Interfacial adhesion in polyester resin concrete

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Silane coupling agents are widely used to improve the interfacial adhesion between the inorganic filler and the organic polymer matrix of polymer concretes. The mechanical properties of the concretes are also found to improve on the addition of silane coupling agents. This paper compares two methods of silane application; pretreatment of aggregates with silane and direct addition of silane to the resin, on the interfacial adhesion in polyester resin concrete for three different silanes. The effects of other parameters, such as the silane loading, predrying of aggregates before silane treatment, addition of $CaCO_3$ microfiller and pH of the silane treatment medium, are also investigated.

Key words: adhesion; compressive strength; concrete mixes; silanes; polyesters.

Owing to their superior properties, polymer concretes are replacing conventional cement concretes for various specific applications[1-5]. Polymer concretes, which are essentially the composite materials of inorganic aggregates and polymeric resin binders, differ widely in their properties depending on the nature of the binder and the aggregate used, and the conditions of preparation. For a given type of polymer concrete, the properties are dependent upon the binder content, aggregate size distribution, nature and content of the microfiller, shrinkage reducing agent used, curing conditions, *etc*. Studies on the effects of these parameters on the properties of a polymer concrete based on polyester resin as binder and crushed quartzite aggregates (called polyester resin concrete) is reported in previous publications.[6,7].

In addition to the above parameters, the adhesion at the binder/aggregate interface governs the properties of these composite materials. Adhesion at the interface, in the absence of any chemical bonding, may be sufficiently good even when it is due to the secondary forces between the two phases.

The use of silane coupling agents, which may provide chemical bonding between the two phases, considerably improves the interfacial adhesion and thereby enhances the mechanical properties of these materials.[8-11]

The bonding mechanism of the resin and the inorganic aggregate through silane has not been fully investigated for the inorganic aggregates studied here. However, a possible mechanism, based on investigations of other systems, for the reaction between the silane and the two components of the composite is shown in Fig. 1. The silanes are of the general structure $R'\text{-Si-}(OR)_3$, where R' is the functional group and R is an alkyl group. Firstly, the alkoxy groups hydrolyse to form reactive silanols, which then further react with the inorganic base; and secondly, the functional group reacts with resin.

The reactivity of the functional groups with the resin may vary depending on the nature of the silane and the resin. This suggests that the choice of silane is highly significant for the interfacial adhesion between the resin and the aggregates.

A wide variety of silane coupling agents is now available, but the choice of a suitable silane for any new composite material becomes a problem as there is not sufficient information available about their suitability for various polymer resins and fillers. The efficiency of any particular silane coupling agent depends on:

- its reactivity with the components of the given polymer concrete, *ie* the properties of a given polymer concrete will depend on the nature of the silane used;
- method of application, and any particular method also depends on the conditions such as the silane content, medium of application *etc.*

Various methods of applying silane coupling agents to such materials are suggested in the literature[12,13]. These include:

i) the surface treatment method[12], which involves the pretreatment of aggregates with a solution of silane in water, or in a mixture of water and methanol, or some other suitable organic solvent.

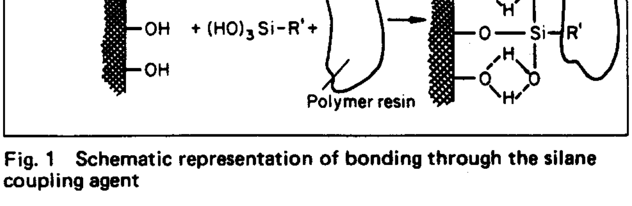


Fig. 1 Schematic representation of bonding through the silane coupling agent

2) the integral blend additive method[12], which involves the addition of silane directly to the binder-aggregate mix.
3) the dry silane concentrate method[13], which involves the exposure of the aggregates to silane vapours, or spraying the silane directly onto the aggregates.

Each of these three methods have their own advantages and disadvantages, hence any one of these may be adopted according to the convenience of the user.

A comparison of the various methods on any given system is not well illustrated in the literature.

In this paper, a study is made of the effect of silane coupling agent on the interfacial adhesion of a particular system, *viz* polyester resin concrete (PC). The efficiency of adhesion at the polymer/aggregate interface is measured in terms of the improvement of mechanical properties, such as compressive strength and tensile strength. PC of constant composition and identical methods of preparation were used in these studies. Two types (*ie* two compositions) of PC samples were investigated; PC without microfiller and PC with $CaCO_3$ microfiller.

A comparison of the effect of methods of application 1) and 2) on the properties of these samples is presented using three different types of silane. The method 3) could not be studied owing to experimental limitations. This study also revealed information about the effect of the nature of the silane on the properties. Finally, the effects of pH of the medium of treatment and the predrying of the aggregate, silane and microfiller were also explored for both the methods of application of the silane coupling agent.

Experimental

Materials

The binder used was a general purpose unsaturated polyester resin, supplied by Crystic (India) Ltd. The catalyst and the accelerator were, respectively, a 50% solution of dimethyl phthalate in methylethylketone peroxide and 1% solution of cobalt naphthenate in styrene, added as 2% by weight of the resin. A mixture of the resin, catalyst and accelerator is termed the resin-mix, or simply the binder, in the subsequent discussion.

The coarse aggregates used were crushed quartzite (specific gravity 2.72 and no organic impurities) of maximum size 10 mm. The fine aggregates used was siliceous sand (locally known as Badarpur sand, of specific gravity 2.6 and no organic impurities) of size which passed through an IS 120 sieve (size 1.2 mm) and was retained on an IS 15 sieve (size 150 μm).

Calcium carbonate ($CaCO_3$) powder, used as a microfiller in some cases, had a particle size ranging from 2.0 to 2.5 μm.

Three silane coupling agents were used, two of which (AMEO and MEMO) were manufactured by Nobel Dynamit Co and the third which was manufactured by Polyscience Inc. The commercial and chemical names and formulae of these three silanes are shown in Table 1.

Method of preparation

The optimum values of aggregate size distribution, binder content and curing conditions, described in previous publications[6,7] were used for the preparation of these PC samples.

PC samples were prepared by mixing together the appropriate quantities of the aggregates and binder. The binder content was 12 wt % and the aggregate grading employed was that with grading modulus $6.42\ mm^{-1}$, mean diameter 4.12 mm, and fineness modulus 4.40[7,14]. The binder-aggregate mix was homogenized, poured into cylindrical moulds and compacted. After room temperature curing for 24 h, the specimens were demoulded and further cured at 70°C for 24 h.

The $CaCO_3$ microfiller, wherever used, was added as 6% by weight of the total weight of the mix, before mixing the aggregates and resinous binder.

Silane coupling agents were applied by either the integral blend method or by direct surface treatment, as described below.

In the direct surface treatment method, the aggregates were treated with 0.5% solution of the silane in water or water-methanol mixture for 1 h and then dried for 4 h at 110°C. In some cases, the pH of the silane treatment medium was adjusted to desired values (from $pH = 4$ to 10) using acetic acid or ammonium hydroxide[15]. The total silane loading in all these surface treatment methods was kept constant at 1% by weight of the binder.

In the integral blend additive method, the silane was added to the resin mix in varying proportions ranging from 0.3 to 1.5% by weight of the binder.

Conditions of preparation of the various samples are shown in Table 2. PC samples without microfiller are denoted as 'PC', while those with $CaCO_3$ microfiller are denoted as 'PC/$CaCO_3$'. The samples without silane treatment are denoted as 'PC-control' or 'PC-untreated'.

Measurement of properties

Compressive strength (σ_c) and split tensile strength (σ_t) were measured on the cylindrical specimens of 50 mm diameter and 100 mm length on an Avery Compression Tester as per Indian Standards IS-516-1959 (with amendment-1)[16] and IS-5816-1970[17], respectively. The loading rates were $140\ kg/cm^2/min$ for the σ_c tests and $15\ kg/cm^2/min$ for the σ_t tests. Measurements were carried out on three to five specimens in each case and the deviation of results around the mean value was less than 5 to 8% in all cases.

Table 1. Details of the three silanes used in this study

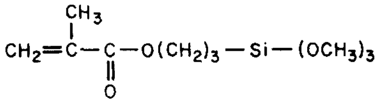
Commercial name	Chemical name	Formula
Dynasilan AMEO	γ-aminopropyltriethoxy silane	$H_2N-CH_2-CH_2-CH_2-Si-(OC_2H_5)_3$
Dynasilan MEMO	γ-methacryloxypropyltrimethoxy silane	 $CH_2=C(CH_3)-C(=O)-O(CH_2)_3-Si-(OCH_3)_3$
Polyscience VTES	vinyltriethoxy silane	$CH_2=CH-Si-(OC_2H_5)_3$

Table 2. Methods of application of silane coupling agent

Method of application	Treatment medium	Type of silane used	Silane concentration (wt %)	pH	Other conditions
Pretreatment of aggregates	Water-methanol mix (60:40)	AMEO	0.5	7	Aggregates were dried for 4 h at 110°C after treatment
		MEMO	0.5	7	
		VTES	0.5	7	
	Water	AMEO	0.5	7, 10.5	Aggregates were dried for 4 h at 110°C after treatment
		MEMO	0.5	7, 4.0	
		VTES	0.5	7	
Integral blend additive	–	AMEO	0.3-1.5*	–	–
	–	MEMO	0.3-1.5*	–	–
	–	VTES	1.0*	–	–

*Indicates content with respect to resin

Results and discussion

Effect of method of application of silane

The compressive strength (σ_c) and split tensile strength (σ_t) of the PC samples prepared by both methods of application of silane are shown in Table 3. It can be seen that the σ_c of the PC-control sample (420 kg/cm^2) increases on application of the silane coupling agent (476 to 675 kg/cm^2) depending on the nature of the silane used and the method of silane application. The σ_t also shows a similar effect. It is further noted that for any given method of applying the coupling agent, the improvement in the properties follows the order: AMEO$<$MEMO$\sim$VTES. For any particular silane, the improvement in the properties is greater for the direct surface treatment method than for the integral blend additive method. Furthermore, in the former method, the silane treatment through water-methanol medium produced greater improvement in properties than the aqueous medium.

In the PC/$CaCO_3$ samples, the nature of the silane and the method of silane application (shown in Table 4) have a similar effect to that found for PC. However, the strengths were somewhat higher for the PC/$CaCO_3$ samples than for the corresponding PC samples.

The role of silanes in improving the adhesion at the aggregate/polyester interface depends on the mechanism of interaction of the functional groups of the silane with the siliceous aggregate and the polyester resin. The present results clearly support this, when they are viewed in the light of the information supplied by the manufacturer of the silanes MEMO and AMEO. AMEO is classified as a 'non-reactive, type, while MEMO is stated as 'reactive' with respect to polyester resin. However, the possibility of secondary bonds should not be ruled out in the non-reactive silane. Hence the adhesion efficiency of these two types of silane would differ such that in MEMO primary bonding at both the reactive ends of the silane may be expected, while in AMEO there might be primary bonding at one end of the silane and secondary bonding at the other end. The lower strengths of the PC samples with AMEO compared with those with MEMO seems to support the role of these silanes. The silane VTES, which is recommended for polyester resin, showed better results than MEMO, probably owing to its greater reactivity with the respective components.

In the direct surface treatment method, the greater improvement in interfacial adhesion observed in the water-methanol medium compared with the pure acueous medium may possibly be due to better wetting of the aggregate surface in the former, and/or due to better hydrolysis of the aggregate surface suitable for bonding with reactive groups of the silane coupling agent.

In the integral blend additive method of application, the efficiency of adhesion would depend on the ease of migration of silane molecules from the resin matrix to the resin/aggregate interface. Though some authors have

Table 3. Effect of method of application of silane coupling agent

Method of application	Type of silane used	Compressive strength, σ_c (kg/cm^2)	Split tensile strength, σ_t (kg/cm^2)
PC-untreated	–	420	110
Pretreatment of aggregates with 0.5% water-methanol solution of silane	AMEO	527	118
	MEMO	657	130
	VTES	675	133
Pretreatment of aggregates with 0.5% aqueous silane solution	AMEO	510	120
	MEMO	574	124
	VTES	578	130
Integral blend additive (1% resin)	AMEO	476	113
	MEMO	540	121
	VTES	555	120

Table 4. Effect of silane coupling agent in PC/$CaCO_3$

Description of specimen	Method of application	Type of silane used	Compressive strength, σ_c (kg/cm^2)	Split tensile strength, σ_t (kg/cm^2)
PC-untreated and no microfiller	–	–	420	110
PC-untreated/$CaCO_3$	–	–	510	108
PC/$CaCO_3$	Pretreatment with water-methanol silane solution	AMEO	615	129
		MEMO	861	162
		VTES	892	168
	Pretreatment with aqueous silane solution	AMEO	592	130
		MEMO	829	162
		VTES	696	138
	Integral blend additive	AMEO	554	115
		MEMO	693	123
		VTES	645	126

stated that the performance of the integral blend additive method was as good as the other methods, these results show this method to be somewhat lower in efficiency compared with the direct surface treatment method. The fact that there is an improvement of mechanical properties confirms that there is a migration of silane from the resin bulk to the interface region. In infra-red spectroscopic studies[18] evidence has been found of bonding at the aggregate surface in the presence of silanes applied through the integral blend additive method.

The lower efficiency of the integral blend additive method might be also due to lower efficiency of migration of silane from the resin bulk to the resin surface, and/or the presence of voids in the structure, in which the silane molecules at the resin surface may not contribute to bonding with aggregate surface. The effect of silane loading was significant in the case of the integral blend additive method, as described below.

Optimization of silane loading

In the integral blend additive method, the ultimate properties of the PC depended on the amount of the silane used (the silane loading). Fig. 2 shows the effect of silane loading on the σ_c and σ_t of PC with the two silanes MEMO and AMEO. As the silane loading increases, both σ_c and σ_t first increase to a maximum value and then decrease. These maxima occur around 0.5-1.0% silane loading in all these cases, and the loading corresponding to these maxima may be called the optimum silane loading.

Below the optimum silane loading, the bonding at the interface apparently increases with silane loading and reaches a maximum at the optimum silane loading. At a silane loading higher than the optimum, the observed low efficiency of adhesion might be due to part of the silane undergoing self-condensation after hydrolysis and leading to the deposition of layers of oligomeric silanols at the aggregate/binder interface[15].

Effect of predrying the aggregates

The role of surface moisture in the bond formation between the silane and aggregate is well known[12,13]. A study of the effect of predrying the aggregates before silane treatment, presented below, confirms this role and provides indirect evidence that bonding occurs through silane at the aggregate surface when the silane is applied by the integral blend additive method.

PC samples (with silanes MEMO and AMEO and without any silane treatment) were prepared with identical compositions of all the constituents but differing in the atmospheric exposure of the aggregates. Two sets of samples were prepared for each composition; one with the aggregates exposed to ambient atmosphere (relative humidity ~65%), and the other with aggregates dried in an oven at 100°C and mixed with the binder, so that the possibility of surface moisture could be minimized.

The σ_c of these samples are shown in Table 5. PC samples without any silane showed no appreciable difference in σ_c when the aggregate type was varied. In the PC samples

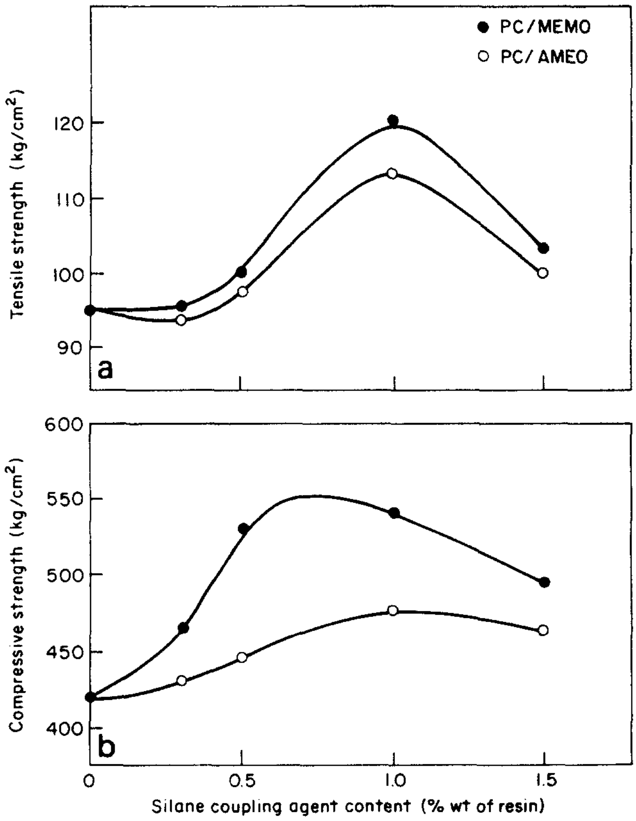


Fig. 2 Variation of (a) split tensile strength and (b) compressive strength with coupling agent content in PC

Table 5. Effect of predrying the aggregates

Description of specimen	Compressive strength, σ_c (kg/cm^2)	
	With oven-dried aggregates	With normal air dried aggregates
PC-untreated	426	420
PC/AMEO	396	476
PC/MEMO	424	540

prepared with oven-dried aggregates, no significant improvement in σ_c was achieved on treatment with either of the two silanes. However, in samples prepared with the aggregates exposed to the ambient atmosphere, σ_c increased on silane treatment, depending on the nature of the silane. This suggests that in the absence of aggregate surface moisture, the silane becomes less effective in improving the interfacial adhesion in these composites.

Effect of silane coupling agent in PC/$CaCO_3$

The results presented in Table 4 illustrate the role of silane coupling agent in PC/$CaCO_3$. The use of $CaCO_3$ microfiller, in general, increases the σ_c and σ_t of PC due to its void-filling property, thus providing a greater possibility of binder-aggregate contact[19]. The σ_c of PC was increased by 70% when $CaCO_3$ was used and an increase of over 100% was observed for the PC/$CaCO_3$/MEMO or VTES system. These improvements may have been due to the simultaneous effects of better adhesion at the aggregate surface through silane bonding and better cohesion of the whole structure produced by the space-filling property of the microfiller. Silanes, however, have no tendency to form chemical bonds at the $CaCO_3$ particle surface.

Effect of the pH of the silane treatment medium

Hydrolysis, which is necessary for the condensation reaction of the silane, depends on concentration, method of application, pH of the treatment medium *etc*[15]. A fast hydrolysis reaction makes the silanols needed for covalent bond formation with the hydroxyl groups of the aggregate surface more readily available. The H^+ and OH^- ion concentration in the aqueous phase also affect the potential on the hydrated mineral surface and thereby influence the orientation (or alignment) of silanols on the aggregate surface. The pH of the medium required is different for each silane as shown in the work of Subramanian and Shu[15] on basalt fibre/polymer composites.

The need to use the appropriate pH for each of the silanes is clearly illustrated in the results obtained on the water-methanol medium *vis-a-vis* the aqueous medium (see Tables 3 and 4). To ascertain the effect of pH, experiments were carried out by controlling the pH of the medium to three fixed values 4, 7 and 10.5 by the addition of suitable chemicals. Values of σ_c of the samples prepared under these differing conditions are shown in Table 6, for the silanes MEMO and AMEO.

The results show that by using a silane medium of appropriate pH, a σ_c as high as 925 kg/cm^2 (more than 200% higher than that of the PC-control sample) can be achieved. Furthermore, adjusting pH to obtain optimum properties is clearly cheaper than adding methanol in the production of PC on a larger scale.

Table 6. Effect of pH of silane medium on the properties of PC

Description of specimen	pH of the medium	Compressive strength, σ_c (kg/cm^2)
PC-untreated	–	420
PC/AMEO	7	510
PC/AMEO	10.5	547
PC/MEMO	7	574
PC/MEMO	4	644
PC/$CaCO_3$/AMEO	7	592
PC/$CaCO_3$/AMEO	10.5	656
PC/$CaCO_3$/MEMO	7	829
PC/$CaCO_3$/MEMO	4	925

Conclusions

The use of silane coupling agent in polyester resin concrete improves its mechanical properties due to improved adhesion between the binder and aggregates at the interface. The direct surface treatment of aggregates with silane in a water-methanol medium gives better properties than the pure aqueous medium of treatment or the integral blend additive method of silane application. By controlling the pH of the silane treatment medium, comparable improvements in properties can be achieved.

In the integral blend additive method, there is an optimum silane loading beyond which the strength diminishes. The effect of surface moisture confirms that bonding at the binder/aggregate interface occurs through the silane. The results also confirm that the microfiller, used to reduce voids, produces a considerable improvement in properties. The silanes VTES and MEMO are more suitable than the silane AMEO for the present binder/aggregate system.

Compressive strengths as high as 800-900 kg/cm^2 can be obtained for the presently studied polyester resin concrete by using the most appropriate aggregate grading, binder content, curing conditions, microfiller content, type of silane coupling agent and the method of application of silane coupling agent. This value of compressive strength is quite comparable to the values reported in the literature[8,9] for various polyester resin concretes (*viz* 700 to 1200 kg/cm^2).

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