JOURNAL OF MATERIALS SCIENCE 21 (1986) 341–345

Polymer impregnated concrete

Part 3 *Effect of corrosive environment on strength and durability properties*

KUMUD R. KIRTANIA*, SUKUMAR MAITI‡
Polymer Materials Division, Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

Methyl methacrylate, styrene and acrylonitrile homopolymer as well as copolymer impregnated concrete specimens were subjected to accelerated durability tests in aqueous sulphuric acid, hydrochloric acid, ammonium chloride, sodium chloride, sodium hydroxide, sea water and crude oil media. The effects of such corrosive stagnant environments on compressive strength, flexural strength, strength of transverse rupture and modulus of elasticity have been studied. A durability mechanism has been proposed to account for the observed behaviour of polymer impregnated concrete.

1. Introduction

It has been observed that the impregnation of cement mortar with polymers results in significant improvement of the mechanical and durability properties of polymer impregnated concrete (PIC). The improvement in mechanical and durability properties of PIC has been suggested to be primarily due to pore filling by the polymer [1]. The impregnated polymer repairs the microcracks and voids, and reinforces the micropores of the cement body by forming an interpenetrating network with the inorganic cementitious silicate structure. However, this pore filling theory fails to explain satisfactorily all the observed behaviour of PICs. Recent studies have indicated that some type of interaction between the host cement matrix and the impregnated organic polymer is also responsible for the superior strength and durability of PICs [2]. Despite some investigations carried out in the field of durability of polymer impregnated concrete, very little understanding has so far been reached regarding the mechanism of durability.

We wish to present some of our results on the effect of corrosive environments on the strength and durability properties of PIC in order to suggest a mechanism of durability of PIC.

2. Experimental methods

The specifications of the materials and the method of preparation of the cement mortar and polymer impregnated concrete have been reported [3]. The strength properties of both ordinary and polymer impregnated concrete were measured, after taking the test specimen out of the corrosive environment, by a non-destructive method of testing using the measurement of ultrasonic pulse velocity. The detailed procedure has been reported elsewhere [3, 4].

2.1. Precoating of sand

Sand was soaked in a 1 wt % solution of polymer (namely polyvinyl acetate in acetone or polystyrene in toluene), and dried to constant weight.

2.2. Preparation of autoclaved concrete

After casting, concrete specimens were cured in an autoclave using a superheated system at 170° C under 15 Pa pressure for 2 h.

2.3. Measurement of porosity

The porosity of the control and composite specimens was determined by a damp–dry technique. The porosity determination was based upon the concept of maximum evaporable water.

2.4. Measurement of durability

Test specimens were immersed in stagnant corrosive environments and the weight losses of the sample were determined at definite intervals of time. Before weighing the specimens were thoroughly washed with water to remove the corrosive solution and then dried to constant weight.

2.5. Surface sealing of pores

The surface pores of specimens were sealed by a thin coating of polystyrene using a 1 wt % solution of polystyrene in styrene monomer.

3. Results and discussion

3.1. Effect of corrosive environment on strength properties

3.1.1. Aqueous HCl solution

The effect of aqueous (1 : 3 vol/vol) HCl solution on the strength properties of ordinary concrete and polymethyl methacrylate (PMMA) impregnated concrete

---

* *Present address*: Oil and Natural Gas Commission, Calcutta, India.
‡ To whom all correspondence should be sent.

0022–2461/86 $03.00 + .12

TABLE I Effect of aqueous HCl environment on strength properties of concrete and PMMA impregnated concrete

Immersion period (days)	Specimen	Compressive strength ($MN\,m^{-2}$)	Flexural strength ($MN\,m^{-2}$)	Transverse rupture strength ($MN\,m^{-2}$)	Modulus of elasticity ($MN\,m^{-2}$)
0	Control	52.8	25.9	34.8	280.1
0	PIC	275.7	49.6	246.9	1463.6
7	Control	49.0	24.0	32.0	262.9
7	PIC	247.8	46.1	219.9	1328.3
14	Control	38.1	18.6	25.1	206.7
14	PIC	218.2	42.4	191.3	1185.0
21	Control	27.5	13.4	18.0	150.8
21	PIC	198.6	39.8	172.4	1090.9
28	Control	15.1	7.4	9.9	70.3
28	PIC	183.9	38.0	158.2	856.7

Concrete composition: sand : cement = 3 : 1; water : cement = 1 : 2. Polymer loading = 14.21%. Aqueous HCl 1 : 3 (vol : vol).

is shown in Table I. As the length of immersion time increases, all four mechanical properties gradually decrease. In due course the highly corrosive HCl solution enters the matrix and attacks the concrete–PMMA bond, thereby weakening the concrete–PMMA interaction. This leads to a gradual decrease in the mechanical properties. The reduction in mechanical properties of ordinary concrete is much greater, for example 72% of compressive strength lost compared with only 34% for PMMA impregnated concrete. The control concrete undergoes a remarkable reduction in structural dimensions but the PIC structure remains almost intact although it suffers appreciable reduction in strength properties.

3.1.2. Effect of sea water

The effect of sea water on the strength properties of ordinary concrete and PIC is pronounced (Table II). The reduction in strength properties is noticed after 14 days of immersion in the case of PMMA impregnated concrete whereas for the control specimen the strength properties decrease almost from the start of immersion.

However, for both the ordinary concrete and polymer impregnated concrete strength properties decrease with increase in duration of immersion. Neither the ordinary concrete nor the PMMA impregnated concrete undergo any noticeable change in structural dimension in sea water after 28 days of immersion.

3.1.3. Effect of crude oil

The effect of crude oil on the strength properties of ordinary concrete and PIC is not very pronounced (Table III). A slight reduction in strength (only about 4% in compressive strength) is noticed in the case of PMMA impregnated concrete whereas in the case of the control concrete the reduction in strength properties is appreciable (about 31%) in 28 days. The structural dimensions of both the ordinary and PMMA impregnated concrete remain unchanged after 28 days of immersion in a crude oil environment.

3.1.4. Effect of NH_4Cl, NaCl and NaOH solutions

The durability behaviour of ordinary concrete and concrete–polystyrene (PS) composite in NH_4Cl, NaCl and NaOH solutions is presented in Table IV. Both the ordinary concrete and polystyrene impregnated concrete undergo weight loss in the first four days in all these media, after which the concrete specimen gradually gains in weight. This is attributed to the salt deposition effect inside the concrete pores. Similar observations were reported by Fukuchi and co-workers [5]. The magnitude of the weight loss in the first four days is less for the concrete–PS composite than for ordinary concrete. The gain in weight after four days of deposition is more pronounced for ordinary concrete than for the concrete–PS composite. This may be explained on the basis of the greater porosity of the ordinary concrete specimens compared with the PS impregnated concrete. Polymer impregnated concrete has lower porosity due to the partial filling up of pores by polymer deposition.

TABLE II Effect of sea water environment on strength properties of control concrete and PMMA impregnated concrete

Immersion period (days)	Specimen	Compressive strength ($MN\,m^{-2}$)	Flexural strength ($MN\,m^{-2}$)	Transverse rupture strength ($MN\,m^{-2}$)	Modulus of elasticity ($MN\,m^{-2}$)
0	Control	52.8	25.7	34.8	280.1
0	PIC	275.7	49.6	246.9	1463.6
7	Control	51.8	25.2	34.1	274.9
7	PIC	275.7	49.6	246.9	1463.6
14	Control	46.3	22.5	30.5	246.0
14	PIC	270.9	49.0	242.3	1440.1
21	Control	43.5	21.2	28.6	233.1
21	PIC	252.2	46.7	224.2	1349.8
28	Control	31.0	17.2	23.2	190.6
28	PIC	239.0	45.0	211.4	1286.1

Concrete composition: sand : cement = 3 : 1; water : cement = 1 : 2. Polymer loading = 13.79%. Sea water from Bay of Bengal at Digha sea beach.

TABLE III Effect of crude oil environment on strength properties of control concrete and PMMA impregnated concrete

Immersion period (days)	Specimen	Compressive strength ($MN m^{-2}$)	Flexural strength ($MN m^{-2}$)	Transverse rupture strength ($MN m^{-2}$)	Modulus of elasticity ($MN m^{-2}$)
0	Control	52.0	25.8	34.0	276.9
0	PIC	266.1	48.5	237.6	1417.5
7	Control	52.0	25.8	34.0	276.9
7	PIC	266.1	48.5	237.6	1417.5
14	Control	49.0	24.3	32.1	261.2
14	PIC	266.1	48.5	237.6	1417.5
21	Control	40.8	20.2	26.7	217.7
21	PIC	261.4	47.9	233.1	1394.6
28	Control	36.1	17.8	23.6	192.8
28	PIC	256.8	47.3	130.5	1372.0

Concrete composition: sand : cement = 3 : 1; water : cement = 1 : 2. Polymer loading = 13.03%. Ankeleswar crude oil (high paraffinic and low flash point).

3.1.5. Durability of autoclaved concrete

The results of the durability tests on ordinary concrete and autoclaved concrete in aqueous H_2SO_4, HCl, NH_4Cl, NaCl and NaOH environments are presented in Table IV. Durability tests of ordinary concrete and autoclaved ordinary concrete in aqueous (1:3) H_2SO_4 solution shows that the latter is more durable than the former. Improved durability of polymer impregnated concrete is also achieved by preparing polymer impregnated autoclaved concrete. Studies on autoclaved concrete–PS composites in H_2SO_4 medium establish the superior durability of autoclaved specimen over ordinary concrete–PS composite. Similar results were obtained in other corrosive environments, namely aqueous (1 : 3) HCl, NH_4Cl, NaCl and NaOH solutions.

TABLE IV Durability of polystyrene impregnated concrete (stagnant environment; temperature 30° C)

Corrosive environment	Concrete specimen*	Time of immersion (days)	Weight loss (%)
Aqueous (1 : 3) H_2SO_4	OC	21	63.0
	AC	21	57.5
	PS-OC	28	32.0
	PS-AC	28	26.5
Aqueous (1 : 3) HCl	OC	28	48.0
	AC	28	41.0
	PS-OC	28	28.0
	PS-AC	28	22.0
NH_4Cl solution (25%)	OC	4	8.4
	AC	4	1.2
	PS-OC	4	2.2
	PS-AC	4	1.8
NaCl solution (25%)	OC	4	9.1
	AC	4	3.3
	PS-OC	4	2.3
	PS-AC	4	1.9
NaOH solution (21.3%)	OC	4	5.9
	AC	4	1.1
	PS-OC	4	2.0
	PS-AC	4	1.0

*Concrete composition: water : cement = 2 : 5; sand : cement = 3 : 1. OC = ordinary concrete cured at 27° C for 7 days under water; AC = autoclaved concrete cured in an autoclave by superheated steam at 170° C under 15 Pa for 2 h; PS-OC = polystyrene impregnated ordinary concrete; PS-AC = polystyrene impregnated autoclaved concrete.

Thus, in all the above corrosive environments the order of durability of the various specimens is

autoclaved concrete–PS > ordinary concrete–PS

> autoclaved concrete > ordinary concrete

The excellent durability of autoclaved concrete and polystyrene impregnated autoclaved concrete is probably due to the formation of a very dense tobermorite microstructure, which offers improved resistance to chemical attack. The formation of tobermorite and free $Ca(OH)_2$ in concrete is enhanced if the curing is performed by superheated steam under pressure inside an autoclave [4]. In the case of curing of concrete in water at room temperature, formation of $Ca(OH)_2$ takes place very slowly and after 7 days it is not complete; formation of very dense tobermorite microstructure is not also possible by this method of curing. The polymer impregnated autoclaved concrete is superior to the autoclaved concrete in resisting chemical attack because of the reinforcement of the

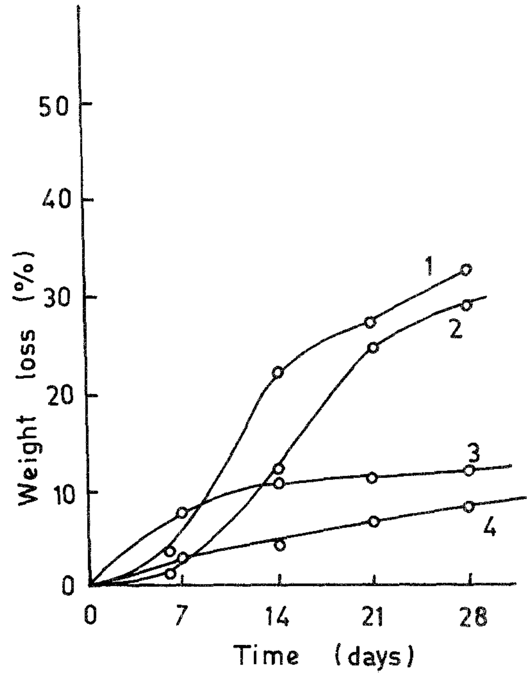

Figure 1 Durability of polymer coated concrete in HCl. 1. Ordinary control; 2. PS-coated control; 3. ordinary concrete–PS; and 4. PS-coated PS–concrete.

TABLE V Effect of precoating of sand on the strength properties of PIC at comparable polymer loading

Specimen (interfaces)*	Compressive strength (Pa)	Flexural strength (Pa)	Transverse rupture strength (Pa)
Ordinary mortar (S–C)	175	51	95
PVAc-coated mortar (S–PVAc–C)	159	43	62
PS-coated mortar (S–PS–C)	154	40	52
Ordinary PMMA composite (S–PMMA–C)	599	223	337
PVAc-coated–PMMA composite (S–PVAc–PMMA–C)	813	267	381
Ordinary PS composite (S–PS_I–C)	337	212	179
PVAc-coated–PS composite (S–PVAc–PS_I–C)	421	253	194
PS-coated–PMMA composite (S–PS–PMMA–C)	679	260	372
PS-coated–PS composite (S–PS–PS_I–C)	373	244	190

*S = ordinary sand surface; C = cement surface; PVAc = polyvinyl acetate-coated sand surface; PS = polystyrene-coated sand surface; PMMA = polymethyl methacrylate (impregnated) surface; PS_I = polystyrene (impregnated) surface.

tobermorite microstructure gel by the impregnated polymer.

3.1.6. Sealing the surface pores

Preventing the entry of the corrosive agent into the concrete or PIC specimens is one of the best ways of increasing the durability. This has been confirmed by sealing the surface pores of the specimen by applying a coating of polystyrene ($\bar{M}_n = 1 \times 10^5$). The durability of both the ordinary concrete and the PS impregnated composite has been improved significantly over the uncoated samples (Fig. 1).

3.1.7. Effect of precoating the sand

In order to ascertain the role of polymer–cement interaction in improving the mechanical strength of PIC, we have studied the effect of precoating the sand on the strength behaviour of mortar–PMMA and mortar–PS systems. Sand was either precoated with a polar polymer such as polyvinyl acetate (PVAc) or with a non-polar polymer such as polystyrene. This precoated sand was used to prepare a mortar, which was impregnated with styrene or methyl methacrylate. The results are shown in Table V. The following observations are made from the data shown in Table V:

1. Mortar prepared with precoated sand has lower strength properties than ordinary mortar (prepared from uncoated sand). The order of strength properties (compressive strength, flexural strength and strength of transverse rupture) is:

$$\text{PS-coated mortar} < \text{PVAc-coated mortar} < \text{uncoated mortar}$$

2. Incorporation of polymer improves all the above strength properties of mortar, and PMMA enhances the properties more than PS does in both cases, namely composite made with coated or uncoated sand.
3. PVAc-coated–PMMA composites have higher strength properties than PS-coated–PMMA composites.
4. Similarly, PVAc-coated–PS composites have higher strength properties than PS-coated–PS composites.

These observations may be explained on the basis of the different natures of the interfacial interactions present in the composites (Table VI). It is evident from the data in Table VI that polar–polar interactions contribute more to the strength of the composites than the polar–non-polar or non-polar–non-polar interactions. PVAc and PMMA are polar polymers whereas PS is a non-polar polymer. It is, therefore, expected that the interaction between the first two polymers will be greater, and consequently contribute more to the enhancement of strength properties, than the interactions with the last. For example, the contribution to compressive strength of the S–PMMA interaction is as high as about 2.5 times that of the S–PS interfacial interaction (S = ordinary sand surface). Similarly, the contribution of the PVAc–PMMA interaction is

TABLE VI Contribution of different interfacial interactions to various strength properties of PIC

Interface	Nature of interaction*	Contribution to strength (Pa)		
		Compressive strength	Flexural strength	Transverse rupture strength
S–PMMA	P–P(I)	424	172	243
S–PS	P–NP(I)	162	161	85
PVAc–PMMA	P–P(O)	214	44	44
PVAc–PS	P–NP(O)	64	41	15
PS_I–PMMA	NP–P(O)	80	37	35
PS_I–PS	NP–NP(O)	80	32	11
S–C	P–P(I)	175	51	94
S–PVAc	P–P(IO)	175	43	–
S–PS_I	P–NP(IO)	154	40	52

*P = polar; NP = non-polar; I = inorganic; O = organic; IO = inorganic–organic.

TABLE VII Ratios of contributions of different interactions to various mechanical strengths of PIC

Interactions	Ratios of contribution to		
	Compressive strength	Flexural strength	Transverse rupture strength
$\frac{\text{S–PMMA}}{\text{PVAc–PMMA}}$	1.98	3.91	5.52
$\frac{\text{S–PS}}{\text{PVAc–PS}}$	1.93	3.92	5.67
$\frac{\text{S–PMMA}}{\text{S–PS}}$	2.62	1.07	2.86
$\frac{\text{PVAc–PMMA}}{\text{PVAc–PS}}$	2.55	1.07	2.93
$\frac{\text{S–PMMA}}{\text{PS}_1\text{–PMMA}}$	5.30	4.07	2.93
$\frac{\text{S–PS}}{\text{PS}_1\text{–PS}}$	4.50	5.03	7.72
$\frac{\text{PS}_1\text{–PMMA}}{\text{PS}_1\text{–PS}}$	2.22	1.16	3.18

also about 2.5 times that of PVAc–PS interaction. Also, the contribution of PS_1–PMMA interaction is about 2.2 times that of the PS_1–PS interaction. Another interesting point to be noted is that for both PS and PMMA composites, the contribution of the S–polymer interaction is about 2 times that of the PVAc–polymer interaction and about 5 times that of the PS_1–polymer interaction. In other words, inorganic–organic interaction is stronger than organic–organic interaction. Ratios of contributions of various interactions to various mechanical properties have been summarized in Table VII.

3.1.8. Durability mechanism

The enhanced durability properties of concrete–polymer composite specimens are most probably due to two major factors, namely (a) sealing of the pores of the concrete by the impregnated polymer, and (b) interfacial interaction between various interfaces existing in the polymer impregnated concrete. Reduction of porosity in the specimen by various means generally results in enhanced durability. By keeping the porosity factor constant, the durability of the PICs can be improved by increasing the interfacial interactions. This could be achieved by increasing the polarity of the polymer to be impregnated. This explains the better durability of PMMA impregnated concrete than that of PS impregnated concrete under identical or very similar polymer loading. The earlier theory of sealing of pores by impregnated polymer alone fails to explain such observation. Our studies on precoated sand lend further support to the importance of interfacial interactions in polymer impregnated concrete. The failure of a specimen subjected to the attack of corrosive agents may, therefore, be explained as follows: first, the corrosive chemical or agent enters through the pores and tries to rupture the concrete–polymer bond, facilitating further entry of the corrosive agent. Second, degradation and/or decomposition of the polymer phase by the corrosive reagent starts, resulting in the failure of the specimen.

Acknowledgements

The authors wish to thank the Department of Atomic Energy for partial financial assistance, and B. Mondal, Metallurgical Engineering Department, U. Bakshi and N. Mallick, Materials Science Centre, for technical assistance.

References

1. A. B. AUSKERN, Brookhaven National Laboratory Report No. BNL-13493, p. 24, US Atomic Energy Commission, 1969.
2. R. N. SWAMY, *J. Mater. Sci.* **14** (1979) 1521.
3. K. R. KIRTANIA, PhD thesis, Indian Institute of Technology, Kharagpur (1984) p. 55.
4. V. K. BHATTACHARYA, K. R. KIRTANIA, M. M. MAITI and S. MAITI, Proceedings of the National Seminar, New Delhi, April 1982, Paper No. III(6).
5. T. FUKUCHI, Y. OHAMA and E. INUISHI, *Proc. Jpn. Congr. Mater. Res.* **21** (1978) 190.

Received 11 October 1984
and accepted 29 March 1985