



Evaluation of Chemical Resistance of Polymer Concrete in Corrosive Environments

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Abstract: Polymer concrete (PC) with suitable mechanical and chemical properties was prepared. The properties of PCs are dependent upon the type of resins and filler materials. This research paper presents an assessment of the chemical resistance of polymer concretes in various chemical compositions. Epoxy resin was used to fabricate PC samples. The sample blocks were exposed to hostile environment in strong acidic and alkali conditions. The loss of compressive strength of the samples exposed to corrosive environment was insignificant. The strength of corrosive environment had significant effect on the chemical resistance of the fabricated PC samples. A desired blend of the optimized chemical composition of epoxy was used and tested in all corrosive environments. These samples were successfully passed all the designed testing conditions.

Key words: Chemical resistance • Polymer concrete • Filler • Epoxy resin • Corrosive environment

INTRODUCTION

Polymer concretes have gained great popularity and used as building materials over the past four decades [1, 2]. PC is a composite material which is composed of resins as a binder of aggregates [3]. They represent a new generation of efficient and chemical resistant materials. Due to their great physical properties such as low porosity and wear resistance, they are used in bridges, tunnel linings, floors, dams, acid tanks and hazardous waste containments [4-6]. The rate of increase in PC strength at earlier ages of their use is low when compared to ordinary Portland cement; in long term, PC may gain equivalent or even higher strengths [7, 8].

Concrete structures may be exposed to corrosive environments. In conventional concretes, the alkaline Portland hydraulic cement forms voids and cracks during hydration. Water can penetrate and crack the concrete. So the concrete can be easily attacked by acidic substances and may fail or damage after only few years of use. However, use of several types of resins such as polyester-styrene, epoxy, furan and vinyl ester eliminates open voids in PC. Also, Polymers are hydrophobic in

nature and resist in hostile environments [9, 10]. Therefore, use of PC in structures under conditions of exposure to various aggressive media without additional chemical protection is recommended. Numerous investigations of the corrosion resistance of polymer concretes of various compositions were carried out.

Mani *et al.* [11] have investigated a comparative study of epoxy and polyester resin-based polymer concretes. They have found that chemical resistance of the polymer concretes is remarkably higher than that of the cement concrete. Polymer concrete showed weak chemical resistance in the presence of CaCO₃ micro filler. Pacheco-Torgal and Jalali [12] have investigated sulphuric acid resistance of plain, polymer modified and fly ash cement concretes. Their results have shown that use of concrete with polymer addition during the mixing phase had minor beneficial effect on durability and acid resistance of the concrete pipe samples. Monteny *et al.* [13] have conducted several chemical and microbiological tests to simulate sulfuric acid corrosion of the polymer-modified concrete. They have used five different concrete compositions in their testing samples, including a reference mixture with high sulfate resistant Portland

cement and four different polymer cement concrete such as acrylic ester and styrene–acrylic ester polymer, styrene butadiene polymer and vinyl copolymer. They have found that concrete composition with the styrene–acrylic ester polymer showed the highest resistance while the compositions with the acrylic polymer and the styrene butadiene polymer had a lower resistance than the reference mixture.

The purpose of present research paper was to investigate chemical resistances of the fabricated PC and define a suitable composition to have strong resistance in extremely corrosive environments.

MATERIALS AND METHODS

Materials

Resin and Hardener: Epoxy resin based on Bisphenol A, supplied by Honsman Company was used for specimen preparation. The principal chemical reaction for epoxy production is shown in Figure 1. No solvent or diluent was added to prevent any possible changes in chemical properties of the samples. A polyamine hardening agent with chemical structure of tetra-amine 3-ethylene with commercial code of HA-11 supplied by Merck (Darmstadt, Germany) was used. The ratio of resin: hardener was 2:1. The resin and hardener specific gravities at 25°C were 1.18 and 1.07 g/cm³, respectively.

Filler and Aggregate: Often, silica powder, calcium carbonate, talc powder, Portland cement, fly ash and calcium sulphate are well-known as fillers. In this study, fly ash and silica powder were used. Fly ash was obtained from coal fire unit. The coal was supplied from Zirab (Mazandaran, Iran) mines. Three different gradation of silica powder which was used in all sets of experiments are as follow:

- Fine silica powder (S₁) with average particle size of 50-60 μm.
- Medium size silica powder (S₂) with average particle size of 600 μm.
- Coarse silica (S₃) with average particle size of 1100 μm.

Four types of blends of fillers were prepared. The F was pure fly ash, type Sa was a combination of S₁ and S₂ silica powder. Type Sb was a mixture of all silica powders and Sc was a blend of S₂ and S₃. The compositions of mixed fillers are summarized in Table 1.

Table 1: Mix proportion and combination of fillers

	F(Fly ash)	S ₁	S ₂	S ₃
F	100%	-	-	-
Sa	-	20%	80%	-
Sb	-	15%	25%	60%
Sc	-	-	40%	60%

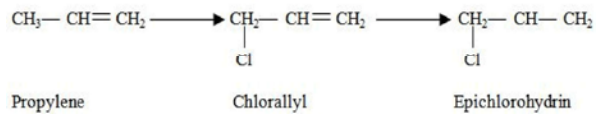


Fig. 1: Chemical reaction for epoxy formation

Considering gradation curve based on ASTM C33 [14], dolomite aggregate was obtained from Ganjafrouz Lahimchi’s crusher (Babol, Mazandaran, Iran). The dolomite particle size was in the range of standard and the particle size was less than 4.75 mm. The size distribution is shown in Figure 2.

Methods: Several specimens with various compositions of resin and filler were prepared. The procedure of specimen formation is illustrated in Figure 3. According to ASTM C579 [15], the compressive strength of the samples with different composition, type of resin and epoxy were measured. Also, based on ASTM C413 [16] and ASTM C905 [17], absorption and apparent density tests were performed. The specimen which had the lowest permeability and the highest density and strength was selected and the chemical strength test according to ASTM C267 [18] was conducted. All specimens dimensions were 5 × 5 × 5 cm and had uniform shape. Chemical strength test was performed in 14-day exposure cycles to an aggressive medium (7-day exposure and 7-day drying in ambient temperature). Before and after each test cycle all specimens were weighed. Prior to immersion, a brief description of the specimen characteristics such as color, surface appearance and the color and clarity of the testing medium was recorded. Then, the specimens were immersed in suitable uniform containers with the related media. For each specimen, 150 ml of aggressive solution was introduced into the container. Rate of chemical degradation was determined after 7, 14, 28 and 56 days of immersion. For every new cycle, the test medium was replaced with fresh media solution. The recorded data were the mean of three individual values for all specimens.

Sodium hydroxide solution (15, 30 and 60 wt%), Hydrochloric acid (15, 30 and 60 wt%), sulfuric acid (15, 30 and 60 wt%), citric acid (15, 30 and 60 wt%) and acetic acid (15, 30 and 60 wt%) were 5 aggressive environments which were used for testing specimens.

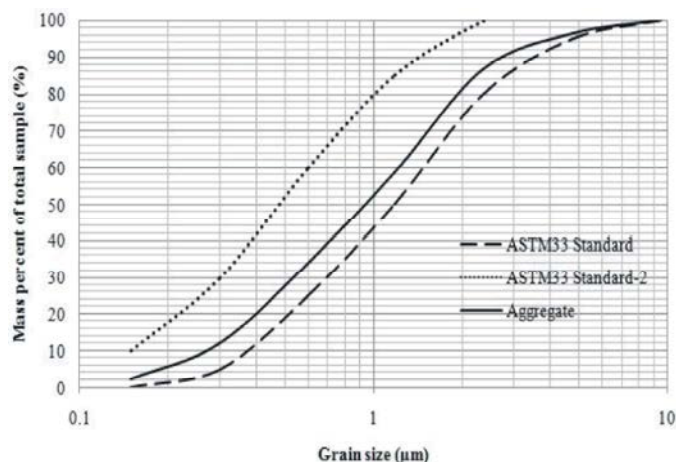


Fig. 2: Gradation curve and size distribution of the used aggregates

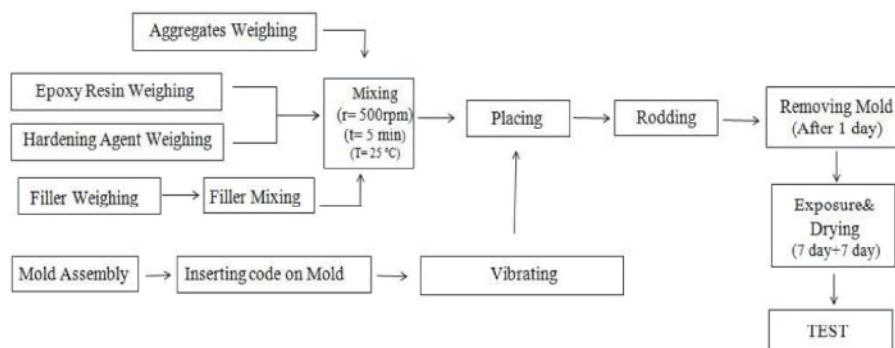


Fig. 3: Polymer concrete specimen production procedure

RESULTS AND DISCUSSION

Epoxy resins and fillers were blended for specimen preparation. The specimen type is represented by a code in which EP is the type of the resin (epoxy) and its subscript shows the percentage of epoxy used in PC sample. The last entry in coding is the type of the filler and the subscript indicates weight percentage of filler in PC. The coding served for recording chemical composition of the prepared samples. The physical properties and various compositions of the tested samples are shown in Table 2. It was clear that changes in type and composition of filler and resin resulted in changes in water absorption, density and strength of PC. Fly ash and silica powders were made of fine particles. This will lead to a dense and low porous mixture. Since the dense and almost non-porous PC sample having limited diffusion, therefore penetration of chemicals and corrosion is reduced. Among the specimens summarized in Table 2, PC type EP₁₅-Sb₂₀₀ due to its high density and low water absorption was selected for testing chemical resistance. Prior to chemical resistance test, the compressive strength, flexural strength and Modulus of

rupture of EP₁₅-Sb₂₀₀ were 70.2, 8.23 and 14.2 MPa, respectively. The composition of the selected specimen (EP₁₅-Sb₂₀₀) is presented in Table 3.

Based on chemical nature of specimen material, the rate of weight and stability changes with respect to time is of more significance than the actual value at any time. Therefore, for evaluation of chemical resistance of the selected PC in different aggressive environments, two parameters were evaluated W.c.% and C.c.s.%, where W.c.% is weight change and C.c.s.% is defined as change in compressive strength of PC. The two parameters are described as follow:

$$W.c.\% = \frac{C_2 - C_1}{C_1} \times 100$$

$$C.c.s.\% = \frac{CS_2 - CS_1}{CS_1} \times 100$$

Which C₂ is weight of specimen before exposure cycle and C₁ is weight of specimen after immersion in aggressive solution. CS₂ and CS₁ are compressive strength of PC before and after the exposure cycle, respectively. The following codes were used in chemical resistance tests:

Table 2: Physical properties of PC specimens

PC type	Water absorption (%)	Density (g/cm ³)	PC type	Water absorption (%)	Density (g/cm ³)	PC type	Water absorption (%)	Density (g/cm ³)
EP ₁₀ -F ₄₀	0.137	2.076	EP ₁₅ -F ₄₀	0.073	2.286	EP ₂₀ -F ₄₀	0.097	2.183
EP ₁₀ -F ₇₀	0.119	2.236	EP ₁₅ -F ₇₀	0.067	2.225	EP ₂₀ -F ₇₀	0.87	2.312
EP ₁₀ -F ₁₀₀	0.086	2.283	EP ₁₅ -F ₁₀₀	0.074	2.17	EP ₂₀ -F ₁₀₀	0.96	2.316
EP ₁₀ -Sa ₁₀₀	0.14	2.252	EP ₁₅ -Sa ₁₀₀	0.085	2.28	EP ₂₀ -Sa ₁₀₀	0.64	2.150
EP ₁₀ -Sa ₁₅₀	0.13	2.283	EP ₁₅ -Sa ₁₅₀	0.081	2.31	EP ₂₀ -Sa ₁₅₀	0.73	2.182
EP ₁₀ -Sa ₂₀₀	0.11	2.156	EP ₁₅ -Sa ₂₀₀	0.096	2.352	EP ₂₀ -Sa ₂₀₀	0.76	2.163
EP ₁₀ -Sb ₁₀₀	0.137	2.153	EP ₁₅ -Sb ₁₀₀	0.073	2.212	EP ₂₀ -Sb ₁₀₀	0.66	2.190
EP ₁₀ -Sb ₁₅₀	0.122	2.226	EP ₁₅ -Sb ₁₅₀	0.06	2.298	EP ₂₀ -Sb ₁₅₀	0.71	2.215
EP ₁₀ -Sb ₂₀₀	0.113	2.203	EP ₁₅ -Sb ₂₀₀	0.054	2.310	EP ₂₀ -Sb ₂₀₀	0.78	2.232
EP ₁₀ -Sc ₁₀₀	0.19	2.103	EP ₁₅ -Sc ₁₀₀	0.12	2.287	EP ₂₀ -Sc ₁₀₀	0.73	2.111
EP ₁₀ -Sc ₁₅₀	0.18	2.118	EP ₁₅ -Sc ₁₅₀	0.09	2.253	EP ₂₀ -Sc ₁₅₀	0.76	2.092
EP ₁₀ -Sc ₂₀₀	0.22	2.27	EP ₁₅ -Sc ₂₀₀	0.11	2.112	EP ₂₀ -Sc ₂₀₀	0.81	2.015

Table 3: Polymer concrete composition used in this study

Polymer matrix components (EP ₁₅ -Sb ₂₀₀)	Composition	Total mass %
Resin	Epoxy, Bisphenol-A (Honsman)	10 ^a
Hardening agent	Tetra-amine 3-ethylene with HA-11 (Merck co.)	50 ^b
Sand	Aggregate of Babol Ganjafrouz Lahimchi	55 ^a
Filler	Silica powder	200 ^c

a Percentage in relation to the mass (resin + hardening agent + sand + filler)

b Percentage in relation to the resin mass

c Percentage in relation to the mass (resin + hardening agent)

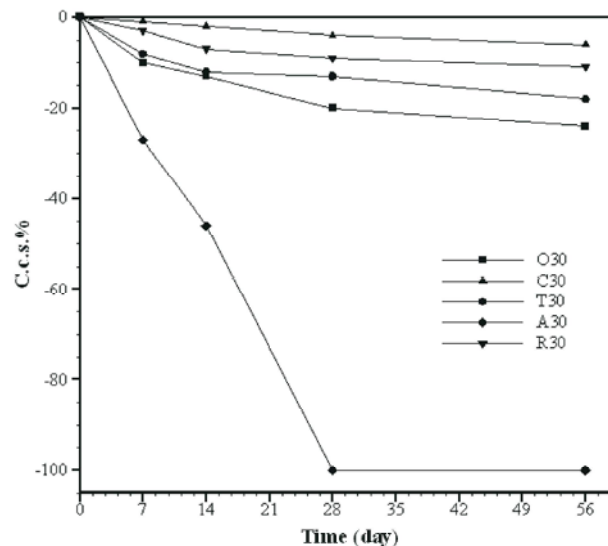


Fig. 4: Effect of various aggressive solutions on C.c.s.% in 30% dilution

A = Acetic acid C = Citric acid O = NaOH R = Hydrochloric acid T = Sulfuric acid and the numbers (15, 30, 60 wt%) present concentrations of the solutions.

The obtained data for the chemical resistance tests are summarized in Table 4. According to ASTM C267 [18], four parameters which are important in chemical resistance tests (weight change percentage, compressive strength change percentage, appearance of specimen and

appearance of the test medium) were evaluated. Based on data presented in the above table it was concluded that, an increase in acid or base concentration has increased the weight changes and compressive strength of the specimens. In most cases except specimens in acetic acid, in concentration below 60 wt% no changes in appearance of the specimens and test medium were observed. However, increasing the concentration above 60 wt% caused surface whitening and slag formation in NaOH solution, color changes in citric acid and hydrochloric

Table 4: Chemical resistance test results

Sodium hydroxide (O)												
Code	O15				O30				O60			
Time (day)	7	14	28	56	7	14	28	56	7	14	28	56
W.c.%	0.1	0.2	0.5	0.9	0.2	0.3	0.5	1	0.5	0.7	0.9	1.3
C.c.s.%	-7	-12	-16	-21	-10	-13	-20	-24	-15	-18	-24	-33
A.s.	a	a	a	a	a	a	a	a	a	a	b	b
A.t.m.	a	a	a	a	a	a	a	a	a	a	d	d
Citric acid (C)												
Code	C15				C30				C60			
Time (day)	7	14	28	56	7	14	28	56	7	14	28	56
W.c.%	0	0	0	0	0	0	0	1	0	0	3	5
C.c.s.%	0	0	-2.2	-5	-1	-2	-4	-6	-2	-3	-6	-7
A.s.	a	a	a	a	a	a	a	a	a	a	c	c
A.t.m.	a	a	a	a	a	a	a	a	a	a	c	c
Sulfuric acid (T)												
Code	S15				S30				S60			
Time (day)	7	14	28	56	7	14	28	56	7	14	28	56
W.c.%	0	0.2	0.5	0.6	0.2	0.5	0.7	0.9	3	5	15	100
C.c.s.%	-5	-8	-10	-12	-8	-12	-13	-18	-10	-18	-33	-100
A.s.	a	a	a	c	a	a	c	c	a	c	g	l
A.t.m.	a	a	a	a	a	a	a	a	a	c	d	l
Hydrochloric acid (R)												
Code	R15				R30				R60			
Time (day)	7	14	28	56	7	14	28	56	7	14	28	56
W.c.%	0	0.1	0.4	0.7	0.2	0.7	1	1.4	0.9	1.6	2.3	3.2
C.c.s.%	0	0	-2.5	-4.2	-1	-3	-4	-5.7	-3.3	-4.2	-5.5	-7.6
A.s.	a	a	a	a	c	c	c	c	a	c	c	c
A.t.m.	a	a	a	a	a	a	a	c	a	a	c	c
Acetic acid (A)												
Code	A15				A30				A60			
Time (day)	7	14	28	56	7	14	28	56	7	14	28	56
W.c.%	-3	-4	-6	-7	-5.2	-7.3	-12	-16.2	-17.9	-20.2	-21	-31.2
C.c.s.%	-13	-19	-24	-42	-27	-46	-100	-100	-43	-64	-100	-100
A.s.	a	c	b	e	f	f	l	l	e	e	g	l
A.t.m.	a	a	a	a	a	c	c	c	a	a	c	c

W.c.%: Weight change %

C.c.s.%: Change in compressive strength %

A.s.: Appearance of specimen

A.t.m.: Appearance of test medium

a: no change

b: surface became white

c: color change

d: slag creation

e: Scab

f: surface Corrosion

g: Protuberance

l: destruction

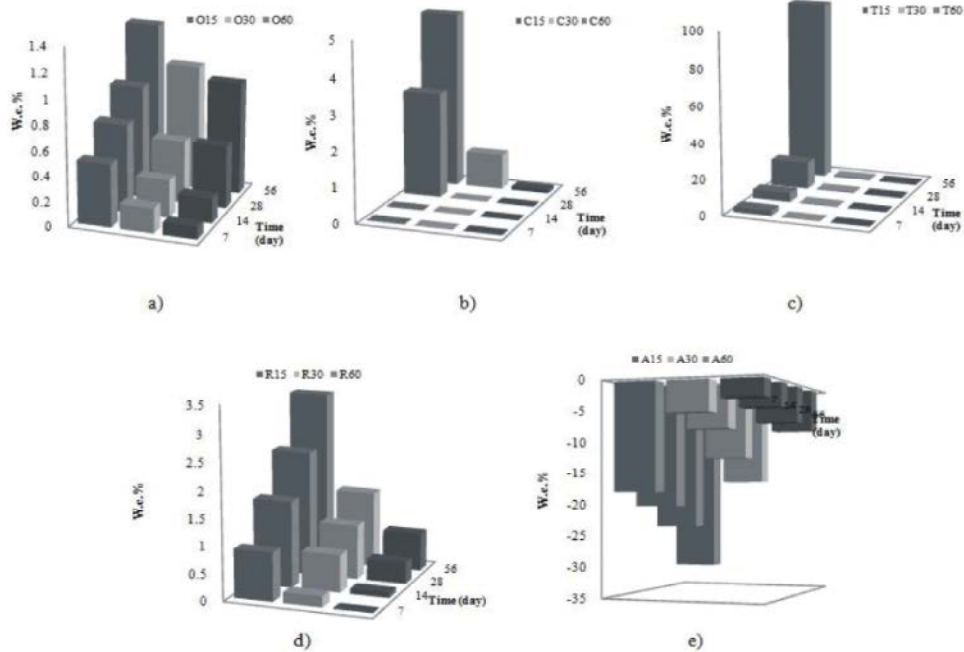


Fig. 5: Weight changes of fabricated samples in a) sodium hydroxide b) citric acid c) Sulfuric acid d) hydrochloric acid e) acetic acid solution

acid solutions, protuberance and destruction in H_2SO_4 and CH_3COOH solution. Furthermore, it was concluded that acetic acid (organic acid) had the toughest effect on weight, compressive strength and appearance change of the specimens.

Figure 4 depicts the effect of various aggressive media on compressive strength changes with respect to time. All the aggressive solutions were 30% diluted. Compressive strength of specimens in inorganic chemical solutions was gradually decreased in duration of immersion cycle (56 days). Loss of the compressive strength of the specimens in contact with 30% solutions of citric and sulfuric acids in a 56 day period was 6 and 18%, respectively. However, specimens in organic solution (acetic acid) had significant losses and the lowest compressive strength and even the entire specimens were degraded after 28 days. The loss of strength in polymer concrete was probably due to the dissociation of the bonds between aggregate material and the polymer matrix. As the chemical strength of the aggressive solution increased the chemical resistances of the PC specimens were progressively decreased.

Figure 5 illustrates the weight loss of various specimens in the aggressive chemicals media. The effect of concentration and types of chemicals were investigated for the duration of 56 days. Figures 5a, 5b and 5d show the chemical resistances of the specimens in NaOH

solution, citric and hydrochloric acids (15, 30 and 60%), respectively. The weight changes of the specimens in NaOH solution, citric and hydrochloric acids (60%) were 1.3, 5 and 3.2%, respectively. Figure 5c represents the chemical resistance of the specimens in sulfuric acid (15, 30 and 60%). Penetration of the diluted acid (H_2SO_4) to PC specimens was limited. As the concentration of the acid increased to 60%, the specimens gained 100% weight, the concentrated acid diffused into the polymer matrices. The weight changes of the PC specimens in acetic acid were negative that was possibly due to molecular size of acetic acid and quick penetration into PC specimens. The weight loss of the specimen is shown in Figure 5e.

CONCLUSIONS

The aim of present study was to evaluate the influence of various chemicals with (15, 30 and 60%) concentrations of aggressive solutions on physical properties (appearance of samples and test medium) and chemical resistance (compressive strength and weight changes) of the fabricated polymer concretes. According to ASTM standards, $EP_{15}-Sb_{200}$ sample was selected for chemical resistance test due to its high density and low permeability. Increasing the concentration of solutions above 60% caused surface whitening and slag formation

in NaOH solution, color changes in citric acid and hydrochloric acid solutions, protuberance and destruction in H₂SO₄ and CH₃COOH solutions. The losses of compressive strength of the samples exposed to acetic acid solution were significant. Furthermore, all the specimens except those in acetic acid solution slightly gained some weight after long duration of immersion in aggressive media. It was concluded that the PC specimens had great chemical resistance in all chemicals except in acetic acid solution; the sample weight lost was about 31%.

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