Influences of Metallic Polymeric Materials on the Properties of Fresh Polyester and Acrylic Polymer Concrete

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ABSTRACT: To investigate the influences of three metallic polymeric materials in polyester and acrylic fresh polymer concretes (PCs), PC-incorporated different levels of these materials have been investigated for their properties of fresh PC. The mix design was made and optimized for workability, strength, and economy, depending on the resin viscosity, the intended use, and the additional quantities of these polymeric materials. The properties investigated include workability, working time, and curing time of fresh PC. It is concluded that these polymeric materials offer the possibility of improving properties of polyester and acrylic fresh polymer concretes. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2337–2343, 2006

Key words: metallic monomers; fresh polymer concrete; workability; working time; curing time

INTRODUCTION

Most polymer concretes (PCs) have high strength in compression and flexure, provides excellent bonding properties, and is waterproof and resistant to corrosion.[1] PC will provide a longer, maintenance-free service life, because the durability and physical properties are superior to those of the portland cement concrete.[2] Also, PC is able to cure within one or two hours. For these reasons, it has been used to repair portland cement concrete and overlay bridge decks, parking garage decks, and industrial floors. Broader utilization of PC in load-bearing elements is presently taking place in machine tool bases, gear pump base plates, and utility vaults.[3]

Metallic monomer powders, products of *S*-company, 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 strength of PC. In addition, metallic elements in molecules will possibly impart an effect on the adhesion between resin and aggregates or steel used in concrete. However, the effect of metallic monomers on fresh PCs has not been documented.

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The purpose of this study was to evaluate the properties of the fresh PC, using the commercial metallic monomer powders.

MATERIALS

Two types of PCs were employed in this research. This section discusses the materials used in making the PC.

Resins or liquid monomers

Two different resins were used in making the PC. 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. Also, polyester PC was made from unsaturated polyester resin, a viscous liquid resin with a styrene monomer content of 43.9.

Initiators

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

Promoters

Also, two promoters were used in each PC. 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. They were zinc diacrylate (ZDA), zinc dimethacrylate (ZMA), and calcium diacrylate (CDA). They are white powders, which do not readily dissolve in resins or monomers.

Aggregates

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

Additives

In this study, polymethyl methacrylate (PMMA) was used for MMA PC as a thickening agent. It is a white substance in the form of small solid particles. The PMMA serves as a thickening agent, which makes the freshly-mixed PC more cohesive and workable. It also results in a skin on the PC surface soon after placement, which reduces evaporation of MMA monomer and minimizes the danger of fire.[4]

MIX DESIGN

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

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. The contents of metallic monomer powder were 0–15% of MMA monomer by weight.

TABLE I
Mix Design for MMA 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	0–15%
DMPT	0.18%
Dibenzoyl peroxide (40% dispersion)	5%
PMMA	3.0% of total sand

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	0–20%
6% cobalt-naphthenate	0.48%
MEKP	2.5%

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 metallic monomer powder contents were 0–20% of polyester resin.

EXPERIMENTAL PROGRAM

Mixing

All PC specimens used throughout this study were made at room temperature (70–75°F).

MMA PC system

The monomers, MMA, TMPTMA, and metallic monomer powder, which were weighed separately, were mixed with DMPT and BZP in a mixer for 1 min. Then, the sand premixed with PMMA was added to the monomer mixture and mixed for 3 min. After mixing, the PC was taken out of the mixer and was cast into molds as soon as possible to prevent the loss of workability. The fresh PC specimens were vibrated using a

TABLE III
Effect of Metallic Monomer Powder on Workability of MMA PC

Metallic monomer content based on resins (wt %)	Workability (flow)		
	ZDA-PC	ZMA-PC	CDA-PC
0.0[a]	194	194	194
2.5	194	192	194
5.0	194	192	194
7.5	194	192	194
10.0	194	191	194
15.0	194	191	194

[a] Control sample without metallic monomer.

TABLE IV
Effect of Metallic Monomer Powder on Workability of Polyester PC

Metallic monomer content based on resins (wt %)	Workability (flow)		
	ZDA-PC	ZMA-PC	CDA-PC
0.0[a]	148	148	148
2.5	149	150	147
5.0	150	152	146
7.5	152	155	144
10.0	154	158	142
12.5	156	160	142
15.0	156	164	140
17.5	158	164	138
20.0	158	165	136

[a] Control sample without metallic monomer.

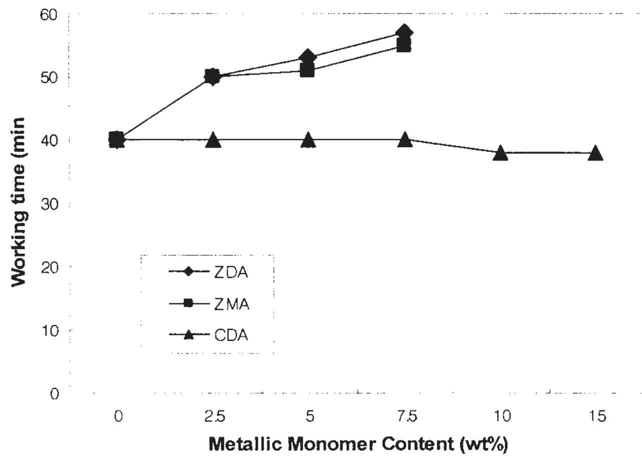

Figure 1 Comparison of working times of MMA PC with three metallic monomer powders.

table external vibrator for 15 s. The PC surfaces were smoothly finished by the use of trowels. All specimens were cured and remained at room temperature before testing.

Polyester PC system

The polyester resin and the metallic monomer, which were weighed separately, were mixed with cobalt and MEKP in a mixer for 1 min. Then, the sand was added to the monomer mixture and mixed for 3 min. After mixing, the same procedure was used as for the MMA PC for placing and curing the polyester PC.

Testing procedure

There are no standard tests that are directly applicable to PC. Therefore, ASTM standards developed for cement-based materials were used as guidelines, whenever applicable.[1,4]

Workability

The workability of fresh PC at room temperature was measured in accordance with ASTM C 230–90 and C 109–92.[5] The fresh PC was uniformly placed into the flow mold at the center of the flow-table top. The mold was gently lifted away from the fresh PC 1 min after completing the mixing operation. Immediately, the flow table was dropped 25 times in 15 s. The flow was then determined by measuring the diameter of the fresh concrete at four equal intervals. The increase in diameter was averaged and workability was expressed as a percentage of the original base diameter.[6]

Working time

The working time of the PC at room temperature was determined using the method described in JIS (Japanese Industrial Standard) A 1186 "Method of Measurement for Working Life of Unsaturated Polyester Resin Concrete."[7] The finger-touch method was used to measure the working life. Samples of the fresh PC in volumes ~20 cm^3 were packed and sealed in polyethylene film bags secured with a rubber band. The moldable PC was monitored at frequent intervals by feeling the sample through the sides of the bag. As soon as the sample became noticeably stiffer in form, the time was noted and recorded as the end of working time. The

TABLE V
Effect of Metallic Monomer Powder on Working Times for MMA PC System

Metallic monomer (wt %)	ZDA-PC		ZMA-PC		CDA-PC	
	Promoter content (wt%)	Working time (min)	Promoter content (wt%)	Working time (min)	Promoter content (wt %)	Working time (min)
0.0[a]	0.0	40	0.0	40	0.0	40
2.5	0.40	50	0.4	50	0.0	40
5.0	0.45	53	0.45	51	0.0	40
7.5	0.50	57	0.50	55	0.0	40
10.0	—	—	—	—	0.0	38
15.0	—	—	—	—	0.0	38

[a] Control sample without metallic monomer.

TABLE VI
Effect of Metallic Monomer Powder on Working Times for Polyester PC System

Metallic monomer (wt %)	ZDA-PC Promoter content (wt %)	ZDA-PC Working time (min)	ZMA-PC Promoter content (wt %)	ZMA-PC Working time (min)	CDA-PC Promoter content (wt %)	CDA-PC Working time (min)
0.0[a]	0.0	40	0.0	40	0.0	40
2.5	0.40	85	0.4	70	0.0	39
5.0	0.45	90	0.45	70	0.0	38
7.5	0.50	80	0.50	65	0.0	34
10.0	0.55	85	0.55	65	0.0	32
12.5	0.60	80	0.60	60	0.0	31
15.0	0.65	80	0.65	60	0.0	31
17.5	0.70	60	0.70	65	0.0	30
20.0	0.75	80	0.75	65	0.0	30

[a] Control sample without metallic monomer.

period from the time of initiation to the end of working time was recorded as the working life.

Curing time

Curing time was measured using the method adopted by The University of Texas Construction Material Research Group (CMRG PC 02), "Method for Determining Cure Times for PC."[8] A thermocouple probe was inserted into the center of mass of the PC specimen while it was still soft. At appropriate intervals, the temperature of the matrix was recorded. The interval between the time of initiation (combination of the initiator and the promoter in the matrix) until the time of peak exotherm (the highest temperature) was considered the curing time.

TEST RESULTS AND DISCUSSION

Workability

It can be seen from Table III that the metallic monomer powders did not have a significant effect on workability of MMA PC. The flow of fresh MMA PC with metallic monomer powder was almost the same as that of the control, regardless of the quantities of metallic monomers. This was related to the fact that all three monomers did not dissolve or swell in MMA monomer, and the viscosity of the MMA monomer was not changed with the addition of those monomers. It was apparent that the workability of fresh MMA PC depends primarily on the MMA monomer content when the fineness modulus of the sand remains constant.

Table IV shows that the metallic monomers have an effect on the workability of polyester PC, especially, when PC incorporated high amount of these materials. Specifically, the workability of fresh polyester PC incorporating ZDA or ZMA increased with increasing levels of ZDA or ZMA. However, the workability of fresh polyester PC incorporating CDA decreased with increasing levels. This was due to the fact that ZDA and ZMA did dissolve in polyester resin, and the viscosity of the resin was decreased with their addition; however, CDA formed small solid particles instead of dissolving in the resin, resulting in loss of workability. Note that the workability of polyester PC depends primarily on the resin to aggregate ratio that remains constant.

Working time

Working time is a very important factor that influences the casting operation and the quality of the product. In general, a feasible cure system for PC is designed for working time (working life) in the range of 15 min to 1 h at normal room temperature (70–75°F).[1] Longer times allow too much monomer evaporation, and faster times do not allow enough batching and placement time.

Table V and Figure 1 show the effects of metallic monomers on working times of MMA PC. The work-

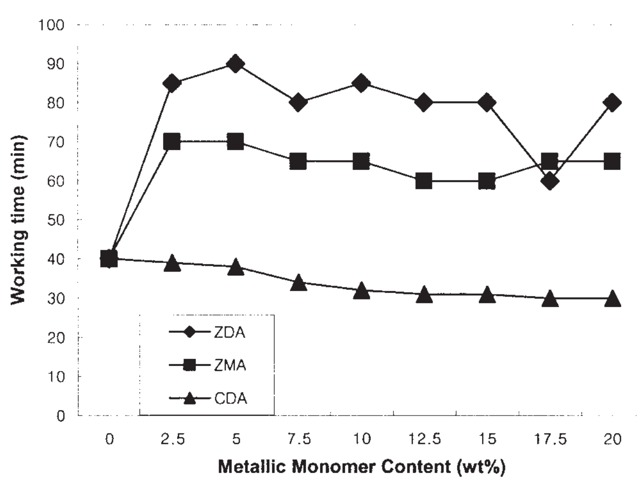

Figure 2 Comparison of working times of polyester PC with three metallic monomer powders.

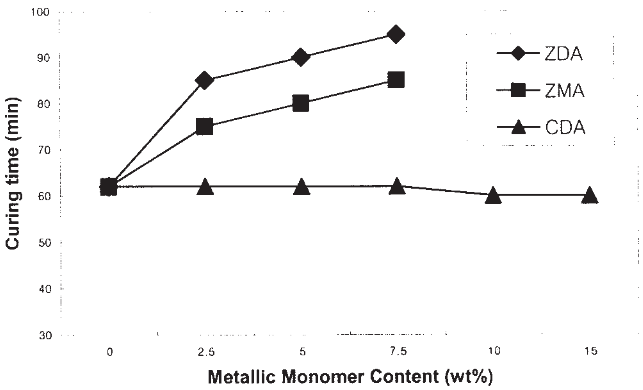

Figure 3 Comparison of working times of PC with and without 5.0 wt % metallic monomer powder.

ing time of the MMA PC without metallic monomer was 40 min. Also, the working time of the MMA PC with CDA was about 40 min, regardless of additional quantities. However, the working times for batches with ZDA and ZMA were increased with increasing additions of ZDA and ZMA. For example, the working time was about 55 min for batches with 7.5 wt % ZDA or ZMA, which is 15 min more than that of the control. It is suggested that ZDA and ZMA delayed chemical reactions, which in turn prolonged the working times.

Basically, metallic monomers had a great effect on the working time of polyester PC as shown in Table VI and Figure 2. It can be seen that the working time was about five times that of the control for the batches with ZDA and ZMA, but a little less than that of the control for the batch with CDA. In other words, ZDA and ZMA significantly increased the working time; however, CDA slightly decreased the working time. Furthermore, ZDA affected working time more than ZMA. The content of the metallic monomer in mix was 5.0% of resin for each of the three materials.

It has been found from Figure 2 that the working times for batches with 5.0% ZDA and ZMA were 2 h at room temperature, which is too long in practice. On the other hand, the working time for batches with 5.0% CDA was about 20 min at room temperature, which is a little short to place PC in practice. Therefore, the quantities of the promoter used in this system were varied in different batches to obtain a target working time of about 1 h, as shown in Tables V and VI, which summarizes the resulting working times corresponding to the quantities of promoter and metallic monomer. Specifically, the amount of promoter used for the batches with ZDA and ZMA was increased with increasing quantities of ZDA and ZMA, since 1 h working time at room temperature was the target value. No promoter was added to the batches with CDA and the control, because the working times of those batches were already in the range expected at room temperature.

It should be noted that polyester used in this study was prepromoted by the manufacturer, and the content of the prepromoter was not released by the manufacturer. Additionally, because the test for working times listed in Table V and VI was performed during summer and the temperature of the test room sometime was much higher than 73°F, longer working times might be expected at room temperature (70–75°F).

Figure 3 shows the comparison of working times for PC with or without 5 wt % metallic monomer.

Curing time

It was observed that the curing times ranged from 1 to 2 h for the system. This is typical for MMA systems with 40–60 min of working time. Tables VII and VIII show the effect of metallic monomer powder on curing times for MMA and Polyester PC. The curing time for controls (without metallic monomer) was 62 min. However, the curing increased with increasing amount of ZDA and ZMA. For example, increases of about 30 and 20 min in curing time were obtained due to the addition of each of 7.5 wt % ZDA and ZMA, respectively. For the batches with CDA, the curing times were almost the same as that of the control. Therefore, it is suggested that to achieve comparable

TABLE VII
Effect of Metallic Monomer Powder on Curing Times for MMA PC System

	ZDA-PC		ZMA-PC		CDA-PC	
Metallic monomer (wt %)	Promoter content (wt %)	Curing time (min)	Promoter content (wt %)	Curing time (min)	Promoter content (wt %)	Curing time (min)
0.0[a]	0.0	62	0.0	62	0.0	62
2.5	0.40	85	0.40	75	0.0	62
5.0	0.45	90	0.45	80	0.0	62
7.5	0.50	95	0.50	84	0.0	62
10.0	—	—	—	—	0.0	60
15.0	—	—	—	—	0.0	60

[a] Control sample without metallic monomer.

TABLE VIII
Effect of Metallic Monomer Powder on Curing Times for Polyester PC System

Metallic monomer (wt %)	ZDA-PC Promoter content (wt %)	ZDA-PC Curing time (min)	ZMA-PC Promoter content (wt %)	ZMA-PC Curing time (min)	CDA-PC Promoter content (wt %)	CDA-PC Curing time (min)
0.0[a]	0.0	85	0.0	85	0.0	85
2.5	0.40	140	0.40	120	0.0	85
5.0	0.45	145	0.45	120	0.0	85
7.5	0.50	135	0.50	125	0.0	80
10.0	0.55	140	0.55	110	0.0	80
12.5	0.60	135	0.60	115	0.0	75
15.0	0.65	135	0.65	110	0.0	70
17.5	0.70	120	0.70	110	0.0	65
20.0	0.75	140	0.75	115	0.0	65

[a] Control sample without metallic monomer.

curing time as MMA PC (Fig. 4), more promoter will be required when ZMA and ZDA are used.

Figure 5 schematically shows that metallic monomers have a significant effect on the curing time of polyester PC. The curing time of the batches with ZDA and ZMA were about three times that of the control, but the curing time for the batch with CDA was shorter than that of the control. In other words, ZDA and ZMA significantly prolonged the curing time, but CDA slightly shortened the curing time. The batches used for curing time tests shown in Figure 5 were the same as the batches used for working time tests shown in Figure 2. In practice, a feasible curing time for PC is about 2 h at normal room temperature (70–75°F). However, when the promoter content was 0.4% of resin in mix, the curing time for batches with 5.0% ZDA and ZMA was found to be more than 3 h at room temperature, which is often too long (Fig. 6). The greater the level of ZDA and ZMA added to PC, the longer was the curing time of PC. On the other hand, when the promoter content was 0.4% of resin in mix, the curing time for batches with 5.0 wt % CDA was about 65 min at room temperature, which is acceptable. Therefore, the quantities of promoter used in this system were varied as shown in Tables VII and VIII, which summarizes the resulting curing times corresponding to the quantities of promoter and metallic monomer. Specifically, the amounts of promoter used for the batches with ZDA and ZMA were increased with increasing additional levels. Two hours curing time at room temperature was desired to avoid loss of resin because of evaporation. No promoter was added to the batches with CDA and the control.

CONCLUSION

The objective of this study was to investigate the influences of three metallic monomers (ZDA, ZMA and CDA) on the properties of fresh PCs and to evaluate the feasibility of commercial use for these materials in PCs. MMA and polyester PCs were used for this study. Laboratory tests were performed to determine

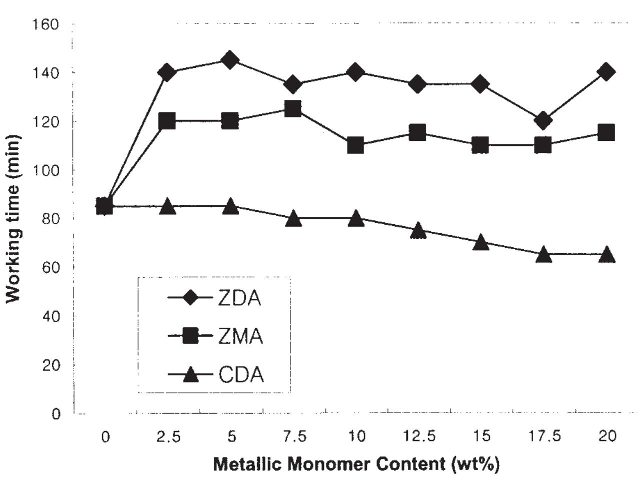

Figure 4 Comparison of curing times of MMA PC with three metallic monomer powders.

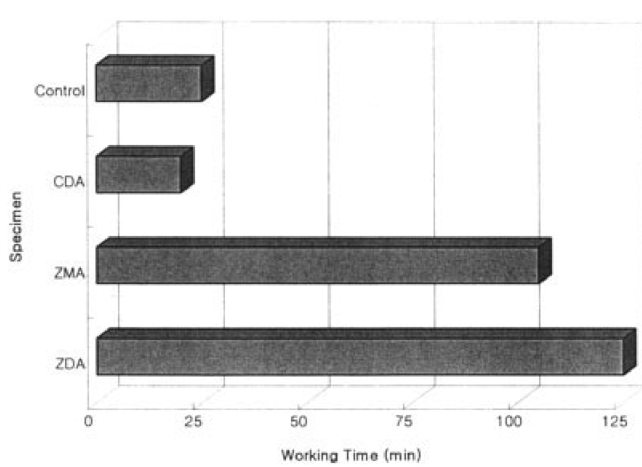

Figure 5 Comparison of curing times of polyester PC with three metallic monomer powders.

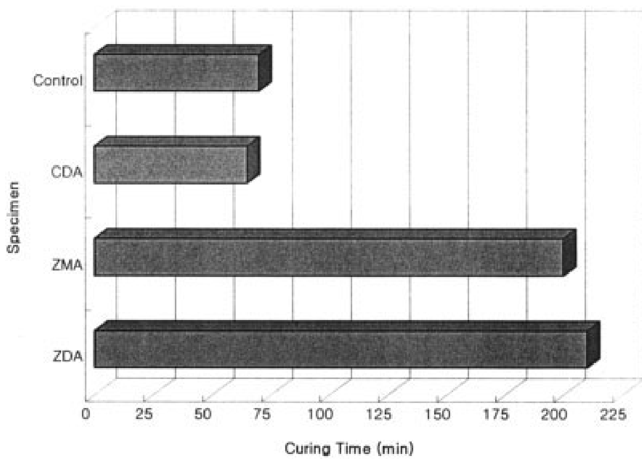

Figure 6 Comparison of curing times of PC with and without 5.0 wt % metallic monomer powder.

the effects of different variables on the workability, working time, and curing time. The variables were the amount of metallic monomer powders.

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

1. All three metallic monomer powders did not dissolve in MMA monomer and did not influence the workability of MMA PC. ZDA and ZMA improved the workability of polyester PC, but CDA reduced the workability of polyester PC.
2. Reasonable working time and curing time can be obtained by adjusting the amount of promoter for the level and type of metallic monomer added to the PC systems. Zinc monomers are retarders for MMA and polyester PC systems, hence more promoter is needed to achieve a feasible cure system whenever a large amount of ZDA and ZMA is used. CDA acts as a promoter or copromoter for polyester systems; hence, few promoters are required to achieve adequate working times and curing times whenever a large amount of CDA is used.
3. ZDA and ZMA may have delayed the strength gain of MMA and polyester PCs, and a post-thermal cure after a 24-h room temperature cure may be necessary to achieve an early strength.

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