Comparative study of epoxy and polyester resin-based polymer concretes

P. Mani, A.K. Gupta and S. Krishnamoorthy

(Indian Institute of Technology, Delhi, India)

This paper presents a comparative evaluation of two types of polymer concretes, prepared with two different polymer binders (epoxy and polyester resins) with an identical aggregate in both cases (crushed quartzite and silica sand). Comparison is also made with a conventional cement concrete. Properties studied include strength (compressive, split-tensile, flexural and impact), setting shrinkage, abrasion and resistance to various chemicals. Both polyester concrete and epoxy concrete show far superior properties than cement concrete. It is further shown that the polyester concrete properties can be improved upon to approach those of the epoxy concrete by modifications such as incorporation of calcium carbonate microfiller and/or addition of a suitable silane coupling agent.

New materials composed of inorganic aggregates and polymeric resin binders are being developed for applications as construction materials with superior properties than the conventional cement concrete. These materials, also known, as polymer concretes, form a wide range depending on the nature of resin binder and the aggregates used and the technology of their preparation. It is well recognized that the properties of these materials are governed mainly by the adhesion between the resin binder and the aggregate, and therefore present day research is directed towards improving the adhesion between the two components, so as to achieve improved strength of the polymer concrete.

Since, for the cost considerations, the binder content used in such composiste materials is quite low, the adhesion of aggregates takes place through a fine layer of resin around the aggregates[1,2]. A larger contact area is therefore desirable, which necessitates a proper space filling of the gaps by smaller aggregates or microfiller particles. Use of a silane coupling agent (which strengthens the adhesion between the resin and the aggregate) and the addition of microfiller (which increases the contact surface area of particles coated with thin layer of the binder) improves the adhesion and thus the ultimate strength of the polymer concretes.

Polymer concretes are finding many applications in various civil engineering fields where the conventional cement concrete is inadequate due to its lower strength, poor chemical resistance, tendency towards crack formation, etc. Furthermore, owing to its improved bondability with old cement concrete[3-5] and more rapid setting than the conventional cement concrete, the polymer concrete may be used in the repair of concrete pavements, highways and airfield runways (where quick setting is desirable) and in the repair of cracks in old buildings[4-10]. Some other applications of polymer concretes may be in the construction of off-shore or hydraulic structures prone to erosion and cavitation, the construction of flooring in chemical industry facilities.

In this paper we present a comparative study of a cement concrete and two polymer concretes — one based on an unsaturated polyester resin binder ('polyester concrete') and the other on an epoxy resin binder ('epoxy concrete'), both with identical aggregate constitutions. Properties studied include: compressive, split-tensile, flexural and impact strengths, abrasion resistance, skid resistance, resistance to various chemicals, water absorption, cavitation resistance and setting shrinkage. Attempts are made to further improve the properties of the polyester concrete by incorporation of a microfiller and a silane coupling

agent, which lead to the encouraging possibility of reaching the properties equivalent to the epoxy concrete by using the less expensive binder (unsaturated polyester resin).

Experimental

Materials

Polymeric binders

The unsaturated polyester resin (Crystic-196, general purpose grade), as supplied by Crystic Resins (India) Pvt Ltd, was used with the catalyst (50% solution of dimethyl phthalate in methyl ethyl ketone peroxide) and the accelerator (1% solution of cobalt naphthanate in styrene). Both catalyst and accelerator were added to 2% by weight of the resin. Acid value, volatile content and initial viscosity of the resin at 25°C were 21 mg KOH/g, 38% and 800–900 cP, respectively.

The epoxy resin (grade GY-257) with polyamide hardener (grade HY-840, Ciba-Geigy) were used maintaining the resin: hardener ratio at 1:0.5. The epoxy value and initial viscosity of the resin at 25°C were 5.2–5.4 Eq/kg and 600 cP, respectively and the initial viscosity of the hardner at 25°C and 4500 cP.

Inorganic aggregates

Coarse aggregates comprising crushed quartzite of size ranging from 10 mm to 2.36 mm, specific gravity 2.72, and negligible organic impurities and moisture content, were used.

Fine aggregates comprising siliceous sand of size ranging from 1.18 mm (sieve size BSS-14) to $150 \mu \sqrt{m}$ (sieve size BSS-100), specific gravity 2.6 and neglegible organic impurities and moisture content were also used.

The size distribution of the aggregates was chosen as shown in Table 1. This is based on our previous studies on polyester resin concrete[11, 12], where the optimum size distribution for maximum mechanical properties such as compressive and split-tensile strengths was found.

Silane coupling agents

As per their suitability for the respective resins as recommended by the manufacturers, two silane coupling agents were used: Dynasil DEMO

Table 1. Grading of aggregate size used for the polymer/concrete

Sieve size	% wt retained	Cumulative wt % passing
10 mm	0	100
4.75 mm	45.00	55
2.36 mm	18.33	37
1.18 mm	3.66	33
600 μm	7.33	26
300 μm	16.50	9
150 μm	9.18	0

Grading modulus[19] = 6.42 mm^{-1}
Mean diameter[19] = 4.12 mm
Fineness modulus[19] = 4.40

(γ-methacryloxy propyl trimethoxy silane) for the polyester resin and Dynasil AMEO (γ-amino propyl triethoxy silane) for the epoxy resin.

Microfiller

Fine calcium carbonate powder (laboratory grade, particle size 2.0 to 2.5 μm, specific gravity 2.7) was used as microfiller in the case of the polyester resin concrete.

Method of preparation

Polymer concretes

Aggregates of appropriate grading were kept in an enamalled tray. The resin mix (ie, resin mixed with catalyst and accelerator or hardner) was poured on the aggregates and a homogenous mixing was done with the help of a spatulla.

The binder aggregate ratio was 12:88 by weight. In the case of samples containing the microfiller, there was 12% binder while the remaining 88% comprised the aggregates and the CaCO$_3$ microfiller in a 94:6 proportion by weight.

Silane coupling agents, wherever used, were added directly to the resin–catalyst–accelerator mix (1% by weight of the resin mix). This method of applying silane coupling agent as a 'integral blend additive', used in previous studies[13-15] on polymer concretes, produced significant improvements in the mechanical properties, which were attributable to the silane coupling agent. However, in comparison with other methods, the 'integral blend additive' method produces 10 to 20% lower compressive strength than the methods involving direct treatment of aggregates with silane in methanol or an aqueous medium[13].

The homogenous pastes thus prepared were placed in the mould and compacted well with a glass rod. After 24 h curing the mould at ambient temperature, the specimens were further cured at 70°C for 24 h in an air oven. Cylindrical specimens of dimensions: (i) 5 cm diameter and 10 cm length (for testing compressive and split-tensile strengths, chemical resistance and water absorption etc.) and (ii) 2.54 cm diameter and 2.54 cm length (for abrasion tests), were cast. Rectangular beams of dimensions: (i) 6 × 6 × 30 cm (for flexural tests), (ii) 2.5 × 2.5 × 25 cm (for setting shrinkage measurements), and (iii) 1 × 1 × 7.5 cm (for impact tests), were cast. Specially curved rectangular specimens were cast in the mould provided with the skid resistance testing instrument.

Cement concrete

As a reference material, cement concrete of the following composition with a medium water–cement ratio (0.55) concrete mix was used. A proportion of 1:1.6:2.4 (cement:sand:aggregates) with Portland cement, silica sand and quartzite aggregates was used. Specimens of the previously described shapes and dimensions were cast after mixing the ingredients of the cement concrete in a mechanical mixer and compacting in a table vibrator. The cast specimens were demoulded after 24 h casting and water cured for 28 days.

Measurements

Compressive, split-tensile and flexural strengths were measured on a Universal testing machine, according to the test procedure BS: 1881 part IV, 1970[16]. Static loading on cylindrical specimens parallel to the axis of the cylinder was used for compressive strength measurements. For split-tensile strength, the cylindrical specimen was kept in the horizontal position and loaded in compression along its diameter until ultimate splitting. Flexural strength tests were conducted on rectangular beam specimens by the three-point bending method maintaining the span length 2.5 cm between the point supports.

Impact tests were carried out on an Izod impact tester, involving cantilever type loading of the rectangular beam specimens through a pendulum hammer. Abrasion tests were conducted on a Dorry's abrasion tester to determine the coefficient of hardness, as per the test procedure IS: 2386, 1963[17]. Skid resistance tests were conducted on the well polished surfaces of the specimens, according to the test procedure BS: 812 Part III, 1975[16] and the results are expressed in terms of the coefficient of friction.

Resistance to chemicals, measured according to the method used by Fukuchi and Ohama[18], is expressed in terms of 'total evaluation points' based on percentage weight loss and surface appearance characteristics of the samples after a prolonged (180 days) exposure of the specimen to the chemical reagent. Reagents used were the following aqueous solutions: 5% HCl, 5% H_2SO_4, 5% CH_3COOH, 15% NaOH, 15% NaCl, and 0.2% $MgSO_4$.

Setting shrinkage was measured at ambient temperature using a Demec strain gauge, of gauge length 20.32 cm (8 inch) with a total range of 2500×10^{-5} strain units, and an accuracy of measurement within 10^{-5} strain units per division. Two Demec points were marked on the specimens at the time of casting. Measurements were made at intervals of 10 min for the first hour and thereafter at intervals of 1 h.

Water absorption tests in cold and boiling water were conducted by immersing the specimens in distilled water at ambient temperature for 72 h (denoted as C_{72}) and in boiling water for 5 h (denoted

as B_5). Cavitation resistance was measured in a Ruemelling utility sand blast cabinet, and represented as the specimens' weight loss due to impingement of the sand.

Results of all tests are presented as average values obtained from measurements on at least five samples in each case. Variation was less than 10% in the results on the various samples for any given test.

Results and discussion

Mechanical properties

Polymer concretes without silane or microfiller

Comparison of compressive, split-tensile, flexural and impact strengths, from the data presented in Table 2, clearly reveals that both the polyester concrete (specimen B) and epoxy concrete (specimen E), without silane and microfiller, have considerably superior properties than the cement concrete (specimen A). Of the two polymer concretes, the epoxy concrete has much superior properties than the polyester concrete (compare, eg, specimens B and E without any silane or microfiller in Table 2).

The split-tensile to compressive strength ratio, which is an important property for the selection of these polymer concretes (specimens B, E) over the cement concrete (specimen A). Thus, in addition to a superior load bearing capacity (owing to high compressive and flexural strengths) these polymer concretes also have a lower crack generation tendency (owing to high split-tensile strength) than the cement concrete.

Impact resistances of both the polyester concrete and the epoxy concrete were also superior to that of the cement concrete. Of the two polymer concretes the epoxy concrete had the greater impact strength over the polyester concrete.

Effect of silane coupling agent

Incorporation of a silane coupling agent further improves the properties of these polymer concretes. Compressive strength goes up by 30% for the polyester concrete (compare specimens B and C) and 36% for the epoxy concrete (compare specimens E and F). Split-

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Table 2. Mechanical properties of cement concrete, polyester concrete and epoxy concrete

Property	Cement concrete	Polyester concrete			Epoxy concrete	
	(A)	(B)[a]	(C)[b]	(D)[c]	(E)[d]	(F)[e]
Compressive strength (MPa)	24.0	41.2	53.0	68.0	71.6	97.7
Split-tensile strength (MPa)	3.2	10.8	11.8	12.1	13.7	18.9
Split-tensile/Compressive strength ratio	0.14	0.26	0.22	0.18	0.21	0.19
Flexural strength (MPa)	3.6	12.2	13.9	19.3	21.0	21.6
Izod impact strength (kg cm $\times$ cm^{-2})	3.3	3.5	4.7	4.3	6.6	7.5

[a]Without silane or filler
[b]With silane MEMO and without filler
[c]With silane MEMO and $CaCO_3$ filler
[d]Without silane
[e]With silane AMEO

tensile, flexural and Izod impact strengths of both polyester and epoxy concretes also improved with the incorporation of the silane coupling agent. This is an expected outcome of the improved interfacial bonding due to the silane coupling agent. The effect of silane coupling agent is more pronounced in the case of the epoxy concrete than in the polyester concrete.

The split-tensile strength to compressive strength ratio decreases on incorporation of the silane coupling agent in both cases, implying a greater improvement of compressive strength than tensile strength in the presence of the coupling agent. Compressive deformation involves displacement of several neighbouring aggregates to create room to allow motion of any two mutually approaching aggregates, whereas in tensile deformation fracture initiating at any site passes through other interfacial areas without involving any cooperative displacement of the aggregates. The stronger binder aggregate bonding in presence of the silane coupling agent would thus produce greater resistance to compressive deformation, owing to the cooperative motion of a large number of aggregates involved in the process of compressive deformation. This explains the observed decrease in split-tensile strength to compressive strength ratio in the presence of the silane coupling agent. Furthermore, a comparison of the compressive strength of these different concretes without silane (specimens B and E) clearly shows that the stronger binder (epoxy resin) gives a higher compressive strength than the weaker binder (polyester resin).

Effect of CaCO₃ microfiller in polyester concrete

From the above comparisons of the mechanical properties of the two polymer concretes, the epoxy resin would seem to be a superior binder to the polyester resin. However, the high cost of epoxy resin may restrict its use to only very exceptional

applications. Further studies on the polyester concrete by incorporation of $CaCO_3$ microfiller indicate a clear possibility of achieving a considerable improvement in the properties of the polyester concrete. The role of the microfiller is to achieve better filling of the spaces between the aggregates so that the resin binder is concentrated on the aggregate interfaces rather than in the empty spaces between the aggregates.

Data on specimens C and D, which differ only in microfiller content, in Tables 2 and 3 reveals the effect of $CaCo_3$ microfiller on the properties of the polyester concrete. The compressive and flexural strengths of the polyester concrete are greatly improved on incorporation of the $CaCO_3$ microfiller (compare specimens C and D). The split-tensile strength shows little change, probably because the split-tensile failure depends on the strength of bonding between the resin and the aggregates, which remains unaltered by the incorporation of $CaCo_3$ microfiller. Higher compressive strength (or lower split-tensile to compressive strength ratio) for specimens with $CaCO_3$ microfiller is owed not necessarily to the stronger bonding but possibly to the greater space filling by the microfiller particles leaving less room for compressive deformation.

Compressive and flexural strength of the polyester concrete on incorporation of $CaCO_3$ microfiller reach values sufficiently comparable with the case of 'epoxy-concrete without silane (specimen E). Impact strength of the polyester concrete, however, is poorer in presence of the $CaCO_3$ microfiller.

Abrasion and skid resistance

The coefficient of hardness of these polymer concretes are slightly superior to that of the cement concrete (Table 3), implying good abrasion resistances for both polyester and epoxy concretes. The epoxy concrete has a somewhat greater abrasion resistance than the polyester concrete.

Table 3. Hardness, friction, setting-shrinkage, cavitation resistance and water absorption properties of the various concretes

Property	Cement concrete	Polyester concrete			Epoxy concrete	
	(A)	(B)[a]	(C)[b]	(D)[c]	(E)[d]	(F)[e]
Coefficient of hardness (Dory's abrasion resistance at 20°C	18.6	18.6	18.8	18.9	19.0	19.0
Coefficient of friction (skid resistance) at 20°C	0.51	0.53	0.55	0.50	0.54	0.55
Setting shrinkage (10⁻⁶ strain units)	*	2900	*	4200	1100	*
Cavitation resistance (wt loss in g)	39.0	28.5	23.0	23.5	*	*
Water absorption (%) in cold water (C_{72})	3.69	0.19	0.14	0.11	0.03	0.03
in boiling water (B_{75})	5.33	0.33	0.26	0.26	0.13	0.13

*Not measured
[a]Without silane and filler
[b]With silane MEMO and without filler
[c]With silane MEMO and CaCO₃ filler
[d]Without silane
[e]With silane AMEO

Coefficients of friction for both polyester and epoxy concretes are distinctly superior to that of the cement concrete, except in the case of polyester concrete containing $CaCO_3$ microfiller. This shows that the skid resistance of these polymer concretes are not inferior to that of the cement concrete.

The abrasion and skid resistance properties are especially relevant for end uses such as bridge-decks, airport runway, motor-highway surfaces. For very specific applications these polymer concretes may prove useful in spite of the high cost of the binders.

Setting shrinkage

Volume change on solidification of the liquid polymeric resins gives rise to significant shrinkage of polymer concretes during the resin setting or curing processes. When measured as a function of time, the shrinkage remains insignificantly small in the first few hours (up to 5 h). After the initial 5 h cure, the shrinkage increases with time and reaches a plateau after 15–20 h. The plateau value of the shrinkage is taken as the 'setting shrinkage'. As shown in Table 3, setting shrinkage of the polyester concrete (specimen B) is much higher than that of the epoxy concrete (specimen E). Addition of $CaCO_3$ microfiller, produces an adverse effect on the setting shrinkage of the polyester concrete (compare specimens B and D).

Use of shrinkage reducing agents is essential, particularly in applications where shrinkage of concrete during setting cannot be accomodated, as for example in the case of polymer concrete mortar used in the repair of cracks in cement concrete structures or in the surfacing of roads and pavements etc. Use of a polymer concrete mortar is sometimes preferable in the repair of the cracks in old cement concrete due to the fact that bonding between old and new cement concrete and the polymer concrete is remarkably good. Studies of shrinkage reduction in polyester concrete, reported in detail in a previous publication[12] showed that the shrinkage could be reduced to zero or could even be negative (ie, expansion), depending on the composition and quantity of 'shrinkage reducing agent' added to the resin. The problem of shrinkage reduction is overcome in a number of ways not only for the concretes but also for many other applications of the binder resins.

Water absorption and cavitation resistance

Both the polymer concretes show considerably smaller water adsorption tendencies than the cement concrete, as shown in Table 3; the epoxy concrete showing a lower water absorption than the polyester concrete. The effects of the silane coupling agent and $CaCO_3$ microfiller on water absorption of the polymer concretes are insignificant. Water absorption, which is greater in boiling water than in cold (ambient temperature) water, is considerably smaller for these polymer concretes than the cement concrete. Amongst the two polymer concretes the epoxy concrete has significantly lower water absorption than the polyester concrete. Incorporation of the silane coupling agent produces a slight decrease in water absorption tendency of the polyester concrete and no significant change in case of the epoxy concrete. Water absorption at these two temperatures (ambient and the boiling

temperature of water) clearly suggest a still lower value of water absorption around the water freezing temperature, thus indicating a greater freeze–thaw resistance for these polymer concretes than the cement concrete.

Tendency to cavitation is compared in terms of the weight loss on sand blasting under identical conditions; the lower value of weight loss implies greater resistance to cavitation. Values shown in Table 3, indicate greater cavitation resistance of the polyester concrete than the cement concrete; silane coupling agent further enhances the cavitation resistance of the polyester concrete, while the $CaCO_3$ microfiller does not produce any significant effect. This suggests better durability under adverse weather conditions of the polyester concrete than the cement concrete.

Resistance to chemicals

The chemical resistance study was carried out with chemical reagents relevant to the general applications of concrete. The six chemical reagents used were HCl, H_2SO_4 CH_3COOH, NaOH, NaCl, $MgSO_4$ representing the effects of strong and weak acids, alkali, saline water and sulphate resistance respectively. Other chemicals relevant to specific end-uses of polymer concrete, such as diesel and petrol for highways or some specific chemicals for polymer concretes used in floor surfacing in chemical industries etc, are not included in this study. Overall resistance to a given chemical is determined after constant exposure for 180 days in all cases and the results are expressed in the units of total evaluation points as defined by Fukuchi and Ohama[18]. The specimens, after exposure to the chemicals, were examined for changes of weight, surface appearance and colour and graded according to the scheme described in Table 4. The total evaluation points were calculated according to expression given in Table 4. Higher values of total evaluation points imply greater resistance to the chemical concerned.

From the results shown in Table 5 it can be seen that, in most cases the chemical resistance of these polymer concretes is superior to that of the cement concrete, with the exception of the resistance to alkali (NaOH) of the polyester concrete. The alkali resistance of the polyester concrete is comparable with that of the cement concrete and is decreased in presence of the $CaCO_3$ microfiller. There is a possibility of saponification of the polyester component in the presence of NaOH, which might be the cause of the lower alkali resistance of the polyester component observed in presence of NaOH, which could explain the lower alkali resistance of the polyester concrete.

Addition of the $CaCO_3$ microfiller decreases the resistance of polyester concrete to, not only the alkali, but to most of the chemicals used. This is unavoidable owing to the considerable reactivity of $CaCO_3$ with these chemical reagents. Thus, although the addition of $CaCO_3$ microfiller enhances the strength of the polyester concrete it does have an adverse effect on its chemical resistance. Hence a compromise of the properties for specific applications, or a search for an alternative microfiller would be necessary.

Epoxy concretes, which show superior resistance to alkali, show somewhat lower resistance to sulphuric acid and acetic acid than the polyester concretes

Table 4.   Evaluation criteria for chemical resistance of polymer concrete

Evaluation item	Standard value for evaluation (Grading points)			
	Excellent (4)	Good (3)	Fair (2)	Poor (1)
Weight change (A)	± 2%	+2 to +15% −2 to −4%	+15 to +20% −4 to −6%	> +20% < −6%
Surface appearance change (B)	No change	Light scaling	Medium scaling	Complete collapse
Colour change (C)	No change	Slight discolouration	Fair discolouration	Remarkable discolouration

$$\text{Total evaluation points} = \frac{1.5A + B + 0.5C}{3}$$

Table 5.   Resistance to various chemicals of the cement concrete and the polymer concretes after 180 days exposure (values expressed in units of total evaluation points described in the text)

Sample number	Reagent	Cement concrete	Polyester concrete			Epoxy concrete without silane
			(A)	(B)	(C)	
1	5% HCl	2.5	4.0	4.0	3.8	4.0
2	5% H_2SO_4	3.0	4.0	4.0	3.8	3.7
3	5% CH_3COOH	2.2	4.0	4.0	3.5	3.7
4	15% NaCl	3.7	4.0	4.0	3.8	4.0
5	15% NaOH	3.0	3.0	3.0	2.5	4.0
6	0.2% $MgSO_4$	3.2	4.0	4.0	3.8	4.0

(A)Without silane or microfiller
(B)With silane MEMO
(C)With $CaCO_3$ and silane MEMO

(without $CaCO_3$ microfiller). Resistance to HCl, saline water and sulphate salt of the epoxy concretes is quite comparable with that of the polyester concretes (without $CaCO_3$ microfiller).

Conclusion

The use of polymeric resin binders, instead of cement, gives stronger concrete than the conventional cement concrete. Polymer concretes based on unsaturated polyester resins and epoxy resin binders show compressive strengths higher by a factor 2 to 4 and split-tensile and flexural strengths higher, by a factor 3 to 6, than the conventional cement concrete. Epoxy concrete is, in general, stronger than polyester concrete but the cost of epoxy resin binder may restrict its use. Present studies show that the compressive, split-tensile and flexural strengths of polyester concrete can be further enhanced by incorporation of a silane coupling agent and the microfiller to reach a level sufficiently comparable with the 'epoxy concrete without silane'. In other properties, such as impact strength and water absorption the polymer concretes are superior to cement concrete while in abrasion and skid resistance they are comparable (or at least not inferior) to cement concrete. Chemical resistance of the polymer concretes is markedly superior to that of the cement concrete, with the exception of the alkali resistance of the polyester concrete and a decrease in chemical resistance in the presence of $CaCO_3$ microfiller.

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Authors

The authors are with the Centre for Materials Science and Technology, Indian Institute of Technolgy, Hauz Khas, New Delhi-110 016, India. P. Mani is presently at the Materials Division, Regional Research Laboratory (CSIR), Trivandrum-695019, India. Inquiries should be directed to Dr Gupta in the first instance.