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Polymer impregnated concrete

Part 2 *Mechanical behaviour of polymer and copolymer impregnated concrete*

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Concrete–polymer composites were prepared by impregnating sand–cement mortar with polymethylmethacrylate, polystyrene and polyacrylonitrile as well as copolymers of styrene–methylmethacrylate, styrene–acrylonitrile, styrene–butyl methacrylate, styrene–butyl acrylate, methyl methacrylate–butyl acrylate, methyl methacrylate–ethyl acrylate, styrene–acrylontrile crosslinked with divinyl benzene, and polystyrene crosslinked with divinyl benzene. Mechanical properties such as compressive strength, flexural strength and in some cases strength of transverse rupture were studied with these polymer and copolymer impregnated concrete. The effects of water/cement ratio, sand/cement ratio, curing temperature and time, polymer loading, and nature of polymer on the compressive and flexural strengths of control concrete and polymer impregnated concrete were studied. For copolymer impregnated concrete the effects of copolymer composition and nature of comonomer pairs on the strength properties of the composite were also investigated.

1. Introduction

Impregnation of concrete by polymers has improved its mechanical properties dramatically. This has led to the development of polymer impregnated concrete (PIC) as a class of modern material with promising technological importance [1–3]. A number of vinyl monomers have been used by various workers for the preparation of such concrete–polymer composite [3–10]. By incorporating a small amount of polymer, generally about 4 to 8%, the strength properties of ordinary cement–sand mortar have been increased by four to five times. We wish to report here the results of our investigations on the mechanical properties of PIC prepared with various vinyl polymers and a number of comonomer pairs.

2. Methods and experiments

Normal Portland cement and Cossy river-bed sand (33.403 American grain fineness specification (AFS)) were used to prepare cement–sand mortar. The mortar specimens were prepared by the standard curing technique [11, 12]. Monomers were freshly distilled before use. Impregnation was carried out with the appropriate monomer or comonomer mixture following the technique described earlier [11]. Benzoyl peroxide (BPO) was used as the initiator for polymerization.

Mechanical strength measurements were carried out in a Universal Testing Machine, Model Fu 10000e (VEB Thuringer Industrie Werk, GDR).

3. Results and discussion

3.1. Effect of water/cement ratio

The effects of water/cement ratio (w/c), porosity, polymer loading, and average polymer density in pores on the compressive strength of composites of concrete with polymethyl methacrylate (PMMA) are summarized in Table I.

The porosity is found to increase with increasing w/c in both the control and test samples. This is expected because with increasing amount of water mixed with the concrete components, much more free water is trapped inside the control concrete, which on drying leaves behind pores inside the concrete. The entry of monomer or monomer pairs into micropores is somewhat restricted and depends upon the size of

TABLE I Effect of various parameters on the compressive strength of control concrete and concrete–PMMA composite

Water/cement ratio	Porosity (%)		Polymer loading (%)	Average polymer density in pores, ($g\,cm^{-3}$)	Compressive strength ($MN\,m^{-2}$)	
	Control	Composite			Control	Composite
0.50	18.98	1.66	5.01	0.347	17.2	56.2
0.45	16.63	1.76	4.93	0.332	18.0	53.7
0.40	14.79	1.22	4.48	0.330	23.8	34.3
0.35	13.67	1.02	4.50	0.356	24.5	53.1
0.30	12.10	0.99	3.95	0.356	34.5	86.3

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TABLE II Effect of various parameters on the flexural strength and flexural modulus of elasticity of control concrete and concrete–PMMA composite

Water/cement ratio	Porosity (%)		Polymer loading (%)	Average polymer density in pores ($g\,cm^{-3}$)	Flexural strength ($MN\,m^{-2}$)		Flexural modulus of elasticity ($MN\,m^{-2}$)	
	Control	Composite			Control	Composite	Control	Composite
0.50	23.00	3.76	7.94	0.848	1.1	18.9	42.2	178.5
0.45	21.85	2.98	7.07	0.784	1.4	18.6	52.4	175.0
0.40	20.00	3.14	5.87	0.742	2.0	15.9	54.0	165.3
0.35	19.13	2.44	5.89	0.756	2.0	18.7	52.7	176.5
0.30	17.77	1.90	6.13	0.832	2.4	21.7	61.5	194.1

the pores, the degree of evacuation of the sample, the impregnation temperature and the time of immersion of the concrete specimen into the monomer.

The average density of PMMA formed inside the pores of various types of concrete specimen shows that the average polymer density first decreases with increasing w/c, reaches a minmum at w/c = 0.40 and finally increases again. The lowest average density of the polymer impregnated in the concrete specimen at w/c = 0.40 may be due to (a) partial or incomplete filling of the micropores and (b) trapping of air bubbles inside the capillary pores.

While the compressive strength of the control specimen decreases with increasing w/c, that of the concrete–PMMA sample first decreases, attains a minimum value at w/c = 0.40 and then increases. The observation in the case of the control specimen is explained by the fact that with increasing w/c the porosity increases, which in turn decreases the strength property. The compressive strength of concrete is, therefore, significantly improved due to pore filling by polymer. Similar arguments have also been advanced by other workers [13].

Similar results are obtained for the influence of w/c, porosity, polymer loading, and average polymer density in the pores on the flexural strength and flexural modulus of elasticity of concrete–PMMA composites (Table II). This may also be due to the filling up of pores in the concrete by polymer. However, improved bonding between sand–cement and polymer may play a significant role in the enhancement of the mechanical properties of the composites.

3.2. Effect of sand/cement ratio

The effect of the sand/cement ratio (s/c) on the compressive and flexural strength of concrete–PMMA composites is shown in Table III. It is found that for a constant w/c, higher value of s/c results in higher strength. This behaviour can be explained in terms of water absorbed by the sand or aggregate. A larger amount of sand or aggregate absorbs a greater quantity of water, thus reducing the effective w/c. As a result the effective w/c in a concrete mix with high s/c is lower than in a rich mix. This in turn results in a lesser porosity and consequently a higher strength.

3.3. Effect of curing temperature

The curing temperature of the mortar sample has a profound effect on its compressive and flexural strengths. With increasing curing temperature the compressive strength of the concrete gradually increases, reaches a maximum at around 80° C and then slowly decreases (Table IV). Up to 80° C the rate of hardening of cement through hydration and hydrolysis is increased with increasing temperature. But above 80° C the concrete structure gradually becomes more and more porous and the increased porosity effect outweighs the effect of faster hydration and hydrolysis. The same trend is also observed in the case of PMMA-impregnated concrete.

3.4. Effect of curing time

The effect of curing time on the compressive and flexural strengths of control and PMMA-impregnated concrete is shown in Table V. With increasing curing time the strength properties of the mortar sample gradually increase. Control samples with sand/cement ratio 1 : 4 and water/cement ratio 0.40 were cured in water at 35° ± 2° C for 3, 7 and 28 days. It was found that maximum strength was developed after 28 days.

Strength development in concrete takes place through the hydration and hydrolysis of the main constituents of cement. During curing, inorganic constituents of cement like CaO (65.3%) and SiO_2 (21.96%) undergo hydrolysis to produce $Ca(OH)_2$ and silicic acid respectivly. At room temperature the hydrolysis reaction is slow and progresses slowly to completion; in 28 days hydrolysis of the above constituents of cement is virtually complete leading to the maximum compressive and flexural strengths. However, the curing time has no effect on the strength properties of PMMA-impregnated concrete. For

TABLE III Influence of sand/cement ratio on the compressive and flexural strengths of concrete–PMMA composite

Sand/cement	Polymer loading (%)	Compressive strength ($MN\,m^{-2}$)	Polymer loading (%)	Flexural strength ($MN\,m^{-2}$)
1 : 9	5.12	43.4	6.24	16.9
1 : 4	3.95	45.3	4.93	19.2
3 : 7	3.76	47.7	3.04	22.3
2 : 3	3.21	57.0	3.94	26.3
1 : 1	2.98	62.1	3.05	31.9

TABLE IV Effect of curing temperature on the compressive and flexural strengths of control concrete and concrete–PMMA composite

Curing temperature (°C)	Polymer loading (%)	Compressive strength ($MN\,m^{-2}$)		Polymer loading (%)	Flexural strength ($MN\,m^{-2}$)	
		Control	Composite		Control	Composite
60	7.03	9.0	27.6	7.81	2.7	10.8
70	7.13	11.1	35.2	4.32	3.0	11.9
80	7.29	12.8	40.0	7.91	3.4	13.9
85	7.18	12.7	39.3	7.03	3.2	13.4
90	7.23	12.5	38.4	7.09	2.9	11.1
95	7.33	12.3	37.8	7.56	2.8	10.5

example, the increment in compressive strength from 3 to 28 days curing is exactly the same, i.e. 3.14 $MN\,m^{-2}$, in both control and PIC samples (Table V).

3.5. Effect of polymer loading and nature of polymer

Table VI presents data for the effect of polymer loading on the compressive and flexural strengths of PMMA-impregnated concrete. It is found that compressive and flexural strengths increase with polymer loading. At comparable polymer loading, the compressive and flexural strengths of polymer impregnated concrete depend on the nature of the impregnating polymer (Table VII). It is found that the strength properties for composites with PMMA, polyacrylonitrile (PAN) and polystyrene (PS) are in the order: concrete–PMMA > concrete–PAN > concrete–PS. This indicates that the polarity of the impregnating monomer has a significant role in enhancing the strength properties of PICs. Polar monomers such as methylmethacrylate (MMA) and acrylonitrile (AN) are able to increase the strength properties of composites more than non-polar styrene under identical polymer loading. The improvement of the adhesion between sand and cement by polymer impregnation will be greater with higher polarity of the monomer.

3.6. Mechanical behaviour of copolymer impregnated concrete

Table VIII shows the compressive and flexural strengths of the composite with copoly(styrene–butyl acrylate) (concrete–P(S–BA)). Samples for strength measurements were prepared with fixed values of s/c and w/c. The comonomer feed composition was varied between 100% styrene (S) and 100% butyl acrylate (BA). Incorporation of butyl acrylate with styrene adversely affects both compressive and flexural strengths initially up to 25% BA. Afterwards the strength properties are found to partially recover their original values (with 100% S).

Similar trends are observed in the compressive and flexural strengths of the composite with copoly(styrene–butyl methacrylate) (concrete–P(S–BMA)) (Table IX). Here also the strength values are minimum at 25% butyl methacrylate (BMA) in the monomer feed.

The situation is completely reversed when MMA is used as a component of the comonomer mixture. For example, the compressive strength of the composite with copoly(methyl methacrylate–butyl acrylate) (concrete–P(MMA–BA)) attains its lowest value at a monomer feed composition of 25% MMA. Similar results are obtained in for the flexural and transverse rupture strengths (Table X).

Table XI lists data for compressive, flexural and transverse rupture strengths of the composite with copoly(methyl methacrylate–ethyl acrylate) (concrete–P(MMA–EA)). Here again all the strength properties attain minimum values at a monomer-feed composition of 25% MMA.

In order to explain why such minima occur in the strength properties as a function of initial monomer composition, and why the minima occur at a higher concentration of styrene in S–BA and S–BMA systems than in MMA–containing composites, it may be argued that the mechanical behaviour of the copolymer is very much affected by segmental alignment in the solid phase, in addition to the influence of the individual homopolymers [14]. The addition of a comonomer usually causes a marked loss in crystallinity, which in turn reduces many physical properties and strength values. In many cases, a rigid fibre-forming polymer is converted into a highly elastic and rubbery product by such minor modification. The dependence of the mechanical properties on copolymer composition in systems which do not crystallize results primarily from changes in intermolecular forces as measured by cohesive energy. Higher cohesive energy results in higher stiffness and hardness, and generally improves the mechanical properties.

The comonomers BA and ethylacrylate (EA) do not crystallize isomorphously with MMA and S. The

TABLE V Effect of curing time on the compressive and flexural strengths of control concrete and concrete–PMMA composite (s/c = 1 : 4, w/c = 0.40)

Curing time (days)	Polymer loading (%)	Compressive strength ($MN\,m^{-2}$)		Flexural strength ($MN\,m^{-2}$)	
		Control	Composite	Control	Composite
3	7.52	10.0	37.1	2.6	10.2
7	7.47	11.9	38.8	2.8	10.4
28	7.38	13.1	40.4	3.4	11.1

TABLE VI Effect of polymer loading on the compressive and flexural strengths of concrete–PMMA composite (s/c = 3 : 1, w/c = 0.35)

Polymer loading (%)	Compressive strength ($MN\,m^{-2}$)	Polymer loading (%)	Flexural strength ($MN\,m^{-2}$)
0 (control)	24.5	0 (control)	5.0
1.85	28.3	1.64	6.7
2.87	33.0	2.85	10.3
3.80	40.2	3.55	15.7
4.50	53.1	3.82	23.9
5.11	54.8	5.05	33.8

copolymers are, therefore, of lower crystallinity than the individual homopolymers, which leads to a lower mechanical strength of the concrete reinforced by them. Also the presence of big pendant groups in polybutyl acrylate (PBA) and polyethyl acrylate (PEA) results in lower cohesive energy in (S–BA), (S–BMA), (MMA–BA) and (MMA–EA) systems, which leads to lower mechanical strength in the concretes reinforced by them. A drastic fall of strength with the incorporation of only 25% BA or BMA in the styrene-based copolymers may be due to much less coherent segmental association in the copolymer. A further increase in the proportion of BA or BMA could, however, slowly restore the cohesion through alignment of a larger proportion of acrylic segments. The variation in strength properties is not very wide in MMA-based copolymer systems. This may be explained by the closer structural similarities between MMA, BA and EA.

Recently Chang *et al.* [15] reported that a significant improvement in strength properties can be achieved by impregnating mortar or concrete with copolymers. For example, a composite impregnated with a 50/50 wt % comonomer mixture of styrene and methyl methacrylate has higher strength properties than when either styrene or methyl methacrylate alone is used for impregnation. Chang *et al.* suggested that copoly (S–MMA) offers enhanced cement–polymer interaction through the polar ester group of MMA, coupled with the ridigity and toughness imparted by the styrene moiety of the copolymer.

TABLE VII Effect of nature of polymer on the compressive and flexural strengths of composites (s/c = 1 : 4, w/c = 0.50)

Monomer used	Monomer polarity*	Polymer loading (%)	Compressive strength ($MN\,m^{-2}$)	Flexural strength ($MN\,m^{-2}$)
MMA	P	7.40	58.4	13.8
AN	P	7.18	46.2	12.3
S	NP	7.35	37.6	11.9

*P, polar; NP, non-polar.

TABLE VIII Compressive and flexural strengths of concrete–P(S–BA) composite (s/c = 1 :4, w/c = 0.50, BPO = 1.1 wt % of total monomer, polymerization for 10 h at 90° C)

Impregnating system	Polymer loading (%)	Compressive strength ($MN\,m^{-2}$)	Polymer loading (%)	Flexural strength ($MN\,m^{-2}$)
100% S	7.20	36.8	6.88	17.6
75% S + 25% BA	7.40	15.3	7.00	3.6
50% S + 50% BA	7.10	19.4	7.08	4.5
25% S + 75% BA	6.99	22.6	7.13	5.9
100% BMA	6.87	24.3	7.32	7.2

TABLE IX Compressive and flexural strengths of concrete–P(S–BMA) composite (s/c = 1 : 4, w/c = 0.50, BPO = 1.1 wt % of total monomer, polymerization for 10 h at 90° C)

Impregnating system	Polymer loading (%)	Compressive strength ($MN\,m^{-2}$)	Polymer loading (%)	Flexural strength ($MN\,m^{-2}$)
100% S	7.20	36.8	6.88	17.6
75% S + 25% BMA	7.15	18.2	6.99	6.2
50% S + 50% BMA	7.35	19.0	7.43	7.3
25% S + 75% BMA	7.23	22.2	7.14	8.6
100% BMA	6.98	25.3	7.32	9.2

TABLE X Compressive, flexural and transverse rupture strengths of concrete–P(MMA–BA) composite (s/c = 1 : 4, w/c = 0.50, BPO = 1.1 wt % of total monomer, polymerization for 10 h at 90° C)

Impregnating system	Polymer loading (%)	Compressive strength ($MN\,m^{-2}$)	Flexural strength ($MN\,m^{-2}$)	Transverse ruputure strength ($MN\,m^{-2}$)
100% M	6.9	50.0	16.4	32.1
75% MMA + 25% BA	7.1	29.8	10.5	19.7
50% MMA + 50% BA	7.4	18.6	5.3	12.2
25% MMA + 75% BA	6.9	7.4	4.6	7.2
100% BA	7.5	14.7	6.5	8.7

TABLE XI Compressive, flexural and transverse rupture strengths of concrete–P(MAA–EA) composite (s/c = 1 : 4, w/c = 0.50, BPO = 1.1 wt % of total monomer, polymerization for 10 h at 90° C)

Impregnating system	Polymer loading (%)	Compressive strength (MN m^{-2})	Flexural strength (MN m^{-2})	Transverse ruputure strength (MN m^{-2})
100% MMA	6.9	50.0	16.4	32.1
75% MMA + 25% EA	7.5	16.1	6.5	22.9
50% MMA + 50% EA	7.3	12.5	4.7	9.6
25% MMA + 75% EA	7.1	8.2	4.3	8.2
100% EA	7.0	14.9	6.3	14.9

However, our data in Table XII fail to substantiate the observation of Chang *et al.* [15]. Our results show that both compressive and flexural strengths of composites reinforced by copolymers are intermediate between those of composites reinforced by the corresponding homopolymers. Thus a composite with a copolymer of styrene with acrylonitrile (S–AN) shows a compressive strength of 40.3 MN m^{-2}, compared with 37.6 and 46.2 MN m^{-2} for concrete–PS and concrete–PAN composites respectively (all three composites being at comparable polymer loading). The same behaviour is observed in the case of concrete reinforced by styrene–methyl methacrylate copolymer (S–MMA). Similarly, the flexural strength of concrete reinforced by a copolymer of styrene and MMA is 13.6 MN m^{-2}, whereas the flexural strengths of concrete–PS and concrete–PMMA specimens are 12 and 13.8 MN m^{-2} respectively.

3.7. Effect of crosslinking agent

If a crosslinking agent is added to either a single monomer or a monomer mixture, the compressive and flexural strengths of the resulting composite become significantly greater. Thus concrete impregnated with a mixture of styrene and divinyl benzene (a crosslinker) shows a compressive strength of 43.9 MN m^{-2}, which is 17% higher than the compressive strength of concrete–PS. Again, concrete impregnated with a mixture of styrene, acrylonitrile and divinyl benzene shows a compressive strength of 48 MN m^{-2} which is 19% higher than that of concrete–PAN. The effect of divinyl benzene as crosslinking agent on the flexural strength is similar; it improves the flexural strength by 12.3% over the non-crosslinked composite.

3.8. Interpretation of results

The effect of various parameters in the impregnation of monomer/monomer mixture, as well as the history of the sand–cement mortar preparation, on its mechanical behaviour has led to the situation where either or both of the following factors are affected. First, the filling up of pores in the concrete–polymer composite can be altered by variation of such parameters. If the conditions are favourable to pore filling, a marked improvement in the physcial properties of the concrete specimen is observed. 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. Second, an enhancment of the mutual interaction between sand–cement and polymer phases may take place. Both greater pore-filling and better interaction between polymer and sand–cement phases result in an enhancement of the mechanical strengths of the polymer-impregnated concrete. Since crosslinking will result in a greater interchain force, the use of a crosslinking agent further improves the mechanical properties of the composite.

However, tight filling of pores will produce a stronger composite than loose filling of pores. When the impregnating polymer chain is poorly aligned and hence more amorphous, the reinforcement achieved is poor compared to that of a perfectly aligned macromolecular chain. Copolymers generally have poorer chain symmetry than homopolymers, and copolymer-impregnated concrete therefore has intermediate strength properties.

Polarity of the monomer or comonomer pair used for impregnation contributes significantly to the interfacial forces between sand–cement and polymer. A highly polar monomer results in a higher interfacial force, and consequently the concrete prepared by using such a monomer as impregnant is stronger. It is observed, therefore, that the polarity of the monomer plays a significant role in the strength properties of a polymer.

TABLE XII Influence of polymer on the compressive and flexural strengths of PIC (s/c = 1 : 4, w/c = 0.5, BPO = 1.1 wt % of total monomer, polymerization for 10 h at 90° C, comonomer composition 50/50 wt % wherever used)

Impregnating system	Polymer loading (%)	Compressive strength (MN m^{-2})	Polymer loading (%)	Flexural strength (MN m^{-2})
S–AN	6.62	40.3	3.72	12.1
S–MMA	7.91	55.0	3.57	13.6
S–DVB*	8.35	43.9	3.50	13.4
S–AN–DVB*	7.04	48.0	3.55	13.2
MMA	7.40	58.4	3.50	13.8
S	7.35	37.6	3.48	11.9
AN	7.18	46.2	3.51	12.3

*DVB = divinyl benzene (used as a crosslinking agent, 2 wt % of total monomer used).

4. Conclusions

The mechanical strength (as measured by compressive strength, flexural strength, strength of transverse rupture and flexural modulus) of sand–cement mortar has been increased by three to five times, by polymer or copolymer impregnation to an extent of only 4 to 8%.

The mechanical strength of a concrete composite impregnated with a copolymer system depends upon the composition of the impregnating comonomer pair and the nature of the comonomers. The mechanical properties of copolymer-impregnated concrete are found to be be intermediate between those of the respective homopolymer-impregnated concretes.

The effects of various parameters in the impregnation of polymers and the preparation of the sand–cement mortar specimen on the mechanical behaviour of the polymer-impregnated concrete may be explained on the basis of two factors: (a) filling up of the pores of the sand–cement mortar by impregnated polymer or copolymer, and (b) improvement of the adhesion between sand and cement through the polymer. Since crosslinking increases the strength of bonding between polymer chains, the addition of crosslinking agent improves the mechanical strength of the concrete–polymer composite.

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