above which the flexural strength tended to decrease.

Bond strength

Twenty-four specimens were cast and tested. The addition of the metallic monomers to polyester PC was 5.0% of the resin for each. The test was performed at ages of 6 and 24 h. The test results are tabulated in Table VI, which indicates that the bond strength of

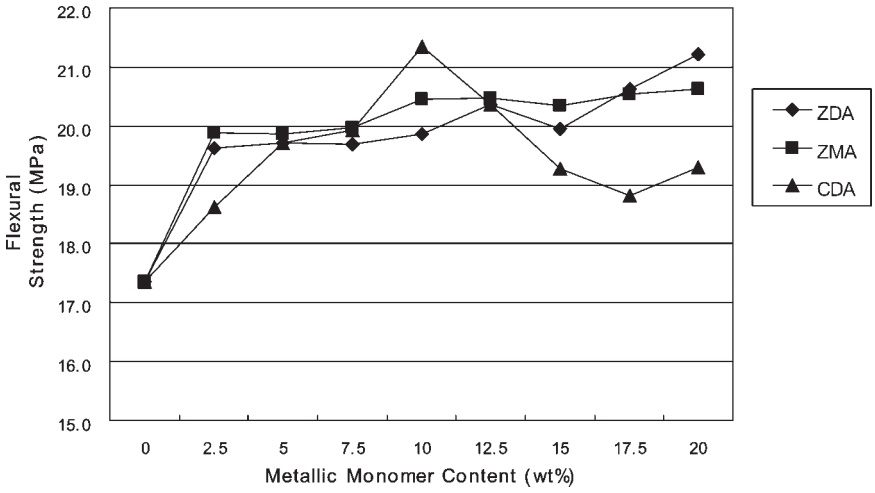

Figure 5 Influence of the metallic monomer on the flexural strength of polyester PC.

polyester PC was significantly increased by the addition of the metallic monomers. At an age of 24 h, for instance, increases of 24, 18, and 27% in the bond strength over the control were obtained for additions of ZDA, ZMA, and CDA, respectively. The significant improvement in the bond strength indicates that metallic-monomer-modified polyester PC offers a better opportunity of being used as a repair material than unmodified polyester PC.

As mentioned before, the typical failure zone occurred at the interface between PC and the steel rod when the steel rod was pulled out.

CONCLUSIONS

On the basis of the test results, the following conclusions can be made.

1. The compressive strength was improved significantly with the addition of all three metallic monomers, except for ZMA in the MMA-based PC system. ZMA had an unpredictable influence on the compressive strength in the MMA-based PC system because of its solubility problem. In the MMA-based PC system, the compressive strength increased with increasing levels of ZDA and CDA. ZDA improved the compressive strength more than CDA at low levels. An increase of about 11% in the compressive strength over the control was obtained with the addition of 7.5 and 15% ZDA and CDA, respectively. In the polyester PC system, the compressive strength was increased with increasing levels of the metallic monomers up to certain amount, which was about 5.0% for ZDA and ZMA and 10.0% for CDA. CDA improved the compressive strength more than the others.
2. All three metallic monomers had a significant effect on the flexural strength in the MMA and polyester PC systems except for ZMA in the MMA system. ZMA had an unpredictable influence on the flexural strength in the MMA-based PC system because of its solubility problem. For the MMA-based PC system, the flexural strength increased with increasing levels of CDA. Also, the flexural strength was increased with additional levels of ZDA up to 5.0%. For the polyester PC system, the flexural strength was increased with increasing levels of ZDA and ZMA. An increase of 20% in the flexural strength over the control was obtained with the additional level of 20% for ZDA and ZMA. In addition, CDA improved the flexural strength more than ZDA and ZMA and imparted the maximum improvement when its concentration was around 10%.
3. The bond strength was increased significantly with the addition of 5.0% of each of the three metallic monomers for the MMA-based and polyester PCs. The metallic monomers improved the bond strength more in the MMA-based PC than the polyester PC. ZDA performed best among the three metallic monomers.

TABLE VI
Summary of the Bond Strength in Polyester PC with 5.0% Metallic Monomer

Specimen	Average bond strength at 6 h [MPa (psi)]	Average bond strength at 24 h [MPa (psi)]	Failure zone
ZDA–PC	2.8 (404)	3.5 (510)	Interface
ZMA–PC	3.0 (440)	3.3 (483)	Interface
CDA–PC	3.1 (453)	3.6 (520)	Interface
Control	1.9 (274)	2.8 (410)	Interface

4. ZDA and ZMA may have delayed the strength gain of MMA-based and polyester PCs, and a postthermal cure after a 24-h room-temperature cure may be necessary to achieve an early strength.

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